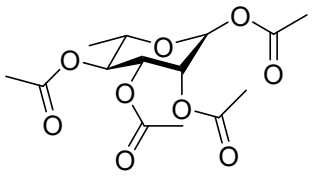
SI.1 General synthetic methods

Commercially available chemicals were used without further purifications. Dry solvent were collected from an Innovative Technology PS-MD-05 solvent drying system. All air and water sensitive reactions were carried out under an inert atmosphere of nitrogen. The plates used for thin layer chromatography (TLC) were Silica gel (60F) coated on aluminum sheets. The TLC plates were analyzed with UV-light and then stained in a 10 % solution of H_2SO_4 in ethanol. Removal of solvents was performed under reduced pressure at 40 °C. Sodium hydride was used as a 60 % dispersion in mineral oil. Purifications by flash column chromatography were carried out by a buchi pure C-815 flash using FlashPure EcoFlex Silica Cartridges.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 500 MHz Ultra Shield Plus spectrograph equipped with a cryoprobe. ^{1}H-NMR were recorded at 500 MHz and ^{13}C-NMR at 126 MHz. The spectra were referenced to the chemical shifts of the deuterated solvents ($CDCl_3$: ^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm), (D_2O: 1H: 4.79 ppm). High-resolution mass spectrometry (HRMS) was performed on a Bruker SolariX XR7T ESI/MALDI-FT-ICR-MS instrument using matrix-assisted laser desorption ionization (MALDI) with dithranol as the matrix.

SI.2 Chemical synthesis

1,2,3,4-tetra-*O*-acetyl-L-rhamnopyranose (SI1)[1]



SI1

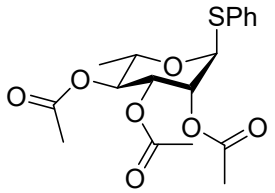
To a suspension of L-rhamnopyranose monohydrate (6.00 g, 32.9 mmol) in pyridine (15 mL) was added acetic anhydride (29.85 g, 292.4 mmol). The reaction was stirred at rt. for 2 hours, where reaction was diluted with DCM. The organic phase was washed twice with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The reaction was not further purified and gave **SI1** (11.02 g, 33.16 mmol, quantitative yield) as a syrup (α/β 1/0.35).

R_f (3/7 EtOAc/Heptane) = 0.56

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.99 (d, *J* = 1.9 Hz, 1H, α-H-1), 5.82 (d, *J* = 1.3 Hz, 0,37H, β-H-1), 5.28 (dd, *J* = 10.1, 3.5 Hz, 1H, H-3), 5.23 (dd, *J* = 3.6, 1.9 Hz, 1H H-2), 5.11 (d, *J* = 10.0 Hz, 1H, H-4), 3.92 (dq, *J* = 7.8, 6.2 Hz, 1H, α-H-5), 3.65 (pd, *J* = 6.3, 4.3 Hz, 0,35H, β-H-5), 2.19 (d, *J* = 7.0 Hz, 3H, CH_3), 2.14 (d, *J* = 5.7 Hz, 3H, CH_3), 2.04 (d, *J* = 1.6 Hz, 3H, CH_3), 1.98 (d, *J* = 2.6 Hz, 3H, CH_3), 1.27 (d, *J* = 6.2 Hz, 1H, α-H-6), 1.21 (dd, *J* = 6.3, 1.6 Hz, 3H, α-H-6).

Spectral data was in accordance with the literature.

Phenyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (SI2)[2]



SI2

Compound **SI1** (11.02 g, 33.16 mmol) was dissolved in DCM (70 mL), whereupon the solution was cooled to 0 °C. To the solution, thiophenol (4.38 g, 39.8 mmol) and BF_3⋅Et_2O (5.67 g, 39.8 mmol) were added and the reaction mixture was allowed to reach rt. After 23 hours, the reaction mixture was quenched with saturated $NaHCO_3$ (aq.). The organic phase was washed with H_2O and with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO2, 100 % toluene to 100 % EtOAc) to give **SI2** (7.65 g, 19.77 mmol, 60 %) as a white solid.

