Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

1 Contents

2 General

Unless otherwise noted all solvents and chemicals were used as received. Solvents used for synthesis were HPLC grade. Anhydrous solvents were taken from an Innovative Technology (IT) apparatus (model PS-MD-05). Sodium iodide was dried by moderate heating under reduced pressure. The 2,6-lutidine used was stored over 3Å molecular sieves for at least 24 hours prior to use. For all reactions in which anhydrous solvents were used the glassware was flame dried prior to use and were carried out under N_2 atmosphere unless stated otherwise.

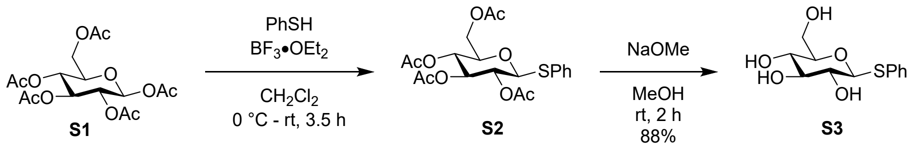
TLC was carried out on aluminium plates pre-coated with Silicagel 60 with fluorescence indicator, visualized by irradiation with UV light (254 nm) and/or H_2SO_4 stain (10% in EtOH) stain. Flash Column Chromatography was carried out using silica gel 60 (40-63 μm) as solid phase. Automated column chromatography was carried out on a Büchi Pure C-815 Flash instrument using Büchi FlashPure columns, loading was done by liquid injection with CH_2Cl_2, eluent gradients were calculated using the instrument Navigator function by inputting TLC data and column size.

^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 MHz Bruker instrument with a non-inverse cryoprobe at 298 K unless notes otherwise. Chemical shifts are reported in ppm and coupling constants (*J*) are reported in Hz. Residual protonated solvent signals were used as internal standards for referencing ^{1}H and ^{13}C NMR spectra (^{1}H: $\delta(CHCl_3)$ = 7.26 ppm (singlet), δ(HDO) = 4.79 ppm (singlet), $\delta(CHD_2CN)$ = 1.94 ppm (pentet), and ^{13}C: $\delta(CDCl_3)$ = 77.16 ppm (triplet), $\delta(CD_3CN)$ = 1.32 ppm (septet)). ^{1}H and ^{13}C NMR assignments were based on 2D ^{1}H-^{1}H COSY and 2D ^{1}H-^{13}C HSQC NMR experiments, aromatic carbon atoms were not assigned. The colors in ^{1}H-^{13}C HSQC spectra indicate even (blue) and odd (red) numbers of hydrogen atoms attached to a carbon atom. Tetramethylsilane was used as internal standard for referencing ^{29}Si NMR spectra (^{29}Si: $\delta(Me_4Si)$ = 0 ppm).

HR-MS (MALDI-TOF) was run on a SolariX ESI/MALDI FTMS spectrometer using dithranol as matrix.

3 Synthetic procedures

Phenyl β-D-thioglucopyranoside (S3)



β-D-glucopyranose pentaacetate **S1** (14.98 g, 38.37 mmol, 1 equiv) was dissolved in anhydrous CH_2Cl_2 (40 ml) to which PhSH (4.80 ml, 46.6 mmol, 1.2 equiv) was added while stirring at 0 °C (ice bath). Then BF_3•OEt_2 (5.70 ml, 46.2 mmol, 1.2 equiv) was added in small portions over the course of 15 minutes followed by stirring at rt for 3.5 hours. Then the reaction was quenched by addition of sat. aqueous $NaHCO_3$ (30 ml). The organic phase was washed with H_2O (2 x 30 ml) and brine (1 x 30 ml) and afterwards dried over Na_2SO_4, filtered and concentrated in vacuo. The mixture was dissolved in PhMe and CH_2Cl_2 and loaded onto a silica plug. The plug was flushed with PhMe until no more PhSH eluted, then pure EtOAc was used to elute the acetylated thioglucopyranoside **S2**. After concentrating *in vacuo*, the sticky white solid was suspended in MeOH (150 ml) and NaOMe (25% in MeOH, 0.50 ml) was added, and the reaction was stirred at rt for 2 hours. The reaction was quenched upon the addition of solid phase acid resin (Amberlite IRC120 H^+ form). The mixture was filtered and concentrated *in vacuo* to yield **S3** as a white foam (9.236 g, 33.9 mmol, 88% over 2 steps).

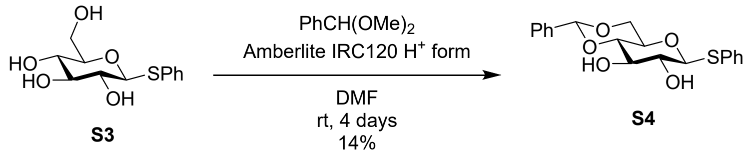
NMR is in accordance with the literature.[2]

^{1}H NMR (500 MHz, D_2O) δ 7.47 – 7.44 (2H, m, **arom.**), 7.31 – 7.26 (3H, m, **arom.**), 4.68 (1H, d, J = 9.9 Hz), 3.77 (1H, dd, J = 12.5, 2.4 Hz), 3.59 (1H, dd, J = 12.5, 5.6 Hz), 3.42 – 3.34 (2H, m), 3.30 – 3.21 (2H, m) ppm. O-H peaks not observed by ^{1}H NMR due to exchange with the D_2O solvent.

^{13}C NMR (126 MHz, D_2O) δ 131.8, 131.4, 129.1, 127.9, 87.1, 79.7, 77.0, 71.5, 69.1, 60.5 ppm.

OH peaks not observed by ^{1}H NMR due to exchange with the D_2O solvent.

Phenyl 4,6-*O*-benzylidene-β-D-thioglucopyranoside (S4)



To a solution of **S3** (9.084 g, 33.36 mmol, 1 equiv) in anhydrous DMF (40 ml) was added a small amount of solid phase acid resin (Amberlite IR 120 H^+ form). Then Benzaldehyde dimethyl acetal (5.70 ml, 37.8 mmol, 1.1 equiv) was added at rt and the reaction was stirred for 23 hours after which TLC analysis showed presence of starting material. Then more benzaldehyde dimethyl acetal (5.0 ml, 33 mmol, 1 equiv) and solid phase acid resin was added, and the reaction stirred at rt for another 24 hours. TLC analysis still showed low conversion so more benzaldehyde dimethyl acetal (3.0 ml, 20 mmol, 0.6 equiv) was added. After 2.5 days solid phase acid resin (Amberlite IR 120 H^+ form, freshly acidified by washing with 1M HCl followed by washing with MeOH) was added and the reaction was stirred at rt. After a total of 4 days the reaction was quenched by the addition of Et_3N (1 ml, 7 mmol) until pH > 7 and the mixture was filtered to remove resin beads. The mixture was diluted with H_2O (100 ml) and extracted with EtOAc (4 x 50 ml). The combined organic phases were washed with H_2O (3 x 40 ml), aqueous HCl (1M, 1 x 40 ml) and brine (2 x 40 ml). The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture was suspended on Celite filter aid and purified by flash column chromatography (1:1 EtOAc/heptane) and further purification of the product-containing fractions by trituration in EtOAc (200 ml) with petroleum ether (700 ml) yielded **S4** as a white powdery solid (1.723 g, 4.78 mmol, 14%).

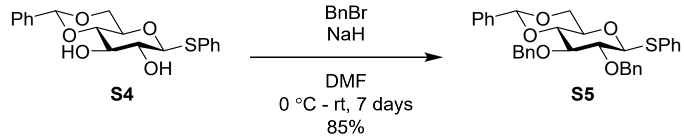
R_F = 0.16 (1:1 EtOAc/heptane)

NMR is in accordance with the literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.54 (2H, m, **arom.**), 7.49 – 7.47 (2H, m, **arom.**), 7.38 – 7.34 (6H, m, **arom.**), 5.54 (1H, s, **PhC<u>H</u>-O,O**), 4.65 (1H, d, *J* = 9.7 Hz, **H1**), 4.39 (1H, dd, *J* = 11.0, 4.1 Hz, **H6**), 3.87 (1H, app. t, *J* = 8.6 Hz, **H3**), 3.81 – 3.77 (1H, m, **H6**), 3.55 – 3.53 (2H, m, **H4**, **H5**), 3.48 (1H, app. t, *J* = 9.7, 8.6 Hz, **H2**), 2.69 (1H, s, **OH**), 2.60 (1H, s, **OH**) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 133.3, 131.3, 129.5, 129.3, 128.7, 128.5, 126.4, 102.1 (**Ph<u>C</u>H-O,O**), 88.8 (**C1**), 80.4 (**C4/5**), 74.7 (**C3**), 72.7 (**C2**), 70.7, 68.7 (**C6**) ppm.

Phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-thioglucopyranoside (S5)



To a solution of benzylidene **S4** (992 mg, 2.75 mmol, 1 equiv) in anhydrous DMF (10 ml) was added NaH (60% in mineral oil, 252.6 mg, 6.32 mmol, 2.3 equiv) at 0 °C (ice bath) while stirring. After 15 minutes BnBr (0.90 ml, 7.6 mmol, 2.8 equiv) was added slowly over the course of 3 minutes followed by stirring the reaction at 0 °C for 1.5 hours. Then the ice bath was removed, and the reaction stirred for another 2 hours at rt. TLC analysis showed starting material present, so NaH (60% in mineral oil, 122.8 mg, 3.07 mmol, 1.1 equiv) and BnBr (0.90 ml, 7.6 mmol, 2.8 equiv) was added at 0 °C (ice bath) followed by stirring the reaction for 7 days with the temperature naturally reaching rt. Then the reaction was quenched by addition of MeOH (1 ml, 24 mmol) and the mixture was stirred at rt for 20 minutes before it was diluted with EtOAc (20 ml). The mixture was washed with H_2O (4 x 20 ml) and brine (1 x 20). The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The combined aqueous phases were extracted with EtOAc (3 x 30 ml) and then the combined organic phases from this extraction were washed with brine (2 x 30 ml) followed by being dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The combined concentrates were purified by flash column chromatography (1:6 EtOAc/heptane then 1:3 EtOAc/heptane) to yield **S5** as a white powdery solid (1.271 g, 2.35 mmol, 85%).

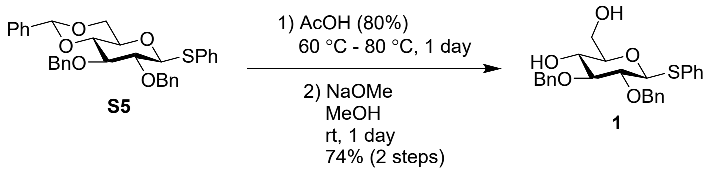
R_F = 0.69 (1:1 EtOAc/heptane)

NMR is in accordance with the literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.52 (2H, m, **arom.**), 7.49 – 7.47 (2H, m, **arom.**), 7.40 – 7.27 (16H, m, **arom.**), 5.59 (1H, s, **PhC<u>H</u>-O,O**), 4.94 (1H, d, J = 11.1 Hz, **C<u>H</u>$_2$Ph**), 4.84 (2H, app. q, J = 14.3, 10.2 Hz, **C<u>H</u>$_2$Ph**), 4.77 (2H, app. t, J = 11.9 Hz, **C<u>H</u>$_2$Ph**, **H1**), 4.39 (1H, dd, J = 10.5, 5.0 Hz, **H6**), 3.86 – 3.78 (2H, m, **H3**, **H6**), 3.71 (1H, app. t, J = 9.4 Hz, **H4**), 3.53 – 3.45 (2H, m, **H2**, **H5**) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.4, 138.2, 137.4, 133.2, 132.5, 129.2, 129.1, 128.6, 128.5, 128.4, 128.4, 128.3, 128.0, 128.0, 127.9, 126.1, 101.3 (**Ph<u>C</u>H-O,O**), 88.4 (**C1**), 83.2 (**C3**), 81.6 (**C4**), 80.6 (**C2**), 76.1 (**<u>C</u>H$_2$Ph**), 75.5 (**<u>C</u>H$_2$Ph**), 70.4 (**C5**), 68.9 (**C6**) ppm.

Phenyl 2,3-di-*O*-benzyl-β-D-thioglucopyranoside (1)



Benzylidene **S5** (772 mg, 1.43 mmol) was suspended in AcOH (80% in H_2O, 20 ml) and the reaction mixture was heated to 60 °C (oil bath) for 21 hours followed by 80 °C for 4 hours. Then the reaction was allowed to cool to rt and was then diluted with EtOAc (25 ml) and a mixture of solid $NaHCO_3$ and NaOH was added until the aqueous phase had pH > 7. The organic phase was washed with H_2O (3 x 25 ml) and brine (2 x 25 ml), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue, containing a mixture of diol **1** and acetylated mono-ol, was suspended in MeOH (30 ml) and then NaOMe (25% in MeOH, 0.30 ml, 1.3 mmol) was added and the reaction was stirred at rt for 24 hours. Then the reaction was quenched by addition of solid phase acid resin (Amberlite IR-120 H^+ form) until the mixture was acidic. The mixture was then filtered and concentrated *in vacuo*. The crude mixture was purified by automated column chromatography (12g silica column, 0 – 100 % EtOAc/heptane) to yield **1** as a white powdery solid (481 mg, 1.062 mmol, 74%).

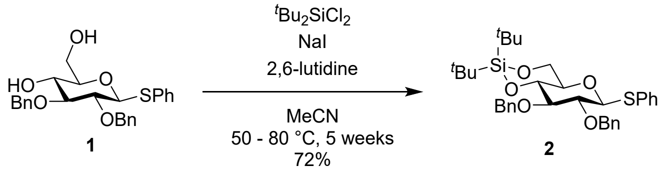
R_F = 0.26 (1:1 EtOAc/heptane)

NMR is in accordance with the literature.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.51 (2H, m, **arom.**), 7.43 – 7.41 (2H, m, **arom.**), 7.37 – 7.28 (11H, m, **arom.**), 4.96 (2H, app. d, *J* = 11.0 Hz, **C<u>H</u>₂Ph**), 4.77 – 4.70 (3H, m, **C<u>H</u>₂Ph**, **H1**), 3.88 (1H, dd, *J* = 11.9, 3.5 Hz, **H6**), 3.75 (1H, dd, *J* = 11.9, 5.4 Hz, **H6**), 3.58 (1H, t, *J* = 9.2 Hz, **H4**), 3.54 – 3.47 (2H, m, **H2**, **H3**), 3.36 (1H, ddd, *J* = 9.2, 5.4, 3.5 Hz, **H5**) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.4, 137.9, 133.6, 131.9, 129.2, 128.9, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 87.9 (**C1**), 86.2 (**C3**), 81.1 (**C2**), 79.3 (**C5**), 75.6 (**<u>C</u>H₂Ph**), 75.6 (**<u>C</u>H₂Ph**), 70.6 (**C4**), 63.0 (**C6**) ppm.

Phenyl 2,3-di-*O*-benzyl-4,6-*O*-di-*tert*-butylsilylene-β-D-thioglucopyranoside (2)



To a solution of **1** (97 mg, 0.215 mmol, 1 equiv) and NaI (108 mg, 0.718 mmol, 3 equiv) in anhydrous MeCN (2 ml) was added 2,6-lutidine (0.08 ml, 0.7 mmol, 3 equiv) while stirring at rt. Then after 10 minutes of stirring at rt $^tBu_2SiCl_2$ (0.05 ml, 0.24 mmol, 1.05 equiv) was added and the reaction was stirred at 50 °C (aluminium block) for 24 hours. Then $^tBu_2SiCl_2$ (0.02 ml, 0.09 mmol, 0.4 equiv) was added as TLC analysis showed almost no conversion of the diol **1**, and the reaction was stirred at 50 °C for another 6 days. The temperature was then increased to 80 °C as TLC analysis showed very little conversion of the diol **1**, and the reaction was stirred for 4 weeks. The reaction was then cooled to rt and quenched by addition of MeOH (2 ml) and diluted with EtOAc (10 ml). The mixture was washed with H_2O (1 x 10 ml), $Na_2S_2O_3$ (10% aqueous solution, 2 x 10 ml), H_2O (2 x 10 ml), and brine (2 x 10 ml). The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (1:4 EtOAc/heptane) yielded **2** as a colorless syrup (92 mg, 0.155 mmol, 72%).

R_F = 0.91 (1:1 EtOAc/heptane)

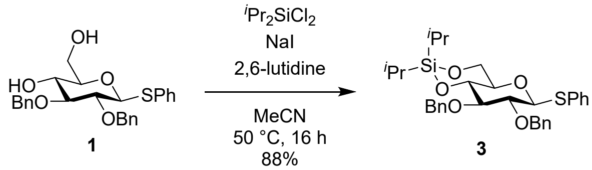
NMR is in accordance with the literature.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.50 (2H, m, **arom.**), 7.43 – 7.27 (13H, m, **arom.**), 5.03 (1H, d, *J* = 10.9 Hz, **C<u>H</u>$_2$Ph**), 4.86 – 4.79 (3H, m, **C<u>H</u>$_2$Ph**), 4.71 (1H, d, *J* = 9.9 Hz, **H1**), 4.22 (1H, dd, *J* = 10.3, 5.0 Hz, **H6**), 3.98 – 3.93 (2H, m, **H3/4**, **H6**), 3.64 (1H, app. t, *J* = 8.7 Hz), 3.47 – 3.42 (2H, m, **H2**, **H5**), 1.11 (9H, s, **$(CH_3)_3CSi$**), 1.01 (9H, s, **$(CH_3)_3CSi$**) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 138.3, 133.4, 132.4, 129.1, 128.5, 128.5, 128.4, 128.3, 127.9, 127.9, 88.4 (**C1**), 86.4 (**C3/4**), 80.1 (**C2/5**), 78.0 (**C3/4**), 75.9 (**<u>C</u>H$_2$Ph**), 75.9 (**<u>C</u>H$_2$Ph**), 74.6 (**C2/5**), 66.4 (**C6**), 27.6 (**(<u>C</u>H$_3$)$_3$CSi**), 27.1 (**(<u>C</u>H$_3$)$_3$CSi**), 22.8 (**Si<u>C</u>(CH$_3$)$_3$**), 20.1 (**Si<u>C</u>(CH$_3$)$_3$**) ppm. One aromatic carbon signal not observed due to overlapping signals.

HRMS (MALDI$^+$): calculated for $C_{34}H_{45}O_5SSi^+$ ($[M+H]^+$) *m/z*: 593.27515, found: 593.27693.

Phenyl 2,3-di-*O*-benzyl-4,6-*O*-di-isopropylsilylene-β-D-thioglucopyranoside (3)



To a solution of **1** (401 mg, 0.885 mmol, 1 equiv) and NaI (417 mg, 2.78 mmol, 3 equiv) in anhydrous MeCN (8 ml) was added 2,6-lutidine (0.31 ml, 2.8 mmol, 3 equiv) while stirring at rt, followed by addition of $^{i}Pr_2SiCl_2$ (0.17 ml, 0.94 mmol, 1.05 equiv). The flask was then fitted with a reflux condenser and the reaction was stirred at 50 °C (oil bath) for 16 hours. The heating was terminated and once the reaction had cooled to rt it was quenched by the addition of MeOH (1 ml). The mixture was then diluted with EtOAc (15 ml), and the organic phase was washed with H_2O (1 x 15 ml), $Na_2S_2O_3$ (10% aqueous solution, 1 x 15 ml), H_2O (2 x 15 ml), and brine (1 x 15 ml). The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The mixture was purified by flash column chromatography (1:3 EtOAc/heptane) to yield **3** as a colorless syrup (440 mg, 0.780 mmol, 88%).

R_F = 0.84 (1:1 EtOAc/heptane)

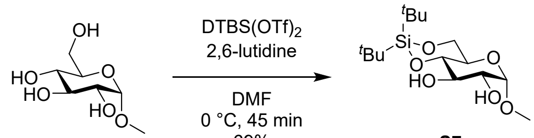
$[\alpha]^{24}_D$ -10 (c 0.758 in $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 -7.49 (2H, m, **arom.**), 7.41 – 7.39 (2H, m, **arom.**), 7.37 – 7.27 (11H, m, **arom.**), 4.98 (1H, d, *J* = 11.0 Hz, **C<u>H</u>$_2$Ph**), 4.84 – 4.77 (3H, m, **C<u>H</u>$_2$Ph**), 4.70 (1H, d, *J* = 9.8 Hz, **H1**), 4.19 (1H, dd, *J* = 10.3, 5.0 Hz, **H6**), 3.92 – 3.86 (2H, m, **H4**, **H6**), 3.62 (1H, t, *J* = 8.7 Hz, **H3**), 3.44 – 3.35 (2H, m, **H2**, **H5**), 1.10 (7H, br. s, **Si-*i*Pr**), 1.00 – 0.98 (7H, m, **Si-*i*Pr**) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 138.3, 133.5, 132.4, 129.1, 128.5, 128.5, 128.4, 128.3, 127.9, 127.9, 127.9, 88.3 (**C1**), 86.1 (**C3**), 80.1 (**C2**), 77.6 (**C4**), 75.9 (**<u>C</u>H$_2$Ph**), 75.8 (**<u>C</u>H$_2$Ph**), 75.0 (**C5**), 66.1 (**C6**), 17.2 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.1 (**(<u>C</u>H$_3$)$_2$CHSi**), 16.7 (**(<u>C</u>H$_3$)$_2$CHSi**), 16.7 (**(<u>C</u>H$_3$)$_2$CHSi**), 13.1 (**Si<u>C</u>H(CH$_3$)$_2$**), 11.9 (**Si<u>C</u>H(CH$_3$)$_2$**) ppm.

HRMS (ESP$^+$): calculated for $C_{32}H_{41}O_5SSi^+$ ($[M+H]^+$) *m/z*: 565.24385, found: 565.24455.

Methyl 4,6-*O*-di-*tert*-butylsilylene-α-D-glucopyranoside (S7)



S7

To a stirred solution of methyl α-D-glucopyranoside (1.078 g, 5.552 mmol, 1.01 equiv) in anhydrous DMF (50 ml) was added 2,6-lutidine (1.80 ml, 15.5 mmol, 3 equiv) while cooling the flask to 0 °C with an ice bath. Then DTBS(OTf)$_2$ (1.80 ml, 5.52 mmol, 1 equiv) was added dropwise. The reaction was stirred at 0 °C for 45 minutes after which it was quenched with MeOH (1 ml, 24 mmol) and allowed to reach rt. The mixture was diluted with EtOAc (80 ml) and washed with H_2O (5 x 75 ml) and brine (1 x 75 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (1:2 EtOAc/heptane) yielded **S7** (1.2745 g, 3.81 mmol, 69%) as a white foam.

R_F = 0.15 (1:1 EtOAc/heptane)

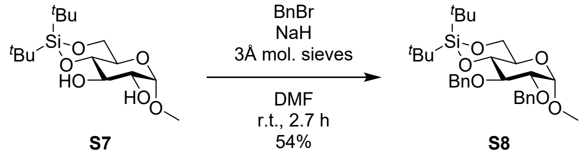
NMR is in accordance with litterature.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.73 (1H, d, *J* = 4.0 Hz, **H1**), 4.11 (1H, dd, *J* = 10.0, 4.8 Hz, **H6**), 3.87 (1H, t, *J* = 10.0 Hz, **H6**), 3.73 – 3.57 (4H, m, **H2-5**), 3.45 (3H, s, **CH_3O**), 2.70 (1H, d, *J* = 1.5 Hz, **C3-OH**), 2.19 (1H, d, *J* = 8.9 Hz, **C2-OH**), 1.06 (9H, s, **$(CH_3)_3CSi$**), 1.00 (9H, s, **$(CH_3)_3CSi$**) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 99.6 (**C1**), 77.3, 74.8, 72.3, 66.7 (**C6**), 66.2, 55.9 (**CH_3O**), 27.6 (**$(\underline{C}H_3)_3CSi$**), 27.1 (**$(\underline{C}H_3)_3CSi$**), 22.9 (**$Si\underline{C}(CH_3)_3$**), 20.1 (**$Si\underline{C}(CH_3)_3$**) ppm.

HRMS (ESP$^+$): calculated for $C_{15}H_{31}O_6Si^+$ ($[M+H]^+$) *m/z*: 335.18844, found: 335.18902.

Methyl 2,3-di-*O*-benzyl-4,6-*O*-di-*tert*-butylsilylene-α-D-glucopyranoside (S8)



To a solution of DTBS acetal **S7** (202 mg, 0.604 mmol, 1 equiv) in anhydrous DMF (5 ml) was added powdered 3Å molecular sieves after which BnBr (0.25 ml, 2.1 mmol, 3.5 equiv) was added at rt. Then NaH (60% in mineral oil, 3 x 20 mg, 1.5 mmol, 2.5 equiv) was added in portions in 20-minute intervals while stirring at rt. After 30 minutes BnBr (0.15 ml, 1.3 mmol, 2.2 equiv) was added and NaH (60% in mineral oil, 2 x 30 mg, 1.5 mmol, 2.5 equiv) was added in portions in 20-minute intervals. The reaction was stirred at rt for 30 minutes after which it was quenched with Et_3N (0.50 ml, 3.6 mmol). The mixture was filtered through a Celite plug and the plug was flushed (60 ml, 2:1 EtOAc/heptane). The mixture was then washed with H_2O (5 x 50 ml) and brine (1 x 50 ml), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (1:8 EtOAc/heptane) yielded **S8** as a colorless syrup (166.4 mg, 0.323 mmol, 54%).

R_F = 0.21 (1:8 EtOAc/heptane)

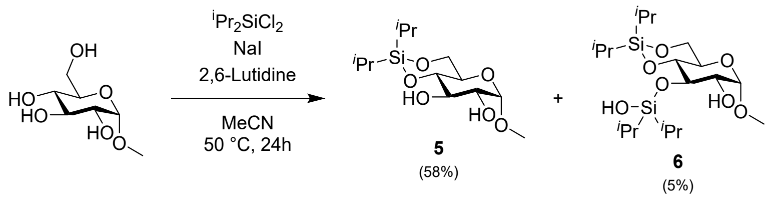
$[\alpha]^{24}_D$ -4.1 (c 0.292 in $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.41 (2H, m, **arom.**), 7.36 – 7.27 (8H, m, **arom.**), 4.97 (1H, d, J = 11.0 Hz, **C<u>H</u>$_2$Ph$_a$**), 4.84 (2H, 2x d, J_a = 11.0 Hz, J_b = 12.1 Hz, **C<u>H</u>$_2$Ph$_{a,b}$**), 4.66 (1H, d, J = 12.1 Hz, **C<u>H</u>$_2$Ph$_b$**), 4.54 (1H, d, J = 3.8 Hz, H1), 4.08 (1H, dd, J = 9.9, 4.8 Hz, **H6**), 3.86 – 3.80 (3H, m, **H3**, **H4**, **H6**), 3.73 (1H, ddd, J = 13.3, 8.5, 4.8 Hz, **H5**), 3.47 – 3.44 (1H, m, **H2**), 3.39 (3H, s, **CH_3O**), 1.08 (9H, s, **$(CH_3)_3C_aSi$**), 1.01 (9H, s, **$(CH_3)_3C_bSi$**) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 138.5, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 99.1 (**C1**), 82.0, 78.8 (C2), 78.5, 75.9 (**<u>C</u>H$_2$Ph$_a$**), 73.9 (**<u>C</u>H$_2$Ph$_b$**), 67.0 (**C6**), 66.3 (**C5**), 55.6 (**CH_3O**), 27.6 (**(<u>C</u>H$_3$)$_3$C$_a$Si**), 27.2 (**(<u>C</u>H$_3$)$_3$C$_b$Si**), 22.8 (**Si<u>C</u>(CH$_3$)$_3$**), 20.1 (**Si<u>C</u>(CH$_3$)$_3$**) ppm.

HRMS (MALDI$^+$): calculated for $C_{29}H_{42}O_6SiNa^+$ ($[M+Na]^+$) m/z: 537.26429, found: 537.26469.

Methyl 4,6-*O*-di-isopropylsilylene-α-D-glucopyranoside (5) / Methyl 3-*O*-hydroxy-di-isopropylsilyl-4,6-*O*-di-isopropylsilylene-α-D-glucopyranoside (6)



Methyl α-D-glucopyranoside (129 mg, 0.663 mmol, 1.2 equiv) and NaI (449 mg, 3.00 mmol, 5.4 equiv) were suspended in anhydrous MeCN (5 ml). Then 2,6-lutidine (0.17 ml, 1.5 mmol, 2.5 equiv) was added while stirring at rt, followed by addition of $^iPr_2SiCl_2$ (0.10 ml, 0.55 mmol, 1 equiv). The flask was fitted with a reflux condenser and stirred while heating to 50 °C (oil bath) for 24 hours. Then the heating was terminated, and the reaction allowed to cool to rt after which the reaction was quenched by addition of MeOH (1 ml, 24 mmol). The mixture was diluted with EtOAc (10 ml), washed with sat. aqueous $NaHCO_3$ (1 x 10 ml), aqueous $Na_2S_2O_3$ (10% solution, 1 x 10 ml), H_2O (1 x 10 ml) and brine (1 x 10 ml). The organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash column chromatography (1:3 EtOAc/heptane then 1:1 EtOAc/heptane) yielded **5** as a white powdery solid (97 mg, 0.32 mmol, 58%) and **6** as a colorless syrup (13 mg, 30 μmol, 5%).

R_F(**5**) = 0.91 (65:35 $CHCl_3$/MeOH), R_F(**6**) = 0.98 (65:35 $CHCl_3$/MeOH)

$[\alpha]^{24}_D$(**5**) 83.9 (c 0.412 in $CHCl_3$)

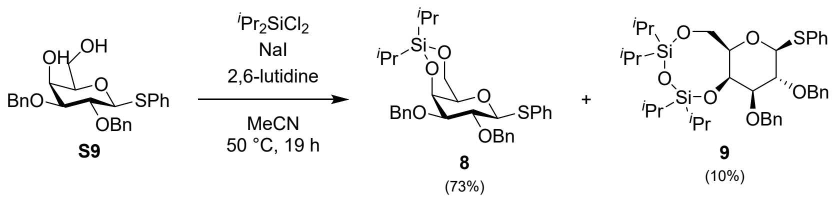
^1H NMR (**5**) (500 MHz, $CDCl_3$) δ 4.73 (1H, d, *J* = 3.9 Hz, **H1**), 4.11 – 4.08 (1H, m, **H6**), 3.87 – 3.83 (1H, m, **H6**), 3.72 (1H, app. br. t, *J* = 8.3 Hz, **H3**), 3.66 – 3.55 (3H, m, **H2**, **H4**, **H5**), 3.45 (3H, s, **CH_3O**), 2.70 (1H, d, *J* = 1.7 Hz, **C3-OH**), 2.19 (1H, d, *J* = 9.1 Hz, **C2-OH**), 1.09 – 1.06 (7H, m, **Si-^{i}Pr**), 1.02 – 0.99 (7H, m, **Si-^{i}Pr**) ppm.
^{13}C NMR (**5**) (126 MHz, $CDCl_3$) δ 99.6 (**C1**), 74.7 (**C3**), 72.3 (**C2/4/5**), 66.8, 66.3 (**C6**), 55.8 (**CH_3O**), 17.2 (**($\underline{C}H_3)_2CHSi$**), 16.7 (**($\underline{C}H_3)_2CHSi$**), 16.6 (**($\underline{C}H_3)_2CHSi$**), 13.2 (**$Si\underline{C}H(CH_3)_2$**), 11.9 (**$Si\underline{C}H(CH_3)_2$**) ppm. One C missing due to overlap with solvent peak.

^1H NMR (**6**) (500 MHz, $CDCl_3$) δ 4.74 (1H, d, *J* = 3.9 Hz, **H1**), 4.12 – 4.09 (1H, m, **H6**), 3.95 – 3.92 (1H, m, **H3**), 3.86 – 3.82 (1H, m, **H6**), 3.66 – 3.63 (2H, m, **H4**, **H5**), 3.54 (1H, ddd, *J* = 9.0, 7.5, 3.9 Hz, **H2**), 3.44 (3H, s, **CH_3O**), 2.37 (1H, d, *J* = 7.5 Hz, **C2-OH**), 1.09 – 1.04 (20H, m, **Si-^{i}Pr**), 1.03 – 1.01 (8H, m, **Si-^{i}Pr**) ppm. Si-OH proton peak not observed.
^{13}C NMR (**6**) (126 MHz, $CDCl_3$) δ 99.6 (**C1**), 77.5 (**C4/5**), 75.2 (**C3**), 73.1 (**C2**), 66.8, 66.5 (**C6**), 55.7 (**CH_3O**), 17.3 (**($\underline{C}H_3)_2CHSi$**), 17.2 (**($\underline{C}H_3)_2CHSi$**), 17.1 (**($\underline{C}H_3)_2CHSi$**), 17.1 (**($\underline{C}H_3)_2CHSi$**), 16.6 (**($\underline{C}H_3)_2CHSi$**), 16.6 (**($\underline{C}H_3)_2CHSi$**), 13.1 (**$Si\underline{C}H(CH_3)_2$**), 12.8 (**$Si\underline{C}H(CH_3)_2$**), 12.6 (**$Si\underline{C}H(CH_3)_2$**), 11.9 (**$Si\underline{C}H(CH_3)_2$**) ppm.

HRMS (**5**) (ESP^+): calculated for $C_{13}H_{27}O_6Si^+$ ($[M+H]^+$) *m/z*: 307.15714, found: 307.15727.

HRMS (**6**) (ESP$^+$): calculated for $C_{19}H_{41}O_7Si_2Na^+$ ([M+Na]$^+$) *m/z*: 459.22048, found: 459.22129.

Phenyl 2,3-di-*O*-benzyl-4,6-*O*-di-isopropylsilylene-β-D-thiogalactopyranoside (8) / Phenyl 2,3-di-*O*-benzyl-4,6-*O*-(1,1,3,3-tetra-isopropyl-1,3-disiloxane-1,3-diyl)-β-D-thiogalactopyranoside (9)



To a solution of **S9** (202 mg, 0.446 mmol, 1 equiv) and NaI (219 mg, 1.46 mmol, 3 equiv) in anhydrous MeCN (4 ml) was added 2,6-lutidine (0.16 ml, 1.4 mmol, 3 equiv) while stirring at rt, followed by addition of ^{i}Pr$_2$SiCl$_2$ (0.09 ml, 0.5 mmol, 1.05 equiv). The reaction was stirred at 50 °C (oil bath) for 19 hours. The heating was terminated and once the reaction had cooled to rt it was quenched by addition of MeOH (1 ml). The mixture was then diluted with EtOAc (15 ml), and the organic phase was washed with H_2O (1 x 15 ml), $Na_2S_2O_3$ (10% aqueous solution, 1 x 15 ml), H_2O (2 x 15 ml), and brine (1 x 15 ml). The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The mixture was purified by automated column chromatography (12g silica, 8-100% EtOAc/heptane) to yield **8** as a colorless syrup (182.8 mg, 0.324 mmol, 73%) and **9** as colorless syrup (31.9 mg, 45.9 µmol, 10%).

R_F(**8**) = 0.23 (1:5 EtOAc/heptane), R_F(**9**) = 0.48 (1:5 EtOAc/heptane)

$[\alpha]^{24}_D$(**8**) -8.6 (c 0.375 in $CHCl_3$)

^{1}H NMR (**8**) (500 MHz, $CDCl_3$) δ 7.57 – 7.54 (2H, m, **arom.**), 7.45 – 7.43 (2H, m, **arom.**), 7.41 – 7.39 (2H, m, **arom.**), 7.37 – 7.22 (9H, m, **arom.**), 4.89 (2H, s, **C<u>H</u>$_2$Ph$_a$**), 4.75 (2H, app. d, **C<u>H</u>$_2$Ph$_b$**), 4.64 (1H, d, *J* = 9.9 Hz, **H1**), 4.39 (1H, d, *J* = 2.9 Hz, **H4**), 4.20 (1H, dd, *J* = 12.3, 1.7 Hz, **H6**), 4.13 (1H, dd, *J* = 12.3, 2.3 Hz, **H6**), 3.85 (1H, app. t, *J* = 9.4 Hz, **H2**), 3.48 (1H, dd, *J* = 9.0, 2.9 Hz, **H3**), 3.30 (1H, app. br. t, *J* = 2.3 Hz, **H5**), 1.16 – 1.15 (3H, m, **Si-*i*Pr**), 1.11 – 1.09 (11H, m, **Si-*i*Pr**) ppm.
^{13}C NMR (**8**) (126 MHz, $CDCl_3$) δ 138.6, 138.4, 134.5, 132.5, 128.9, 128.6, 128.5, 128.5, 128.0, 127.9, 127.9, 127.5, 88.6 (**C1**), 83.0 (**C3**), 77.2 (**C2**), 76.1 (**<u>C</u>H$_2$Ph$_a$**), 75.1 (**C5**), 71.7 (**<u>C</u>H$_2$Ph$_b$**), 70.1 (**C4**), 67.0 (**C6**), 17.4 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.3 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.2 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.0 (**(<u>C</u>H$_3$)$_2$CHSi**), 14.0 (**Si<u>C</u>H(CH$_3$)$_2$**), 12.7 (**Si<u>C</u>H(CH$_3$)$_2$**) ppm.

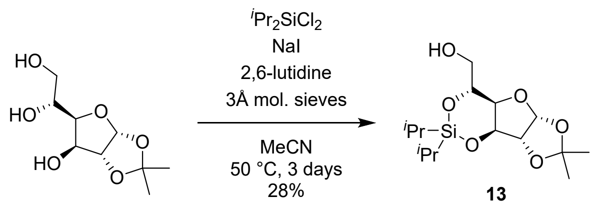
^{1}H NMR (**9**) (500 MHz, $CDCl_3$) δ 7.56 – 7.54 (2H, m, **arom.**), 7.40 – 7.38 (2H, m, **arom.**), 7.34 – 7.21 (11H, m, **arom.**), 4.73 (1H, s, **<u>C</u>H$_2$Ph**), 4.72 (1H, s, **<u>C</u>H$_2$Ph**), 4.70 (2H, s, **C<u>H</u>$_2$Ph**), 4.59 (1H, d, J = 9.6 Hz, **H1**), 4.27 (1H, d, J = 2.8 Hz, **H4**), 3.88 – 3.82 (3H, m, **H2**, **H6**), 3.58 – 3.49 (2H, m, **H3**, **H5**), 1.14 – 0.97 (28H, m, **^{i}PrSi**) ppm.

^{13}C NMR (**9**) (126 MHz, $CDCl_3$) δ 138.5, 138.3, 134.1, 131.6, 129.0, 128.5, 128.4, 128.4, 128.2, 127.8, 127.7, 127.2, 87.6 (**C1**), 82.9 (**C3/5**), 77.9, 76.5 (**C2**), 75.4 (**$\underline{C}H_2Ph$**), 73.3 (**$\underline{C}H_2Ph$**), 66.6 (**C4**), 59.4 (**C6**), 17.8 (**$(\underline{C}H_3)_2CHSi$**), 17.6 (**$(\underline{C}H_3)_2CHSi$**), 17.5 (**$(\underline{C}H_3)_2CHSi$**), 17.4 (**$(\underline{C}H_3)_2CHSi$**), 17.3 (**$(\underline{C}H_3)_2CHSi$**), 17.2 (**$(\underline{C}H_3)_2CHSi$**), 17.2 (**$(\underline{C}H_3)_2CHSi$**), 14.2 (**$Si\underline{C}H(CH_3)_2$**), 13.4 (**$Si\underline{C}H(CH_3)_2$**), 12.9 (**$Si\underline{C}H(CH_3)_2$**), 12.6 (**$Si\underline{C}H(CH_3)_2$**) ppm.

HRMS (**8**) (ESP$^+$): calculated for $C_{32}H_{41}O_5SSi^+$ ($[M+H]^+$) *m/z*: 565.24385, found: 565.24624.

HRM (**9**) (MALDI$^+$): calculated for $C_{38}H_{55}O_6SSi_2^+$ ($[M+H]^+$) *m/z*: 695.32524, found: 695.32684.

1,2-*O*-isopropylidene-3,5-*O*-di-isopropylsilylene-α-D-glucofuranose (13)



1,2-*O*-isopropylidene-α-D-glucofuranose (397 mg, 1.80 mmol, 1 equiv), NaI (812 mg, 5.41 mmol, 3 equiv), and 3Å molecular sieves were suspended in anhydrous MeCN (8 ml). Then 2,6-lutidine (0.64 ml, 5.5 mmol, 3 equiv) was added while stirring at rt followed by addition of $^{i}Pr_2SiCl_2$ (0.34 ml, 1.9 mmol, 1.05 equiv). The reaction was stirred at 50 °C (oil bath) for 3 days. The heating was terminated and once the reaction had cooled to rt it was quenched by addition of MeOH (1 ml). The mixture was then diluted with EtOAc (15 ml) and filtered through a Celite plug and flushed with EtOAc. The organic phase was washed with H_2O (1 x 25 ml), $Na_2S_2O_3$ (10%, 2 x 20 ml), H_2O (2 x 20 ml), and brine (2 x 20 ml). The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by automated column chromatography (12g silica, 22-100% EtOAc/heptane) yielded **13** as a colorless syrup (169 mg, 0.508 mmol, 28%).

R_F = 0.61 (1:1 EtOAc/heptane)

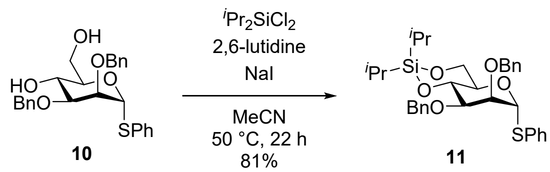
$[\alpha]^{24}_D$ 22.3 (c 0.826 in $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (1H, d, J = 3.8 Hz, **H1**), 4.54 (1H, d, J = 3.8 Hz, **H2**), 4.43 (1H, d, J = 2.7 Hz, **H3**), 4.32 (1H, ddd, J = 7.0, 4.2, 2.3 Hz, **H5**), 4.08 (1H, app. t, J = 2.5 Hz, **H4**), 3.76 (1H, ddd, J = 11.3, 7.9, 4.2 Hz, **H6**), 3.67 (1H, ddd, J = 11.3, 7.0, 4.5 Hz, **H6**), 2.02 (1H, dd, J = 7.9, 4.5 Hz, **C6-OH**), 1.48 (3H, s, **$C(CH_3)_{2,a}$**), 1.32 (3H, s, **$C(CH_3)_{2,b}$**), 1.03 – 1.01 (14H, m, **Si-^{i}Pr**) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 111.8 (**<u>C</u>(CH$_3$)$_2$**), 104.4 (**C1**), 86.0 (**C2**), 77.9 (**C4**), 76.1 (**C3**), 73.3 (**C5**), 65.5 (**C6**), 26.8 (**(<u>C</u>H$_3$)$_2$C$_a$**), 26.3 (**(<u>C</u>H$_3$)$_2$C$_b$**), 17.0 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.0 (**(<u>C</u>H$_3$)$_2$CHSi**), 16.9 (**(<u>C</u>H$_3$)$_2$CHSi**), 16.8 (**(<u>C</u>H$_3$)$_2$CHSi**), 13.3 (**Si<u>C</u>H(CH$_3$)$_2$**), 13.2 (**Si<u>C</u>H(CH$_3$)$_2$**) ppm.