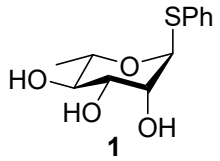
R_f (4/6 EtOAc/Heptane) = 0.5

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dt, *J* = 8.0, 1.3 Hz, 2H, ArH), 7.34 – 7.27 (m, 3H, ArH), 5.49 (dd, *J* = 3.3, 1.6 Hz, 1H, H-2), 5.41 – 5.40 (m, 1H, H-1), 5.29 (ddd, *J* = 10.0, 3.3, 1.2 Hz, 1H, H-3), 5.14 (td, *J* = 9.9, 1.2 Hz, 1H, H-4), 4.36 (dq, *J* = 9.6, 6.2 Hz, 1H, H-5), 2.14 (d, *J* = 1.3 Hz, 3H, CH_3), 2.08 (d, *J* = 1.3 Hz, 3H, CH_3), 2.01 (d, *J* = 1.3 Hz, 3H, CH_3), 1.24 (d, *J* = 6.2 Hz, 3H, H-6).

HRMS (MALDI+): Calculated for $C_{18}H_{22}SO_7Na^+$ 405.09784 m/z found 405.09743 m/z.

Spectral data was in accordance with the literature.

Phenyl 1-thio-α-L-rhamnopyranoside (1)[3]



1

Compound **SI2** (3.04 g, 7.95 mmol) was dissolved in MeOH (75 mL). Na_2CO_3 (0.168 g, 1.59 mmol) was added to the reaction mixture. The reaction mixture was stirred at rt. for 2 hours, whereupon the reaction was stopped by adding washed acid resin (Amberlite IR120 hydrogen form). The solution was filtered and evaporated to dryness to give **1** (2.01 g, 7.84 mmol, quantitative yield) as a white solid.

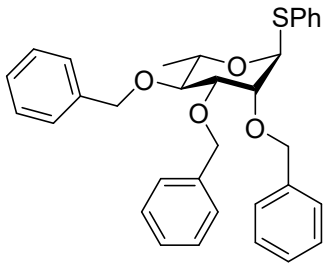
R_f (EtOAc) = 0.58

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H, ArH), 7.31 – 7.27 (m, 3H, ArH), 5.49 (d, *J* = 1.4 Hz, 1H, H-1), 4.23 (s, 1H, H-2), 4.20 – 4.12 (m, 1H, H-5), 3.81 (d, *J* = 9.3 Hz, 1H, H-3), 3.57 (dt, *J* = 10.9, 5.3 Hz, 1H, H-4), 3.30 (s, 1H, 3-OH), 3.12 (s, 1H, 2-OH), 2.95 (s, 1H, 4-OH), 1.33 (d, *J* = 6.2 Hz, 3H, H-6).

HRMS (MALDI+): Calculated for $C_{12}H_{16}SO_4Na^+$ 279.06625 m/z found 279.06706 m/z.

Spectral data was in accordance with the literature.

Phenyl 2,3,4-tri-*O*-benzyl-1-thio-α-L-rhamnopyranoside (2)[4]



2

Compound **1** (1.02 g, 3.98 mmol) was dissolved in DMF (10 mL) and the reaction mixture was cooled to 0 °C. NaH (0.94 g, 23.4 mmol) was added the reaction mixture and then stirred at 0 °C for 30 minutes whereupon benzyl bromide (4.0 g, 23.4 mmol) was added. The cooling was removed and the reaction mixture was stirred at room temperature for 3 hours after which the reaction was stopped by adding MeOH (3 mL). The reaction mixture was then extracted with EtOAc and the combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. The product was purified using flash column chromatography, (SiO_2, 0% to 10% EtOAc in heptane) to give **2** (1.72 g, 3.27 mmol, 82%) as a clear syrup.

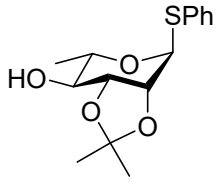
$\boldsymbol{R_f}$ (3/7 EtOAc/Heptane) = 0.6

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 20H, ArH), 5.51 (d, *J* = 1.8 Hz, 1H, H-1), 4.98 (d, *J* = 10.9 Hz, 1H, CH_2), 4.74 (d, *J* = 12.4 Hz, 1H, CH_2), 4.70 – 4.65 (m, 2H, CH_2), 4.62 (d, *J* = 4.3 Hz, 1H, CH_2), 4.59 (d, *J* = 7.3 Hz, 1H, CH_2), 4.16 (dq, *J* = 9.6, 6.3 Hz, 1H, H-5), 4.01 (dd, *J* = 3.1, 1.8 Hz, 1H, H-2), 3.85 (dd, *J* = 9.3, 3.1 Hz, 1H, H-3), 3.70 (t, *J* = 9.3 Hz, 1H, H-4), 1.37 (d, *J* = 6.2 Hz, 3H, H-6).