HRMS (MALDI$^+$): calculated for $C_{15}H_{28}O_6SiNa^+$ ([M+Na]$^+$) *m/z*: 355.15474, found: 355.15536.

Phenyl 2,3-di-*O*-benzyl-4,6-*O*-di-isopropylsilylene-α-D-thiomannopyranoside (11)



To a solution of the diol **10** (103 mg, 228 µmol, 1 equiv) and NaI (137 mg, 911 µmol, 4 equiv) in anhydrous MeCN (3 ml) was added 2,6-lutidine (79 µl, 239 µmol, 3 equiv) at rt, followed by addition of iPr_2SiCl_2 (44 µl, 239 µmol, 1.05 equiv) and the reaction was heated to 50 °C (aluminum block) while stirring for 20 hours. The heating was terminated and once the reaction had cooled to rt it was quenched by the addition of MeOH (1 ml). The mixture was then diluted with EtOAc (15 ml), and the organic phase was washed with H_2O (1 x 15 ml), $Na_2S_2O_3$ (10% aqueous solution, 1 x 15 ml), H_2O (2 x 15 ml), and brine (1 x 15 ml). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography (0-100% EtOAc/heptane) yielded **11** as a colorless syrup (104 mg, 911 µmol, 81%)

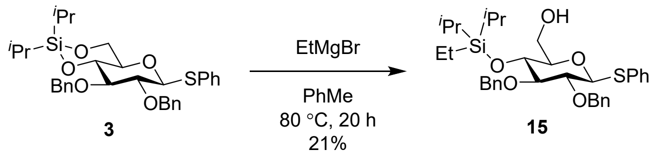
R_F = 0.82 (1:1 EtOAc/heptane)

^{1}H NMR (500 MHz, CDCl3) δ 7.51 – 7.08 (15H, m, **arom.**), 5.43 (1H, d, *J* = 1.7 Hz, **H1**), 4.88 (1H, d, *J* = 12.3 Hz, **CH$_2$Ph**), 4.77 – 4.65 (3H, m, **CH$_2$Ph**), 4.39 (1H, td, *J* = 9.4, 1.5 Hz, **H4**), 4.10 (1H, td, *J* = 9.7, 4.5 Hz, **H5**), 4.07 – 4.00 (1H, m, **H6**), 3.99 – 3.97 (2H, m, **H2, H6**), 3.69 (1H, dd, *J* = 9.4, 3.1 Hz, **H3**), 1.15 – 0.95 (14H, m, **Si-^{i}Pr**) ppm.

^{13}C NMR (126 MHz, CDCl3) δ 139.0, 138.1, 134.3, 131.4, 129.3, 128.5, 128.4, 128.2, 127.9, 127.7, 127.6, 127.6, 87.0 (**C1**), 78.8 (**C3**), 78.0 (**C2**), 75.0 (**C4**), 73.4 (**<u>C</u>H$_2$Ph**), 72.9 (**<u>C</u>H$_2$Ph**), 69.7 (**C5**), 66.2(**C6**), 17.2 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.2(**(<u>C</u>H$_3$)$_2$CHSi**), 16.9 (**(<u>C</u>H$_3$)$_2$CHSi**), 16.8 (**(<u>C</u>H$_3$)$_2$CHSi**), 13.2 (**Si<u>C</u>H(CH$_3$)$_2$**), 12.1 (**Si<u>C</u>H(CH$_3$)$_2$**) ppm.

HRMS (MALDI$^+$): calculated for $C_{32}H_{40}O_5SSi^+$ ([M+H]$^+$) m/z: 565.24385, found: 565.24139.

Phenyl 2,3-di-*O*-benzyl-4-*O*-ethyl-di-isopropylsilyl-β-D-thioglucopyranoside (15)



To a solution of **3** (99 mg, 0.175 mmol, 1 equiv) in anhydrous THF (0.4 ml) under an Ar atmosphere was added EtMgBr (1 M in THF, 0.90 ml, 0.90 mmol, 5 equiv) and the reaction was stirred for 5 minutes. Then the solvent was evaporated by a stream of dry N_2 gas followed by addition of anhydrous PhMe (1.0 ml), and the reaction was stirred at 80 °C (aluminium block) for 20 hours after which the heating was terminated. Once the reaction had cooled to rt it was quenched by addition of saturated NH_4Cl (aq) (1 ml). The mixture was diluted with PhMe (5 ml) and the organic phase washed with H_2O (2 x 5 ml) and brine (2 x 5 ml), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by automated column chromatography (4g silica, 0-100% EtOAc/heptane) yielded **15** as a colorless syrup (22 mg, 37 μmol, 21%).

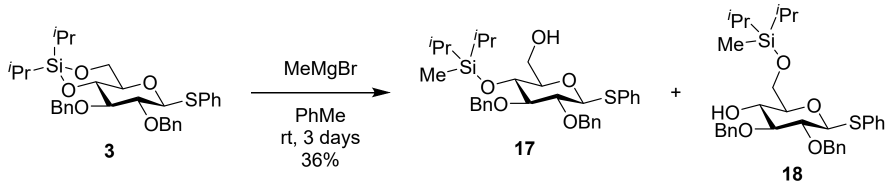
R_F = 0.39 (1:1 EtOAc/heptane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.49 (2H, m, **arom.**), 7.34 – 7.27 (13H, m, **arom.**), 5.06 (1H, d, *J* = 11.7 Hz, **C<u>H</u>$_2$Ph$_a$**), 4.91 (1H, d, *J* = 10.1. Hz, **C<u>H</u>$_2$Ph$_b$**), 4.81 – 4.77 (1H, m, **H1**), 4.72 (1H, d, *J* = 11.7 Hz, **C<u>H</u>$_2$Ph$_a$**), 4.61 (1H, d, *J* = 10.1. Hz, **C<u>H</u>$_2$Ph$_b$**), 3.89 (1H, ddd, *J* = 11.8, 7.0, 2.8 Hz, **H6**), 3.77 – 3.69 (2H, m, **H3/4**, **H6**), 3.54 – 3.49 (2H, m, **H2**, **H3/4**), 3.37 (1H, ddd, *J* = 9.0, 6.0, 2.8 Hz, **H5**), 1.95 (1H, t, *J* = 7.0 Hz, **C6-OH**), 1.00 – 0.93 (17H, m, **Si-^{i}Pr**, **C<u>H</u>$_3$CH$_2$Si**), 0.63 (2H, q, *J* = 7.6, 7.4 Hz, **SiC<u>H</u>$_2$CH$_3$**) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 137.8, 134.0, 131.6, 129.2, 128.5, 128.3, 128.3, 128.0, 127.7, 127.3, 126.7, 87.7 (**C1**), 86.7 (**C2/3/4**), 82.0, 81.0 (**C5**), 75.3 (**<u>C</u>H$_2$Ph$_b$**), 74.9 (**<u>C</u>H$_2$Ph$_a$**), 71.1, 62.6 (**C6**), 18.0 (**(<u>C</u>H$_3$)$_2$CHSi**), 18.0 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.9 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.9 (**(<u>C</u>H$_3$)$_2$CHSi**), 13.2 (**Si<u>C</u>H(CH$_3$)$_2$**), 12.8 (**Si<u>C</u>H(CH$_3$)$_2$**), 7.5 (**<u>C</u>H$_3$CH$_2$Si**), 3.5 (**Si<u>C</u>H$_2$CH$_3$**) ppm.

HRMS (MALDI$^+$): calculated for $C_{34}H_{46}O_5SSiNa^+$ ($[M+Na]^+$) *m/z*: 617.27274, found: 617.27411.

Phenyl 2,3-di-*O*-benzyl-4-*O*-di-isopropylmethylsilyl-β-D-thioglucopyranoside (17) / Phenyl 2,3-di-*O*-benzyl-6-*O*-di-isopropylmethylsilyl-β-D-thioglucopyranoside (18)



To a solution of **3** (103 mg, 0.183 mmol, 1 equiv) in anhydrous THF (0.4 ml) under an Ar atmosphere was added MeMgBr (3.0 M in Et_2O, 0.3 ml, 0.9 mmol, 5 equiv) and the reaction stirred at rt for 10 minutes. Then the solvents were evaporated by a stream of dry N_2 gas followed by addition of anhydrous PhMe (1.0 ml), and the reaction was stirred at rt for 3 days after which it was quenched by addition of saturated NH_4Cl (aq) (1 ml). The mixture was diluted with PhMe (4 ml) and the organic phase was washed with H_2O (2 x 5 ml) and brine (2 x 5 ml), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by automated column chromatography (4g silica, 0-100% EtOAc/heptane) yielded a mixture of **17** and **18** as a colorless syrup (38 mg, 65.2 μmol, 36%) in a ratio ≥1:0.3 of **17** to **18**.

R_F = 0.44 (1:1 EtOAc/heptane)

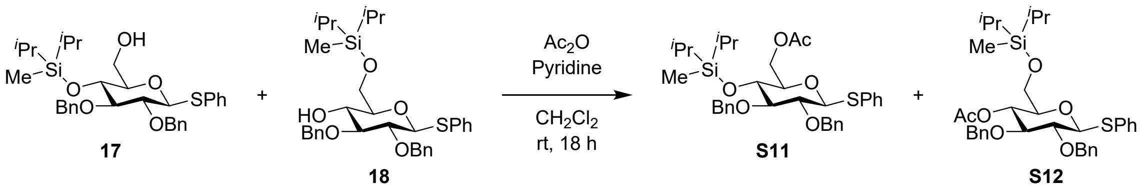
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.50 (2H, m, **arom.**), 7.42 – 7.40 (1H, m, **arom.**), 7.37 – 7.27 (12H, m, **arom.**), 5.02 (1H, d, *J* = 11.7 Hz, **C<u>H</u>$_2$Ph$_a$**), 4.96 (1H, d, *J* = 10.1 Hz, **C<u>H</u>$_2$Ph***), 4.90 (1H, d, *J* = 10.1 Hz, **C<u>H</u>$_2$Ph$_b$**), 4.78 – 4.75 (2H, m, **C<u>H</u>$_2$Ph$_a$**, **H1**), 4.63 (1H, d, *J* = 10.1 Hz, **C<u>H</u>$_2$Ph$_b$**), 3.88 (1H, dd, *J* = 11.7, 2.7 Hz, **H6**), 3.74 – 3.68 (2H, m, **H3/4**, **H6**), 3.54 – 3.48 (2H, m, **H2**, **H3/H4**), 3.35 (1H, tt, *J* = 6.0, 2.7 Hz, **H5**), 0.97 (7H, app. d, *J* = 4.4 Hz, **Si-^{i}Pr**), 0.92 (7H, app. d, *J* = 3.9 Hz, **Si-^{i}Pr**), 0.01 (3H, s, **SiCH$_3$**)

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 138.4, 137.9, 137.9, 133.9, 133.7, 131.9, 131.6, 129.2, 128.9, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 127.7, 127.3, 126.8, 87.9 (*****), 87.7 (**C1**), 86.8 (**C2/3/4**), 86.2 (*****), 81.8, 81.0 (*****), 80.9 (**C5**), 79.3 (*****), 75.6 (*****), 75.6 (*****), 75.4 (**<u>C</u>H$_2$Ph**), 75.2 **<u>C</u>H$_2$Ph**, 71.1, 70.6 (*****), 62.9 (*****), 62.5 (**C6**), 17.9 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.8 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.7 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.6 (**(<u>C</u>H$_3$)$_2$CHSi**), 13.7 (**Si<u>C</u>H(CH$_3$)$_2$**), 13.3 (**Si<u>C</u>H(CH$_3$)$_2$**), -7.0 (**SiCH$_3$**) ppm.

The * designates NMR signals resulting from the minor product, the **18** regioisomer.

HRMS (ESP$^+$): calculated for $C_{33}H_{45}O_5SSi^+$ ([M+H]$^+$) *m/z*: 581.27515, found: 581.27917.

Phenyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-di-isopropylmethylsilyl-β-D-thioglucopyranoside (S11) / Phenyl 4-*O*-acetyl-2,3-di-*O*-benzyl-6-*O*-di-isopropylmethylsilyl-β-D-thioglucopyranoside (S12)



The mixture of **17** and **18** (38 mg, 65 μmol) was dissolved in CH_2Cl_2 (1 ml) and then Ac_2O (0.50 ml, 5.2 mmol) and pyridine (0.50 ml, 6.2 mmol) was added while stirring at rt. The reaction was stirred at rt for 18 hours after which it was co-evaporated multiple times with PhMe to remove reagents. Yield not calculated.

R_F = 0.52 (1:1 EtOAc/heptane)

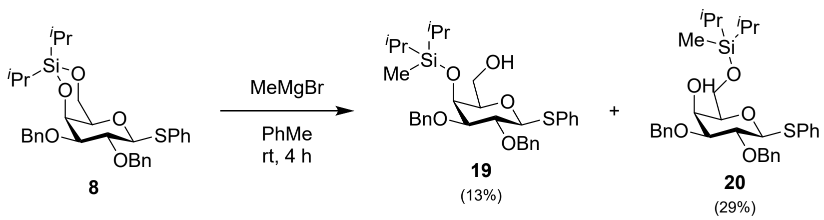
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.53 (2H, m, **arom.**), 7.40 – 7.39 (1H, m, **arom.**), 7.35 – 7.24 (12H, m, **arom.**), 5.05 – 5.01 (1H, m, **C<u>H</u>$_2$Ph$_a$**), 4.91 (1H, d, *J* = 10.0 Hz, **C<u>H</u>$_2$Ph$_b$**), 4.82 (1H, d, *J* = 11.4 Hz, **C<u>H</u>$_2$Ph***), 4.75 – 4.70 (2H, m, **C<u>H</u>$_2$Ph$_a$**, **H1**), 4.66 (1H, d, *J* = 9.8 Hz, **C<u>H</u>$_2$Ph***), 4.61 (1H, d, *J* = 10.0 Hz, **C<u>H</u>$_2$Ph$_b$**), 4.46 (1H, dd, *J* = 11.8, 2.2 Hz, **H6**), 4.14 (1H, dd, *J* = 11.8, 6.2 Hz, **H6**), 3.76 – 3.72 (1H, m, **H3/4**), 3.52 – 3.47 (3H, m, **H2**, **H5**), 2.08 (3H, s, **CH_3C=O**), 2.07 (3H, s, **CH_3C=O***), 0.98 – 0.95 (7H, m, **Si-^{i}Pr**), 0.91 (7H, br. s, **Si-^{i}Pr**), -0.01 (3H, s, **$SiCH_3$**) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (**<u>C</u>(=O)CH_3**), 169.7 (**<u>C</u>(=O)CH_3***), 138.8, 138.1 (*), 137.9 (*), 137.9, 134.2, 133.3 (*), 132.4 (*), 131.8, 131.0 (*), 129.2 (*), 129.1 (*), 129.0, 128.6 (*), 128.5, 128.4 (*), 128.3, 128.3, 128.1 (*), 128.0, 128.0 (*), 127.9 (*), 127.6, 127.3, 126.8, 125.4 (*), 87.8 (**C1**), 87.7 (*), 86.7 (**C2/3/4/5**), 84.0 (*), 81.7, 80.7 (*), 78.6, 76.0 (*), 75.7 (*), 75.6 (*), 75.3 (**<u>C</u>H$_2$Ph**), 75.1 (**<u>C</u>H$_2$Ph**), 71.3, 69.9 (*), 63.8 (**C6**), 62.8 (*), 21.0 (**<u>C</u>H$_3$C=O**), 17.9 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.7 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.7 (**(<u>C</u>H$_3$)$_2$CHSi**), 17.6 (**(<u>C</u>H$_3$)$_2$CHSi**), 13.7 (**Si<u>C</u>H(CH_3)$_2$**), 13.3 (**Si<u>C</u>H(CH_3)$_2$**), -7.0 (**$SiCH_3$**) ppm. One too many aromatic signals observed from the minor product.

The * designates NMR signals resulting from the minor product, the **S12** regioisomer.

HRMS (MALDI$^+$): calculated for $C_{35}H_{46}O_6SSiNa^+$ ($[M+Na]^+$) *m/z*: 645.26766, found: 645.26992.

Phenyl 2,3-di-*O*-benzyl-4-*O*-di-isopropylmethylsilyl-β-D-thiogalactopyranoside (19) / Phenyl 2,3-di-*O*-benzyl-6-*O*-di-isopropylmethylsilyl-β-D-thiogalactopyranoside (20)



To a solution of **8** (26 mg, 46 μmol, 1 equiv) in anhydrous THF (0.2 ml) under an Ar atmosphere was added MeMgBr (3.0 M in Et_2O, 0.08 ml, 0.24 mmol, 5 equiv) and the reaction was stirred at rt for 5 minutes. Then the solvents were evaporated by a stream of dry N_2 gas followed by addition of anhydrous PhMe (0.25 ml). The reaction was stirred at rt for 4 hours after which it was quenched by addition of saturated NH_4Cl (aq) (0.5 ml). The mixture was diluted with EtOAc (5 ml), and the organic phase was washed with H_2O (3 x 5 ml) and brine (1 x 5 ml), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (1:3 EtOAc/heptane, then 100% EtOAc) yielded **19** as a colorless syrup (3.5 mg, 6.0 μmol, 13%) and **20** as a colorless syrup (7.6 mg, 13 μmol, 29%).

R_F(**19**) = 0.53 (1:3 EtOAc/heptane), R_F(**20**) = 0.91 (1:3 EtOAc/heptane)

^{1}H NMR (**19**) (500 MHz, $CDCl_3$) δ 7.59 – 7.57 (2H, m, **arom.**), 7.38 – 7.36 (2H, m, **arom.**), 7.33 – 7.22 (11H, m, **arom.**), 4.74 – 4.67 (4H, m, **C<u>H</u>₂Ph**), 4.62 (1H, d, *J* = 9.5 Hz, **H1**), 4.09 (1H, d, *J* = 2.6 Hz, **H4**), 3.94 (1H, dd, *J* = 11.2, 7.9 Hz, **H6**), 3.87 (1H, app. t, *J* = 9.4 Hz, **H2**), 3.64 (1H, br. dd, *J* = 11.2, 4.3 Hz, **H6**), 3.50 (1H, dd, *J* = 7.9, 4.3 Hz, **H5**), 3.45 (1H, dd, *J* = 9.2 Hz, 2.6 Hz, **H3**), 1.84 (1H, br. s, **C6-OH**), 1.00 – 0.96 (7H, m, **Si-^{i}Pr**), 0.93 (7H, app. t, *J* = 6.2 Hz, **Si-^{i}Pr**), 0.00 (3H, s, **$SiCH_3$**) ppm.
^{13}C NMR (**19**) (126 MHz, $CDCl_3$) δ 138.3, 138.1, 133.9, 131.6, 129.0, 128.5, 128.4, 128.1, 127.9, 127.8, 127.3, 87.4 (**C1**), 83.7 (**C3**), 80.2 (**C5**), 75.5 (**$\underline{C}H_2Ph$**), 73.8 (**$\underline{C}H_2Ph$**), 69.7 (**C4**), 63.1 (**C6**), 18.0 (**$(\underline{C}H_3)_2CHSi$**), 17.9 (**$(\underline{C}H_3)_2CHSi$**), 17.9 (**$(\underline{C}H_3)_2CHSi$**), 17.8 (**$(\underline{C}H_3)_2CHSi$**), 14.0 (**$Si\underline{C}H(CH_3)_2$**), 13.7 (**$Si\underline{C}H(CH_3)_2$**), -6.7 (**$SiCH_3$**) ppm. Signal missing from **C2** due to overlap with solvent signal. One aromatic carbon signal not observed due to overlapping signals.

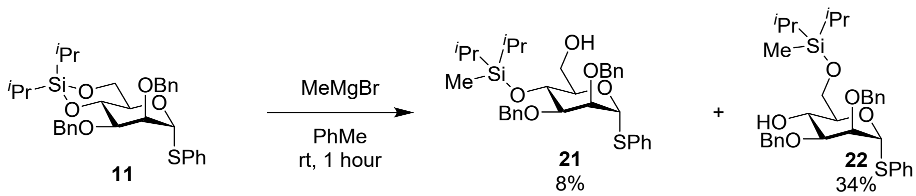
^{1}H NMR (**20**) (500 MHz, $CDCl_3$) δ 7.58 – 7.56 (2H, m, **arom.**), 7.42 – 7.40 (2H, m, **arom.**), 7.36 – 7.22 (11H, m, **arom.**), 4.82 (1H, d, *J* = 10.4 Hz, **$C\underline{H}_2Ph$**), 4.76 – 4.72 (3H, m, **$C\underline{H}_2Ph$**), 4.63 (1H, d, *J* = 9.8 Hz, **H1**), 4.12 (1H, d, *J* = 3.2 Hz, **H4**), 3.95 (1H, dd, *J* = 10.3, 6.2 Hz, **H6**), 3.88 (1H, dd, *J* = 10.3, 5.2 Hz, **H6**), 3.78 (1H, app. t, *J* = 9.4 Hz, **H2**), 3.56 (1H, dd, *J* = 8.9, 3.2 Hz, **H3**), 3.42 (1H, app. t, *J* = 5.7 Hz, **H5**), 2.72 (1H, br. s, **C4-OH**), 1.02 – 0.96 (14H, m, **Si-^{i}Pr**), 0.05 (3H, s, **$SiCH_3$**) ppm.
^{13}C NMR (**20**) (126 MHz, $CDCl_3$) δ 138.4, 138.0, 134.2, 131.9, 129.0, 128.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.4, 88.0 (**C1**), 82.9 (**C3**), 78.2 (**C5**), 75.9 (**$\underline{C}H_2Ph$**), 72.2 (**$\underline{C}H_2Ph$**),

66.9 (**C4**), 63.0 (**C6**), 17.5 ((**<u>C</u>H$_3$)$_2$CHSi**), 17.5 ((**<u>C</u>H$_3$)$_2$CHSi**), 17.5 ((**<u>C</u>H$_3$)$_2$CHSi**), 13.0 (**Si<u>C</u>H(CH$_3$)$_2$**), 13.0 (**Si<u>C</u>H(CH$_3$)$_2$**), -8.5 (**SiCH$_3$**) ppm. Signal missing from **C2** due to overlap with solvent signal.

HRMS (**19**) (MALDI$^+$): calculated for $C_{33}H_{44}O_5SSiNa^+$ ($[M+Na]^+$) *m/z*: 603.25709, found: 603.25813.

HRMS (**20**) (MALDI$^+$): calculated for $C_{33}H_{45}O_5SSi^+$ ($[M+H]^+$) *m/z*: 581.27515, found: 581.27624.

Phenyl 2,3-di-*O*-benzyl-4-*O*-di-isopropylmethylsilyl-α-D-thiomannopyranoside (21) / Phenyl 2,3-di-*O*-benzyl-6-*O*-di-isopropylmethylsilyl-α-D-thiomannopyranoside (22)



To a solution of **11** (97 mg, 172 µmol mmol, 1 equiv) in anhydrous THF (0.50 ml) under a N_2 atmosphere was added MeMgBr (3.0 M in Et_2O, 0.30 ml, 0.90 mmol, 5.2 equiv) and the reaction stirred at rt for 5 minutes. Then the solvents were evaporated by a stream of dry N_2 gas followed by addition of anhydrous PhMe (1.0 ml), and the reaction was stirred at rt for 1 hour. The reaction was then quenched by addition of sat. aq. NH_4Cl (2 ml), and then diluted with EtOAc (10 ml). The organic phase was washed with H_2O (3 x 10 ml) and brine (1 x 10 ml), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification first by flash column chromatography (1:5 EtOAc/heptane) then product containing fractions purified again by flash column chromatography (1:8 EtOAc/heptane) yielded **22** as a colorless syrup (34.1 mg, 58.7 µmol, 34%) and **21** as a colorless syrup (8.5 mg, 14.6 µmol, 8%).

R_F(**22**) = 0.61 (1:3 EtOAc/heptane)

R_F(**21**) = 0.53 (1:3 EtOAc/heptane)

^{1}H NMR (**22**) (500 MHz, $CDCl_3$) δ 7.45 (2H, dt, *J* = 5.8, 1.7 Hz, **arom.**), 7.36 – 7.25 (13H, m, **arom.**), 5.57 (1H, d, *J* = 1.6 Hz, **H1**), 4.67 (1H, d, *J* = 12.2 Hz, **C<u>H</u>$_2$Ph**), 4.61 (1H, d, *J* = 11.9 Hz, **C<u>H</u>$_2$Ph**), 4.58 (1H, d, *J* = 11.9 Hz, **C<u>H</u>$_2$Ph**), 4.55 (1H, d, *J* = 12.2 Hz, **C<u>H</u>$_2$Ph**), 4.13 – 4.08 (2H, m, **H4**, **H5**), 3.98 (1H, dd, *J* = 3.0, 1.6 Hz, **H2**), 3.95 – 3.89 (2H, m, **H6**), 3.69 (1H, dd, *J* = 9.0, 3.0 Hz, **H3**), 2.84 (1H, s, **C4-OH**), 1.02 – 0.95 (14H, m, **Si-^{i}Pr**), 0.04 (3H, s, **SiCH$_3$**) ppm.

^{13}C NMR (**22**) (126 MHz, $CDCl_3$) δ 138.2, 138.0, 134.7, 131.6, 129.1, 128.7, 128.5, 128.1, 128.0, 128.0, 127.8, 127.5, 86.0 (**C1**), 79.7 (**C3**), 76.0 (**C2**), 73.3 (**C4/5**), 72.1 (**$\underline{C}H_2Ph$**), 72.1 (**$\underline{C}H_2Ph$**), 68.9, 64.4 (**C6**), 17.5 (**$(\underline{C}H_3)_2CHSi$**), 17.5 (**$(\underline{C}H_3)_2CHSi$**), 13.0 (**$Si\underline{C}H(CH_3)_2$**), -8.5 (**$SiCH_3$**) ppm.

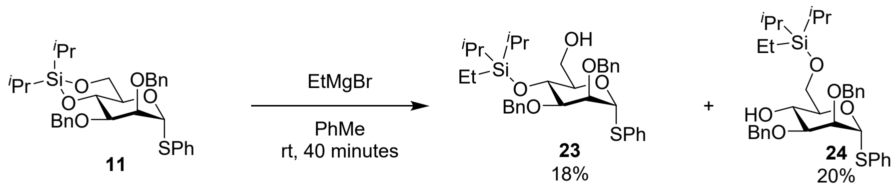
^{1}H NMR (**21**) (500 MHz, $CDCl_3$) δ 7.44 – 7.42 (2H, m, **arom.**), 7.37 – 7.25 (13H, m, **arom.**), 5.50 (1H, d, J = 2.5 Hz, **H1**), 4.61 – 4.54 (4H, m, **$C\underline{H}_2Ph$**), 4.16 (1H, t, J = 8.8 Hz, **H4**), 4.05 (1H, ddd, J = 8.8, 5.3, 2.8 Hz, **H5**), 3.96 (1H, t, J = 2.5 Hz, **H2**), 3.83 (1H, dd, J = 11.5, 2.8 Hz, **H6**), 3.77 (1H, dd, J = 11.5, 5.3 Hz, **H6**), 3.64 (1H, dd, J = 8.8, 2.5 Hz, **H3**), 1.80 (1H, s, **C6-OH**), 1.00 – 0.97 (7H, m, **Si-^{i}Pr**), 0.95 – 0.93 (7H, m, **Si-^{i}Pr**), 0.03 (3H, s, **$SiCH_3$**) ppm.

^{13}C NMR (**21**) (126 MHz, $CDCl_3$) δ 138.3, 138.2, 134.2, 132.1, 129.3, 128.5, 128.4, 127.8, 127.8, 127.8, 127.7, 86.3 (**C1**), 80.7 (**C3**), 76.3 (**C2**), 75.0 (**C5**), 72.6 (**$\underline{C}H_2Ph$**), 71.9 (**$\underline{C}H_2Ph$**), 68.3 (**C4**), 62.5 (**C6**), 17.9 (**$(\underline{C}H_3)_2CHSi$**), 17.8 (**$(\underline{C}H_3)_2CHSi$**), 17.7 (**$(\underline{C}H_3)_2CHSi$**), 17.7 (**$(\underline{C}H_3)_2CHSi$**), 13.8 (**$Si\underline{C}H(CH_3)_2$**), 13.4 (**$Si\underline{C}H(CH_3)_2$**), -7.0 (**$SiCH_3$**) ppm.

HRMS (**22**) (ESP^+): calculated for $C_{33}H_{44}O_5SSiNa^+$ ($[M+Na]^+$) *m/z*: 603.25709, found: 603.25667.

HRMS (**21**) (ESP^+): calculated for $C_{33}H_{44}O_5SSiNa^+$ ($[M+Na]^+$) *m/z*: 603.25709, found: 603.25642.

Phenyl 2,3-di-*O*-benzyl-4-*O*-ethyl-di-isopropylsilyl-α-D-thiomannopyranoside (23) / Phenyl 2,3-di-*O*-benzyl-6-*O*-ethyl-di-isopropylsilyl-α-D-thiomannopyranoside (24)



To a solution of **11** (116 mg, 206 µmol mmol, 1 equiv) in anhydrous THF (0.50 ml) under a N_2 atmosphere was added EtMgBr (1.0 M in THF, 1.0 ml, 1.0 mmol, 4.9 equiv) and the reaction stirred at rt for 5 minutes. Then the solvents were evaporated by a stream of dry N_2 gas followed by addition of anhydrous PhMe (1.0 ml), and the reaction was stirred at rt for 40 minutes. The reaction was then quenched by addition of sat. aq. NH_4Cl (2 ml), and then diluted with EtOAc (10 ml). The organic phase was washed with H_2O (3 x 10 ml) and brine (1 x 10 ml), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (1:8 EtOAc/heptane) yielded **24** as a colorless syrup (24.2 mg, 40.7 µmol, 20%) and **23** as a colorless syrup (21.6 mg, 36.3 µmol, 18%).

R_F(**24**) = 0.71 (1:3 EtOAc/heptane)

R_F(**23**) = 0.66 (1:3 EtOAc/heptane)

^{1}H NMR (**24**) (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (2H, m, **arom.**), 7.36 – 7.25 (13H, m, **arom.**), 5.56 (^{1}H, d, J = 1.6 Hz, **H1**), 4.67 (^{1}H, d, J = 12.2 Hz, **C<u>H</u>$_2$Ph**), 4.61 (2H, s, **C<u>H</u>$_2$Ph**), 4.56 (^{1}H, d, J = 12.2 Hz, **C<u>H</u>$_2$Ph**), 4.13 – 4.11 (2H, m, **H4**, **H5**), 3.98 (^{1}H, dd, J = 3.0, 1.6 Hz, **H2**), 3.96 – 3.91 (2H, m, **H6**), 3.72 – 3.69 (^{1}H, m, **H3**), 2.94 (^{1}H, s, **C4-OH**), 1.04 – 0.99 (17H, m, **Si-^{i}Pr**, **C<u>H</u>$_3$CH$_2$Si**), 0.68 (2H, q, J = 8.0 Hz, **SiC<u>H</u>$_2$CH$_3$**) ppm.

^{13}C NMR (**24**) (126 MHz, $CDCl_3$) δ 138.2, 138.0, 134.7, 131.7, 129.1, 128.6, 128.5, 128.1, 128.0, 128.0, 127.8, 127.5, 86.1 (**C1**), 79.6 (**C3**), 76.1 (**C2**), 73.2 (**C4/5**), 72.2 (**<u>C</u>H$_2$Ph**), 72.2 (**<u>C</u>H$_2$Ph**), 69.3, 64.8 (**C6**), 17.8 (**(<u>C</u>H$_3$)$_2$CHSi**), 12.4 (**Si<u>C</u>H(CH$_3$)$_2$)**), 12.3 (**Si<u>C</u>H(CH$_3$)$_2$)**), 7.3 (**<u>C</u>H$_3$CH$_2$Si**), 2.2 (**Si<u>C</u>H$_2$CH$_3$**) ppm.

^{1}H NMR (**23**) (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (2H, m, **arom.**), 7.36 – 7.25 (13H, m, **arom.**), 5.52 (^{1}H, d, J = 2.5 Hz, **H1**), 4.60 (^{1}H, d, J = 12.0 Hz, **C<u>H</u>$_2$Ph**), 4.59 (^{1}H, d, J = 11.7 Hz, **C<u>H</u>$_2$Ph**), 4.54 (^{1}H, d, J = 12.0 Hz, **C<u>H</u>$_2$Ph**), 4.53 (^{1}H, d, J = 11.7 Hz, **C<u>H</u>$_2$Ph**), 4.20 (^{1}H, t, J = 8.7 Hz, **H4**), 4.06 (^{1}H, ddd, J = 8.7, 5.3, 2.7 Hz, **H5**), 3.99 (^{1}H, t, J = 2.5 Hz, **H2**), 3.85 (^{1}H, dd, J = 11.7, 2.7 Hz, **H6**), 3.80 (^{1}H, dd, J = 11.7, 5.3 Hz, **H6**), 3.65 (^{1}H, dd, J = 8.7, 2.5 Hz, **H3**), 1.82 (^{1}H, s, **C6-OH**), 1.04 – 0.95 (17H, m, **Si-^{i}Pr**, **C<u>H</u>$_3$CH$_2$Si**), 0.69 – 0.59 (2H, m consisting of two dq, J = 11.6, 8.1, 7.6 Hz, **SiC<u>H</u>$_2$CH$_3$**) ppm.

^{13}C NMR (**23**) (126 MHz, $CDCl_3$) δ 138.3, 138.2, 134.2, 132.1, 129.3, 128.5, 128.4, 127.8, 127.8, 127.8, 127.7, 127.7, 86.2 (**C1**), 80.8 (**C3**), 76.1 (**C2**), 75.1 (**C5**), 72.5 (**<u>C</u>H$_2$Ph**), 71.7

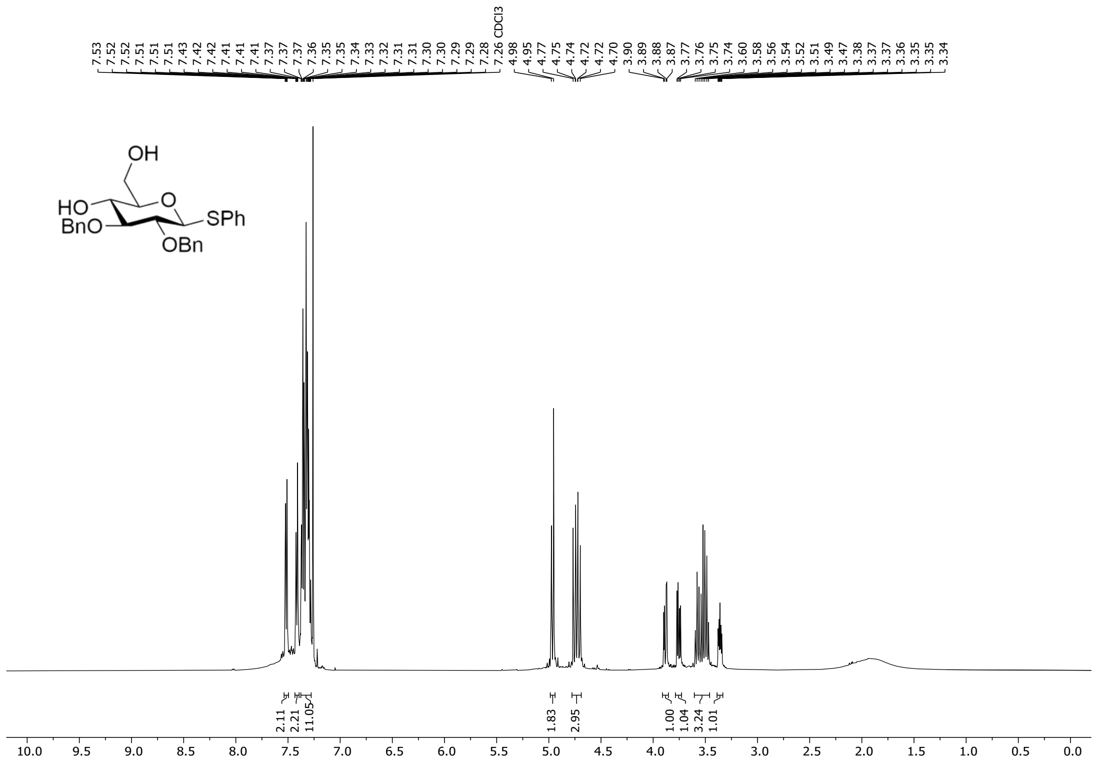
(**$\underline{C}H_2Ph$**), 68.4 (**C4**), 62.5 (**C6**), 18.1 (**($\underline{C}H_3)_2CHSi$**), 18.0 (**($\underline{C}H_3)_2CHSi$**), 18.0 (**($\underline{C}H_3)_2CHSi$**), 17.9 (**($\underline{C}H_3)_2CHSi$**), 13.1 (**$Si\underline{C}H(CH_3)_2)$**), 12.8 (**$Si\underline{C}H(CH_3)_2)$**), 7.5 (**$\underline{C}H_3CH_2Si$**), 3.4 (**$Si\underline{C}H_2CH_3$**) ppm.

HRMS (**24**) (ESP^+): calculated for $C_{34}H_{46}O_5SSiNa^+$ ($[M+Na]^+$) *m/z*: 617.27274, found: 617.27224.

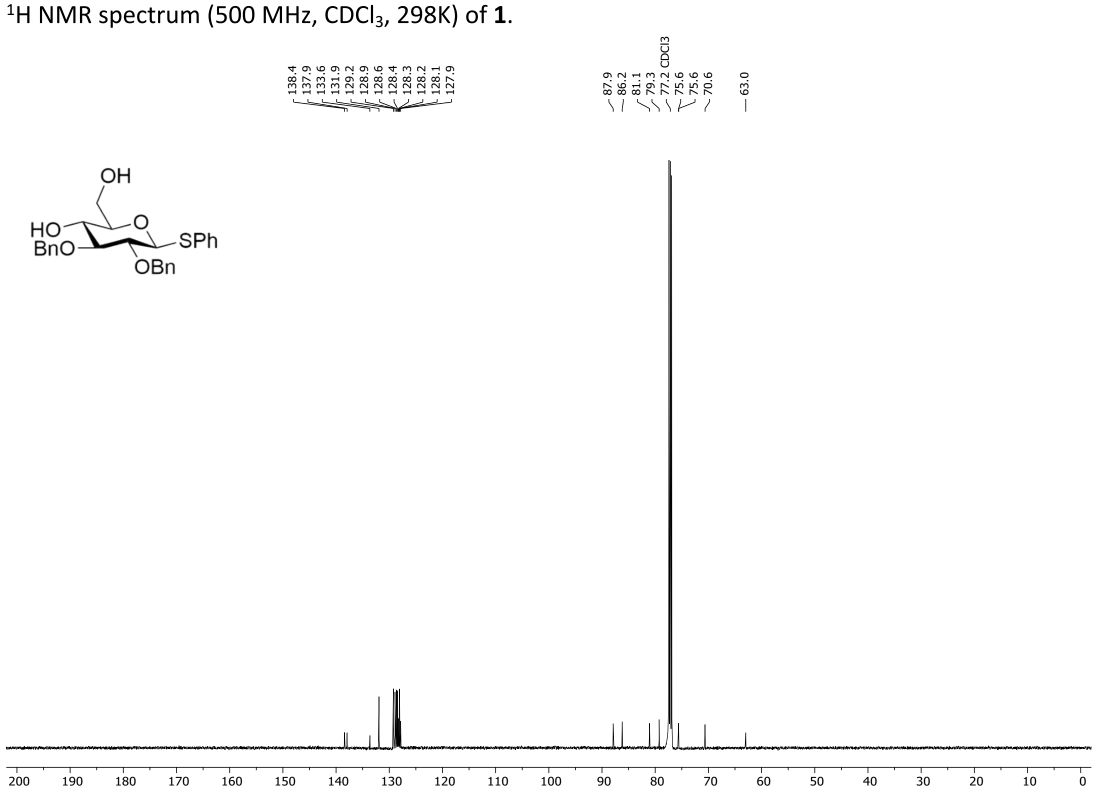
HRMS (**23**) (ESP^+): calculated for $C_{34}H_{46}O_5SSiNa^+$ ($[M+Na]^+$) *m/z*: 617.27274, found: 617.27215.

4 NMR Spectra of Characterized Compounds

NMR spectra of 1

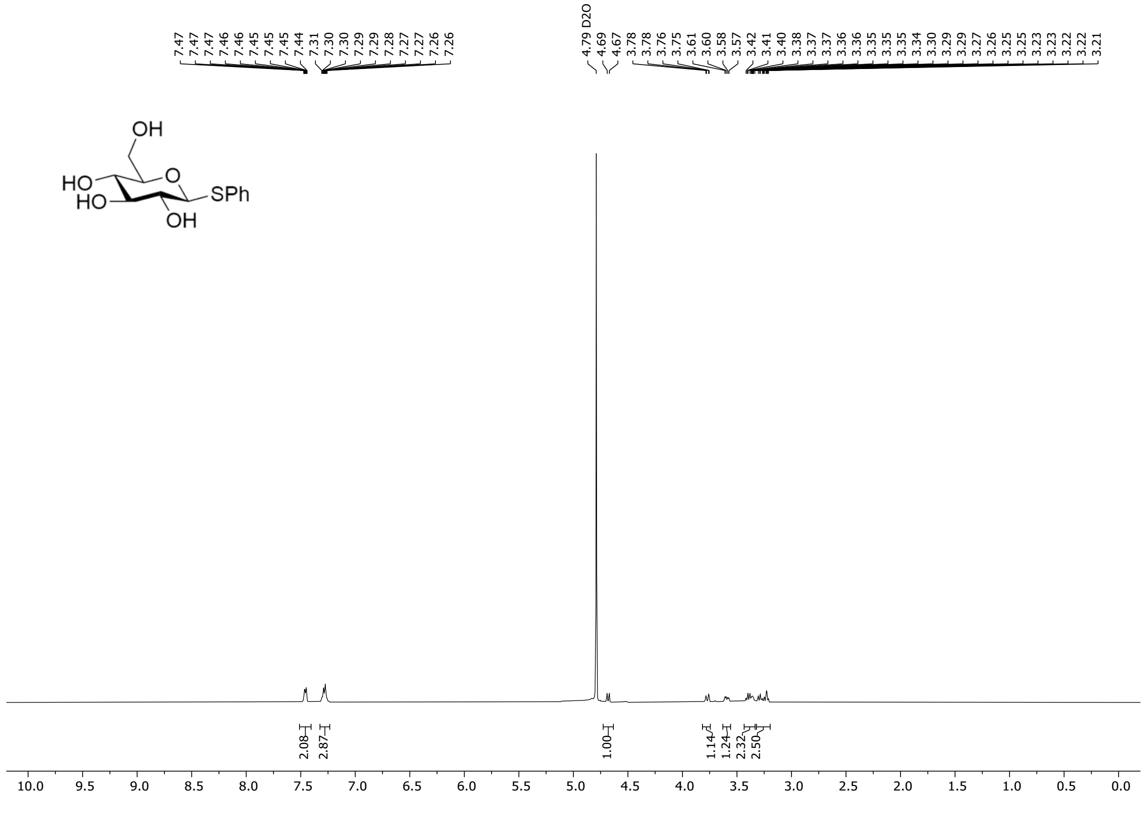


[1]H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **1**.

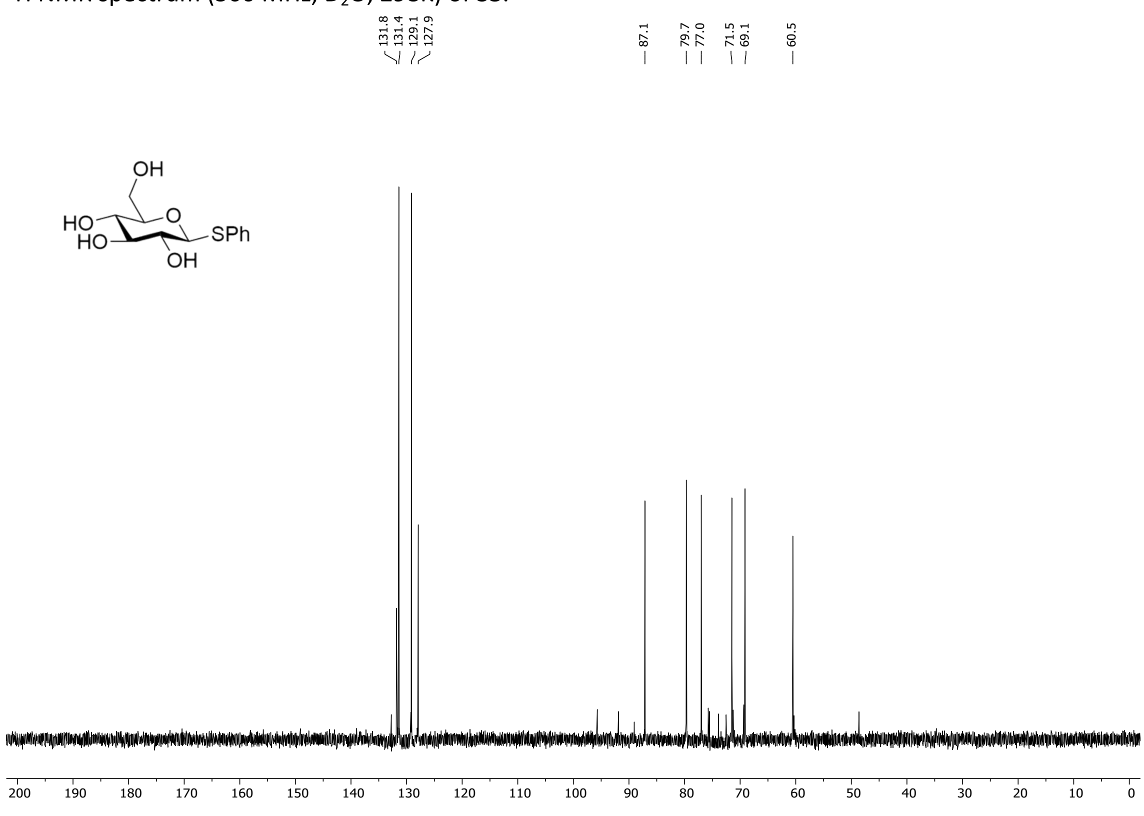


[13]C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **1**.

NMR spectra of S3

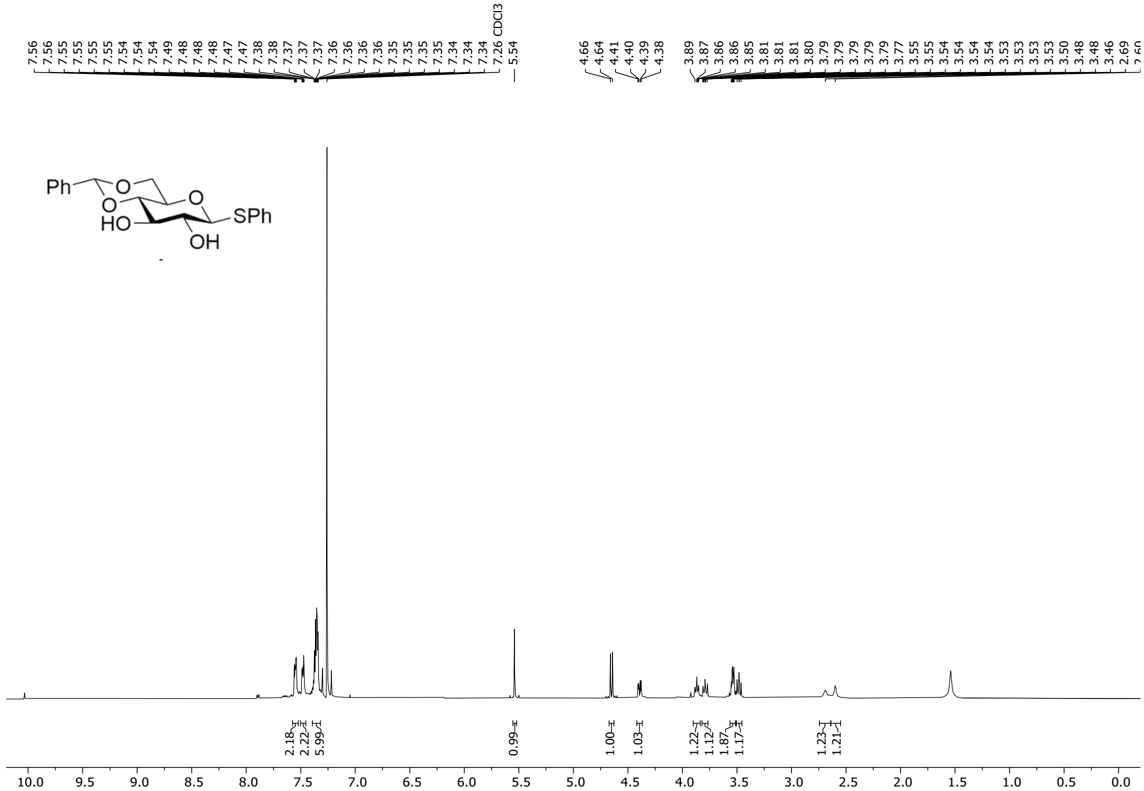


^{1}H NMR spectrum (500 MHz, D_2O, 298K) of **S3**.

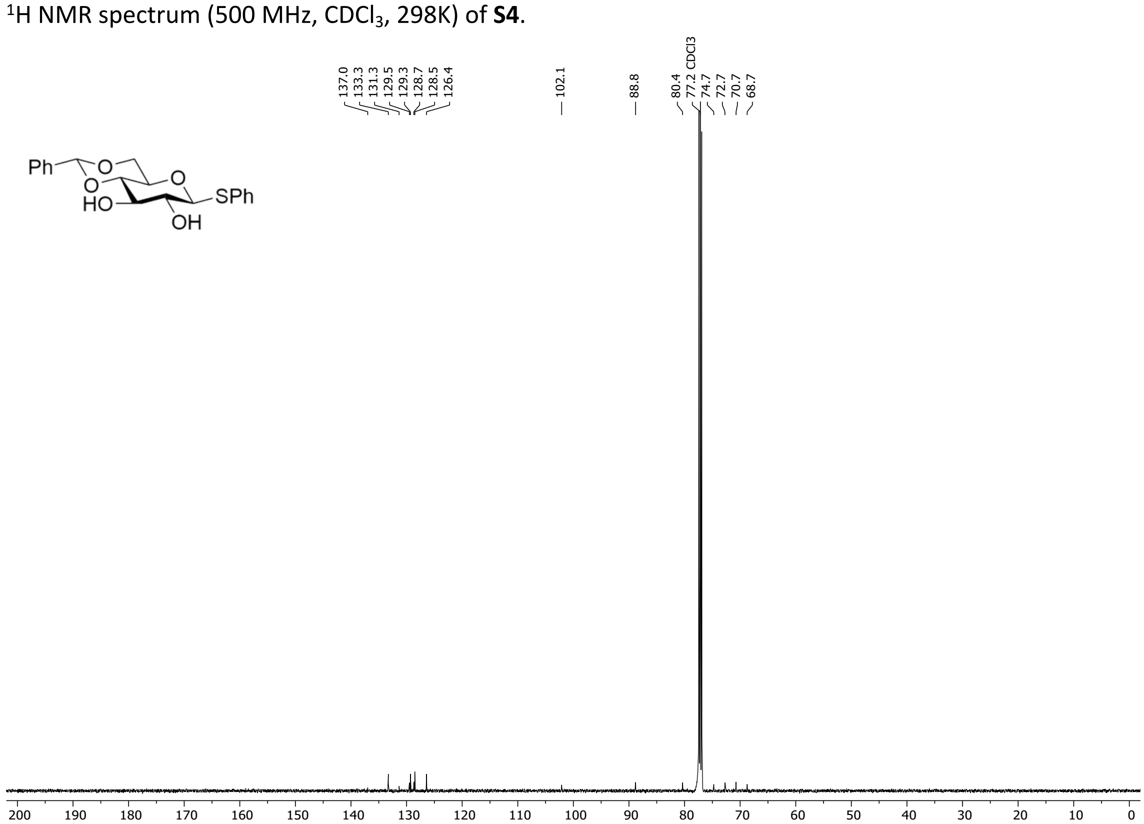


^{13}C NMR spectrum (126 MHz, D_2O, 298K) of **S3**.

NMR spectra of S4

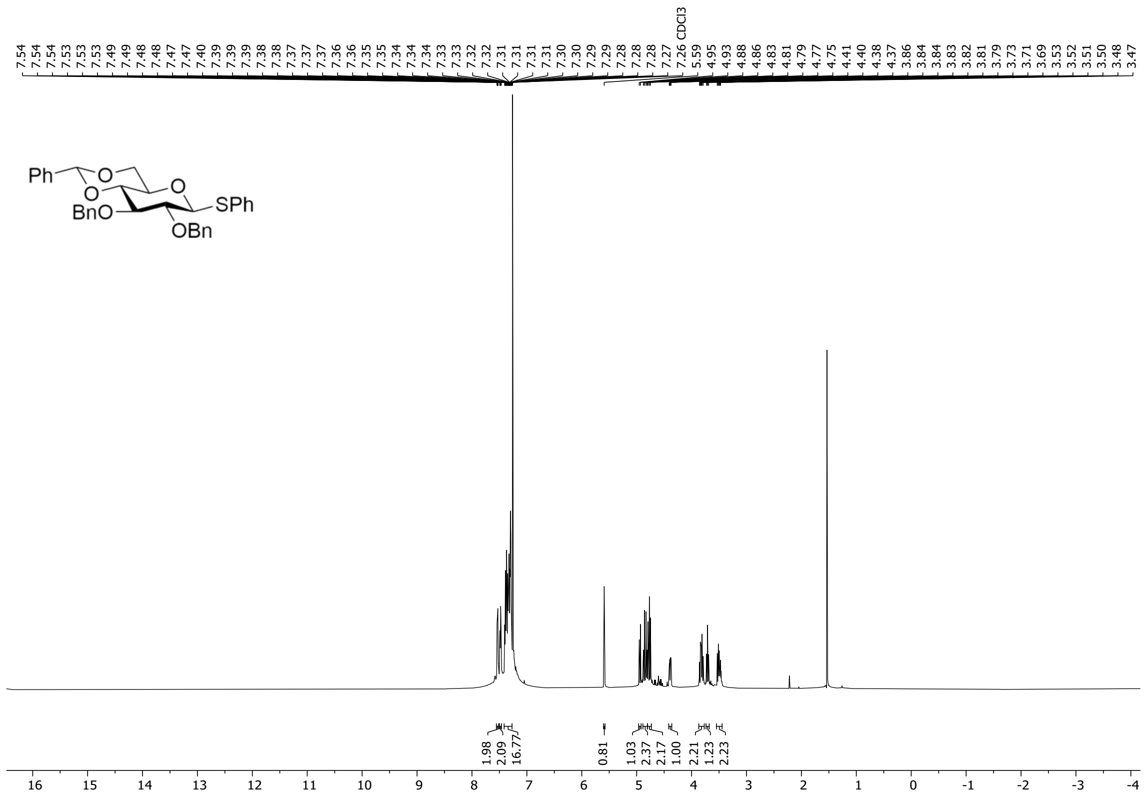


^1H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **S4**.

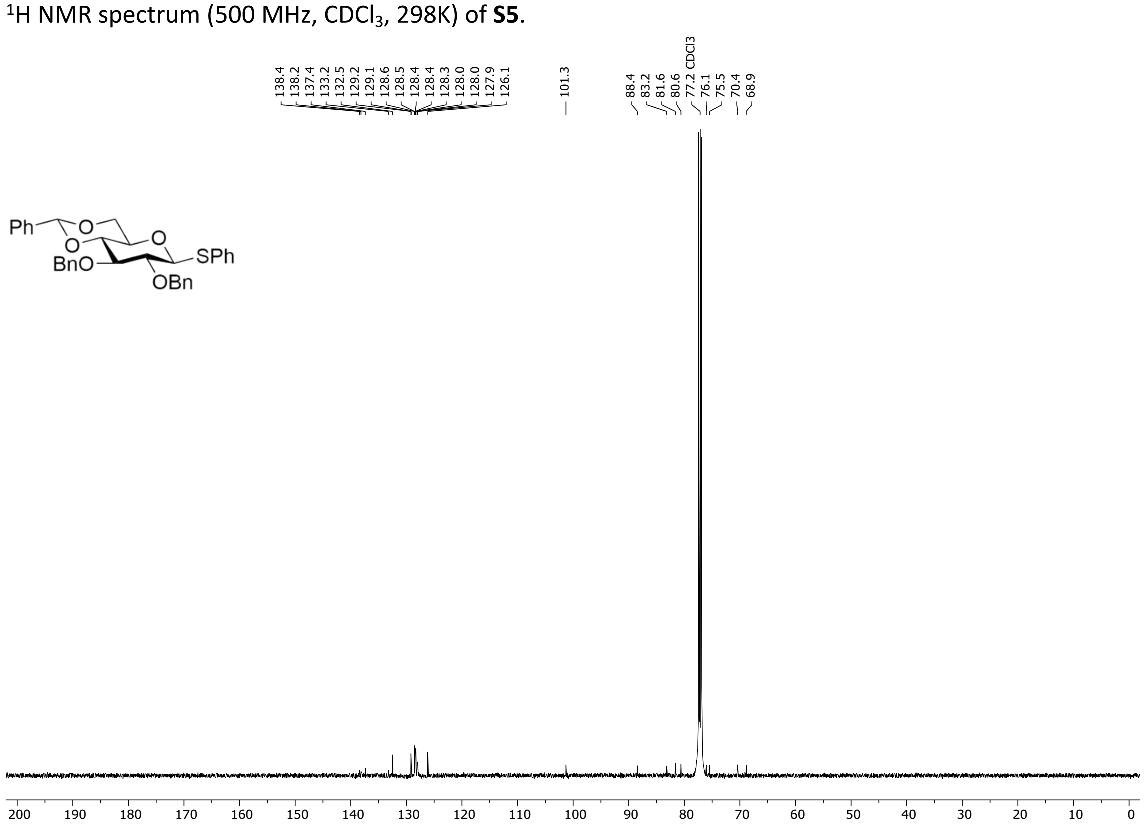


^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **S4**.

NMR spectra of S5

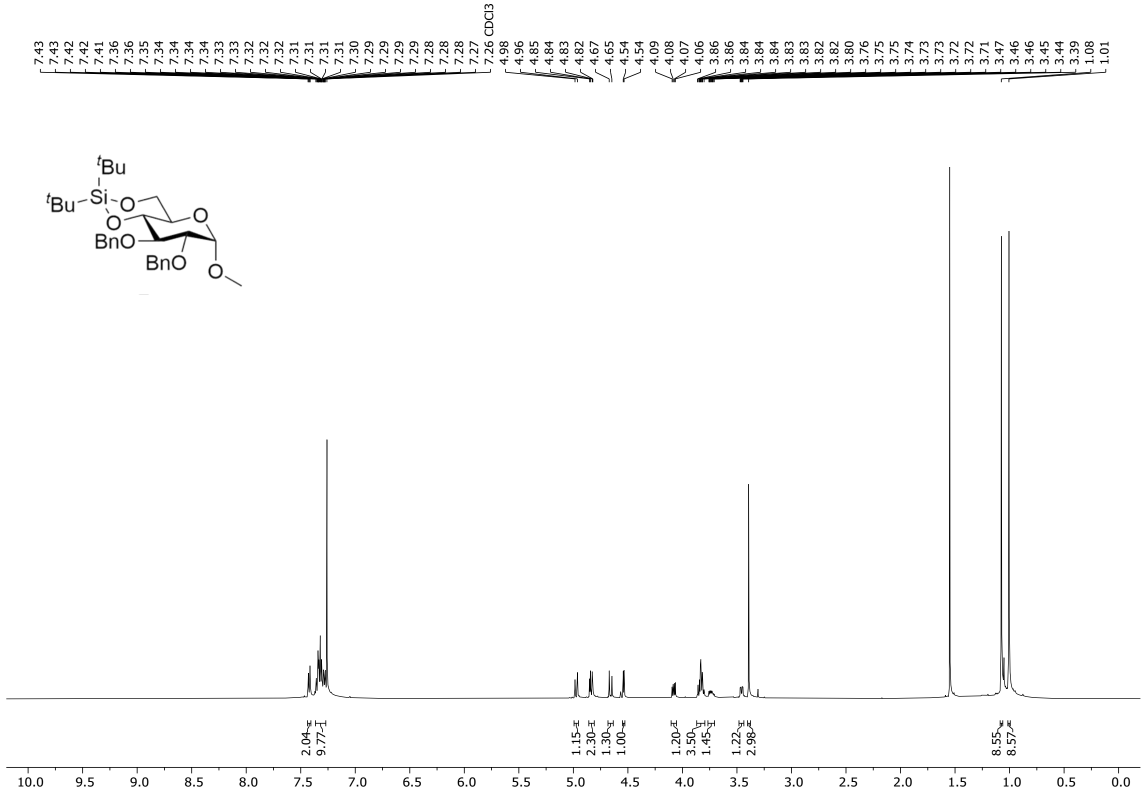


^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **S5**.

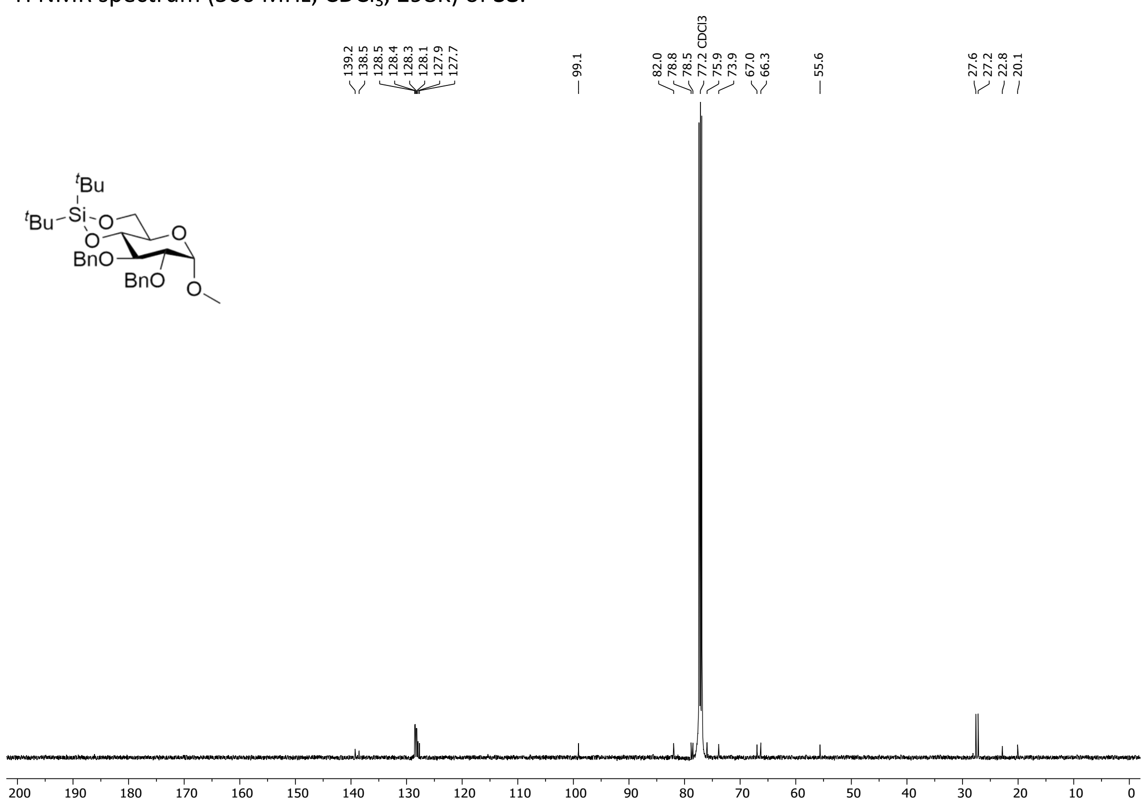


^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **S5**.

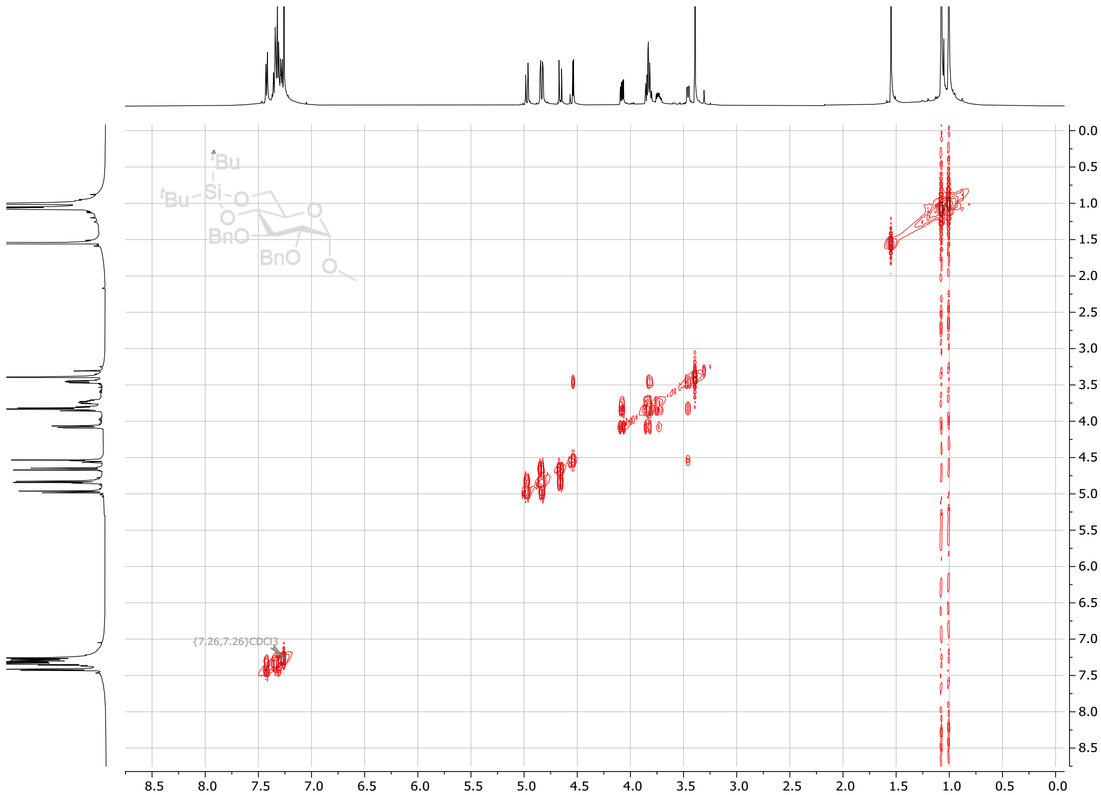
NMR spectra of S8



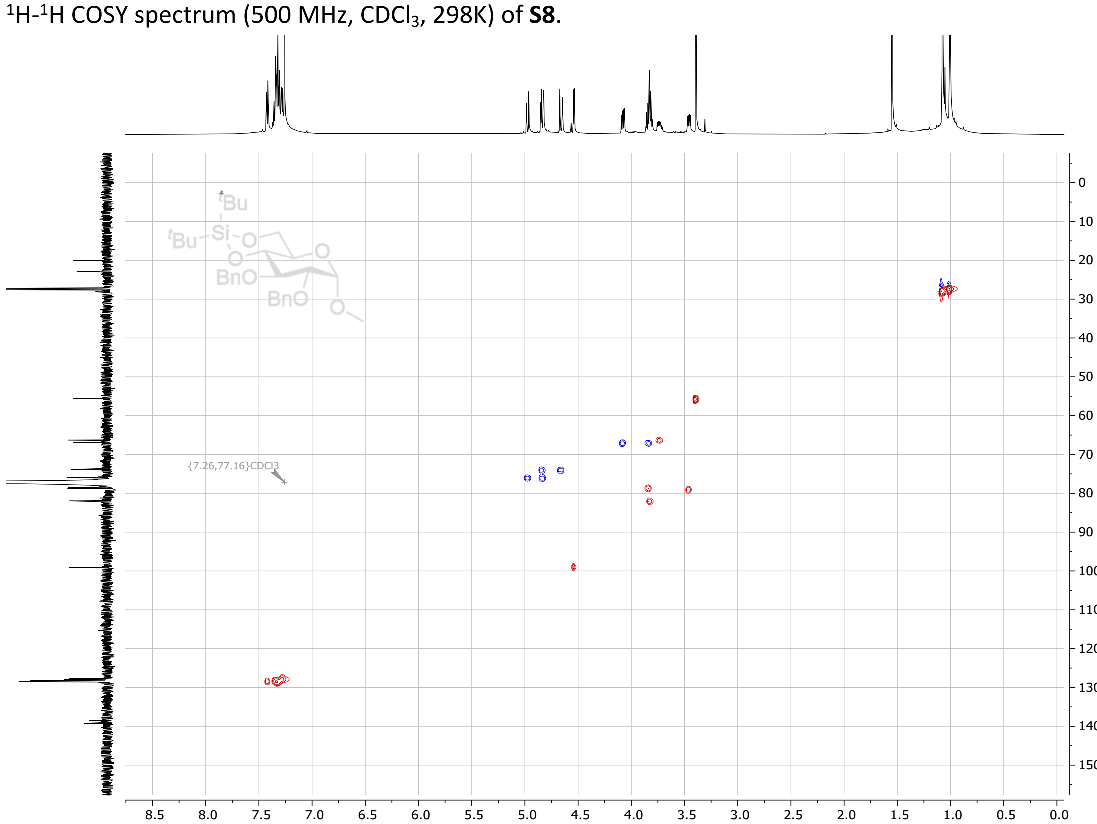
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **S8**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **S8**.

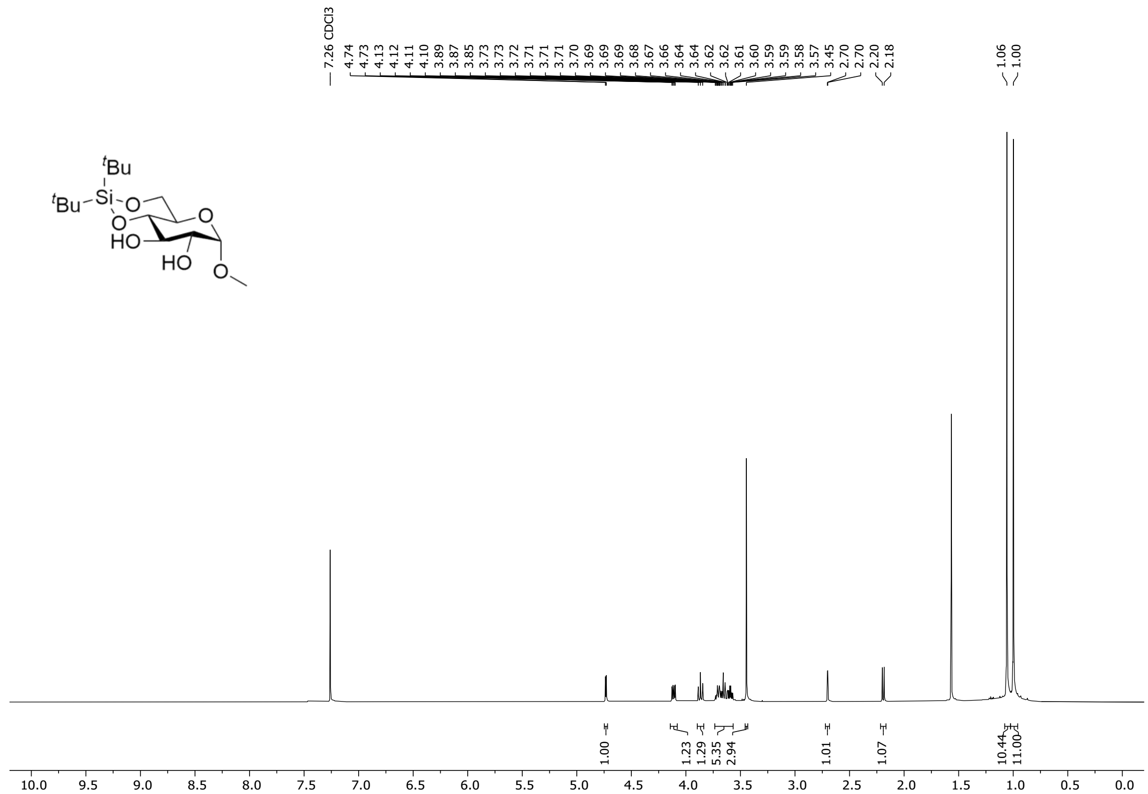


^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **S8**.

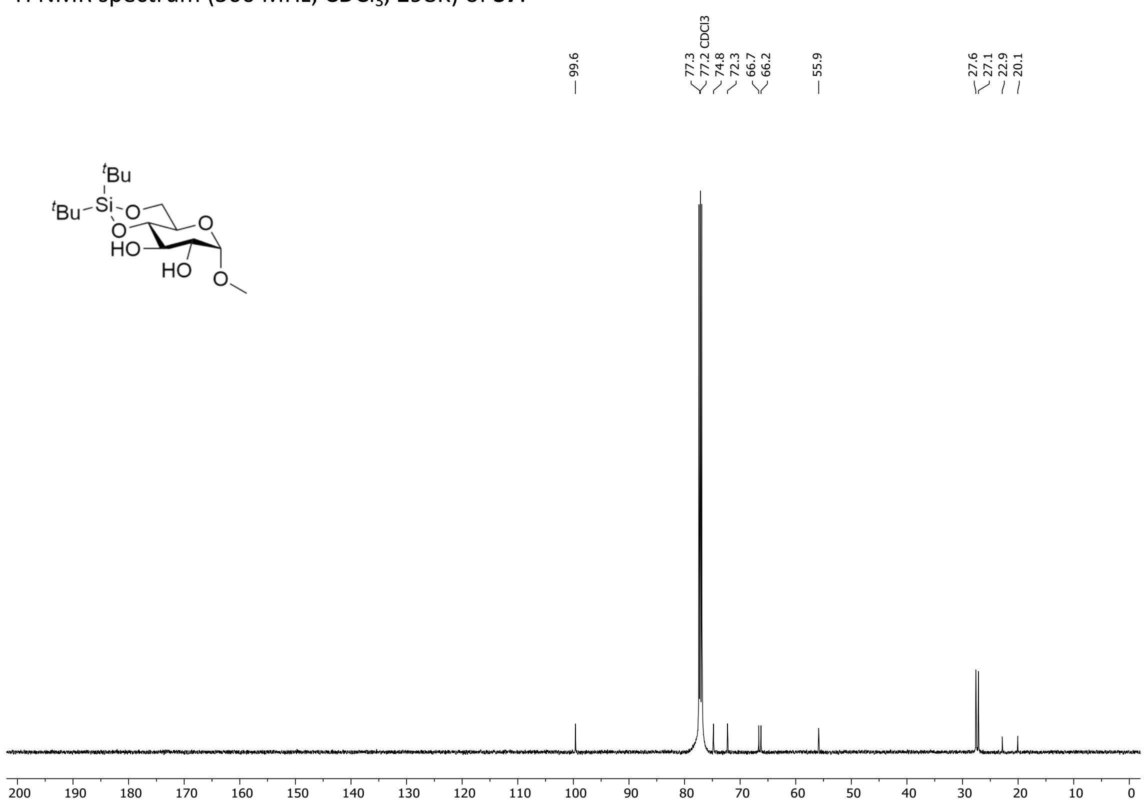


^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **S8**.

NMR spectra of S7

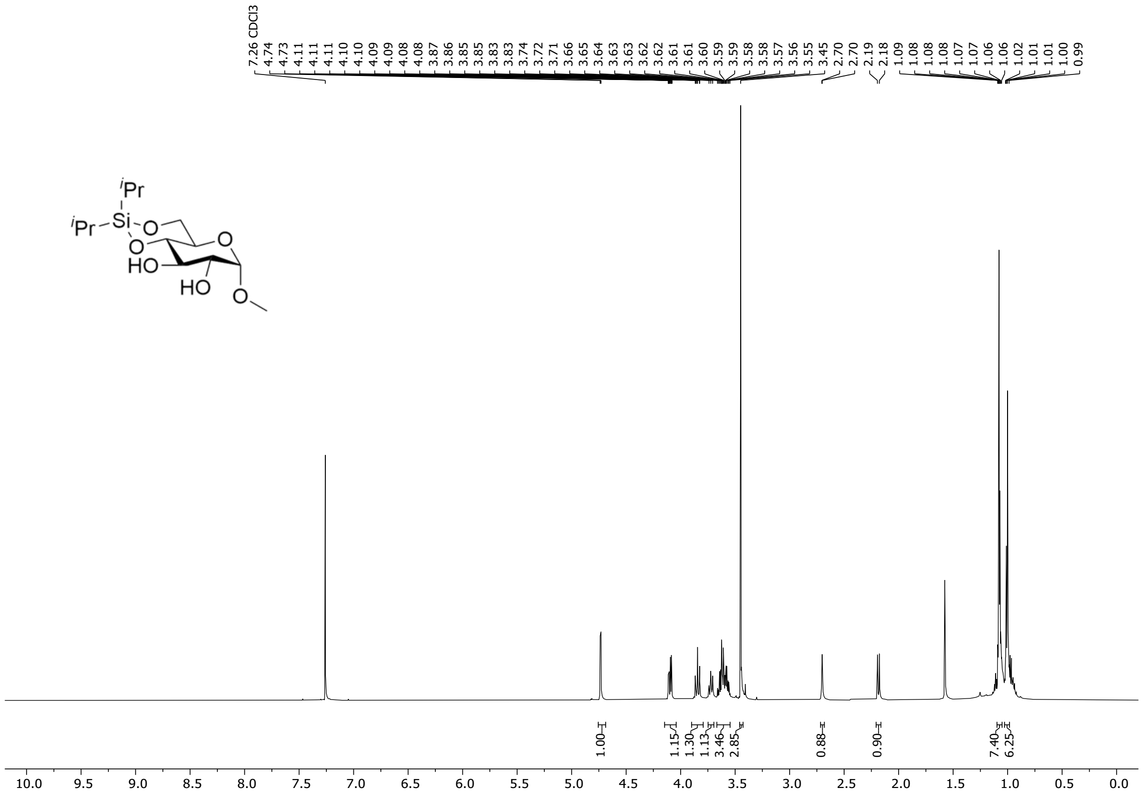


[1]H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **S7**.

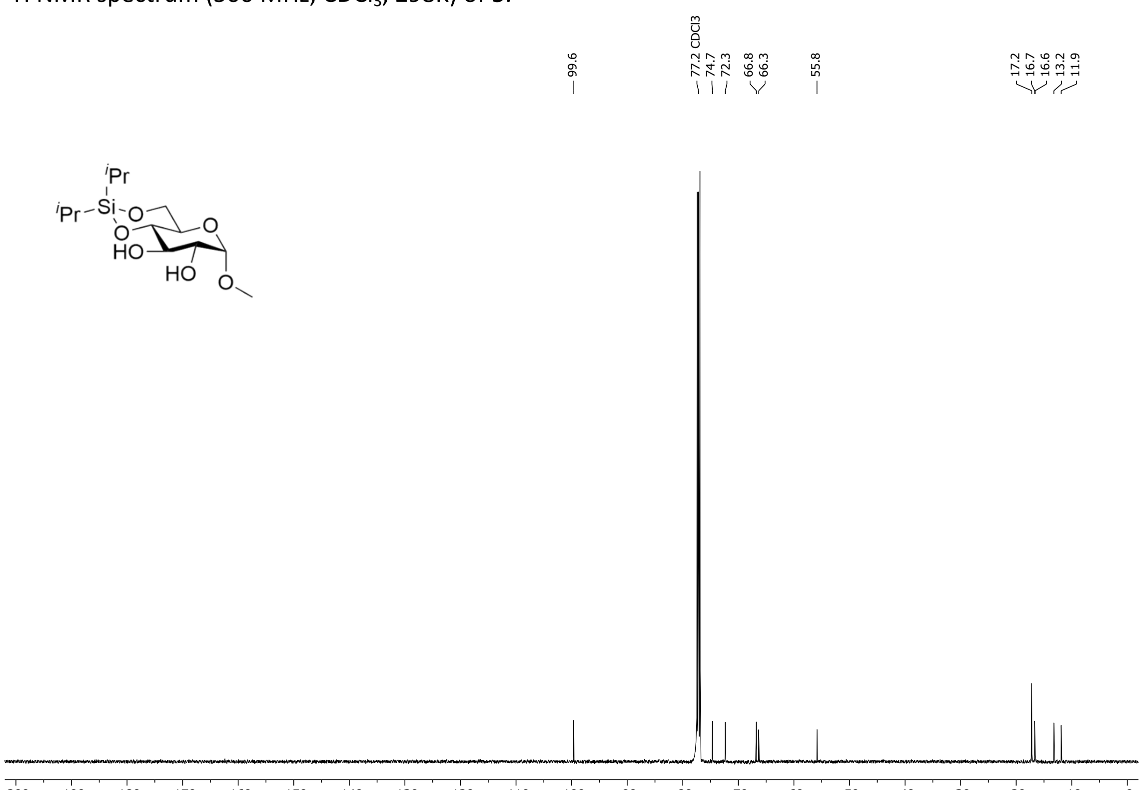


[13]C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **S7**.

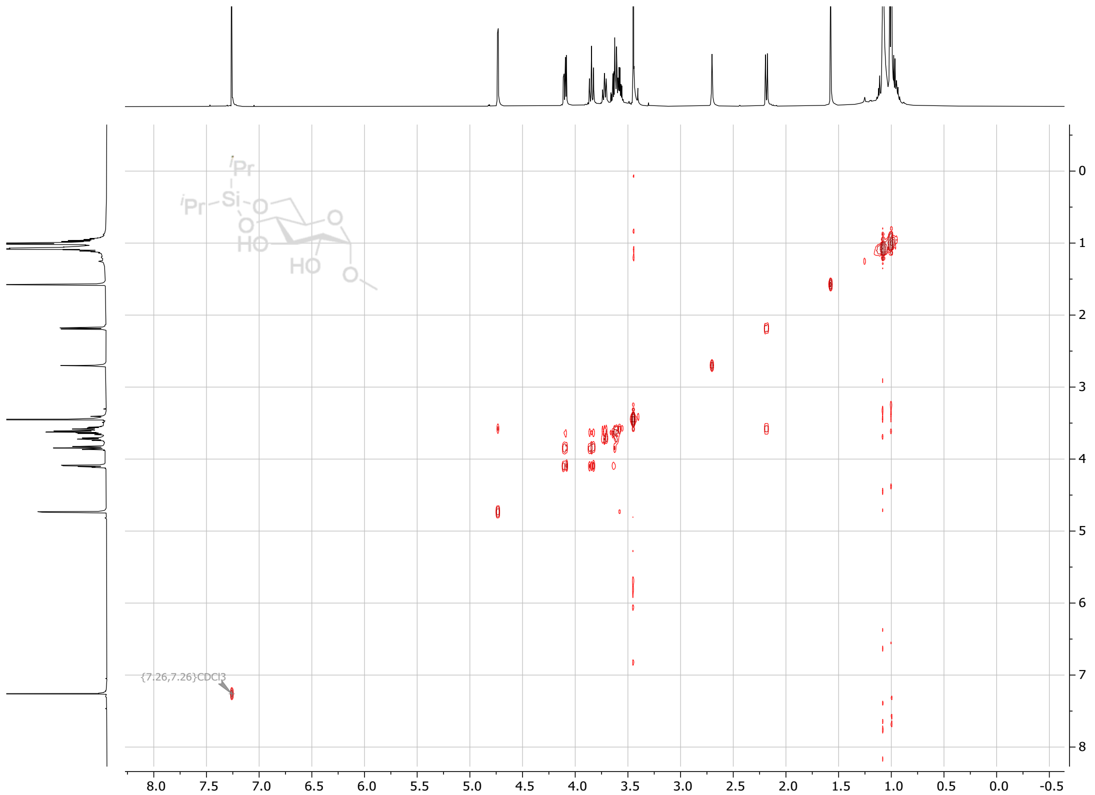
NMR spectra of 5



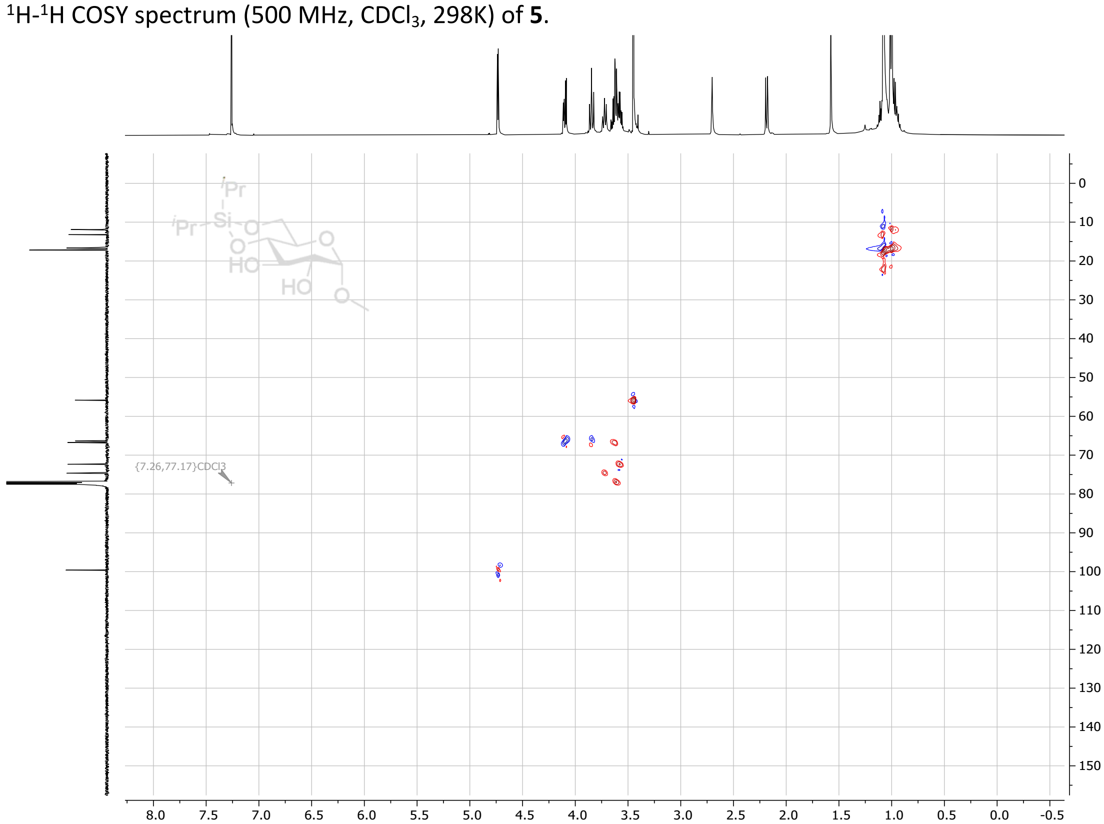
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **5**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **5**.