HRMS (MALDI+): Calculated for $C_{33}H_{34}SO_4Na^+$ 549.20700 m/z found 549.20664 m/z.

Spectral data was in accordance with the literature.

Phenyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (3)[5]



3

Compound **1** (1.03 g, 4.02 mmol) and p-toluene sulfonic acid monohydrate (0.152 g, 0.80 mmol) was dissolved in acetone (7 mL). To the reaction mixture was added 2,2-dimethoxypropane (7.31 g, 70.2 mmol) and the reaction mixture was stirred at rt. for 19 hours whereupon the reaction was quenched with triethylamine (1 mL). The solution was concentrated, and the residue was dissolved in DCM. The organic phase was washed twice with H_2O, and once with brine. The organic phase

was then dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO2, 30% EtOAc in heptane) to give **3** (0.87 g, 2.94 mmol, 75 %) as a light yellow solid.

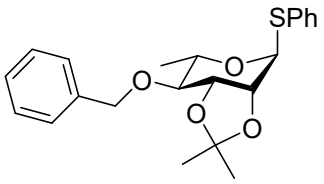
R_f (3/7 EtOAc/Heptane) = 0.28

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H, ArH), 7.34 – 7.27 (m, 3H, ArH), 5.75 (s, 1H, H-1), 4.35 (dd, *J* = 5.5, 0.9 Hz, 1H, H-2), 4.15 – 4.02 (m, 2H, H-3 and H-5), 3.48 (ddd, *J* = 9.7, 7.6, 4.1 Hz, 1H, H-4), 2.14 (d, *J* = 4.0 Hz, 1H, OH-4), 1.54 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.25 (d, *J* = 6.2 Hz, 3H, H-6).

HRMS (MALDI+): Calculated for $C_{15}H_{20}SO_4Na^+$ 319.09745 m/z found 319.09757 m/z.

Spectral data was in accordance with the literature.

Phenyl 4-*O*-benzyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (SI3)[6]



SI3

Compound **3** (0.510 g, 1.72 mmol) was dissolved in DMF (4 mL) and the solution was cooled to 0 °C. NaH (0.134 g, 3.37 mmol) was added to the reaction mixture and the reaction was stirred at 0 °C for 30 minutes. Then benzyl bromide (0.588 g, 3.44 mmol) was added to the reaction, whereupon the cooling were removed. After 2 hours at rt. the reaction was quenched with MeOH and reaction mixture was extracted with EtOAc. The organic phase was washed three times with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 17 % to 100 % EtOAc in heptane) to give **SI3** (0.662 g, 1.73 mmol, quantitative yield) as an off white solid.

R_f (3/7 EtOAc/Heptane) = 0.64

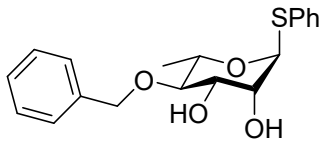
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H, ArH), 7.38 – 7.34 (m, 4H, ArH), 7.32 – 7.27 (m, 4H, ArH), 5.73 (s, 1H, H-1), 4.92 (d, *J* = 11.5 Hz, 1H, OCH_2), 4.64 (d, *J* = 11.5 Hz, 1H, OCH_2),

4.36 (dd, *J* = 5.6, 0.9 Hz, 1H, H-3), 4.32 (dd, *J* = 7.0, 5.7 Hz, 1H, H-2), 4.14 (dt, *J* = 9.7, 6.2 Hz, 1H, H-5), 3.30 (dd, *J* = 9.8, 7.1 Hz, 1H, H-4), 1.52 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.23 (d, *J* = 6.2 Hz, 3H, H-6).

HRMS (MALDI+): Calculated for $C_{22}H_{26}SO_4H^+$ 387.16246 m/z found 387.16298 m/z.

Spectral data was in accordance with the literature.