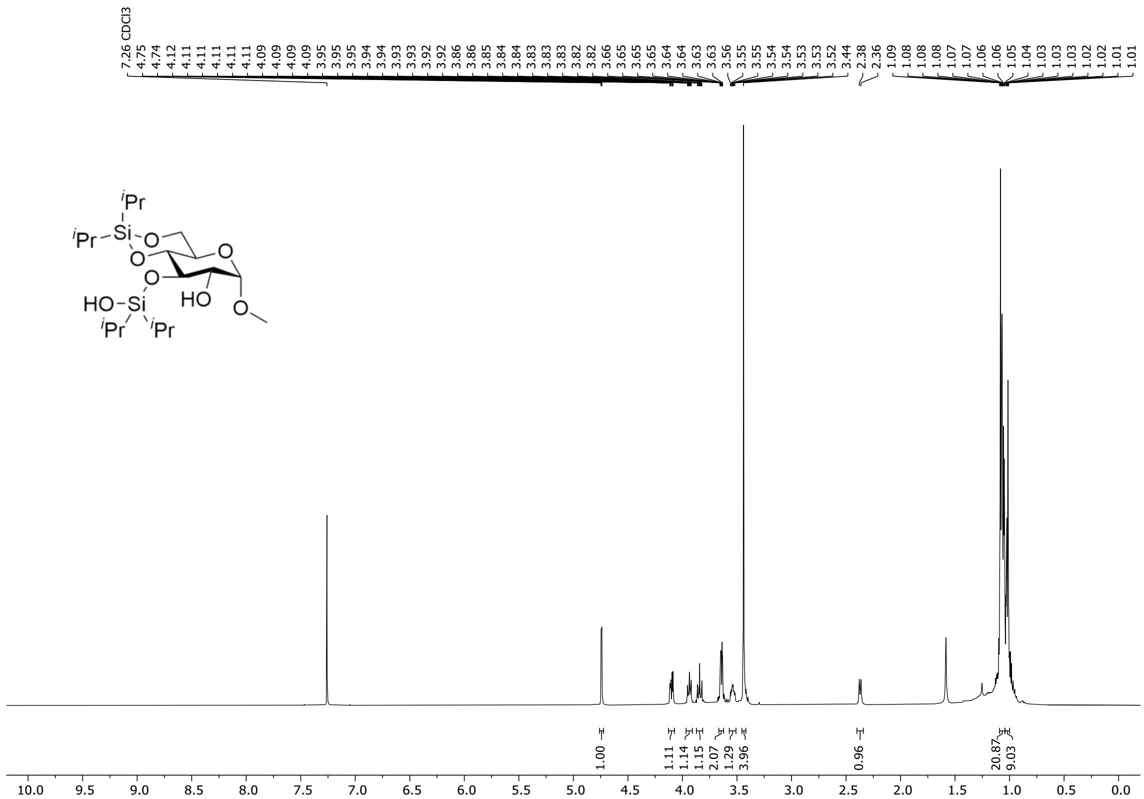


^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **5**.

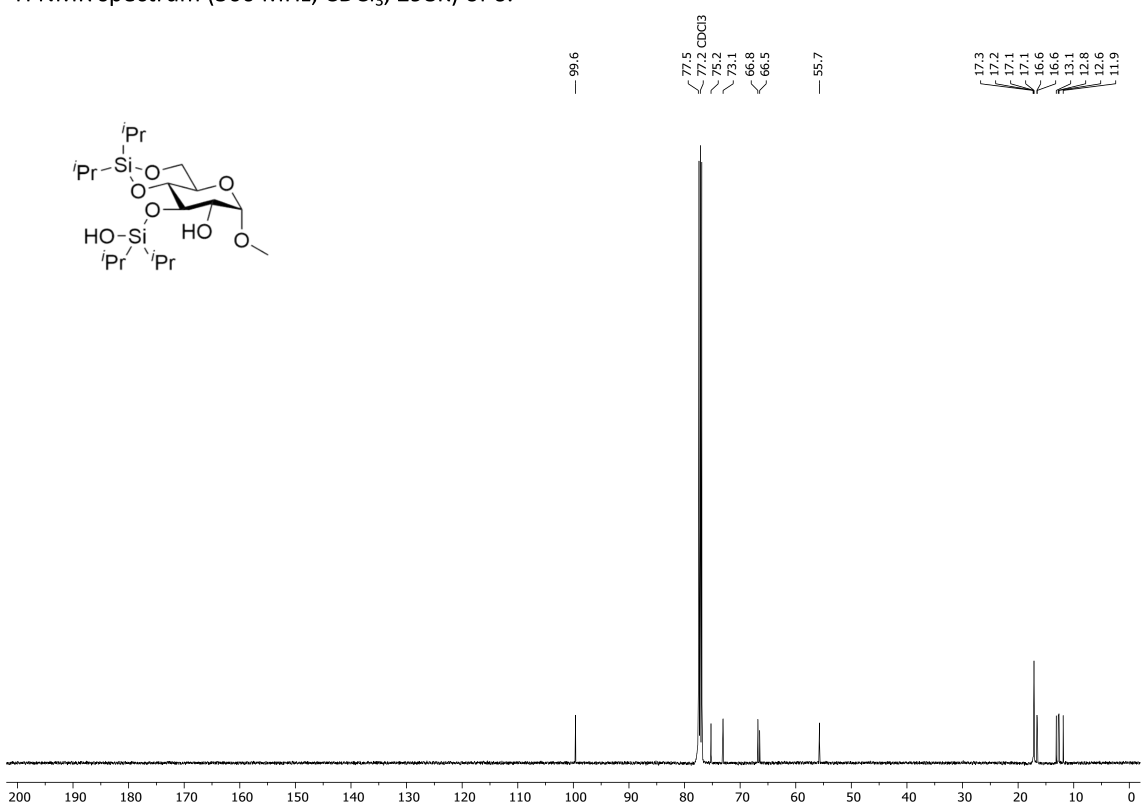


^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **5**.

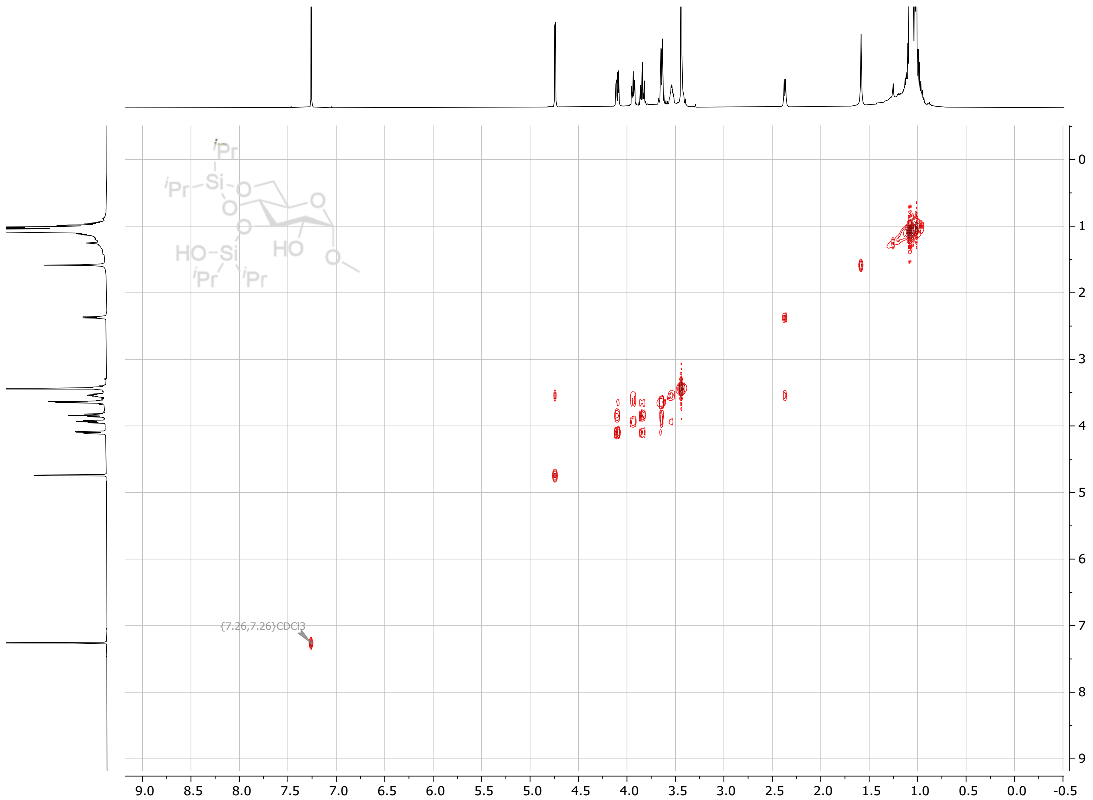
NMR spectra of 6



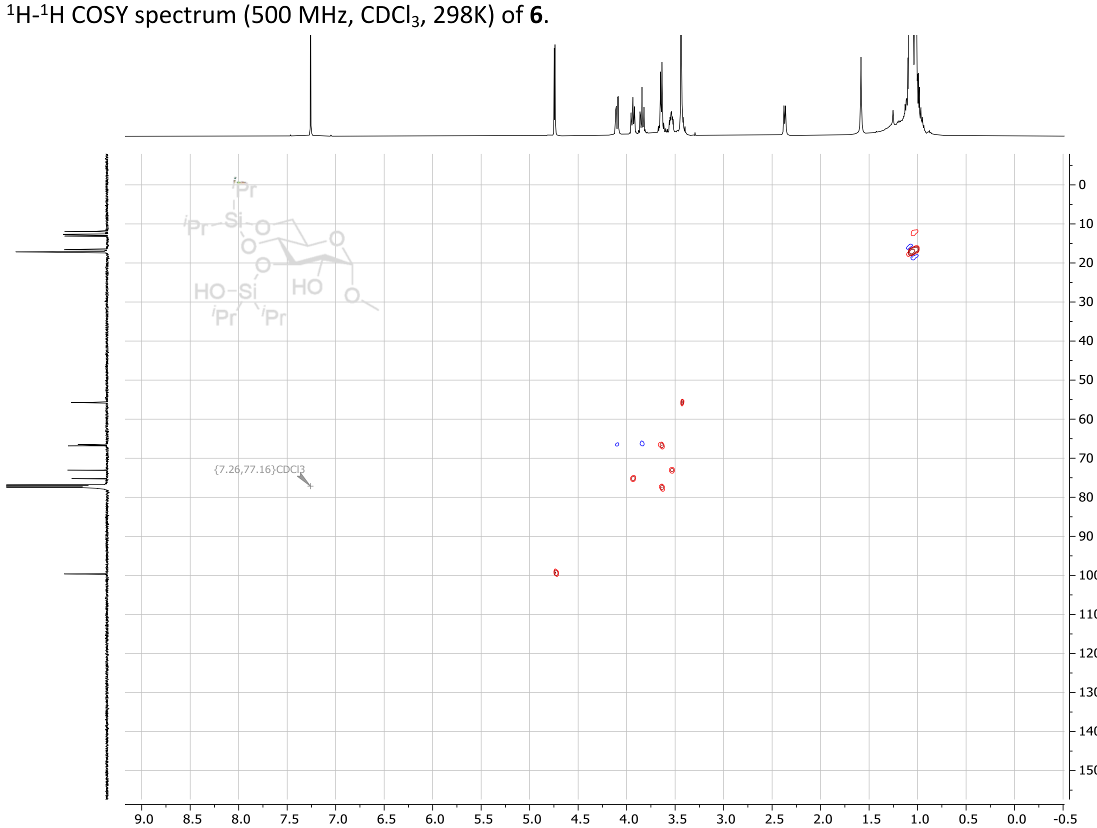
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **6**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **6**.

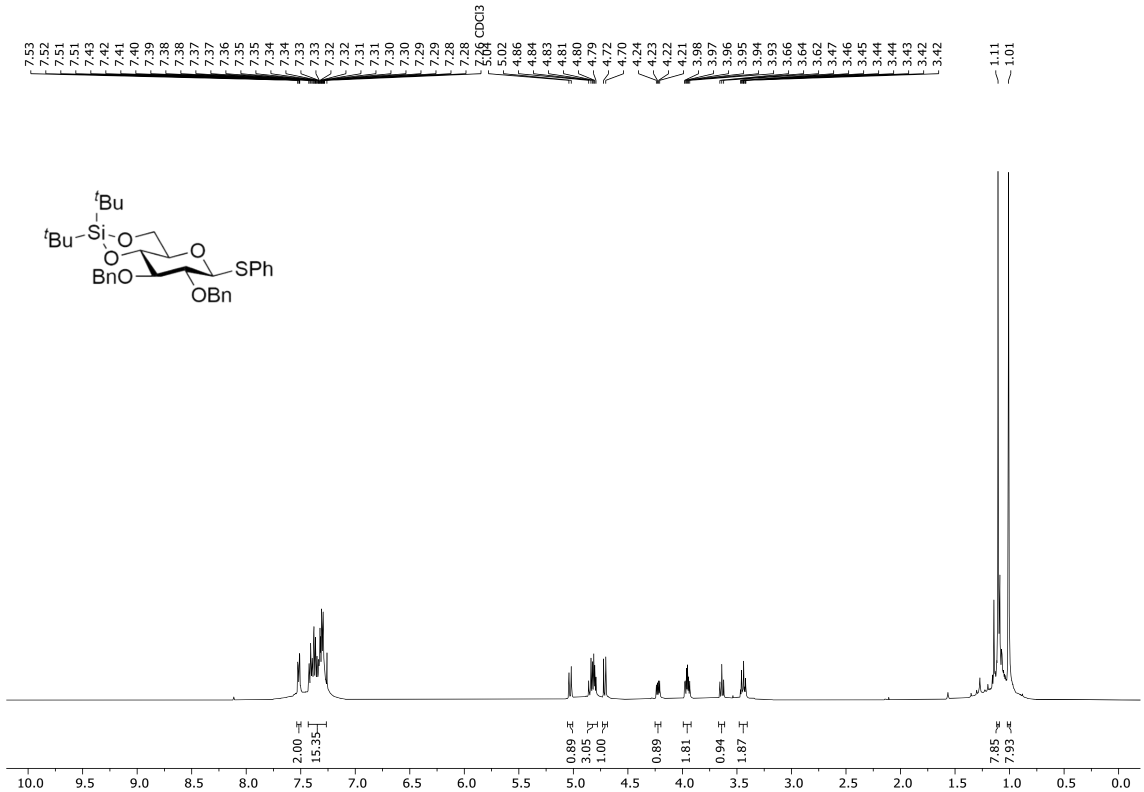


^1H-^1H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **6**.

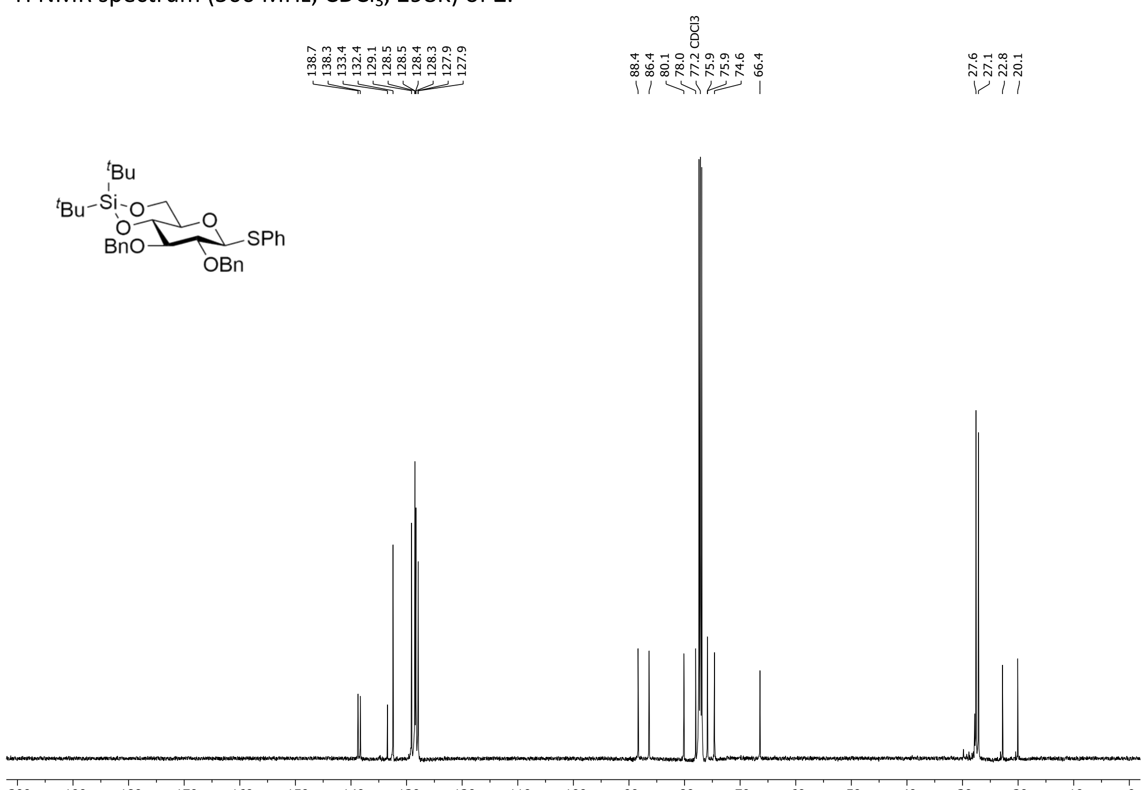


^1H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **6**.

NMR spectra of 2

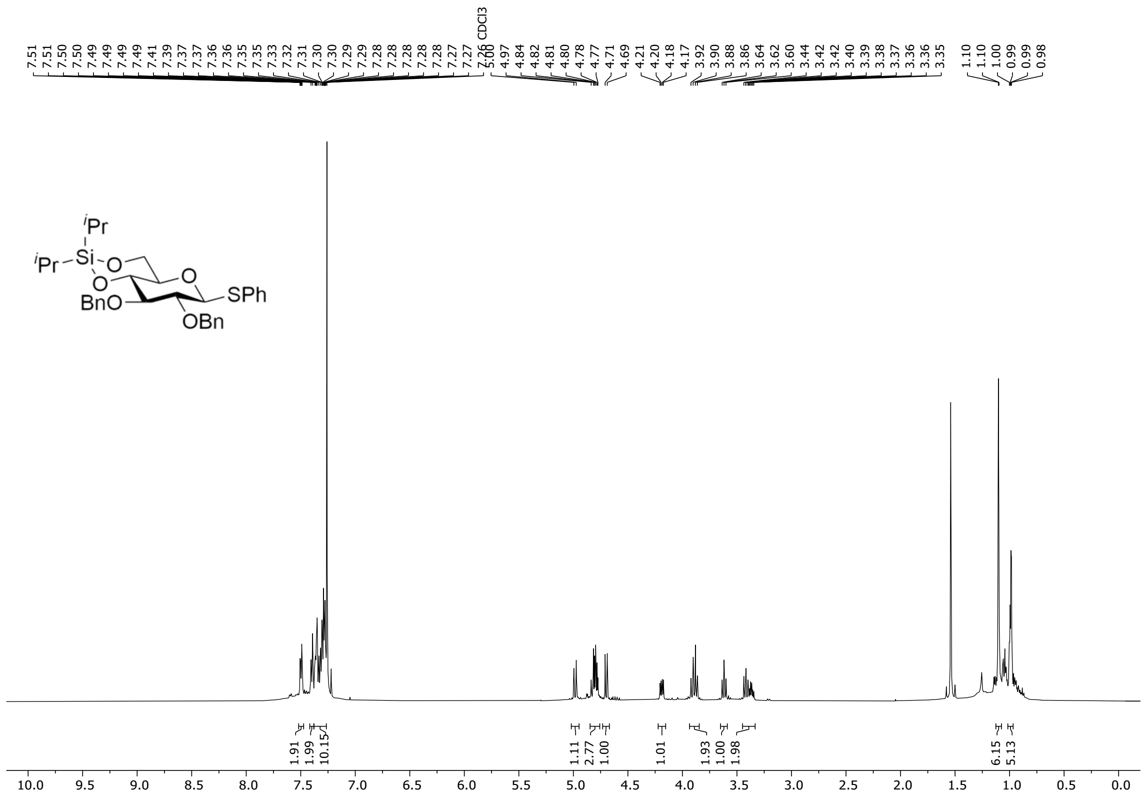


^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **2**.

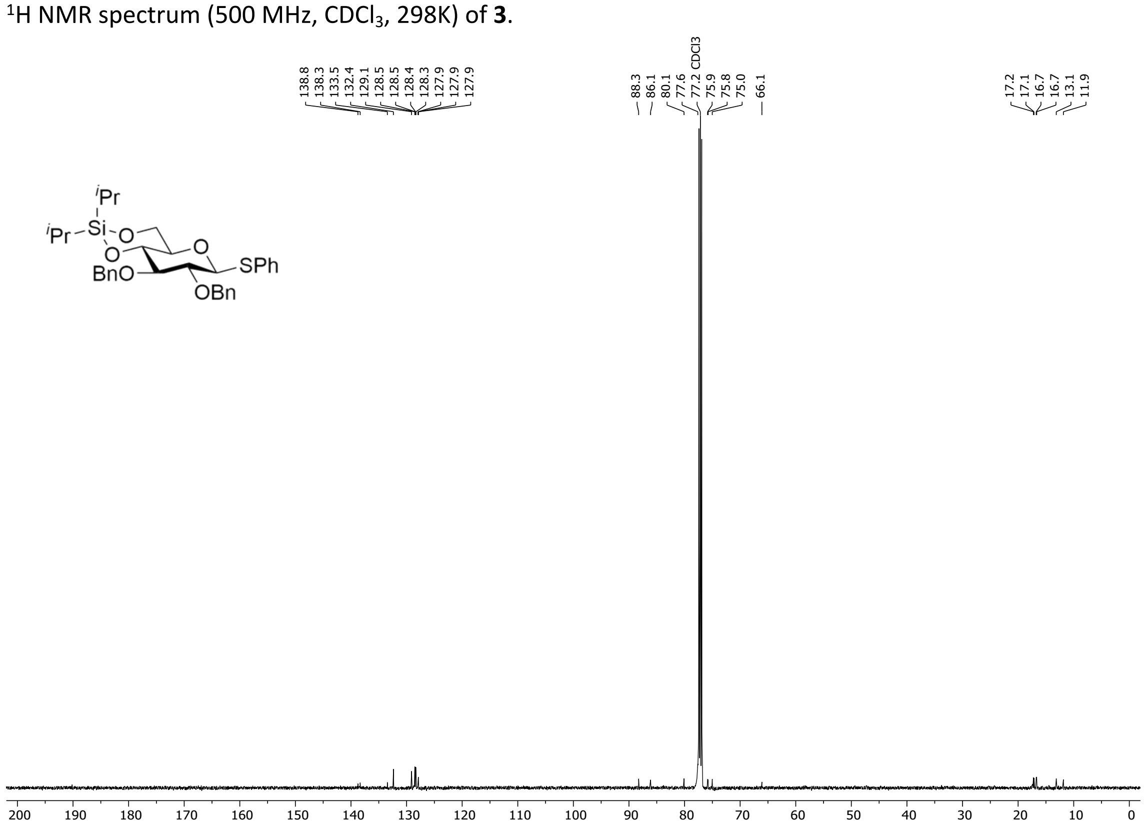


^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **2**.

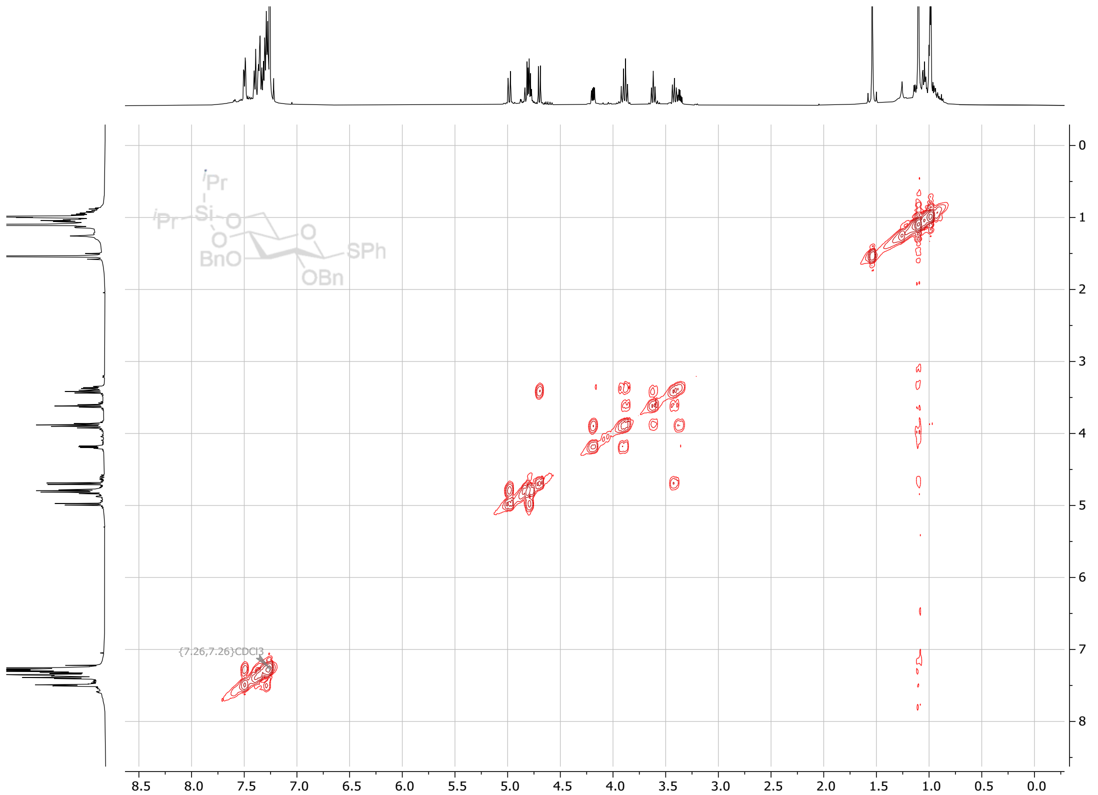
NMR spectra of 3



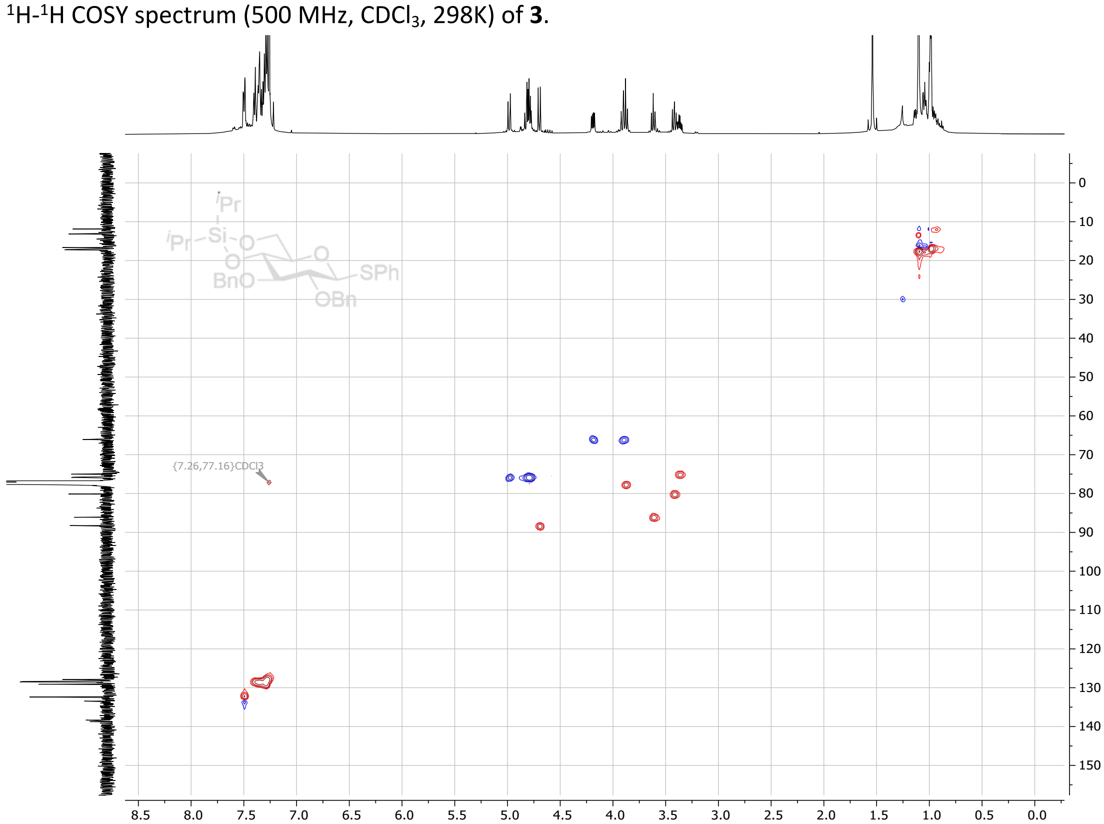
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **3**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **3**.

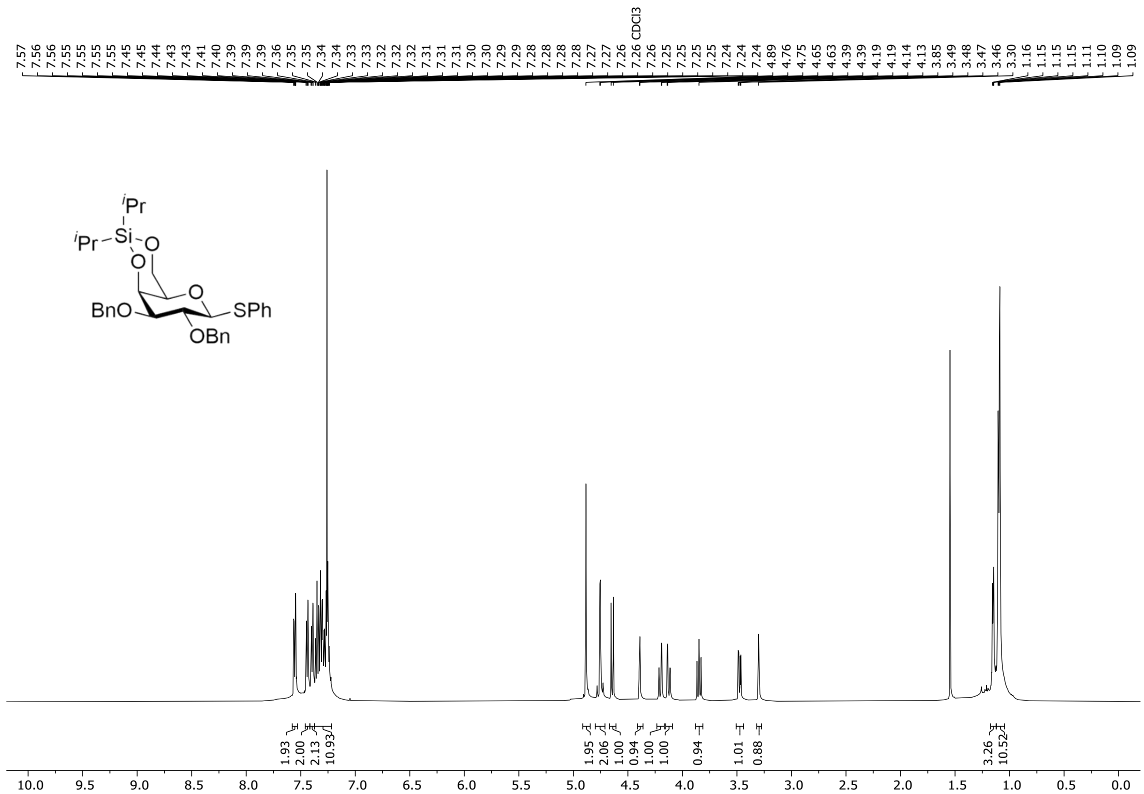


^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **3**.

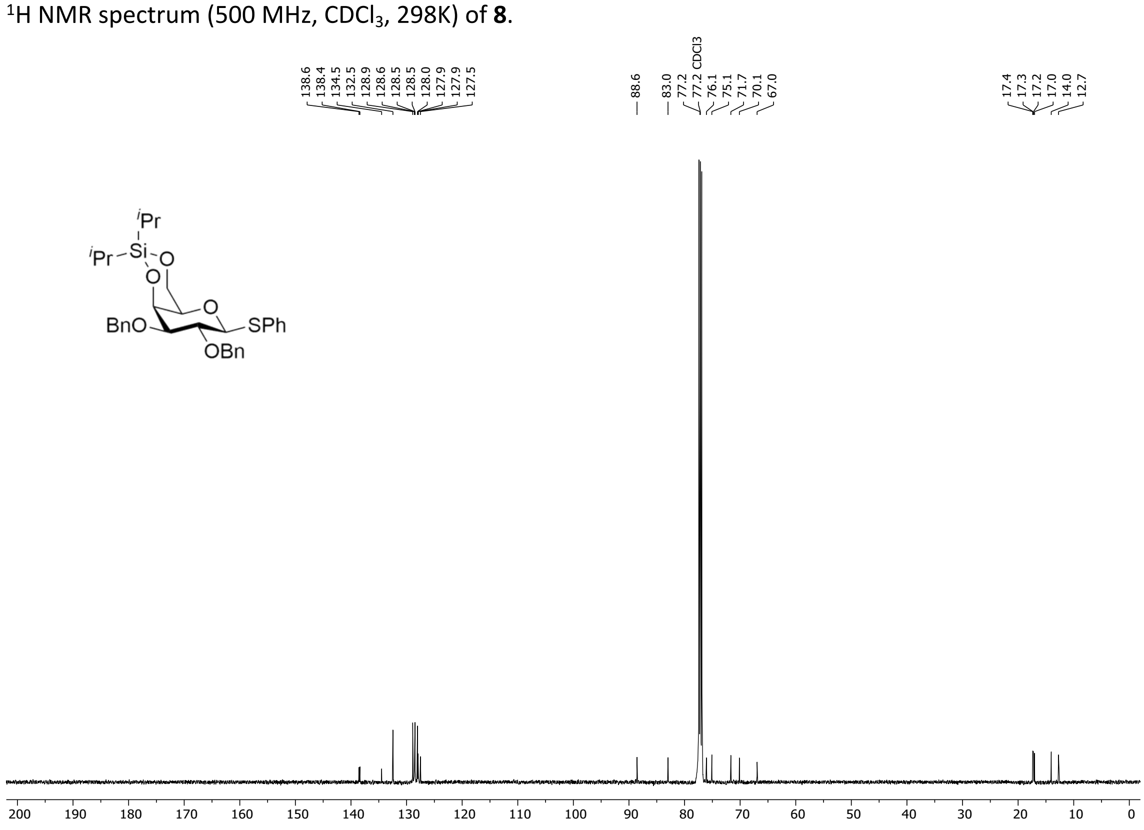


^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **3**.

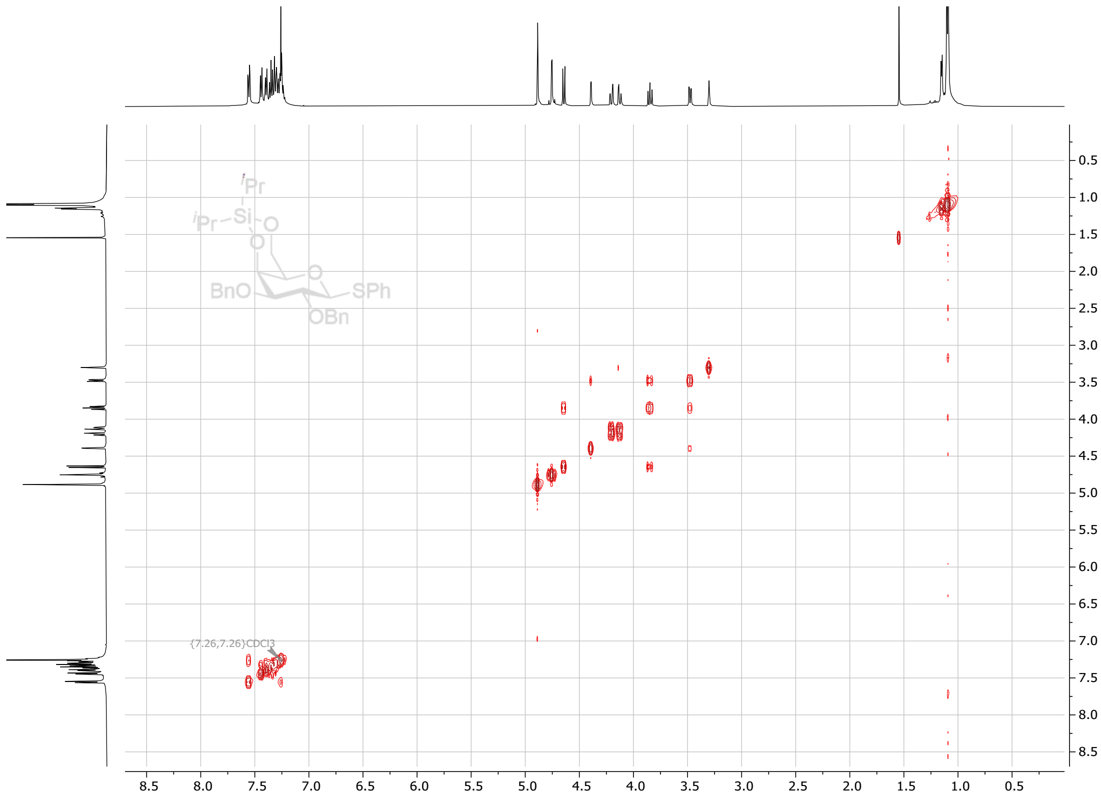
NMR spectra of 8



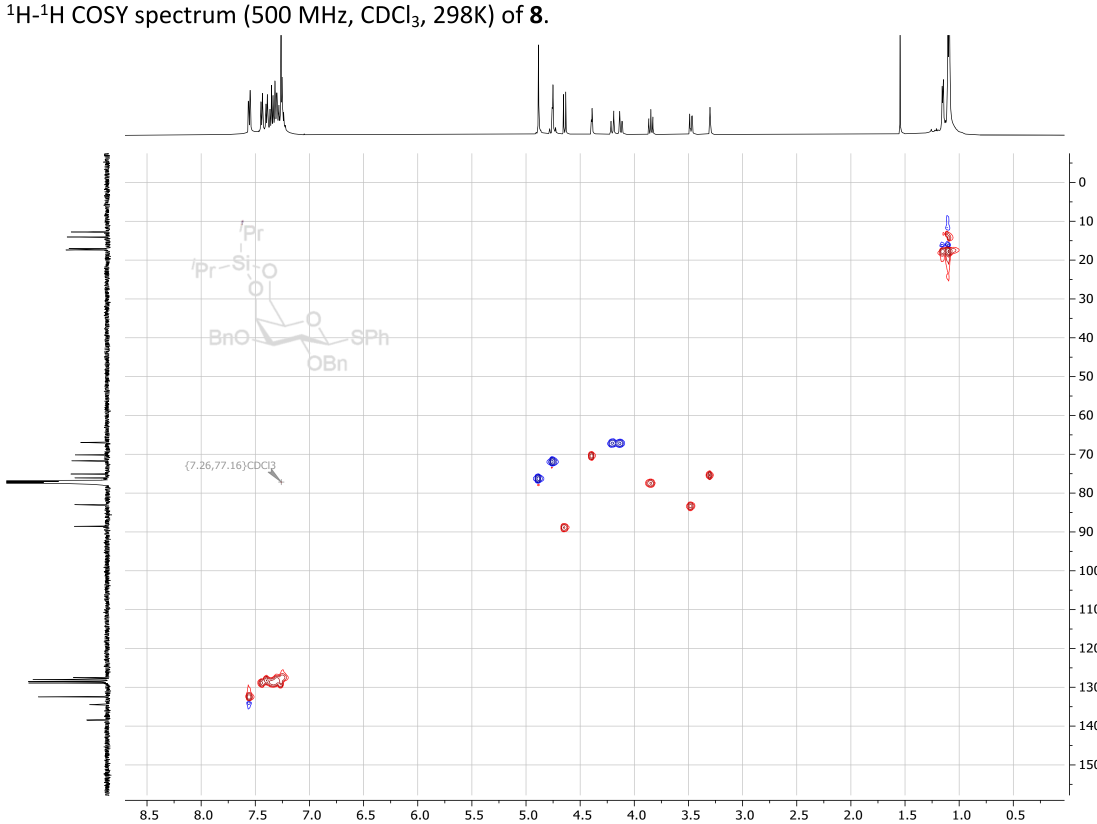
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **8**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **8**.

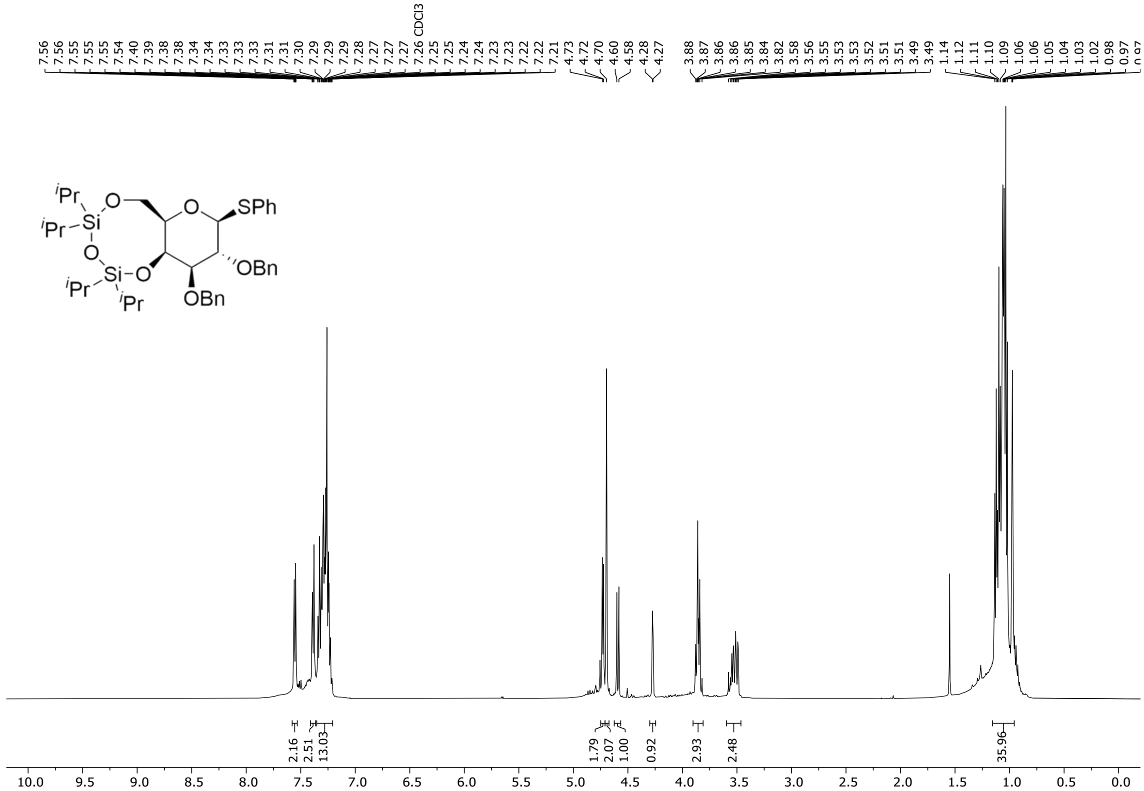


^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **8**.

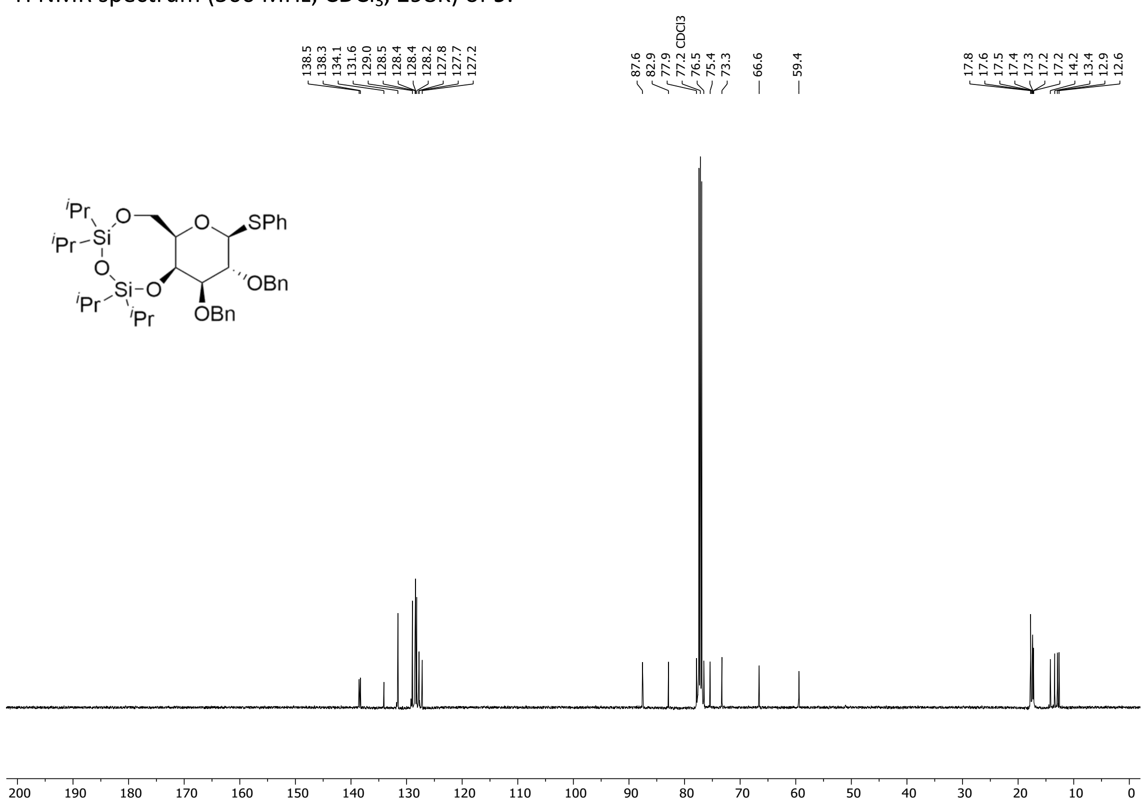


^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **8**.

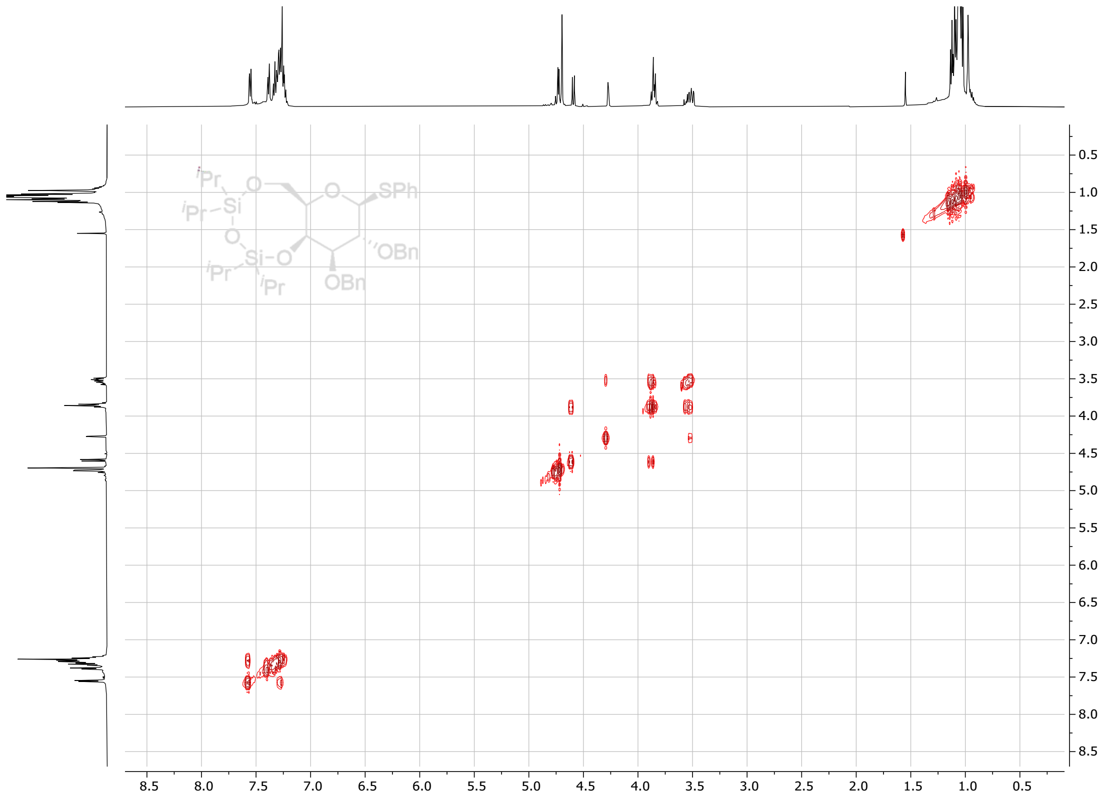
NMR spectra of 9



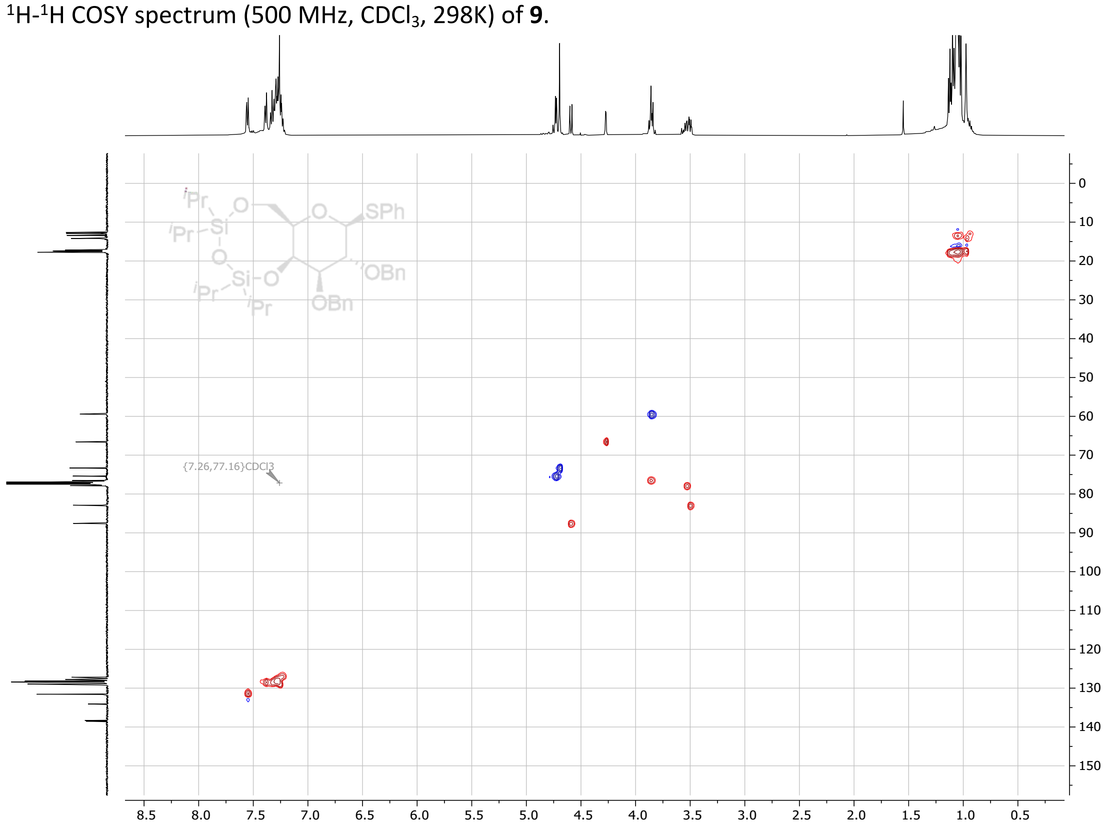
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **9**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **9**.

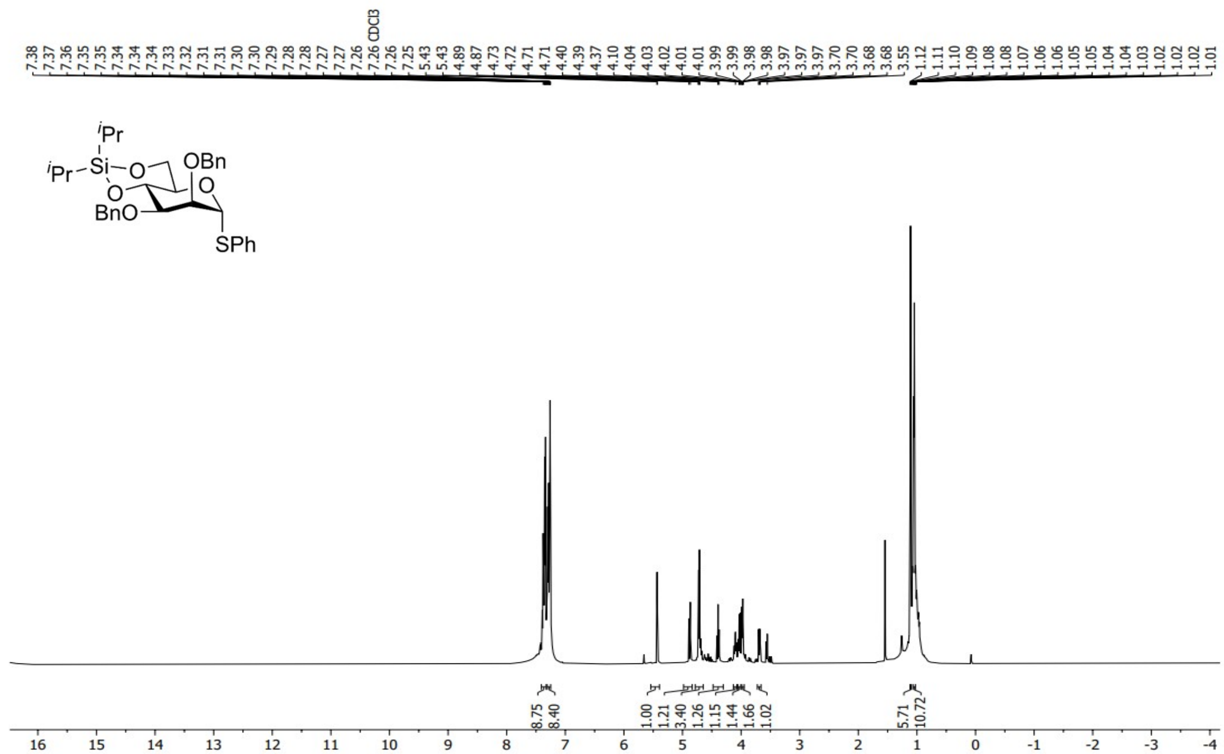


^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **9**.

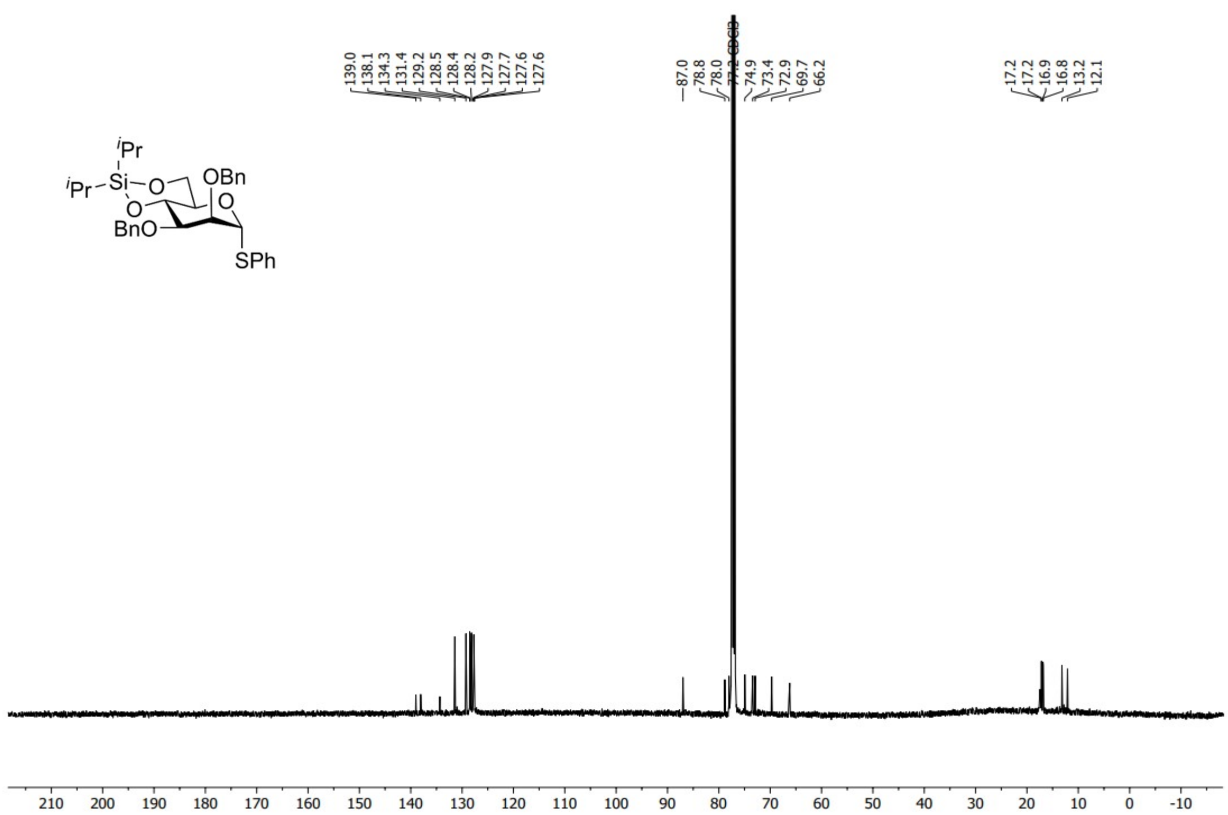


^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **9**.

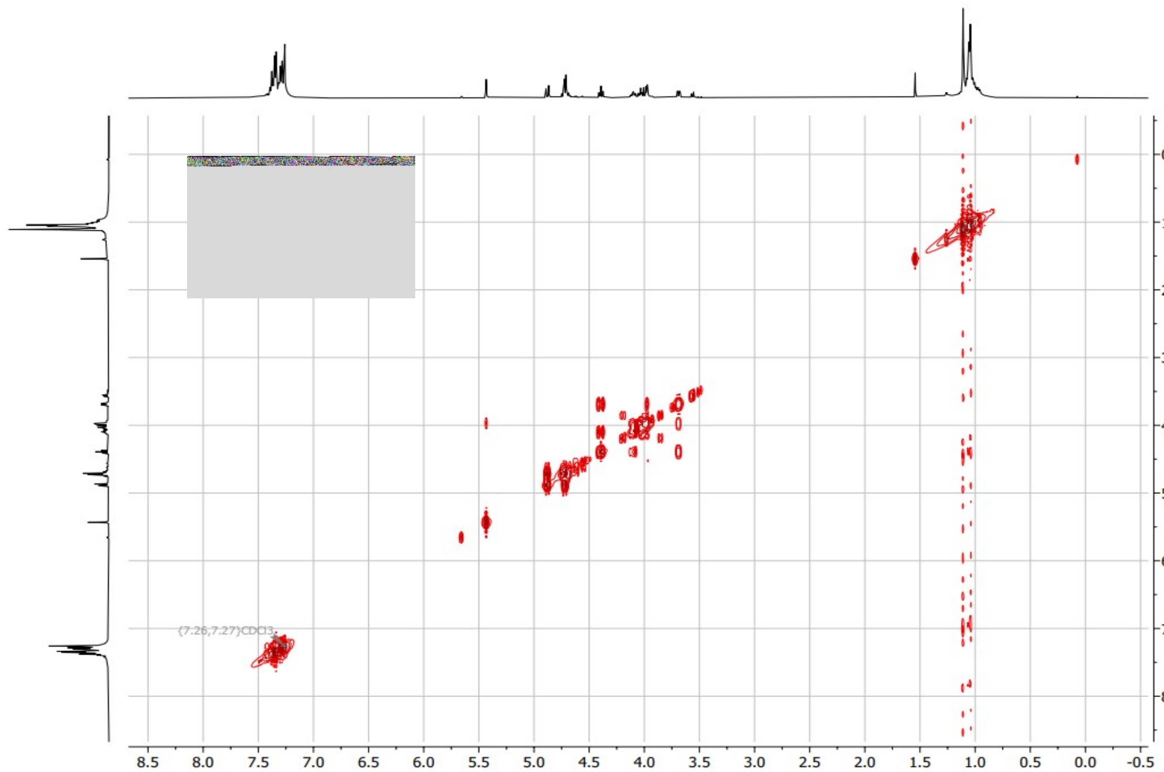
NMR spectra of 11



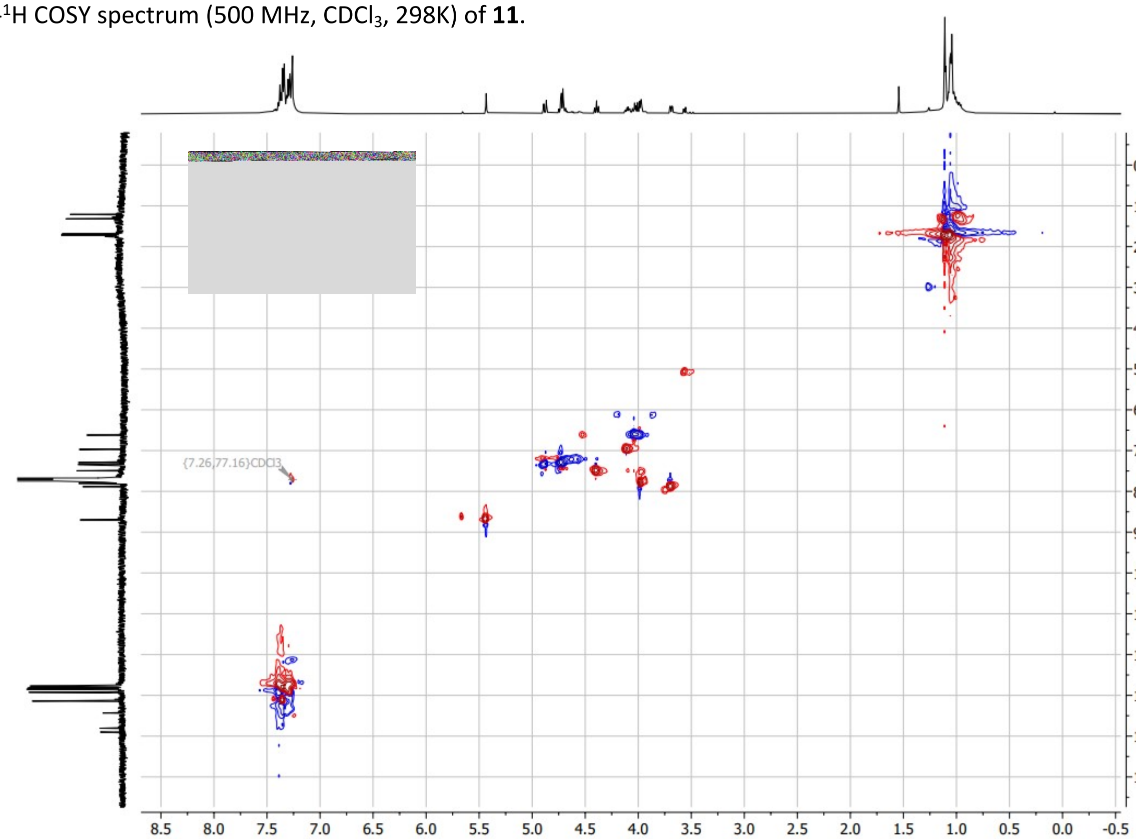
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **11**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **11**.

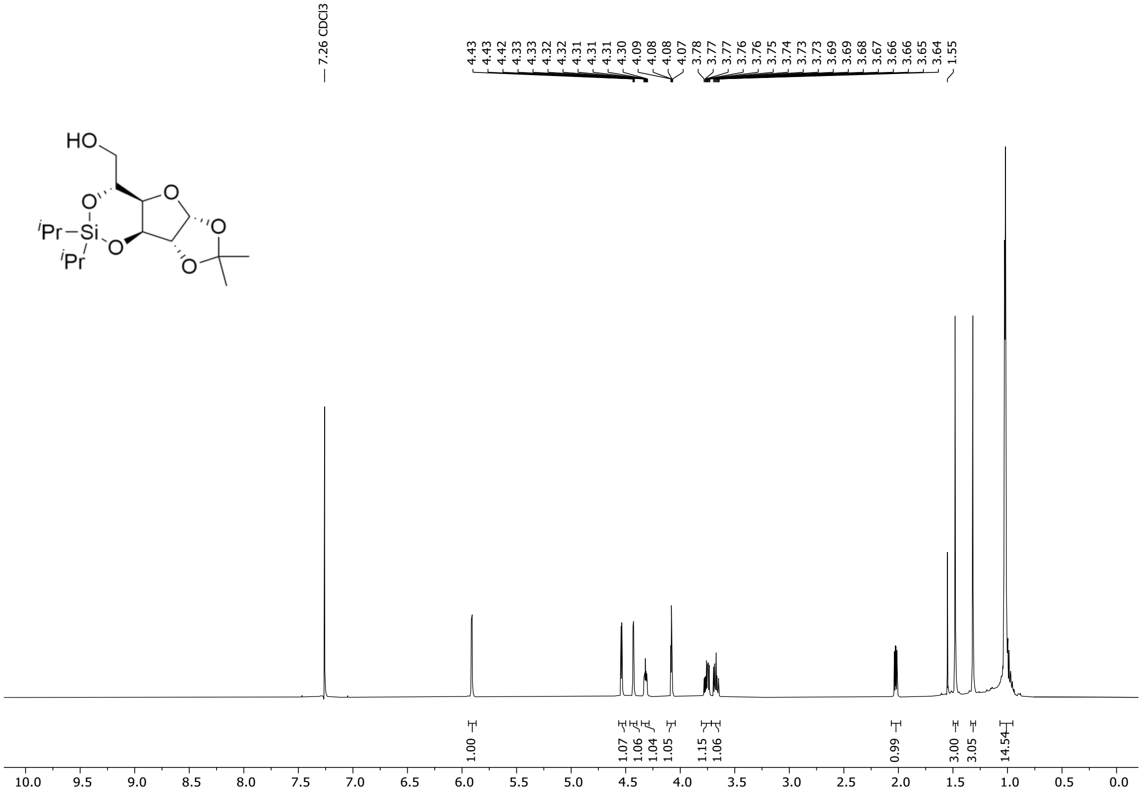


^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **11**.

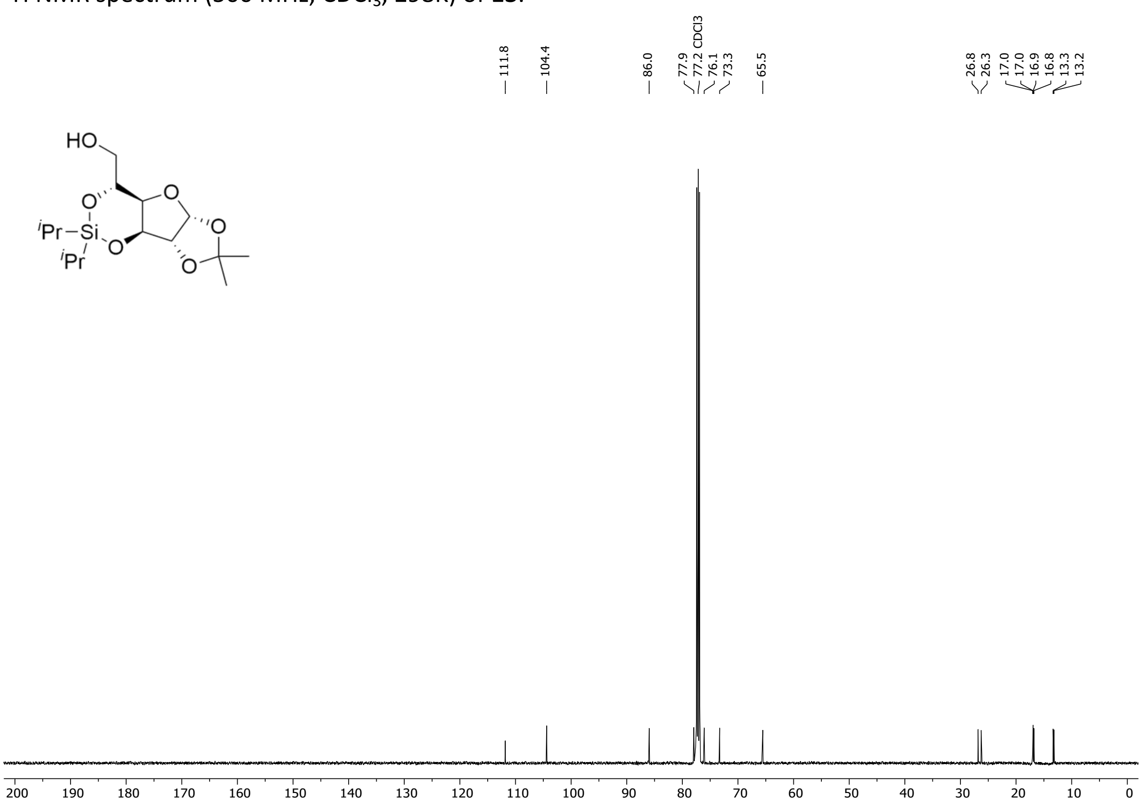


^{1}H-^{13}C HSQC spectrum (500/126 MHz, $CDCl_3$, 298K) of **11**.

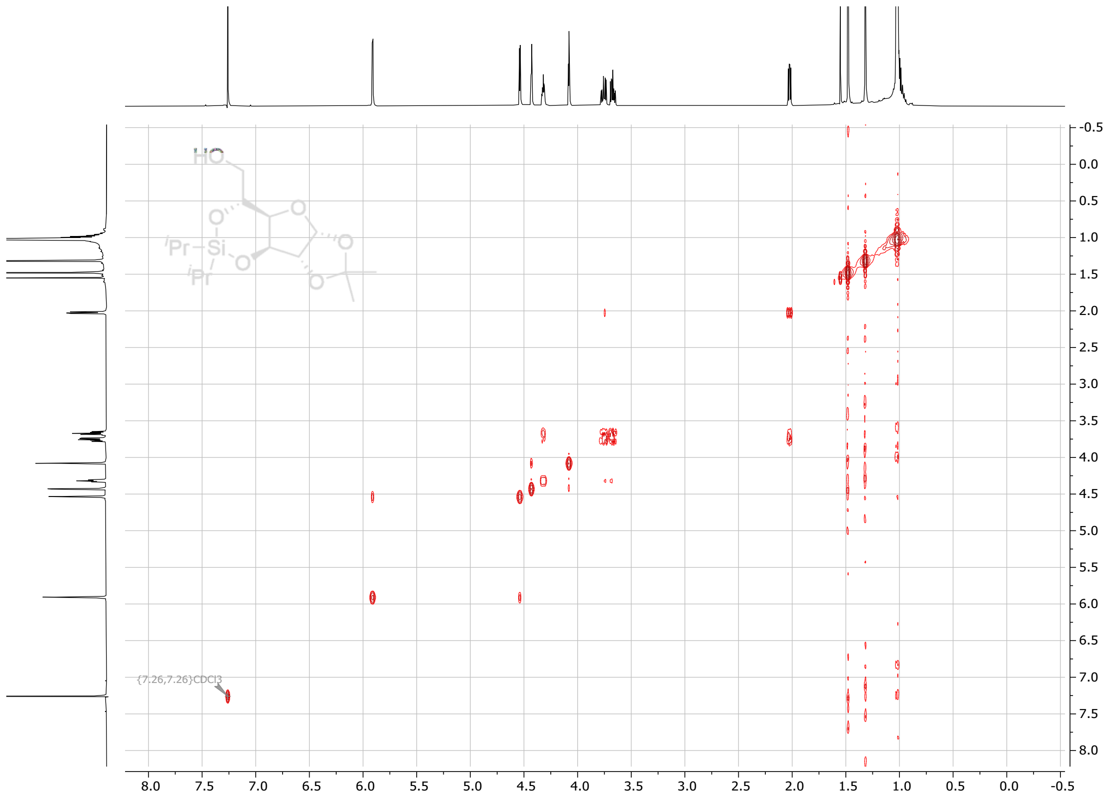
NMR spectra of 13



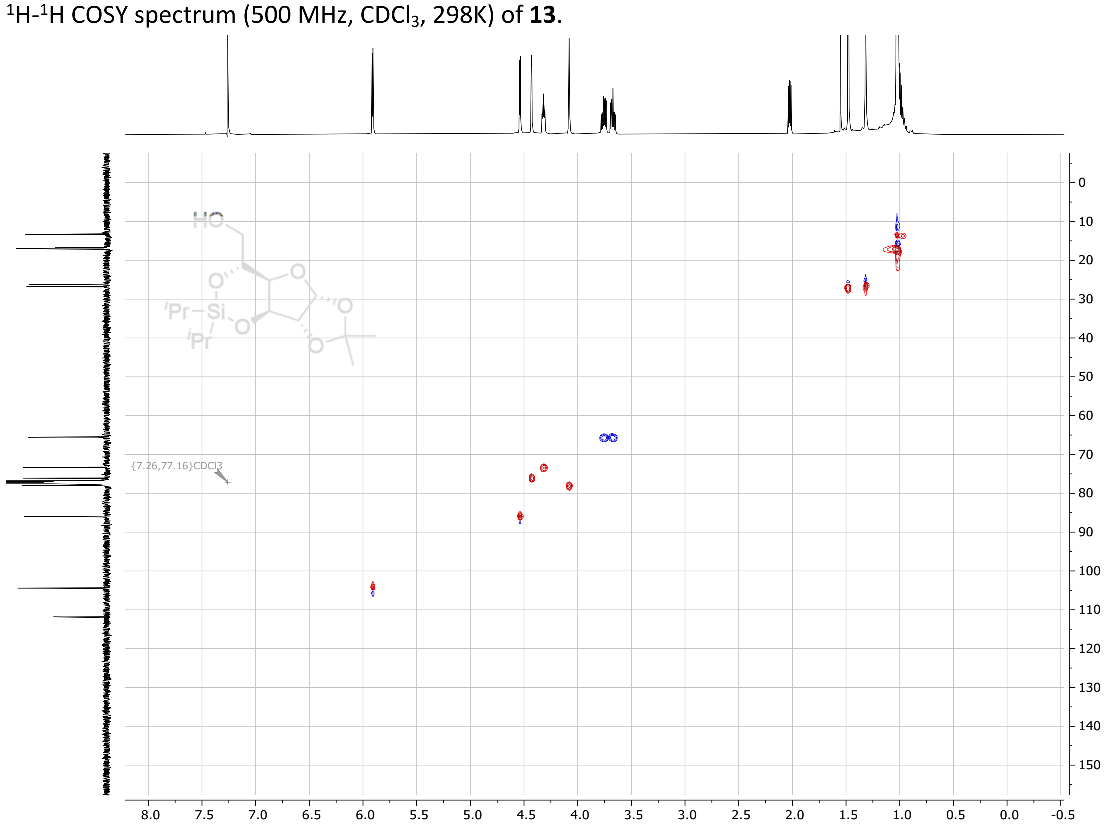
^1H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **13**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **13**.

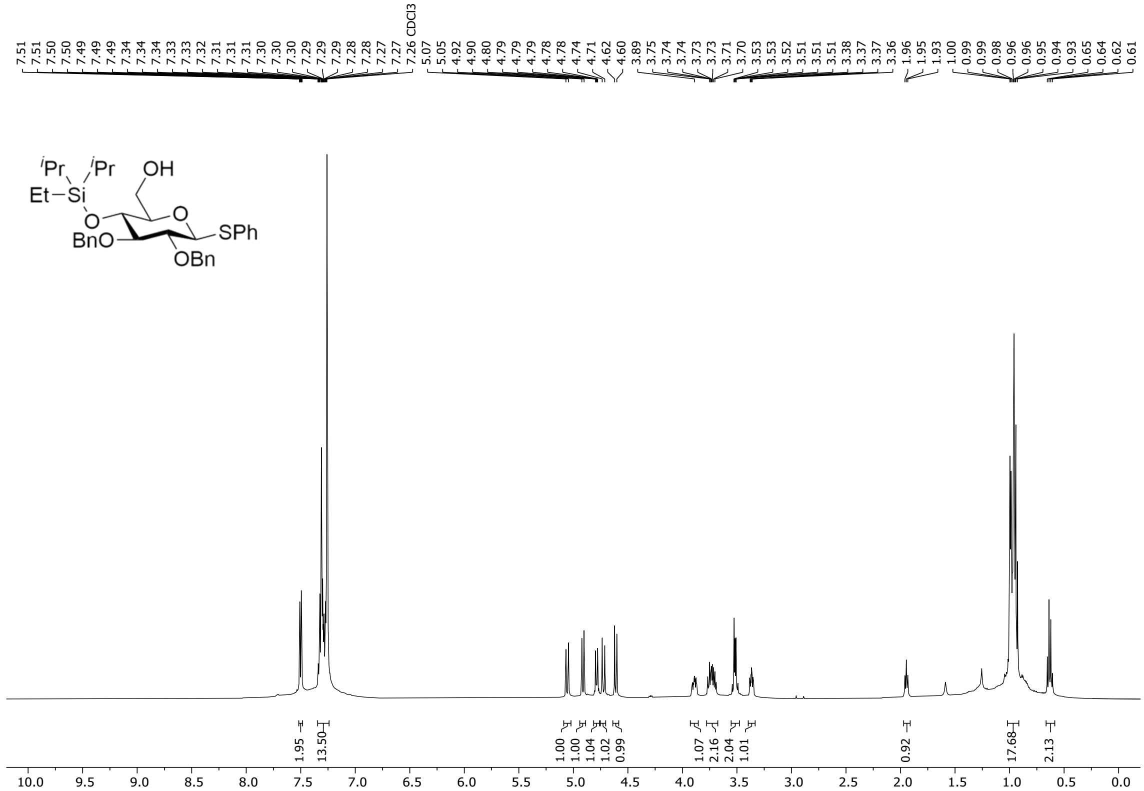


^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **13**.

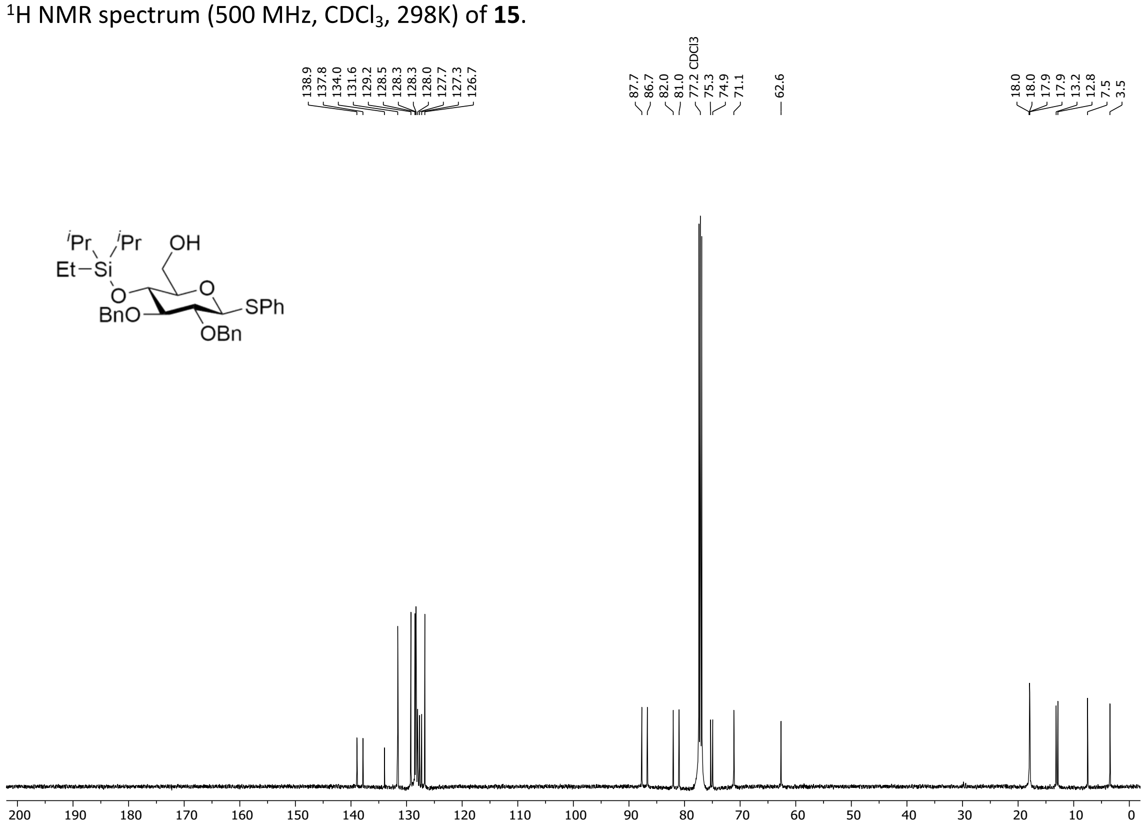


^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **13**.

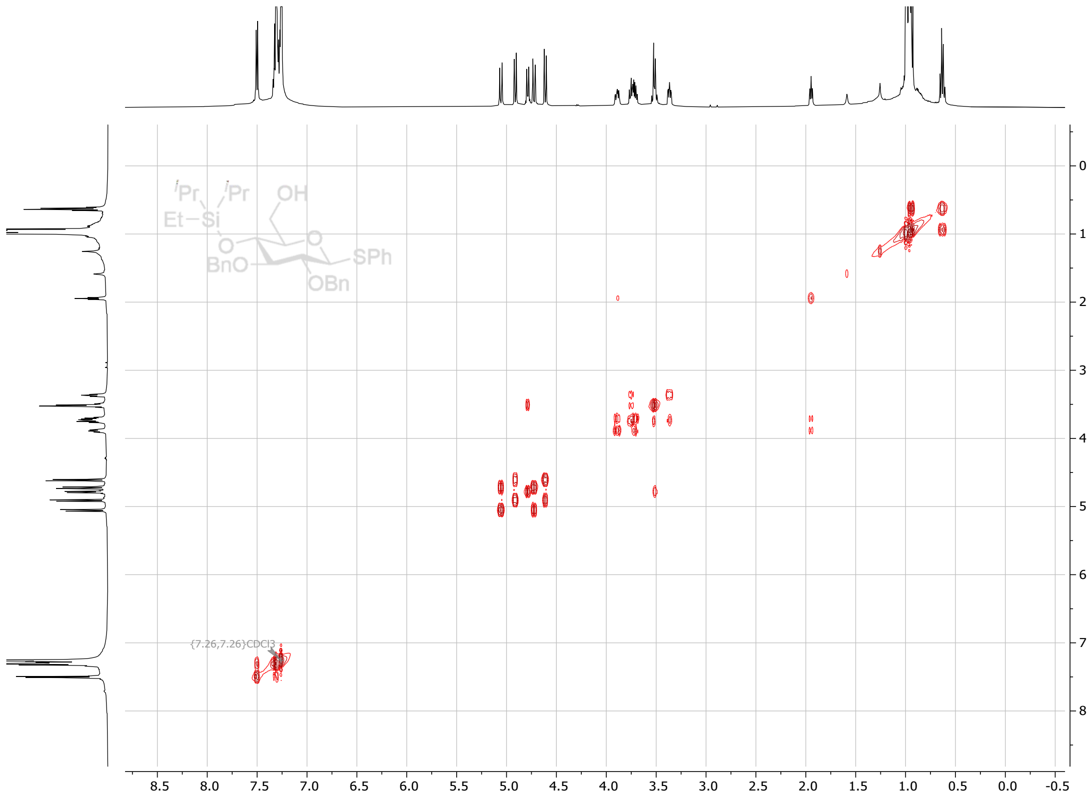
NMR spectra of 15



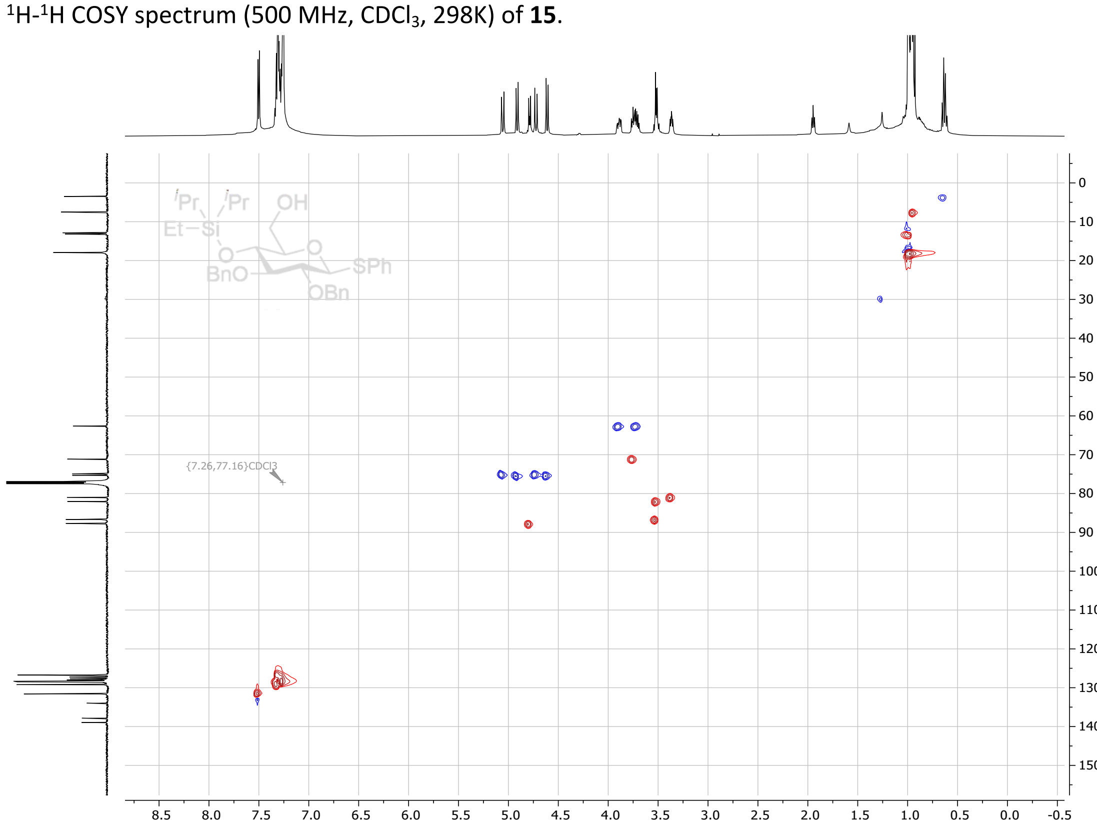
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **15**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **15**.