Phenyl 4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (4)[7]



4

Compound **SI3** (0.666 g, 1.71 mmol) was dissolved in aqueous acetic acid (80%, 15 mL) and the reaction mixture were stirred at 70 °C overnight. The heating was removed and the reaction mixture was cooled down to rt, where it was concentrated and the crude product was then purified with flash column chromatography, (SiO_2, 12 % to 100 % EtOAc in heptane) to give **4** (0.525 g, 1.52 mmol, 89 %) as a white solid.

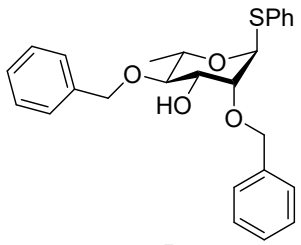
R_f (1/1 EtOAc/Heptane) = 0.37

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H, ArH), 7.39 – 7.36 (m, 4H, ArH), 7.34 – 7.27 (m, 4H, ArH), 5.48 (d, *J* = 1.5 Hz, 1H, H-1), 4.82 – 4.70 (m, 2H, OCH_2), 4.26 – 4.18 (m, 2H, H-5 and H-2), 3.93 (dd, *J* = 9.1, 3.3 Hz, 1H, H-3), 3.43 (t, *J* = 9.2 Hz, 1H, H-4), 1.37 (dd, *J* = 6.2, 0.9 Hz, 3H, H-6).

HRMS (MALDI+): Calculated for $C_{19}H_{22}SO_4H^+$ 369.11310 m/z found 369.11375 m/z.

Spectral data was in accordance with the literature.

Phenyl 2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (5)[8]



5

Compound **4** (0.310 g, 0.894 mmol) was dissolved in DCM (3 mL) followed by the addition of 10 % NaOH aq. (2 mL) and TBAI (0.066 g, 0.179 mmol) resulting in a two phase system. Benzyl bromide (0.918 g, 5.37 mmol) was added to the reaction mixture, which was stirred at rt. for 17 hours. The reaction mixture was then diluted with DCM and the organic phase was washed twice with H_2O and once with brine, followed by drying over $MgSO_4$ and concentration in vacuo. The product was purified with flash column chromatography, (SiO_2, 2 % to 100 % EtOAc in heptane) to give **5** (0.313 g, 0.716 mmol, 80 %) as a clear syrup.

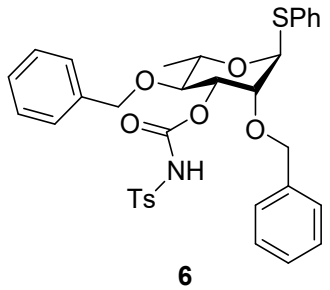
$\boldsymbol{R_f}$ (1/1 EtOAc/Heptane) = 0.46

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.24 (m, 15H, ArH), 5.56 (s, 1H, H-1), 4.93 (d, *J* = 11.1 Hz, 1H, CH_2), 4.76 (d, *J* = 11.7 Hz, 1H, CH_2), 4.68 (d, *J* = 11.0 Hz, 1H, CH_2), 4.54 (d, *J* = 11.6 Hz, 1H, CH_2), 4.17 (dq, *J* = 9.6, 6.2 Hz, 1H, H-5), 4.00 (dd, *J* = 3.7, 1.5 Hz, 1H, H-2), 3.99 – 3.95 (m, 1H, H-3), 3.41 (t, *J* = 9.2 Hz, 1H, H-4), 2.37 (s, 1H, 3-OH), 1.35 (d, *J* = 6.2 Hz, 3H, H-6).

HRMS (MALDI+): Calculated for $C_{26}H_{28}SO_4Na^+$ 459.16005 m/z found 459.16046 m/z.

Spectral data was in accordance with the literature.

Phenyl 2,4-di-*O*-benzyl-3-*O*-tosylcarbamate-1-thio-α-L-rhamnopyranoside (6)



6

Compound **5** (0.300 g, 0.687 mmol) was dissolved in DCM (3 mL), whereupon the solution was cooled down to 0 °C. Tosyl isocyanate (0.16 g, 0.82 mmol) was added to the reaction mixture and after which the cooling was removed. The reaction mixture was stirred at rt. For further 2 hours after which it was diluted with DCM. The organic phase was washed twice with H_2O and once with brine, the dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash column chromatography, (SiO_2, 0 % to 100 % EtOAc in heptane) to give **6** (0.358 g, 0.564 mmol, 82 %) as a white solid.