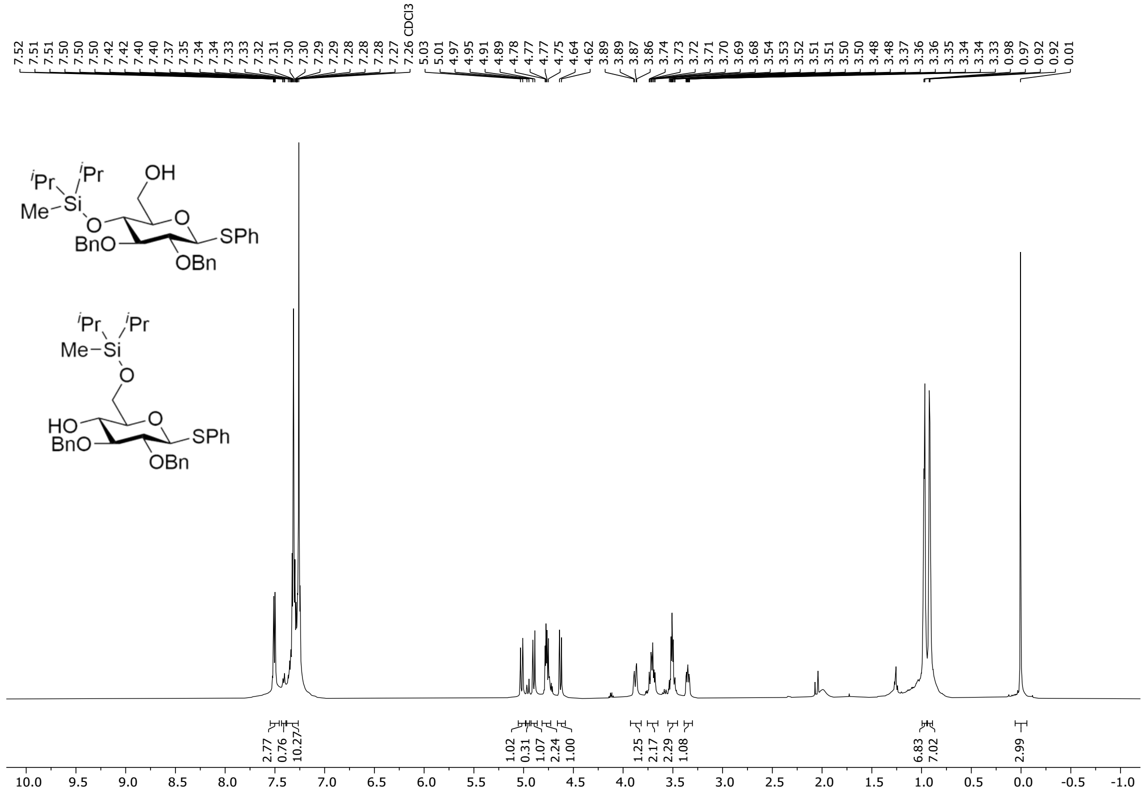


^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **15**.

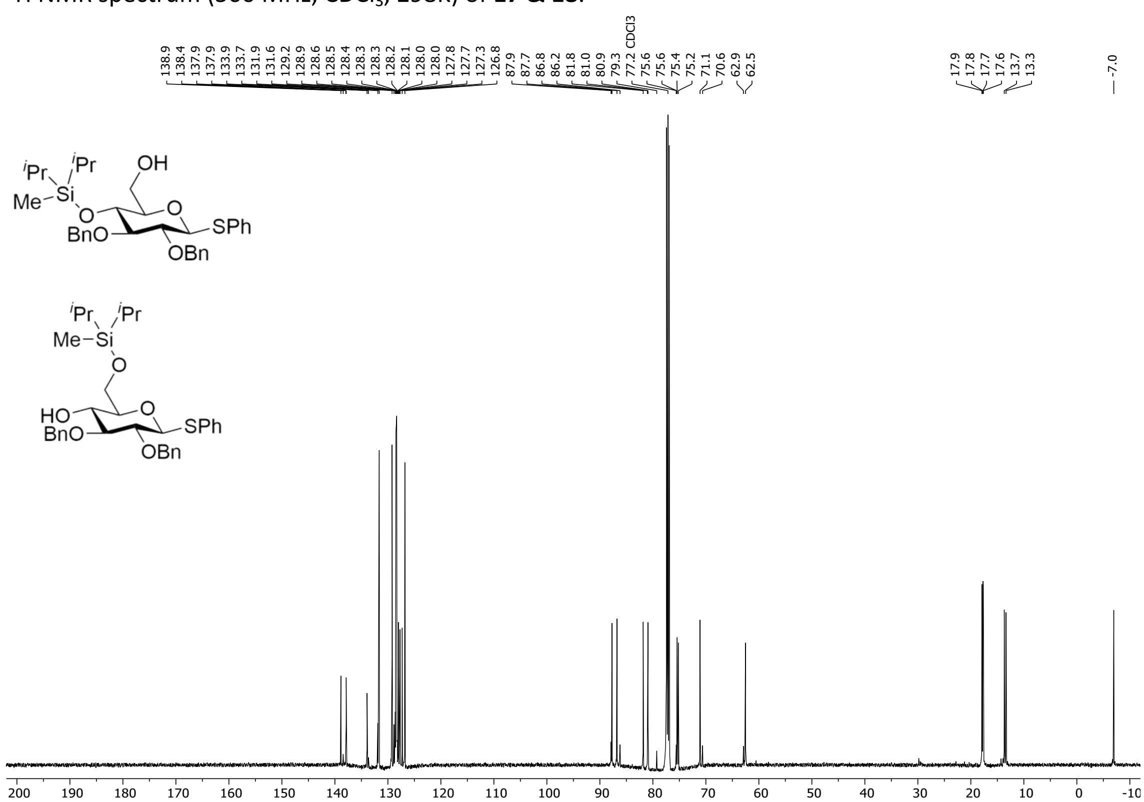


^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **15**.

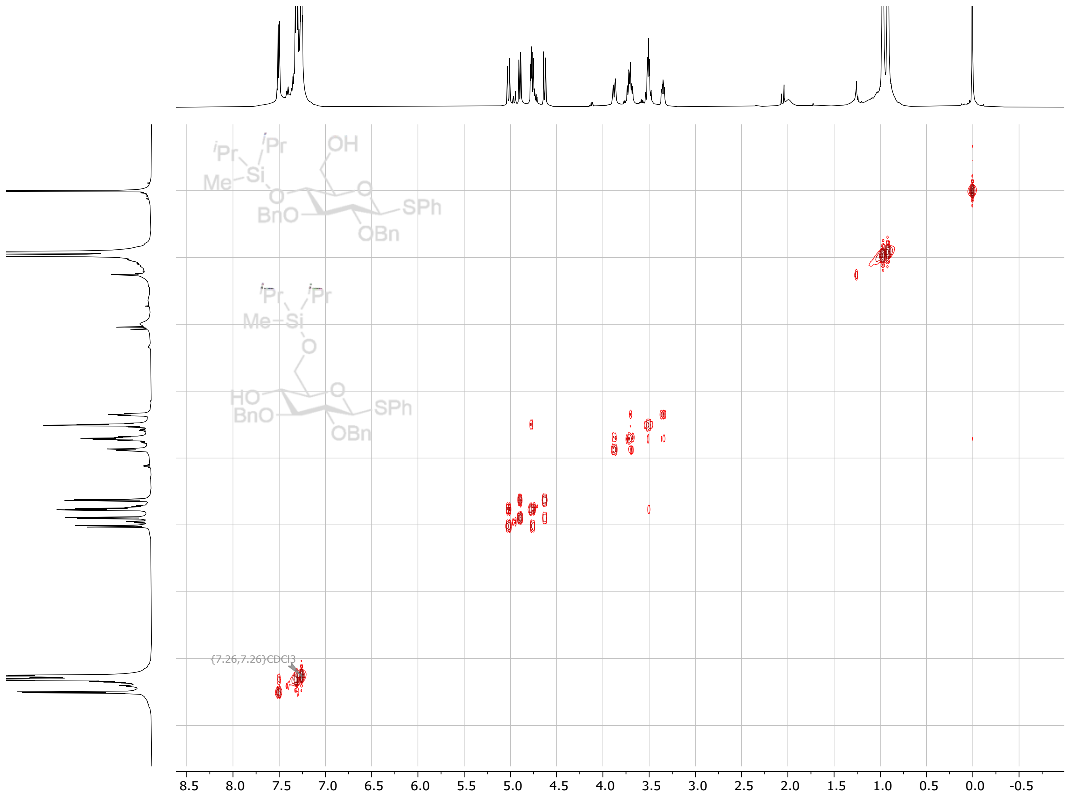
NMR spectra of 17 & 18 (15 being the major component)



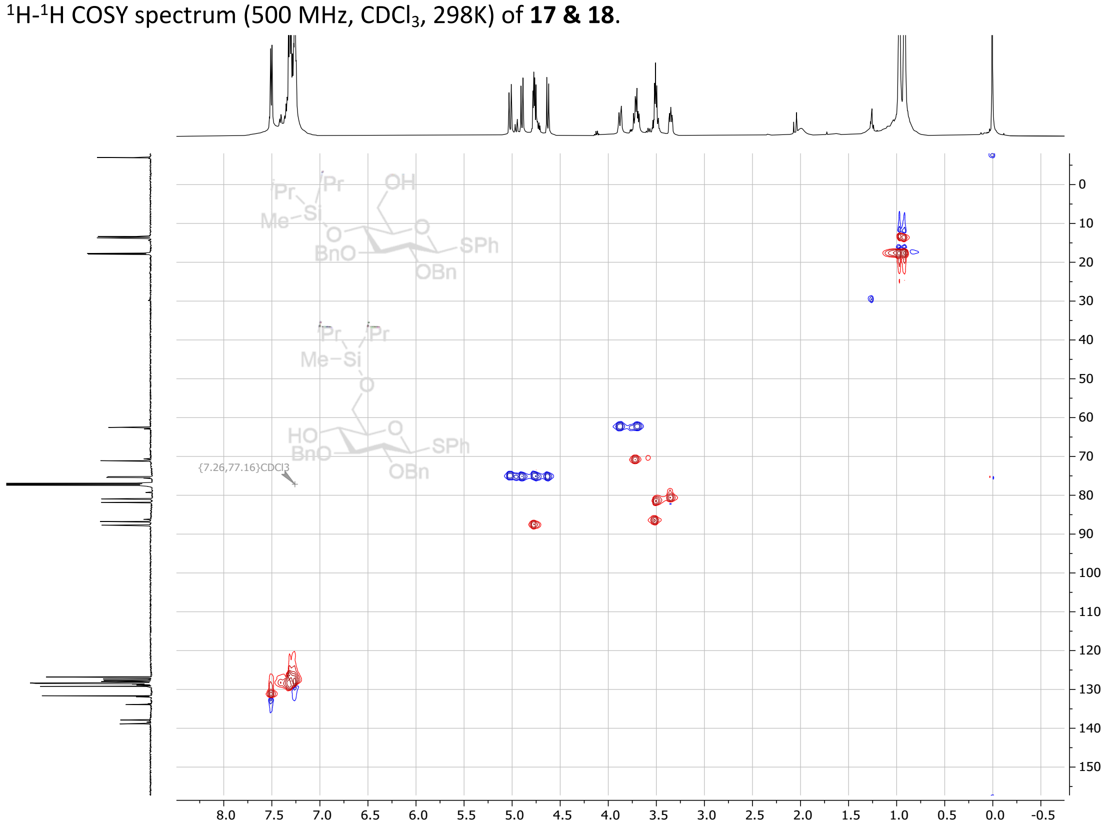
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **17 & 18**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **17 & 18**.

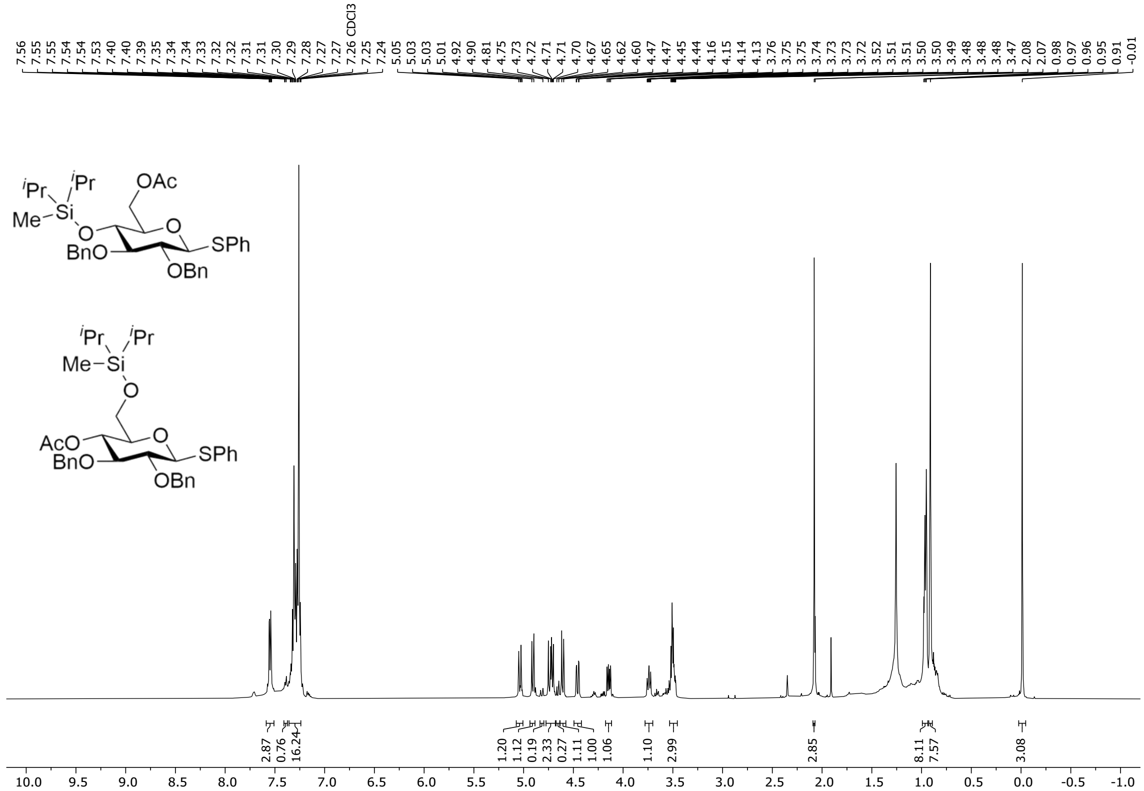


^1H-^1H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **17 & 18**.

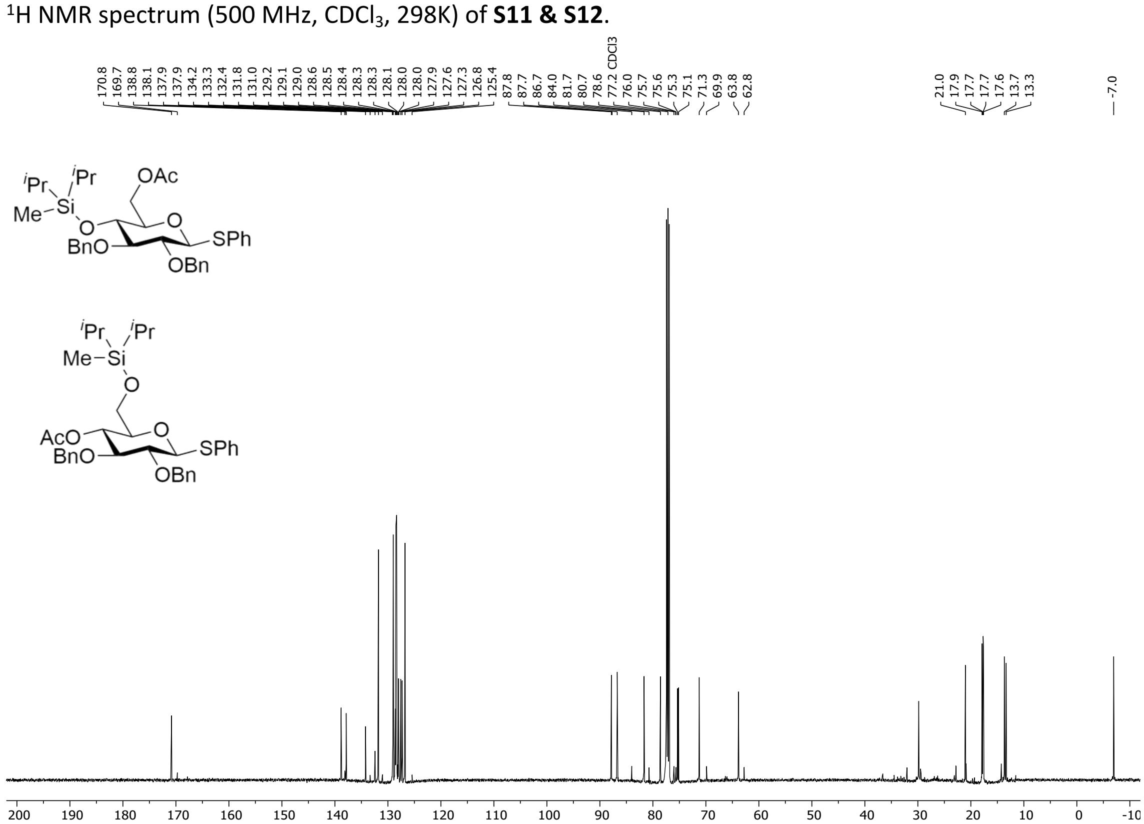


^1H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **17 & 18**.

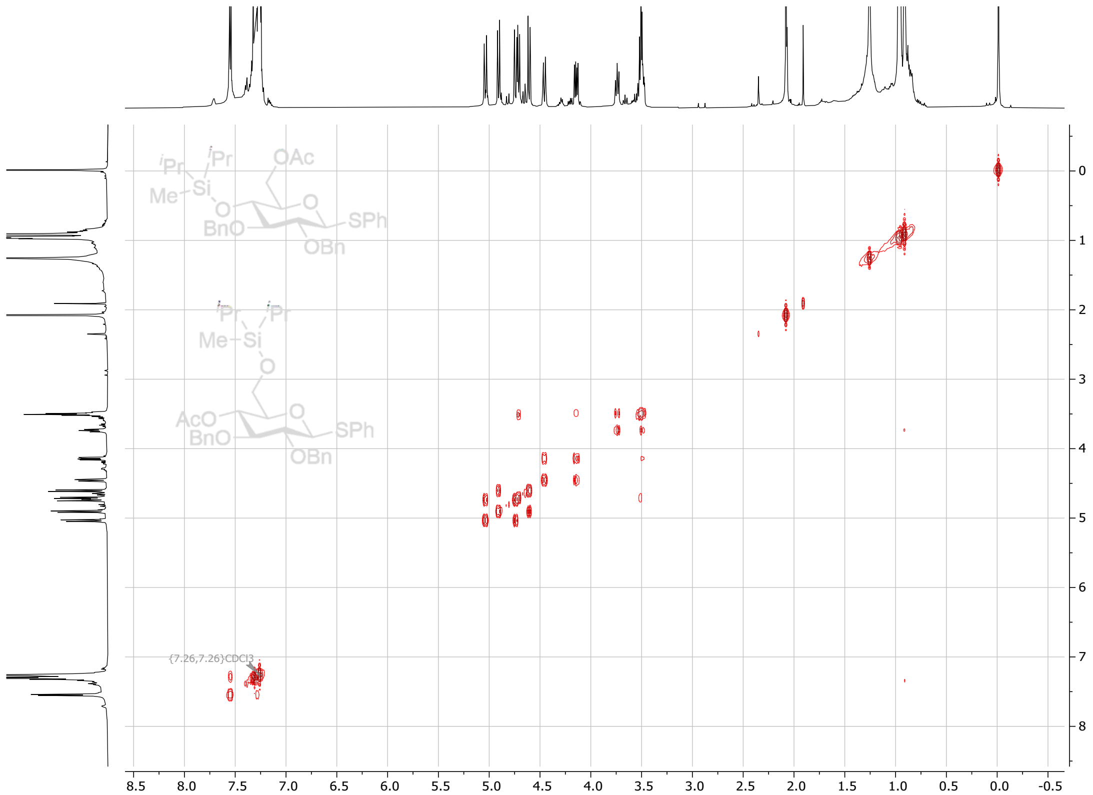
NMR spectra of S11 & S12 (S11 being the major component)



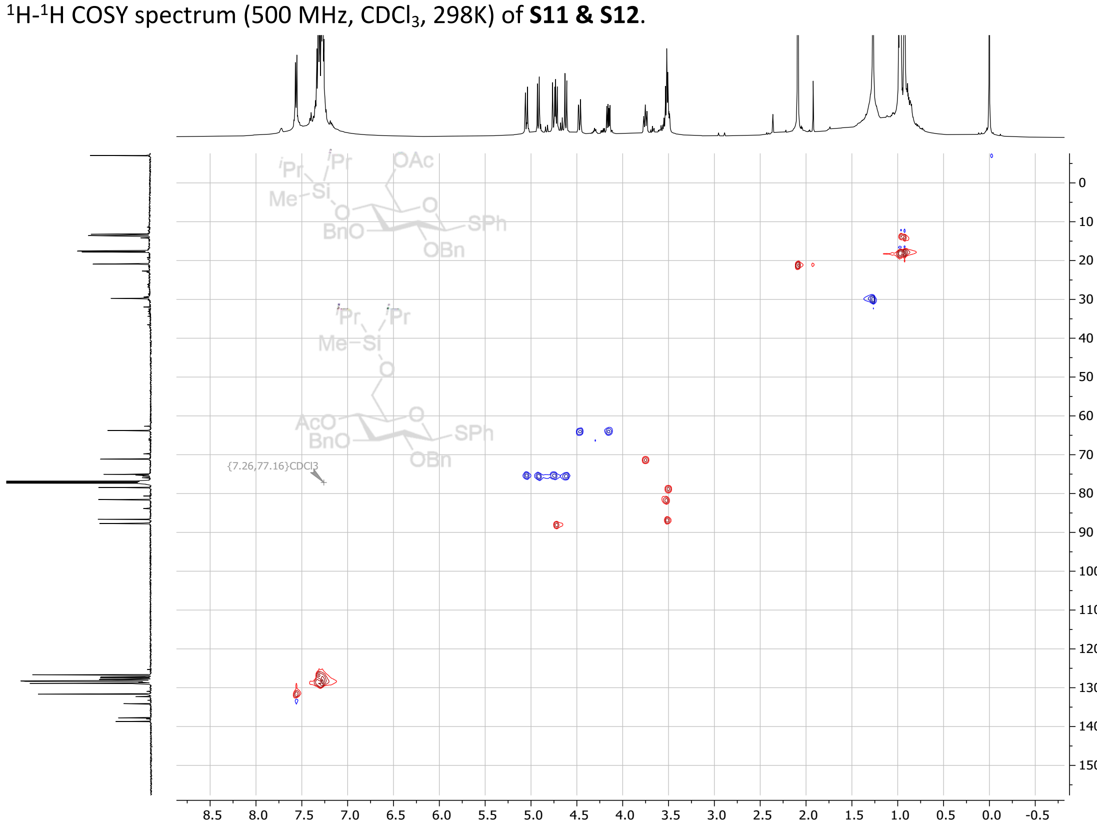
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **S11 & S12**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **S11 & S12**.

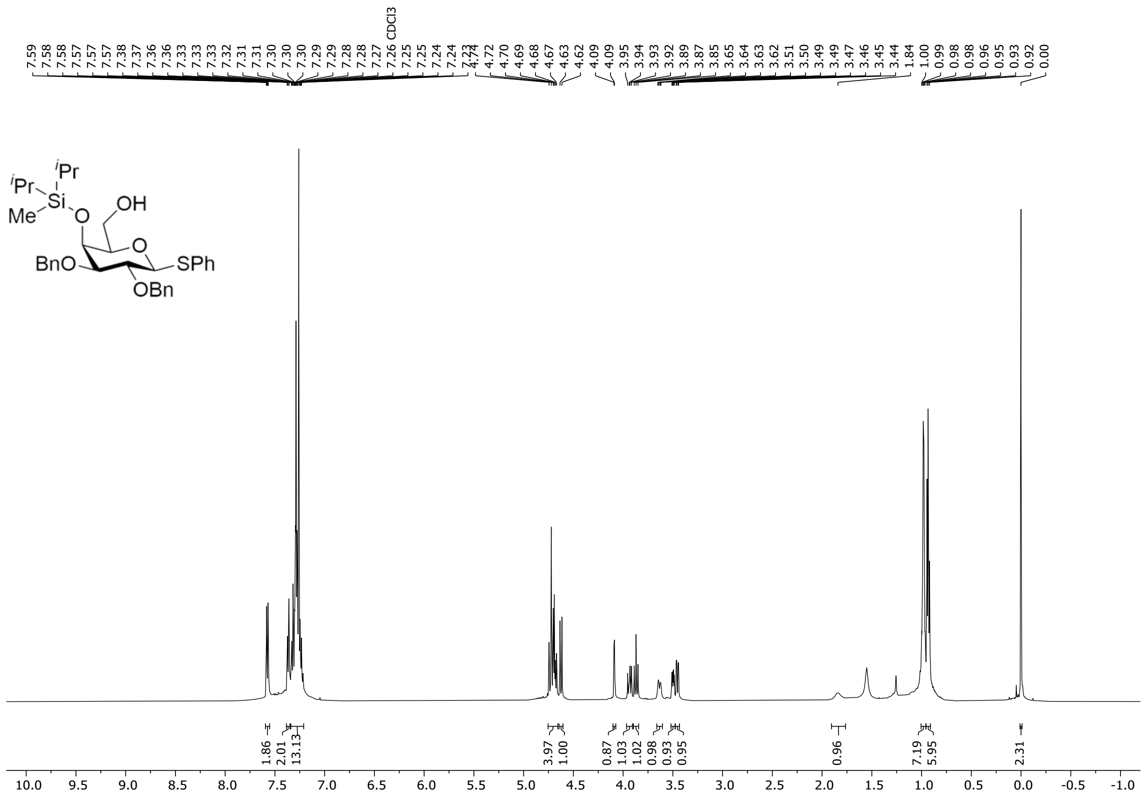


^1H-^1H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **S11 & S12**.

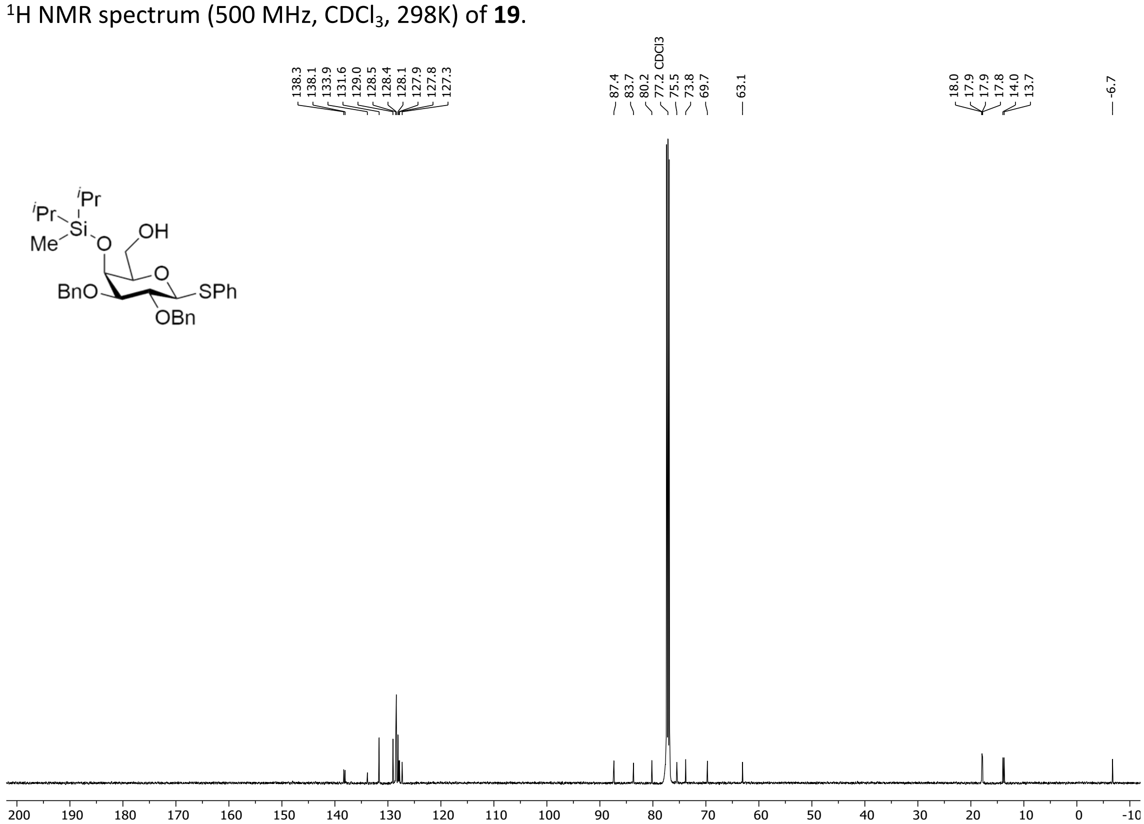


^1H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **S11 & S12**.

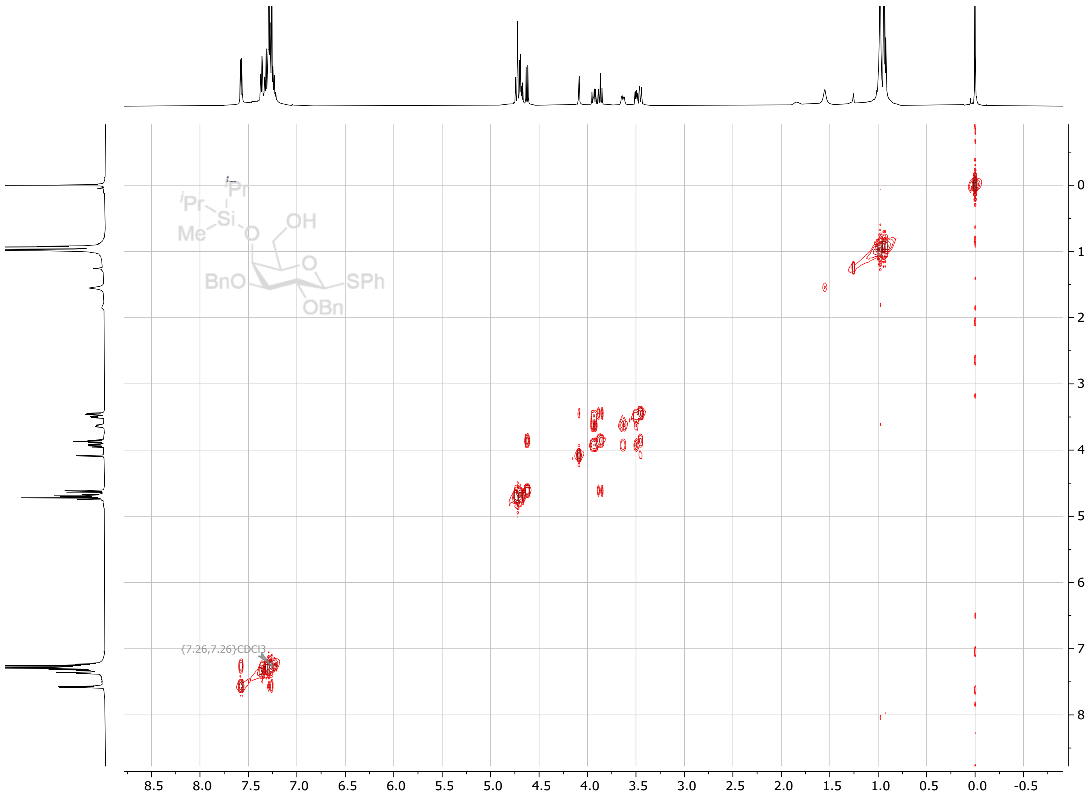
NMR spectra of 19



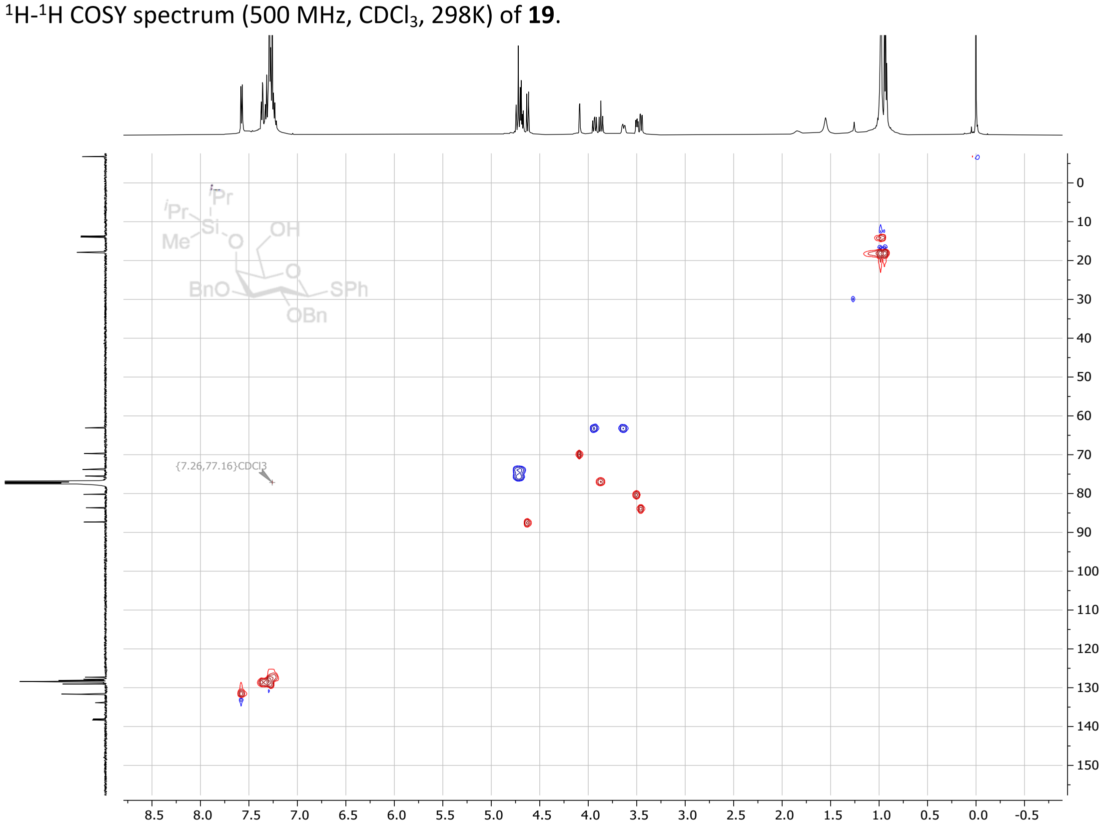
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **19**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **19**.

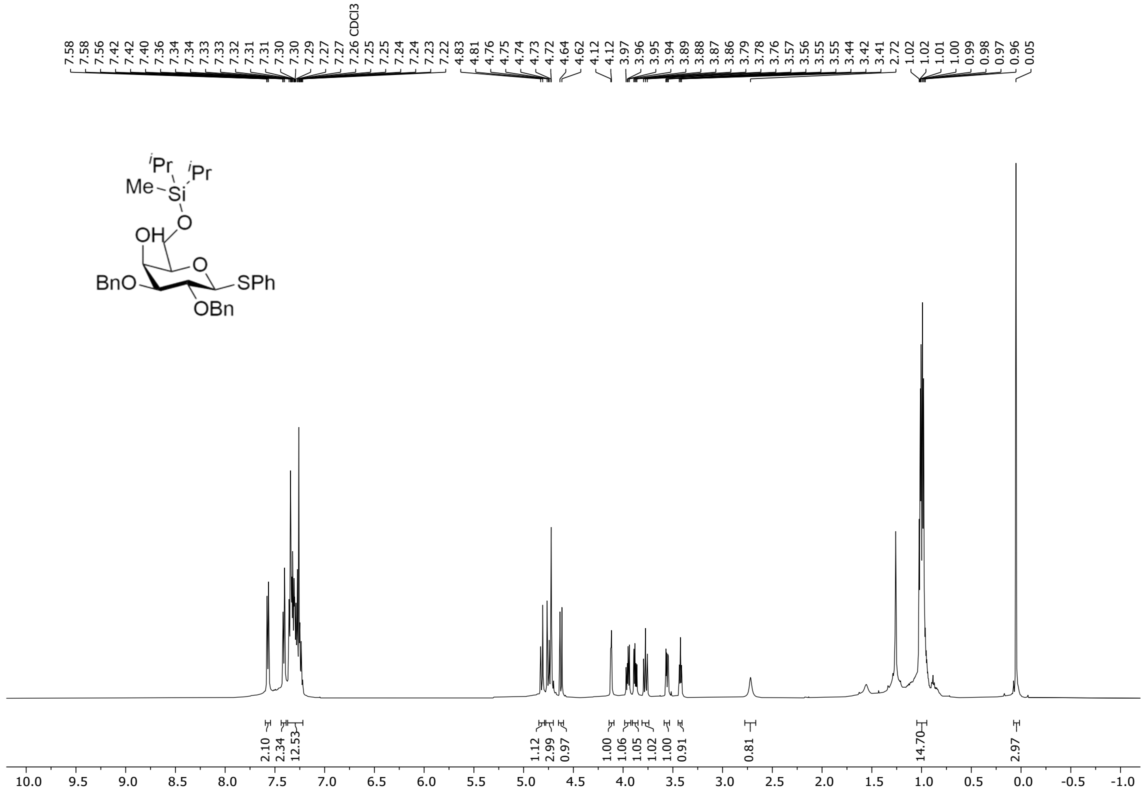


^1H-^1H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **19**.

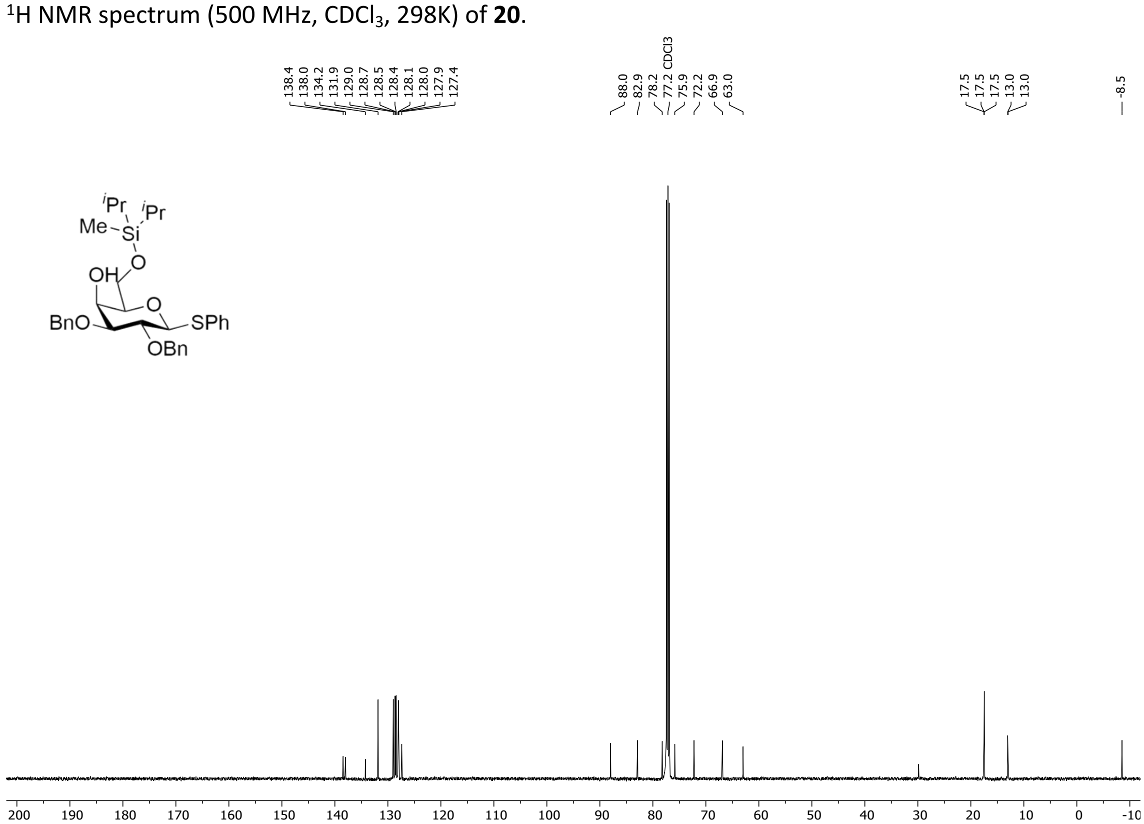


^1H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **19**.