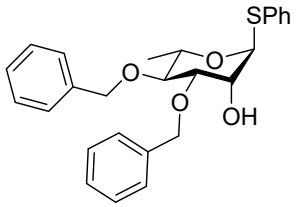
$\boldsymbol{R_f}$ (1/1 EtOAc/Heptane) = 0.4

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H, ArH), 7.39 – 7.17 (m, 17H, ArH), 5.38 (d, *J* = 2.0 Hz, 1H, H-1), 5.00 (dd, *J* = 9.4, 3.2 Hz, 1H, H-3), 4.54 (dd, *J* = 24.3, 11.6 Hz, 2H, CH_2), 4.41 (dd, *J* = 11.6, 5.1 Hz, 2H, CH_2), 4.18 – 4.12 (m, 1H, H-5), 4.06 (dd, *J* = 3.3, 2.0 Hz, 1H, H-2), 3.58 (t, *J* = 9.4 Hz, 1H, H-4), 2.40 (s, 3H, CH_3), 1.32 (d, *J* = 6.2 Hz, 3H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.58 (C=O), 145.29 (ArC), 138.03 (ArC), 137.53 (ArC), 135.52 (ArC), 134.23 (ArC), 85.63 (C-1), 79.03 (C-4), 77.56 (C-2), 75.98 (C-3), 75.08 (CH_2), 72.88 (CH_2), 68.89 (H-5), 21.85 (CH_3), 17.85 (C-6).

HRMS (MALDI+): Calculated for $C_{34}H_{35}NS_2O_7Na^+$ 656.17471 m/z found 656.17597 m/z.

Phenyl 3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (7)[9]



7

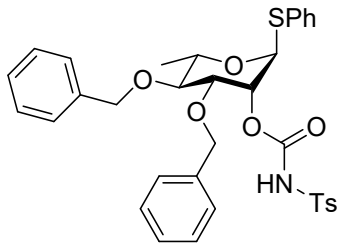
To a suspension of **4** (0.20 g, 0.58 mmol) in toluene (3 mL) was added dibutyltin oxide (0.17 g, 0.69 mmol). The reaction was heated to 105 °C and stirred for 23 hours. The toluene was removed under reduced pressure and the residue was dissolved in DMF (2 mL). To the reaction mixture was added benzyl bromide (0.13 g, 0.75 mmol) and cesium fluoride (0.17 g, 0.12 mmol). The reaction was stirred at rt. for 4 hours where after it was extracted with EtOAc. The combined organic phases were washed three times with H_2O and once with brine, then dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash column chromatography, (SiO_2, 5 % to 100 % EtOAc in heptane) to give **7** (0.22 g, 0.52 mmol, 89 %) as a clear syrup.

$\boldsymbol{R_f}$ (1/1 EtOAc/Heptane) = 0.63

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H, ArH), 7.30 – 7.27 (m, 6H, ArH), 7.24 – 7.16 (m, 7H, ArH), 5.45 (d, *J* = 1.6 Hz, 1H, H-1), 4.82 (d, *J* = 10.9 Hz, 1H, CH_2), 4.64 (s, 2H, CH_2), 4.58 (d, *J* = 10.9 Hz, 1H, CH_2), 4.17 (dt, *J* = 3.5, 1.8 Hz, 1H, H-2), 4.12 (dq, *J* = 9.6, 6.2 Hz, 1H, H-5), 3.78 (dd, *J* = 9.0, 3.3 Hz, 1H, H-3), 3.45 (t, *J* = 9.3 Hz, 1H, H-4), 2.58 (s, 1H, 2-OH), 1.23 (d, *J* = 6.2 Hz, 3H, H-6).

HRMS (MALDI+): Calculated for $C_{26}H_{28}SO_4Na^+$ 459.16005 m/z found 459.16110 m/z.