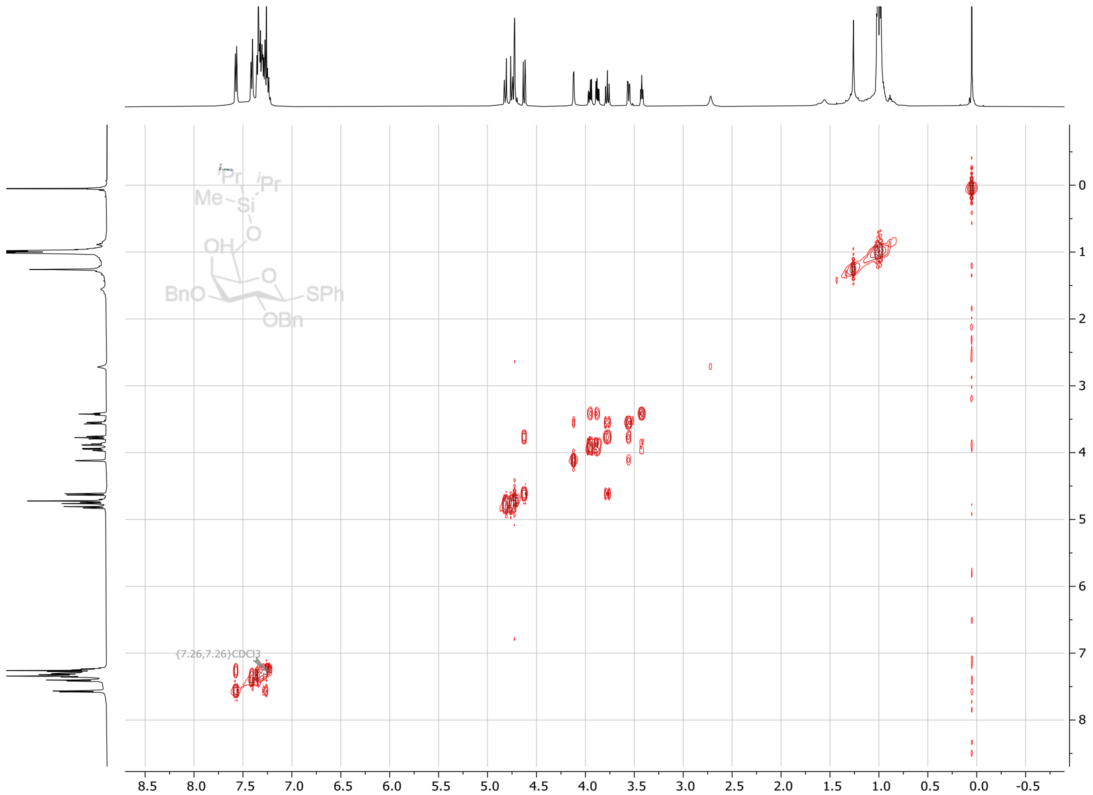
NMR spectra of 20



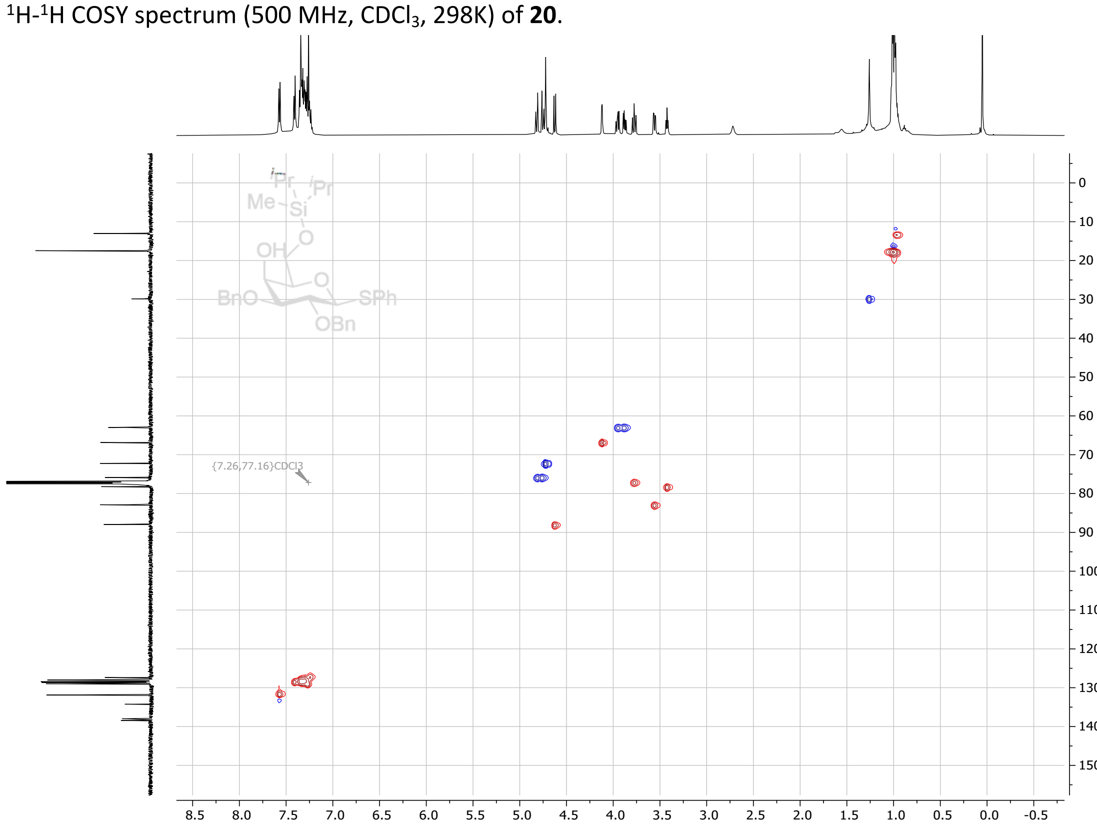
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **20**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **20**.

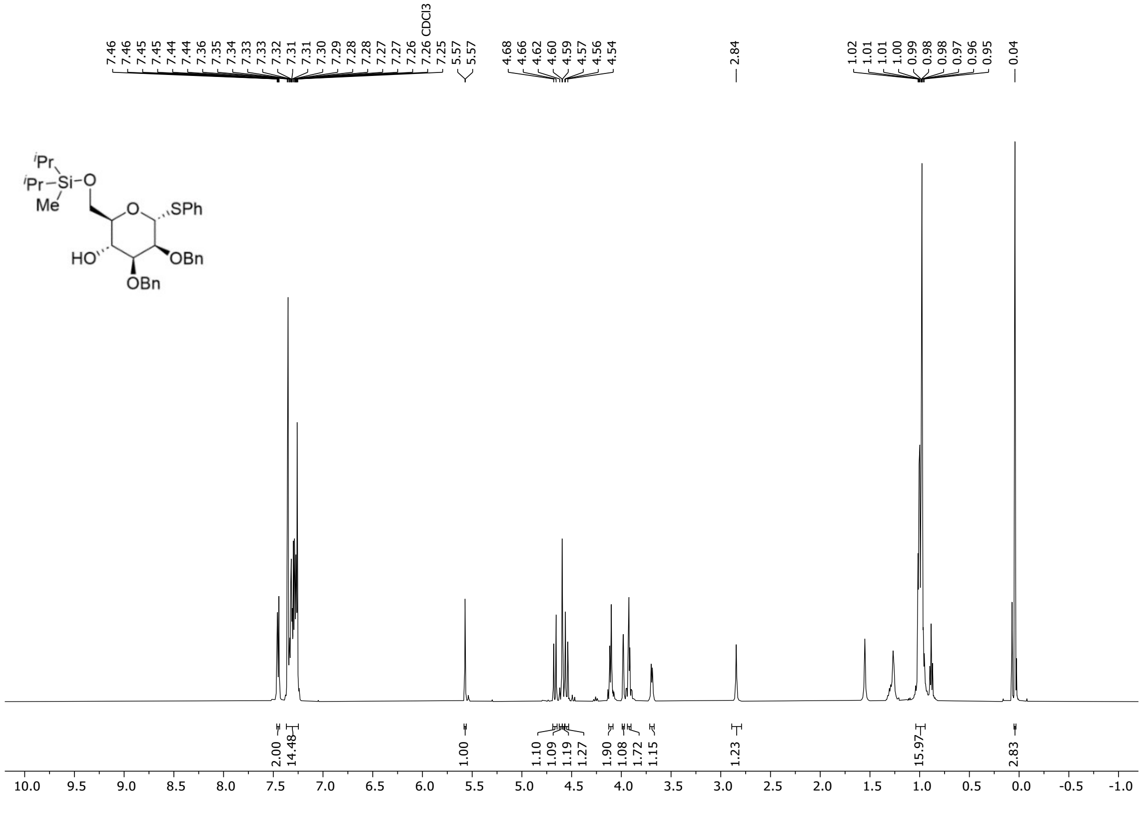


^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **20**.

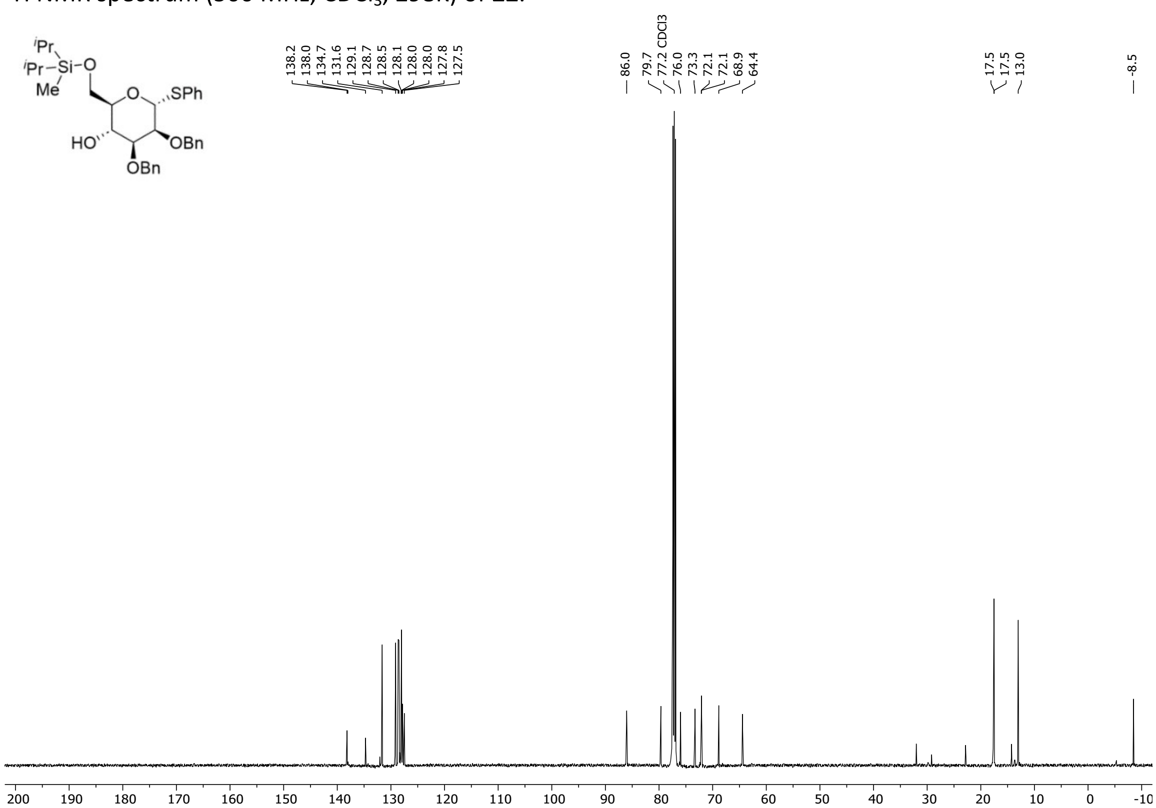


^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **20**.

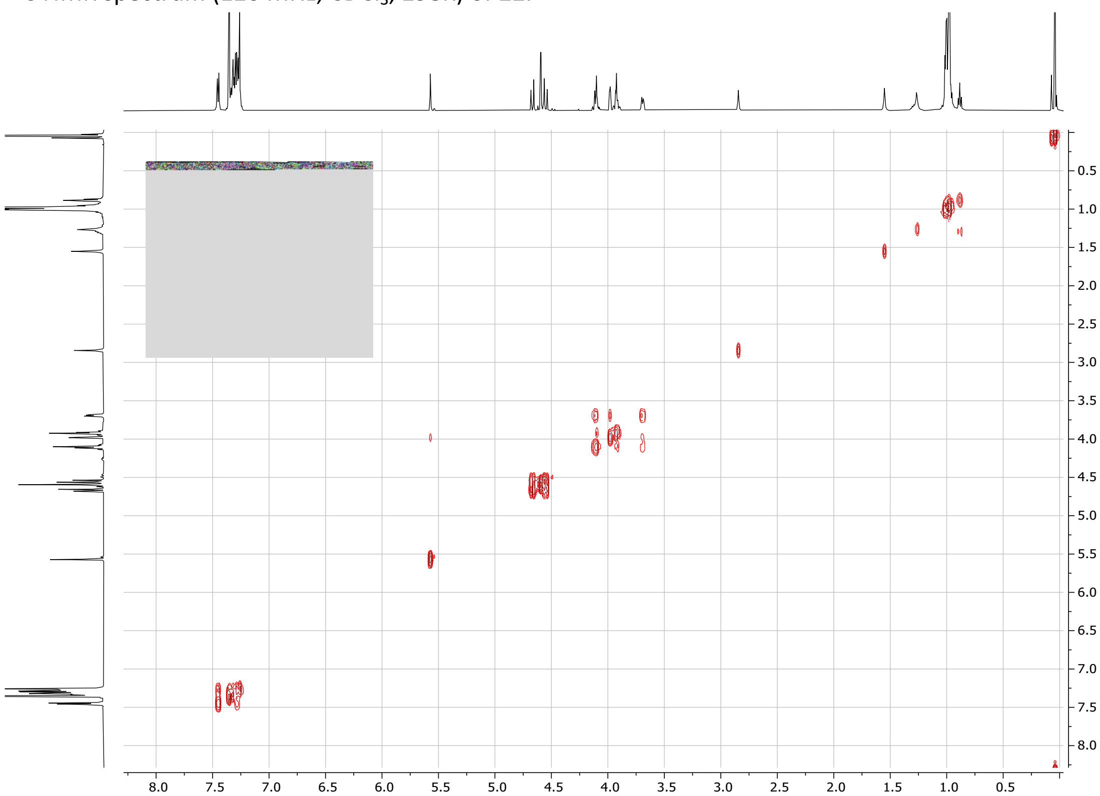
NMR spectra of 22



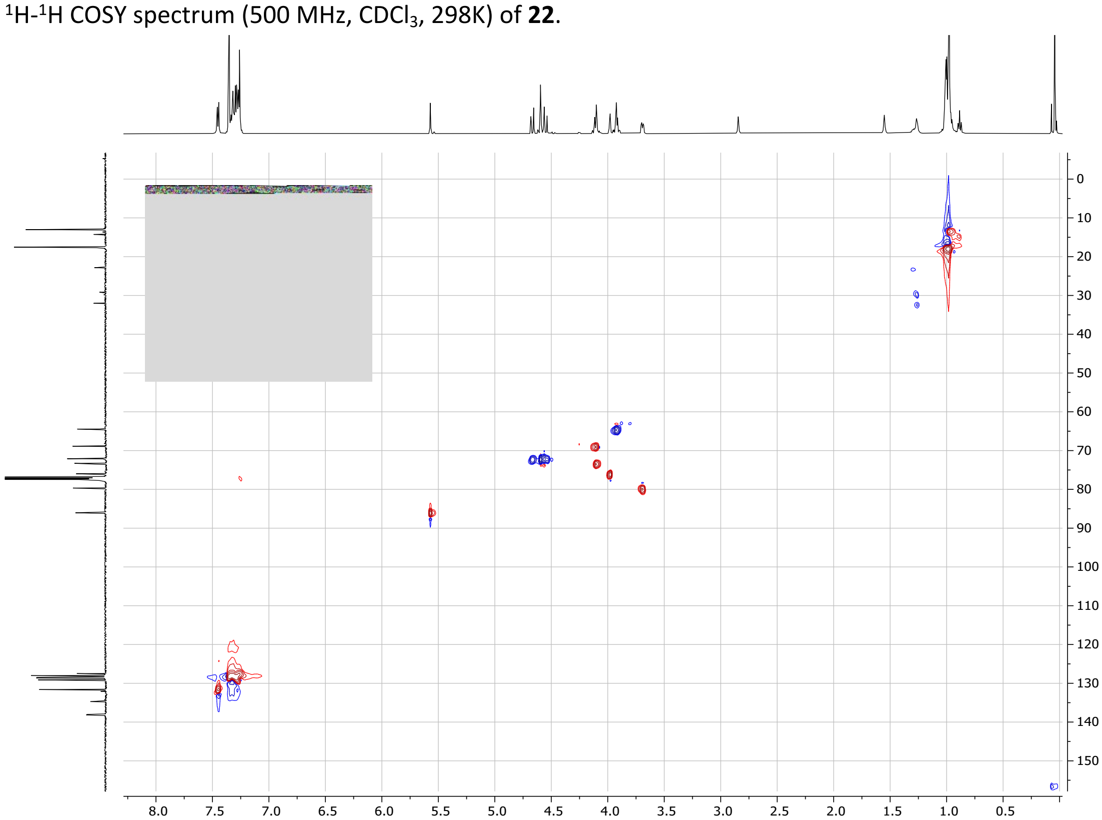
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **22**.



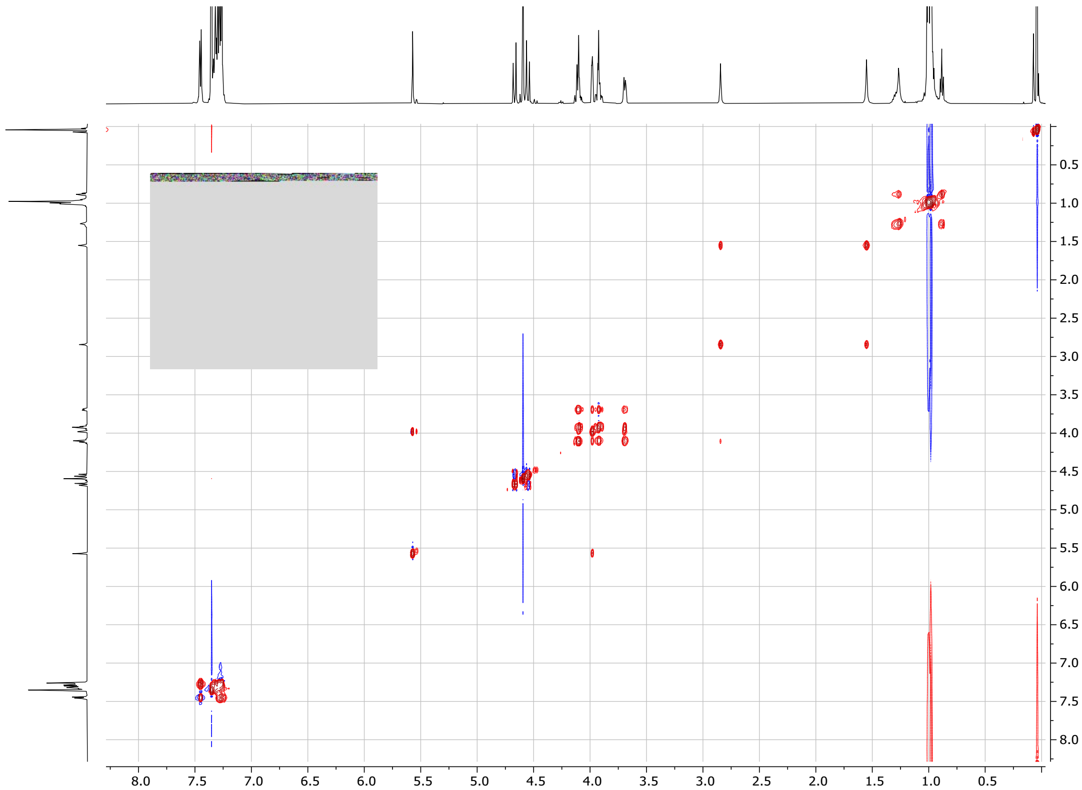
^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **22**.



^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **22**.

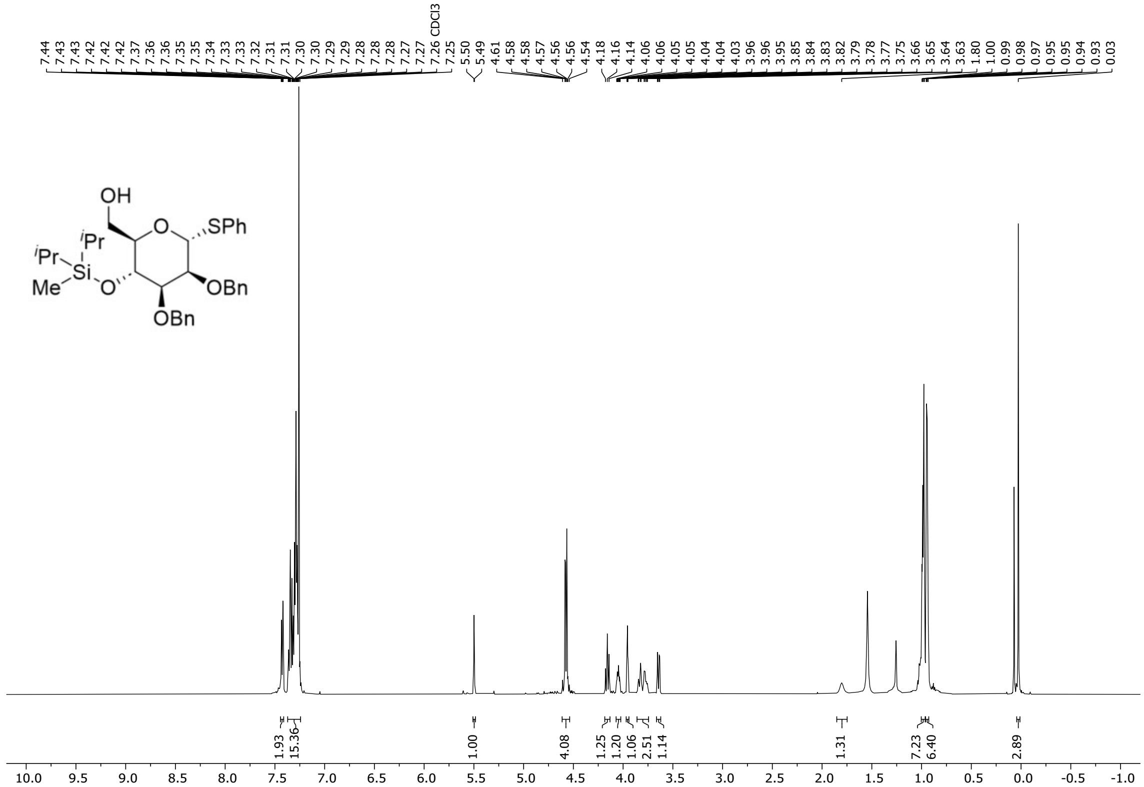


^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **22**.

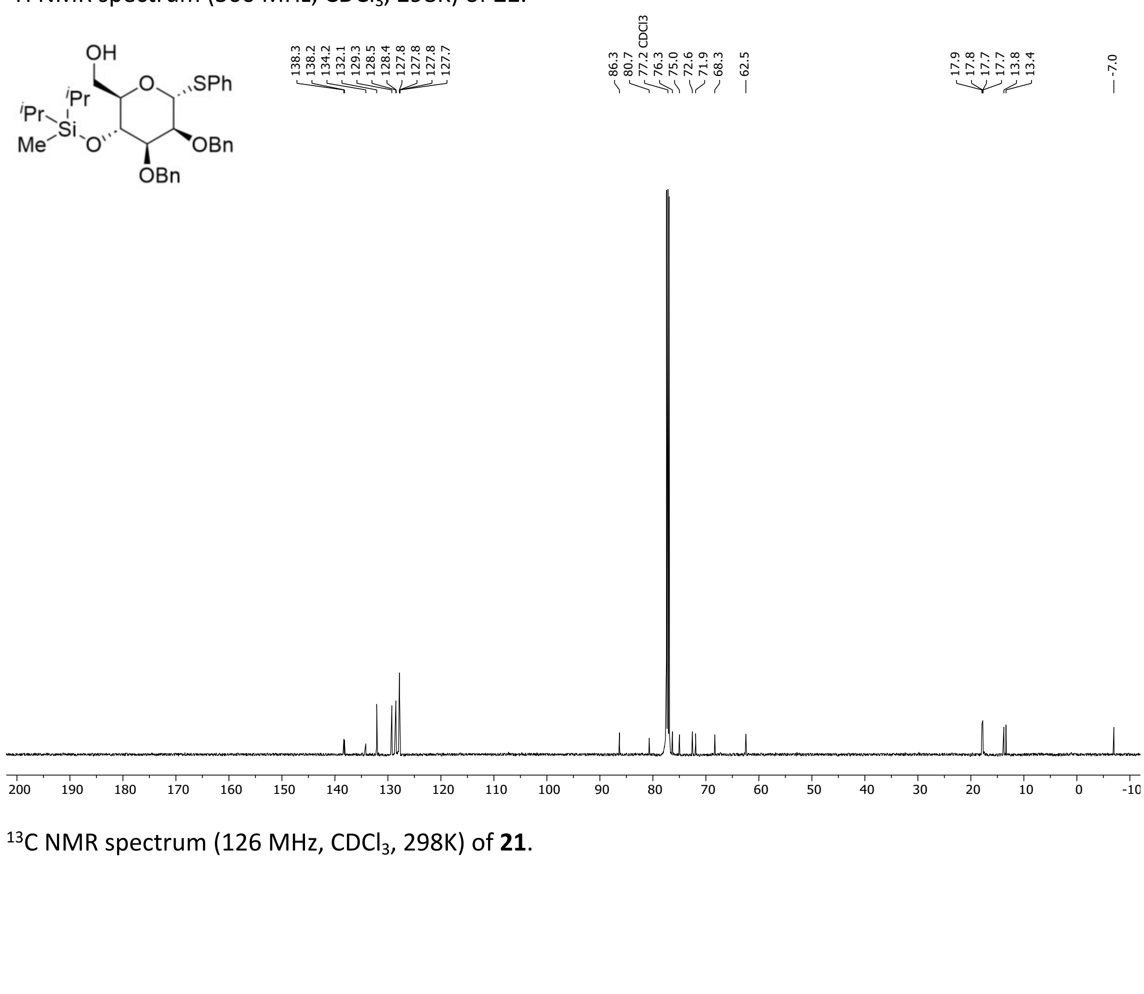


^1H-^1H TOCSY spectrum (500 MHz, $CDCl_3$, 298K) of **22**.

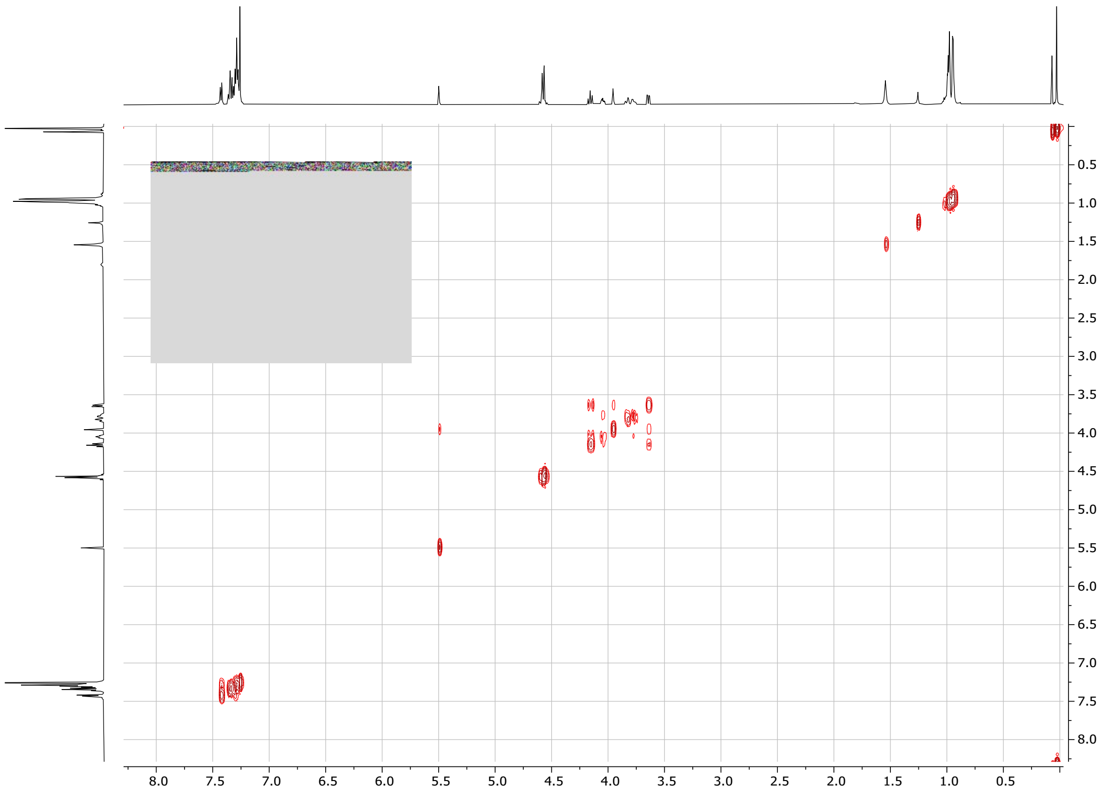
NMR spectra of 21



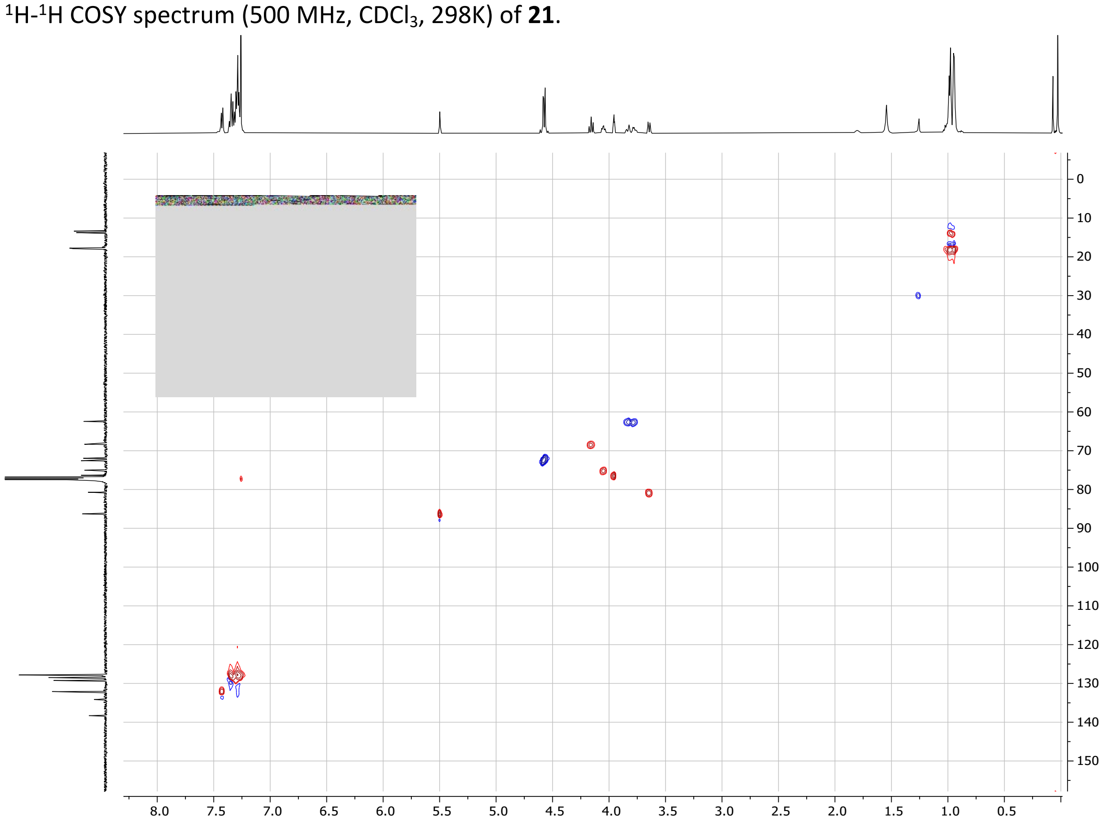
[1]H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **21**.



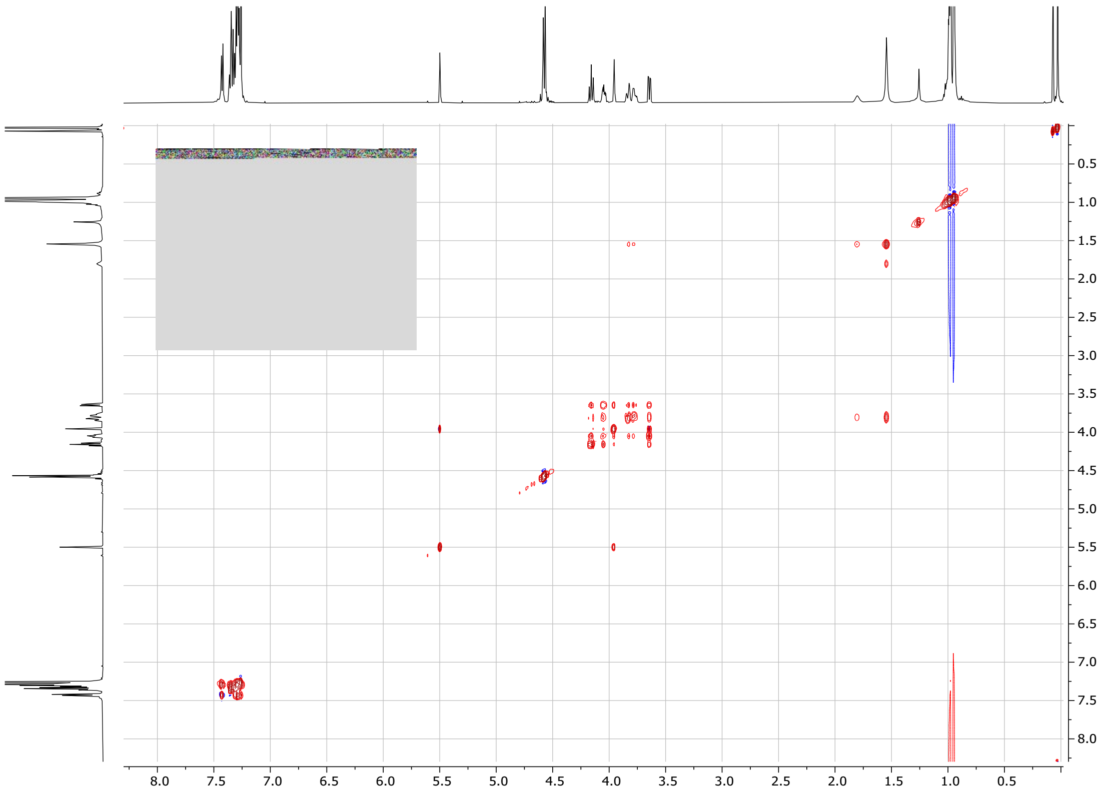
[13]C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **21**.



^1H-^1H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **21**.

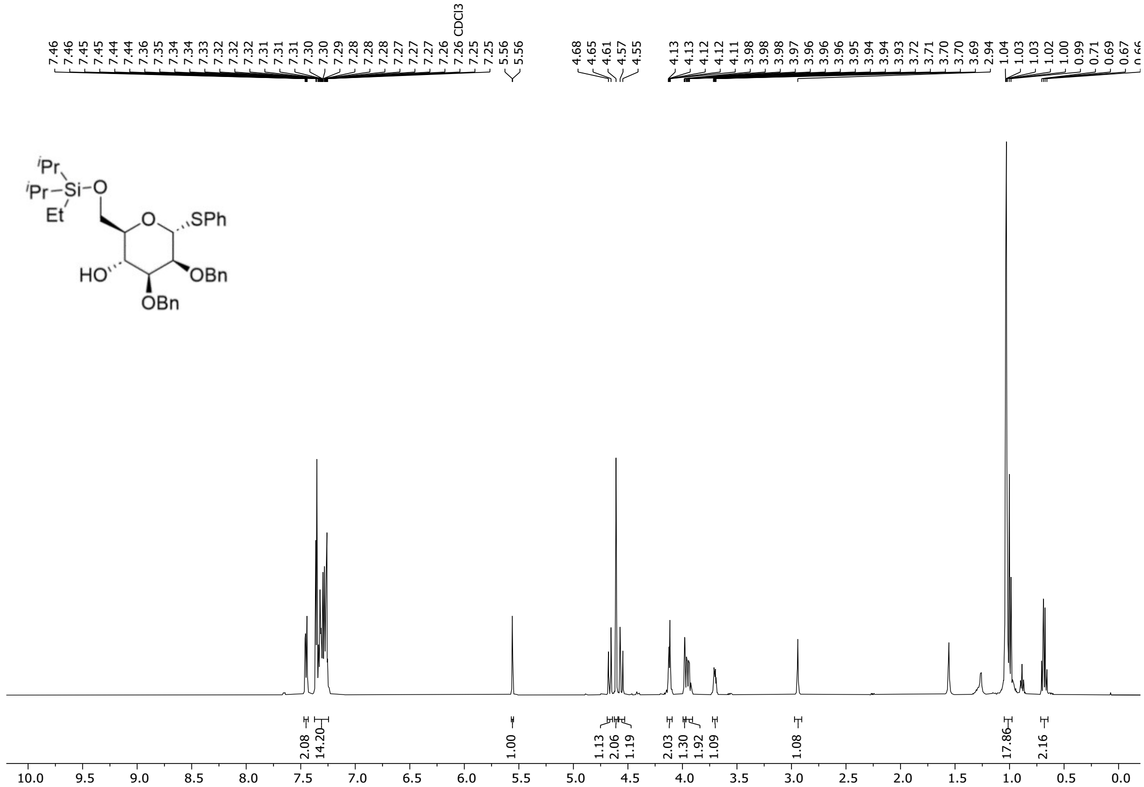


^1H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **21**.

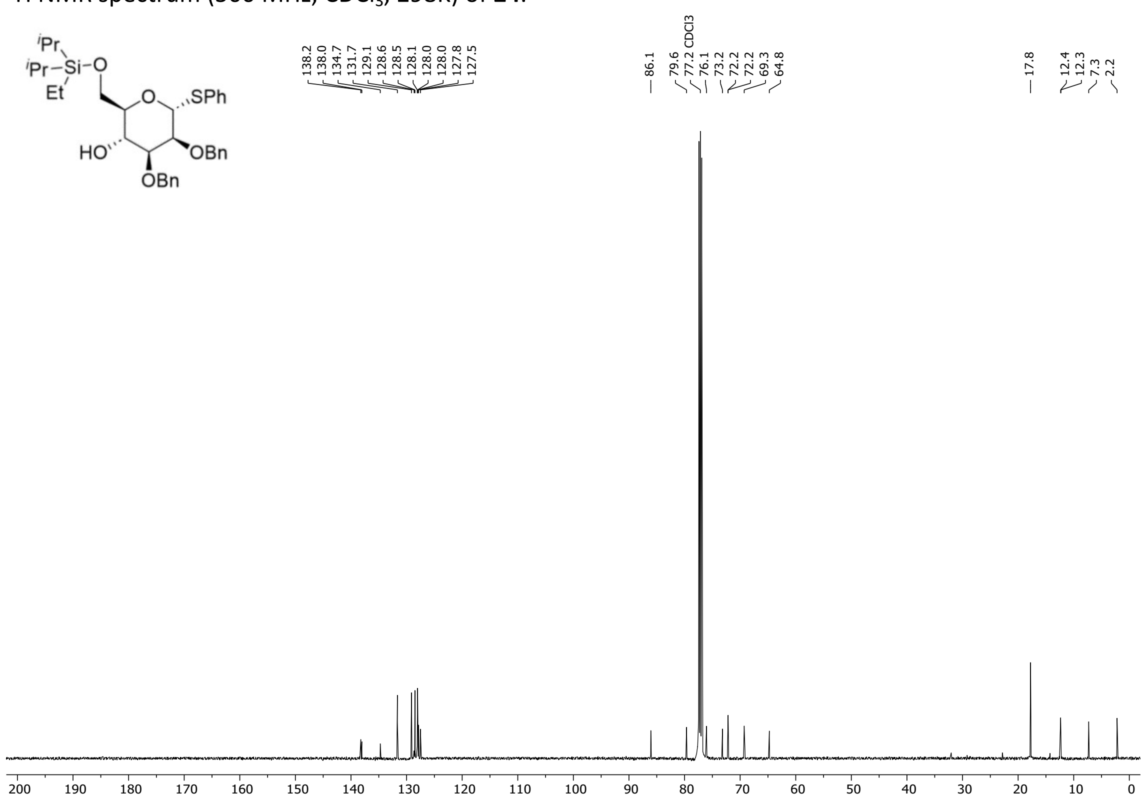


^{1}H-^{1}H TOCSY spectrum (500 MHz, $CDCl_3$, 298K) of **21**.