Phenyl 3,4-di-*O*-benzyl-2-*O*-tosylcarbamate-1-thio-α-L-rhamnopyranoside (8)



8

Compound **7** (0.22 g, 0.52 mmol) was dissolved in DCM (2 mL) and then cooled down to 0 °C, where tosyl isocyanate (0.12 g, 0.62 mmol) was added to the reaction mixture, after which the cooling was removed. The reaction was stirred at rt. for 2 hours before it was diluted with DCM. The organic phase was washed twice with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated followed by purification by flash column chromatography, (SiO_2, 0 % to 100 % EtOAc in heptane) to give **8** (0.29 g, 0.47 mmol, 91 %) as a white solid.

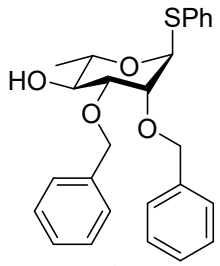
R_f (4/6 EtOAc/Heptane) = 0.51

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H, ArH), 7.45 (d, *J* = 2.2 Hz, 2H, ArH), 7.40 – 7.36 (m, 3H. ArH), 7.34 – 7.20 (m, 12H, ArH), 5.41 (td, *J* = 2.9, 1.6 Hz, 1H, H-2), 5.31 (d, *J* = 2.2 Hz, 1H, H-1), 4.84 (dd, *J* = 10.8, 2.2 Hz, 1H, CH_2), 4.63 (dd, *J* = 11.1, 2.3 Hz, 1H, CH_2), 4.57 (dd, *J* = 10.8, 2.2 Hz, 1H, CH_2), 4.46 (dd, *J* = 11.0, 2.2 Hz, 1H, CH_2), 4.16 (ddt, *J* = 10.1, 6.3, 3.2 Hz, 1H, H-5), 3.83 (dt, *J* = 9.3, 2.9 Hz, 1H, H-3), 3.41 (td, *J* = 9.4, 2.3 Hz, 1H, H-4), 2.39 (s, 3H), 1.30 (dd, *J* = 6.3, 2.3 Hz, 3H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.72 (C=O), 145.28 (ArC), 138.32 (ArC), 137.52 (ArC), 135.60 (ArC), 133.66 (ArC), 131.95 (ArC), 129.80 (ArC), 129.27 (ArC), 128.58 (ArC), 128.32 (ArC), 128.18 (ArC), 127.96 (ArC), 85.71 (H-1), 80.01 (H-4), 78.21 (H-3), 75.73 (CH_2), 73.60 (CH_2), 72.18 (H-2), 69.25 (H-5), 21.83 (CH_3), 17.94 (H-6).

HRMS (MALDI+): Calculated for $C_{34}H_{35}NS_2O_7Na^+$ 656.17471 m/z found 656.17631 m/z.

Phenyl 2,3-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (9)[10]



9

Compound **1** (0.303 g, 1.18 mmol) was dissolved in DCM (3 mL) and 10 % NaOH aq. (2 mL) and TBAI (0.087 g, 0.236 mmol) were added resulting in a two phase system. Benzyl bromide (1.21 g, 7.09 mmol) was then added to the reaction mixture, which was stirred at rt. for 21 hours. After diluting with DCM the organic phase was washed twice with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 17 % to 100 % EtOAc in heptane) to give **9** (0.240 g, 0.549 mmol, 47 %) as a clear syrup.

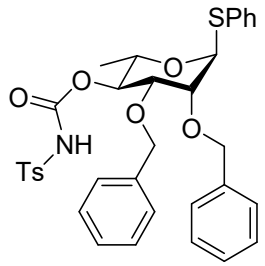
$\boldsymbol{R_f}$ (3/7 EtOAc/Heptane) = 0.32

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dq, *J* = 6.9, 1.2 Hz, 2H, ArH), 7.33 – 7.20 (m, 13H, ArH), 5.51 (d, *J* = 1.6 Hz, 1H, H-1), 4.65 (d, *J* = 12.2 Hz, 1H, CH_2), 4.50 (dd, *J* = 11.9, 7.0 Hz, 2H, CH_2), 4.38 (d, *J* = 11.6 Hz, 1H, CH_2), 4.06 (dq, *J* = 9.3, 6.2 Hz, 1H, H-5), 3.98 (dt, *J* = 2.5, 1.2 Hz, 1H, H-2), 3.75 (t, *J* = 9.4 Hz, 1H, H-4), 3.59 (ddd, *J* = 9.6, 3.1, 0.8 Hz, 1H, H-3), 2.29 (s, 1H, 4-OH), 1.30 (dd, *J* = 6.1, 0.8 Hz, 3H, H-6).