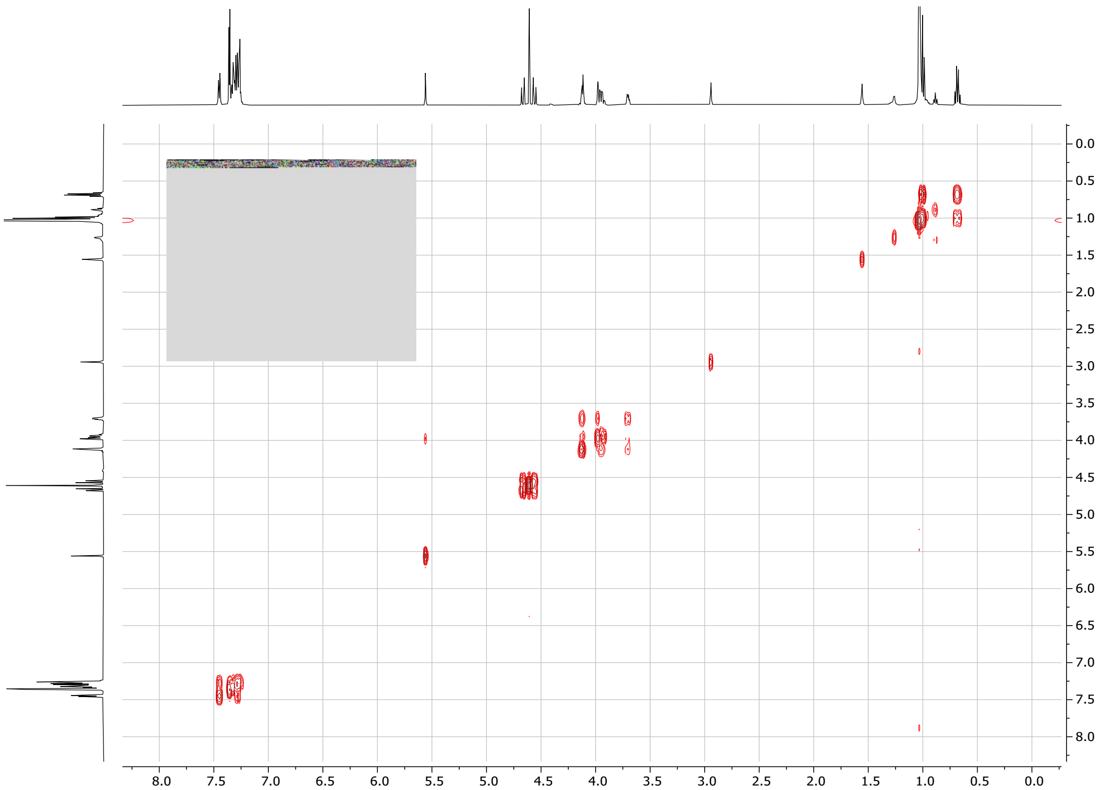
NMR spectra of 24



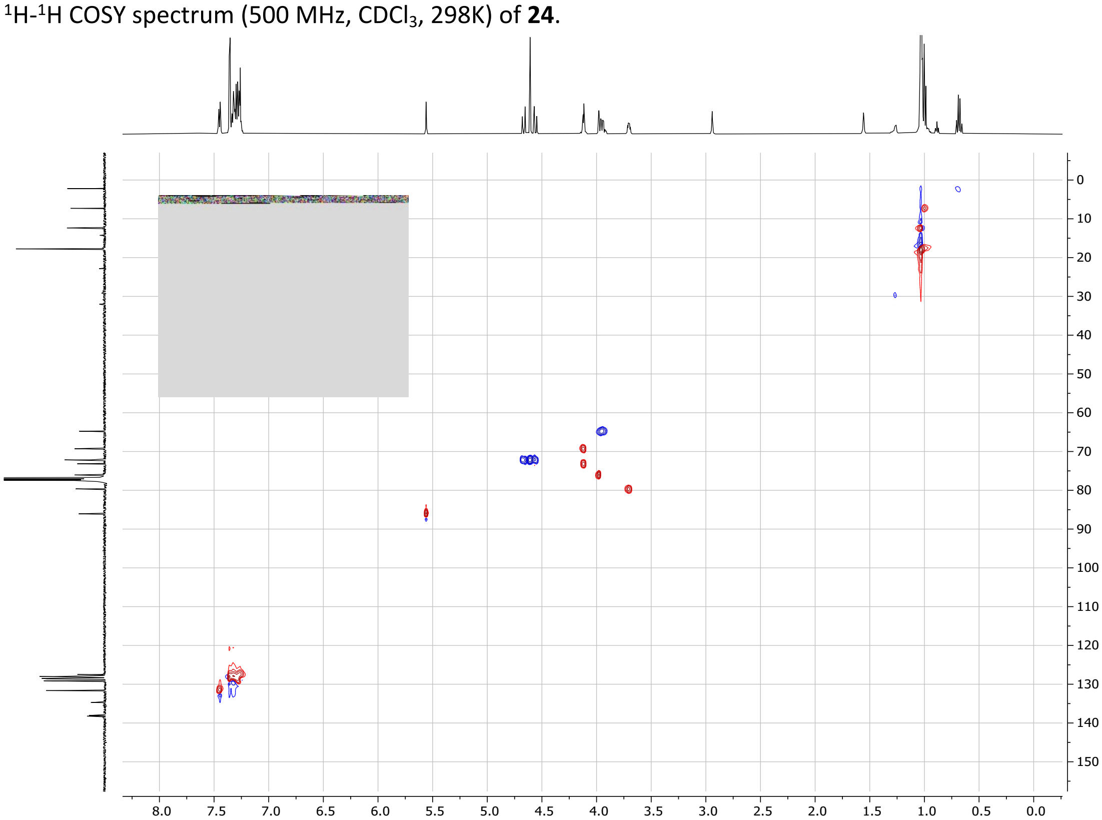
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **24**.



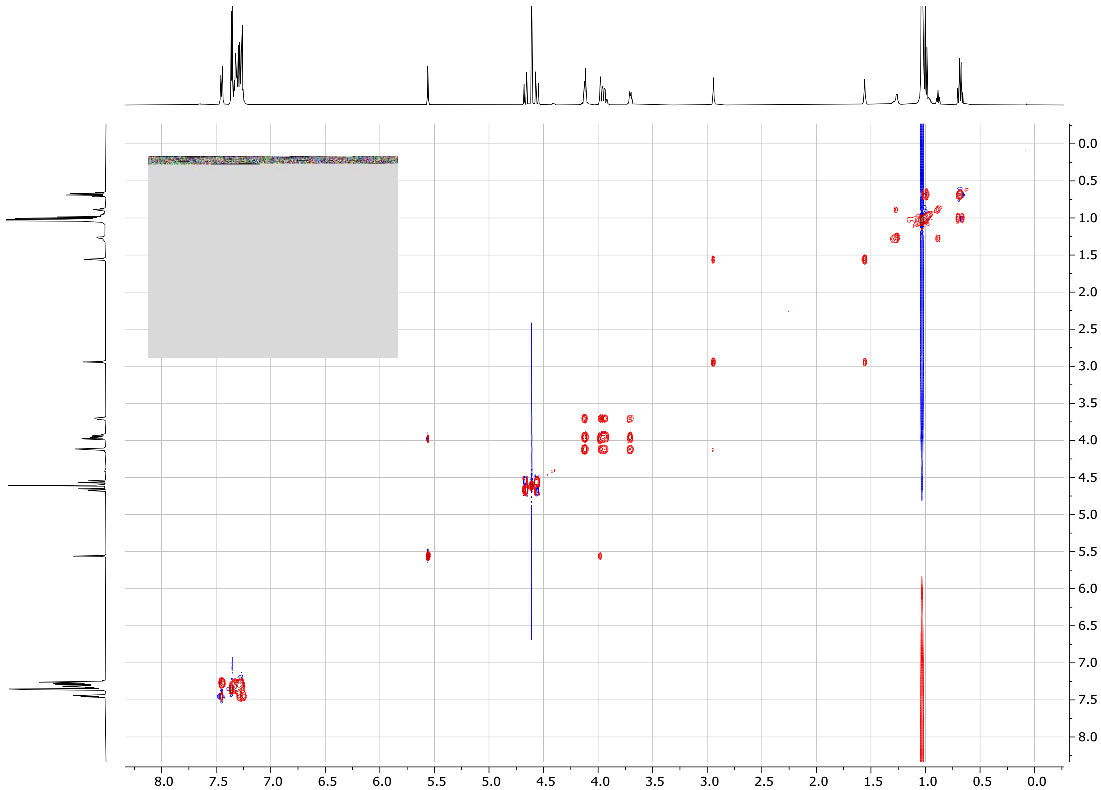
^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **24**.



^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **24**.

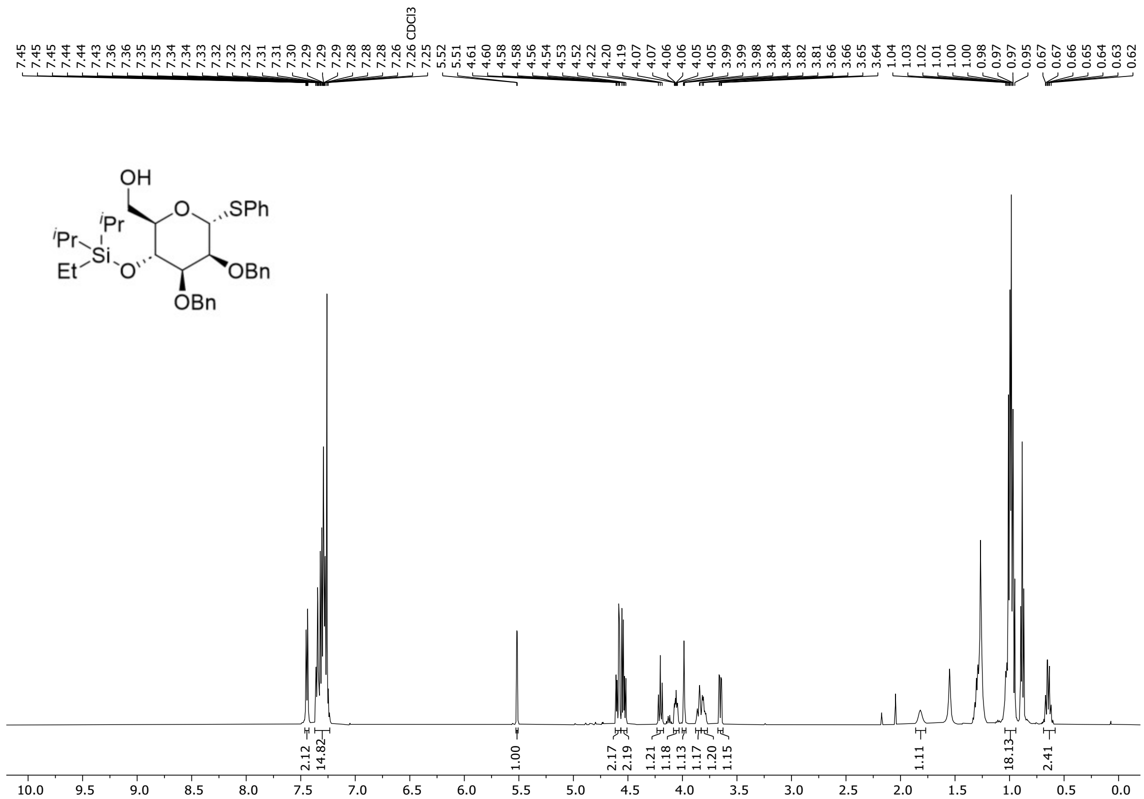


^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **24**.

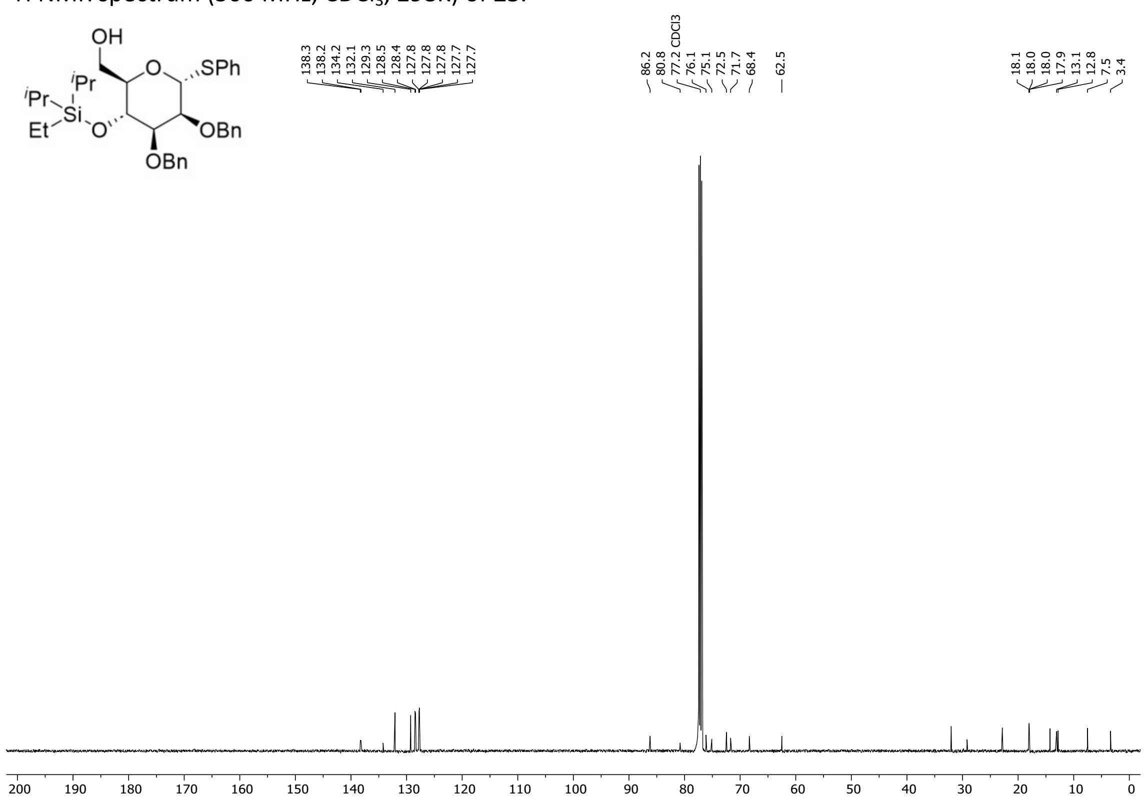


[1]H-[1]H TOCSY spectrum (500 MHz, $CDCl_3$, 298K) of **24**.

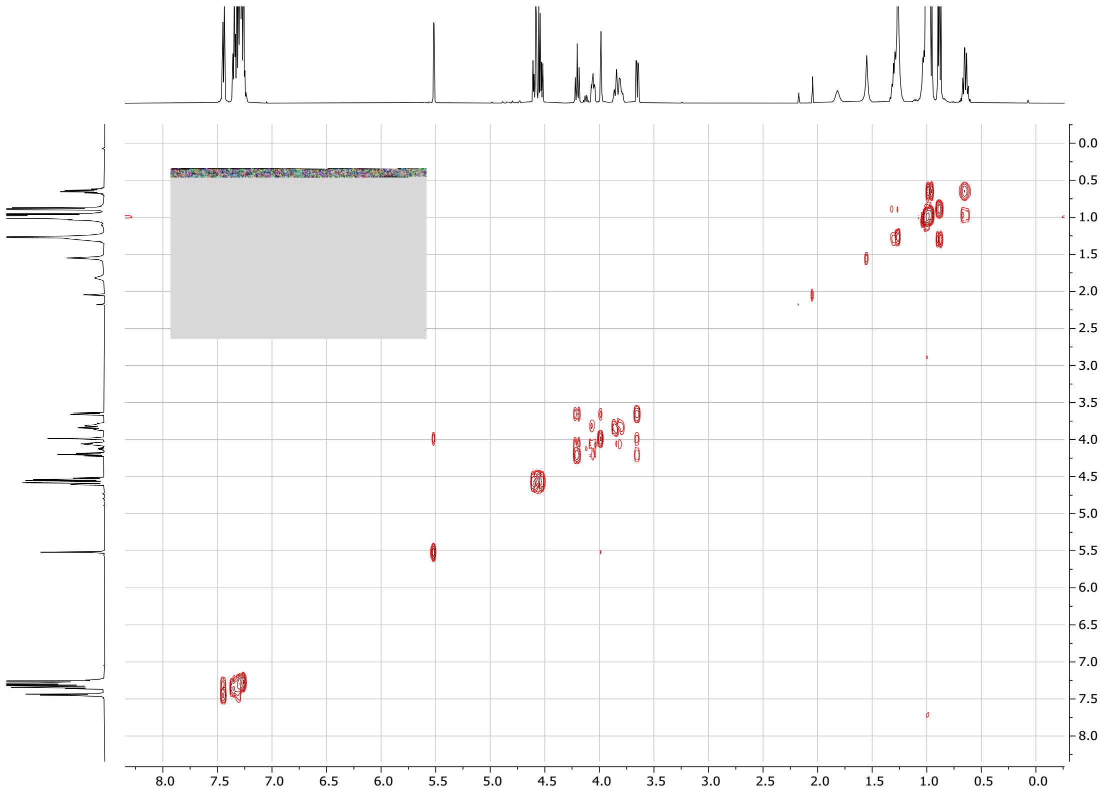
NMR spectra of 23



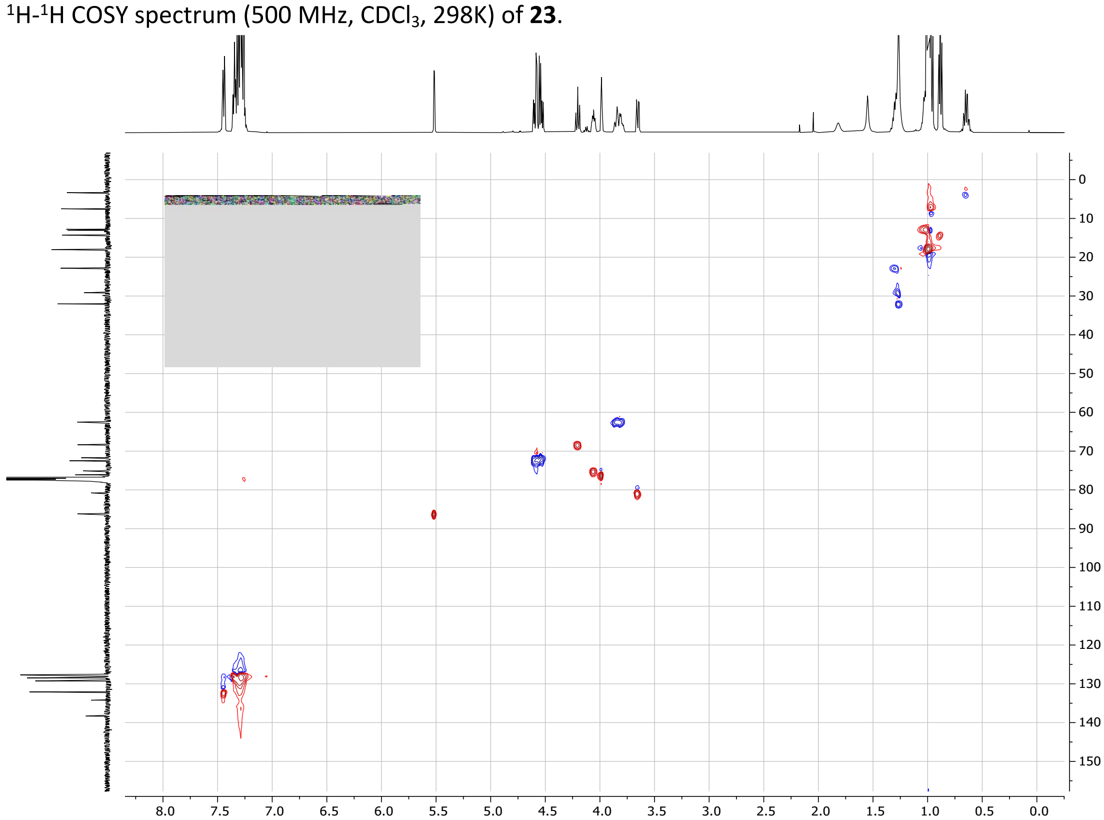
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **23**.



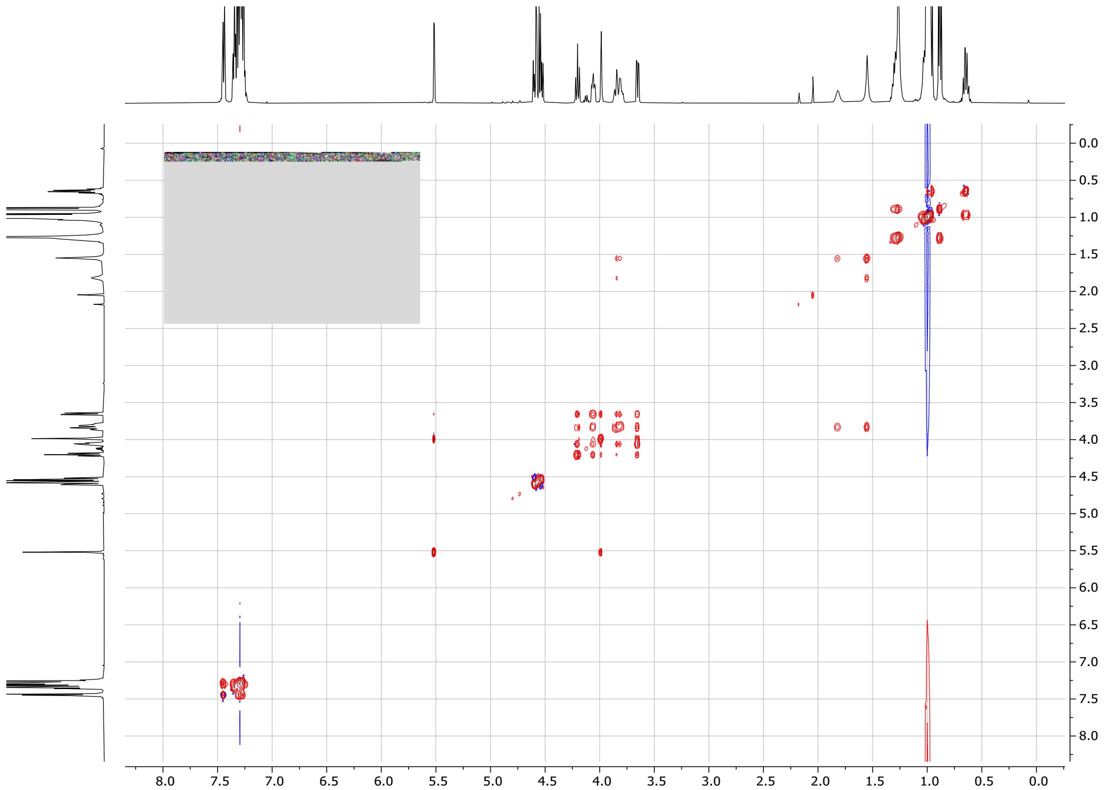
^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298K) of **23**.



^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298K) of **23**.



^{1}H-^{13}C HSQC spectrum (500 / 126 MHz, $CDCl_3$, 298K) of **23**.



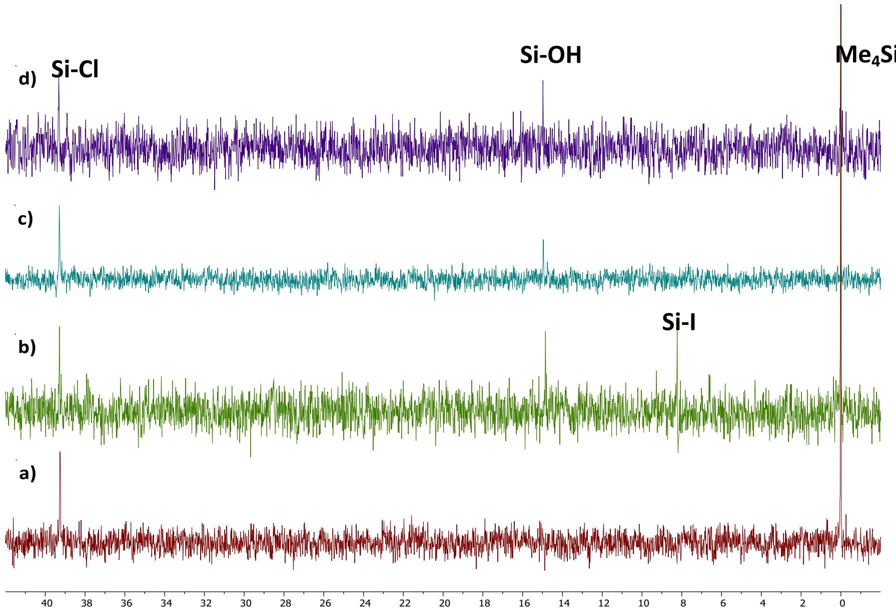
^1H-^1H TOCSY spectrum (500 MHz, $CDCl_3$, 298K) of **23**.

5 Solubility of selected alkali metal halides

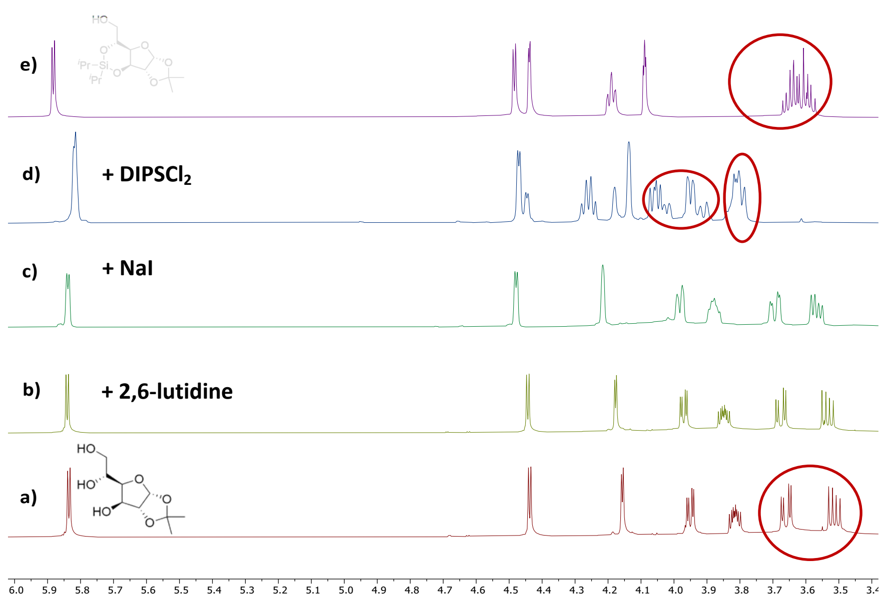
Solubility of selected alkali metal halides in some common organic solvents. Values are grams of salt per 100 grams of solvent. Obtained from J. Burgess, *Metal Ions in Solution*, Ellis Horwood Limited, Chichester, 1978.

	Methanol	**Sulfolane**	**Acetonitrile**	**Acetone**	**DMF**
LiCl	21.0	1.5	0.14	0.83	11
NaCl	1.40	$5.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-4}$	$4.2 \cdot 10^{-5}$	0.04
KCl	0.53	$4.0 \cdot 10^{-3}$	2.4·10-3	$9.1 \cdot 10^{-5}$	0.017
NaI	62.5	N/A	24.9	28.0	3.7

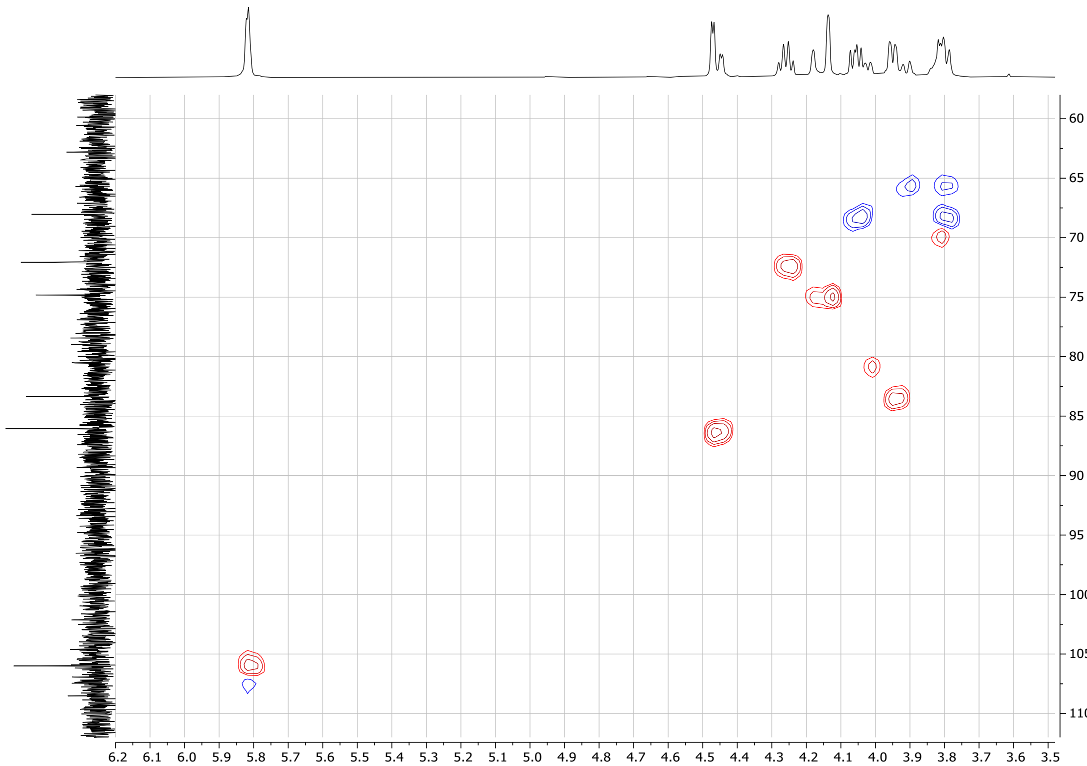
6 NMR experiments to study the "Silyl-Finkelstein" reaction mechanism



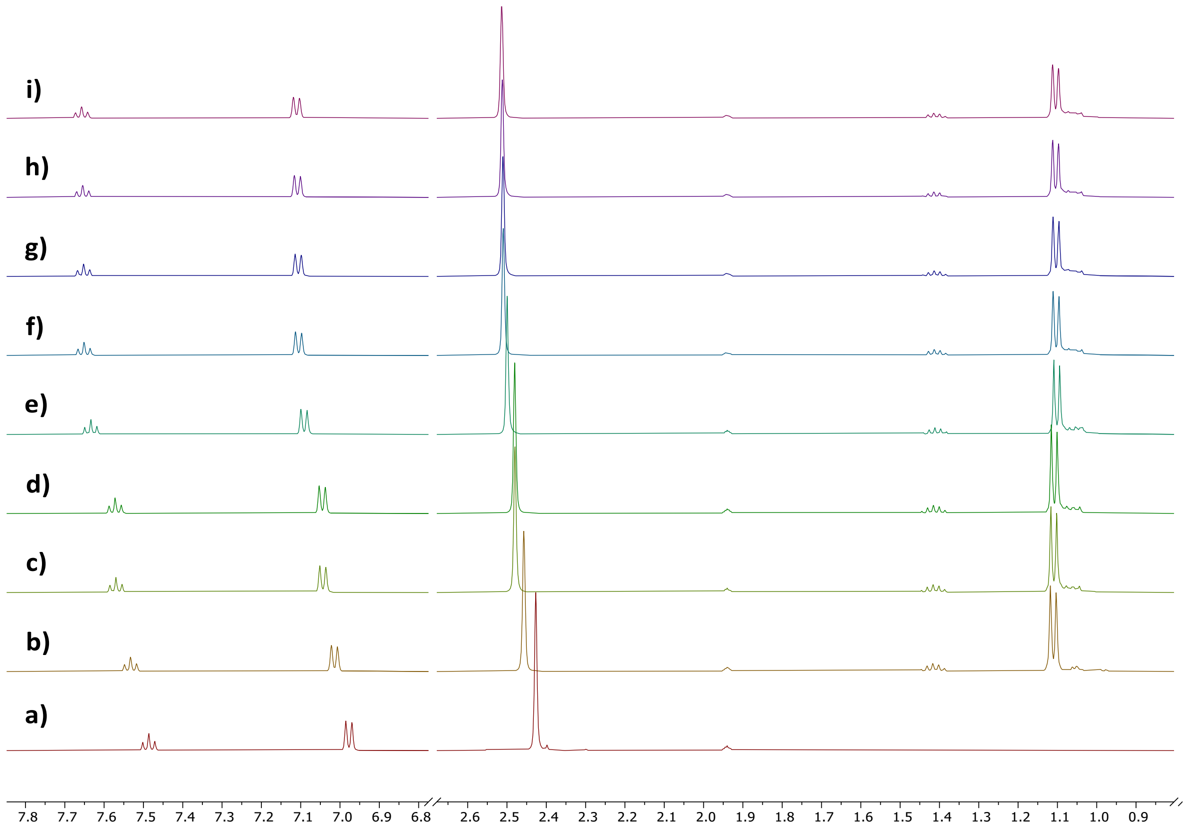
Zoom of stacked [29]Si-DEPT NMR spectra (99 MHz, CD_3CN, 300K) with internal Me_4Si as reference. a) $DIPSCl_2$. b) $DIPSCl_2$ with NaI added. c) 0.2 M $DIPSCl_2$. d) 0.1 M $DIPSCl_2$. The peak at 14.9 ppm is from the reaction of $DIPSCl_2$ with water from the air.



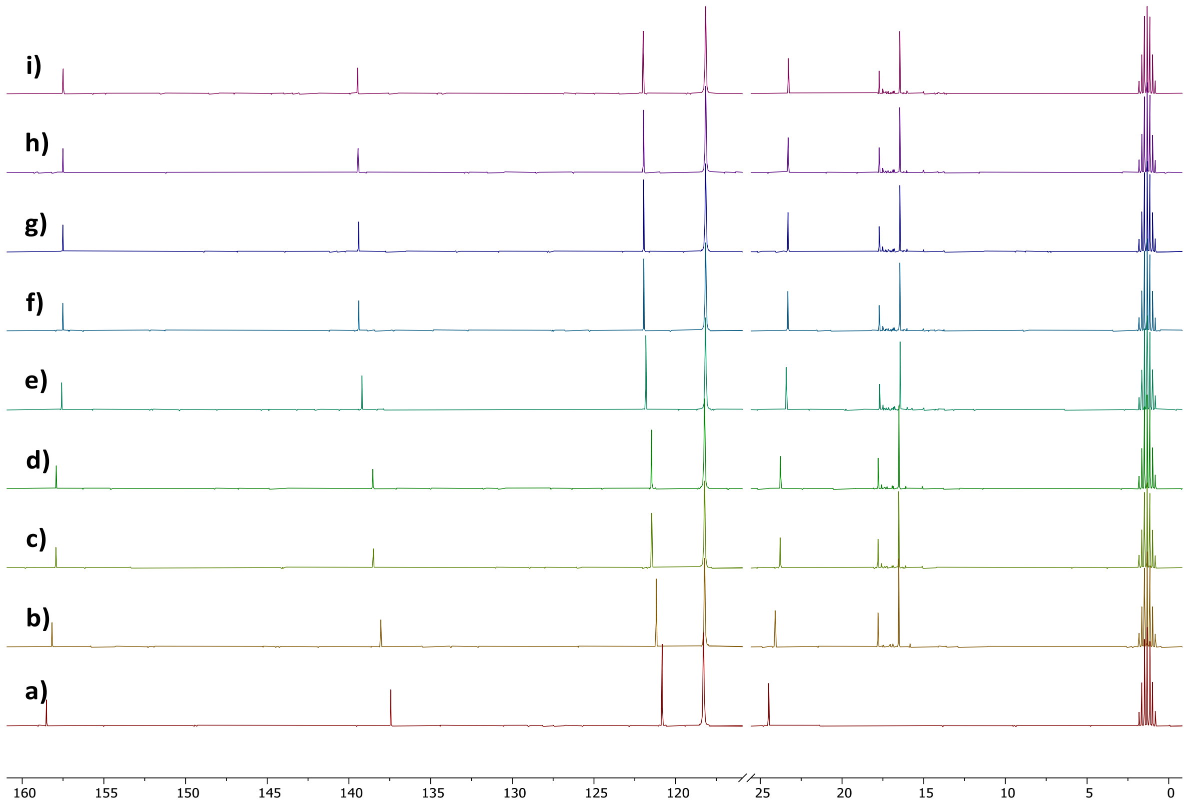
Zoom of stacked [1]H NMR spectra (500 MHz, CD_3CN) of a) 1,2-isopropylidene-α-D-glucofuranose with sequential addition of b) 2,6-lutidine, c) NaI, d) $DIPSCl_2$. e) purified **11**. Spectra a, b, and e obtained at 298K, spectra c and d obtained at 300K. Signals assigned to H6 protons are circled in red.



^1H-^{13}C HSQC spectrum (500 / 126 MHz, CD_3CN, 300K) of mixture of 1,2-*O*-isopropylidene-D-glucofuranose, 2,6-lutidine, NaI, and $DIPSCl_2$ (d from above).

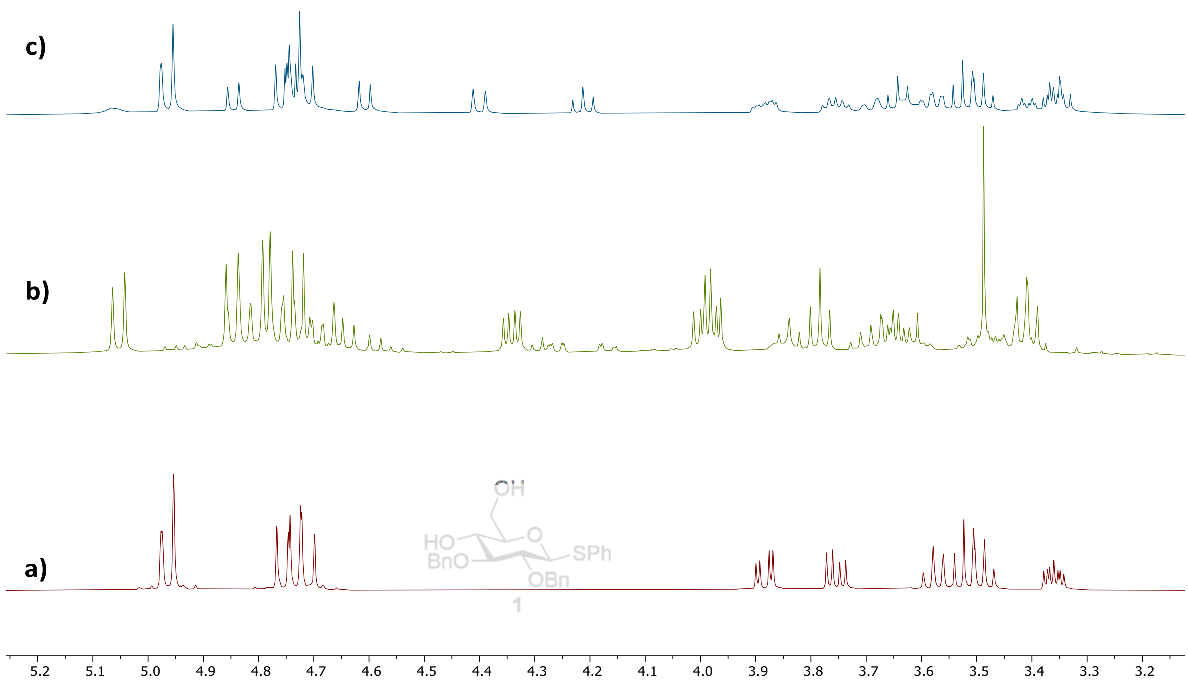


Zoom of stacked ^{1}H NMR spectra (500 MHz, CD_3CN, 300K) of a) 2,6-lutidine, b) 2,6-lutidine and $DIPSCl_2$ right after addition of $DIPSCl_2$, c) 2,6-lutidine and $DIPSCl_2$ 18 hours after addition of $DIPSCl_2$, d) 2,6-lutidine and $DIPSCl_2$ 22 hours after addition of $DIPSCl_2$, e) 2,6-lutidine, $DIPSCl_2$, and NaI right after addition of NaI, f) 2,6-lutidine, $DIPSCl_2$, and NaI 18 hours after addition of NaI, g) 2,6-lutidine, $DIPSCl_2$, and NaI 22 hours after addition of NaI, h) 2,6-lutidine, $DIPSCl_2$, and NaI 42 hours after addition of NaI, i) 2,6-lutidine, $DIPSCl_2$, and NaI 72 hours after addition of NaI.

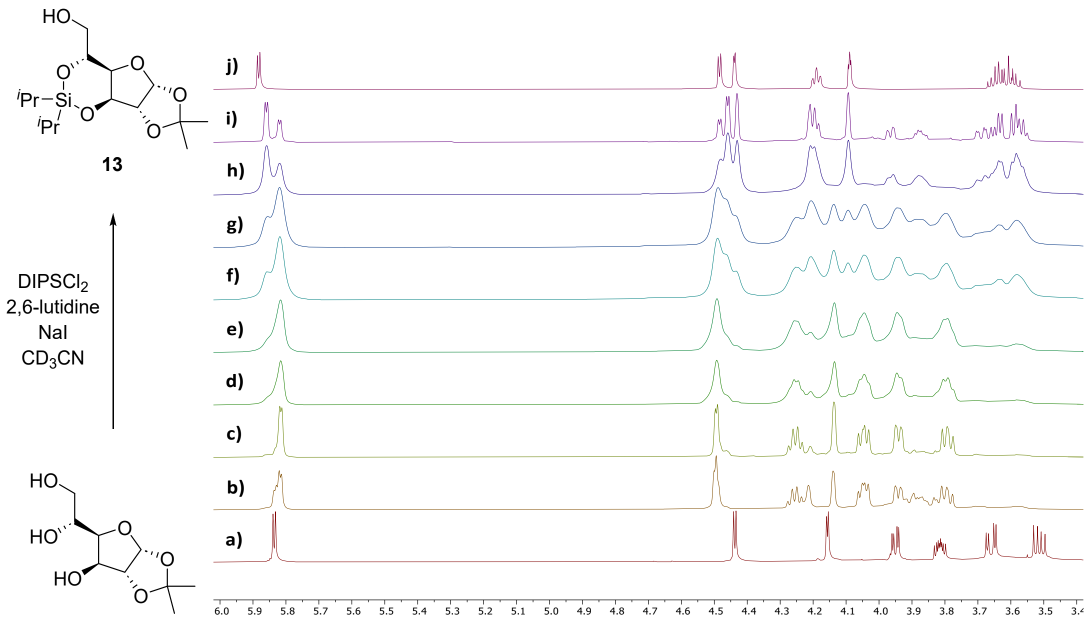


Zoom of stacked ^{13}C NMR spectra (126 MHz, CD_3CN, 300K) of a) 2,6-lutidine, b) 2,6-lutidine and $DIPSCl_2$ right after addition of $DIPSCl_2$, c) 2,6-lutidine and $DIPSCl_2$ 18 hours after addition of $DIPSCl_2$, d) 2,6-lutidine and $DIPSCl_2$ 22 hours after addition of $DIPSCl_2$, e) 2,6-lutidine, $DIPSCl_2$, and NaI right after addition of NaI, f) 2,6-lutidine, $DIPSCl_2$, and NaI 18 hours after addition of NaI, g) 2,6-lutidine, $DIPSCl_2$, and NaI 22 hours after addition of NaI, h) 2,6-lutidine, $DIPSCl_2$, and NaI 42 hours after addition of NaI, i) 2,6-lutidine, $DIPSCl_2$, and NaI 72 hours after addition of NaI.

7 Monitoring reactions by NMR



Zoom of stacked ^{1}H NMR spectra (500 MHz, CD3CN, 298K) of a) diol **1**, b) crude mixture of the "silyl Finkelstein" type reaction of diol **1** with dichlorodiphenylsilane, c) recovered impure diol 2 from flash column chromatography on aluminium oxide.



Zoom of stacked ^{1}H-NMR spectra (500 MHz, CD3CN) of a) 1,2-isopropylidene-α-D-glucofuranose, b) The reaction mixture for synthesis of 19 obtained directly after addition of DIPSCl2, c) Reaction mixture after 110 minutes at rt, d) Reaction mixture heated at 50 °C for 45 minutes, e) Reaction mixture heated at 50 °C for 105 minutes, f) Reaction mixture heated at 50 °C overnight, g) Reaction mixture ultra-sonicated for 160 minutes while heating at 50 °C, h) Reaction mixture heated at 50 °C for another 4 days, i) Reaction mixture after being left at rt for another 9 days, j) purified **13**. All spectra were obtained at 300K, except for spectra a and j which were obtained at 298K.

8 References

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