HRMS (MALDI+): Calculated for $C_{26}H_{28}SO_4Na^+$ 459.16005 m/z found 459.16072 m/z.

Spectral data was in accordance with the literature.

Phenyl 2,3-di-*O*-benzyl-4-*O*-tosylcarbamate-1-thio-α-L-rhamnopyranoside (10)



10

Compound **9** (0.240 g, 0.549 mmol) was dissolved in DCM (2 mL) and the solution was cooled to 0 °C. Tosyl isocyanate (0.131 g, 0.659 mmol) was then added and the reaction mixture was allowed to reach rt., where it was kept for 2 hours. When TLC indicated full conversion the reaction mixture was diluted with DCM and washed twice with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0 % to 100 % EtOAc in heptane) to give **10** (0.218 g, 0.343 mmol, 62 %) as a white solid.

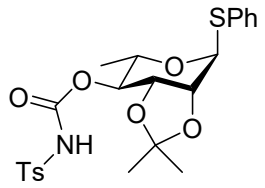
$\boldsymbol{R_f}$ (4/6 EtOAc/Heptane) = 0.39

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H, ArH), 7.39 – 7.25 (m, 17H, ArH), 5.44 (d, *J* = 1.8 Hz, 1H, H-1), 5.03 (t, *J* = 9.7 Hz, 1H, H-4), 4.65 – 4.58 (m, 2H, CH_2), 4.39 (d, *J* = 12.0 Hz, 1H, CH_2), 4.27 (d, *J* = 12.0 Hz, 1H, CH_2), 4.06 (dd, *J* = 9.6, 6.2 Hz, 1H, H-5), 3.92 (dd, *J* = 3.1, 1.8 Hz, 1H, H-2), 3.61 (dd, *J* = 9.7, 3.1 Hz, 1H, H-3), 2.42 (s, 3H, CH_3), 1.09 (d, *J* = 6.2 Hz, 3H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.54 (C=O), 145.30 (ArC), 137.79 (ArC), 137.73 (ArC), 135.75 (ArC), 134.25 (ArC), 131.28 (ArC), 129.80 (ArC), 129.29 (ArC), 128.57 (ArC), 128.53 (ArC), 128.07 (ArC), 127.99 (ArC), 127.94 (ArC), 127.65 (ArC), 85.90 (C-1), 76.61 (C-3) 76.33 (C-4), 76.01 (C-2), 72.44 (CH_2), 71.88 (CH_2), 67.70 (C-5), 21.82 (CH_3), 17.43 (C-6).

HRMS (MALDI+): Calculated for $C_{34}H_{35}NS_2O_7Na^+$ 656.17471 m/z found 656.17484 m/z.

Phenyl 2,3-*O*-isopropylidene-4-*O*-tosylcarbamate-1-thio-α-L-rhamnopyranoside (11)



11

Compound **3** (0.40 g, 1.35 mmol) was dissolved in DCM (3 mL) and the solution cooled to 0 °C. Tosyl isocyanate (0.399 g, 2.02 mmol) was added to the reaction mixture and then the cooling was removed. The reaction mixture was stirred at rt. for 15 hours before it was diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 3/7 to 4/6 EtOAc/heptane) to give **11** (0.63 g, 1.28 mmol, quantitative yield) as a white solid.

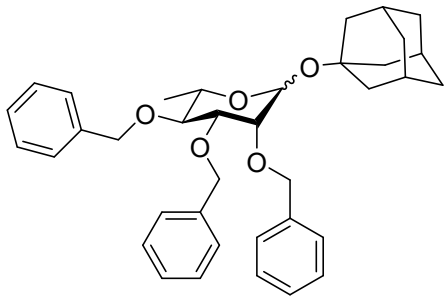
R_f (1/1 EtOAc/Heptane) = 0.47

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H, ArH), 7.47 – 7.43 (m, 2H, ArH), 7.37 – 7.28 (m, 5H, ArH), 5.73 – 5.69 (m, 1H, H-1), 4.71 (dd, *J* = 9.9, 7.7 Hz, 1H, H-4), 4.31 (dd, *J* = 5.3, 1.0 Hz, 1H, H-2), 4.14 – 4.05 (m, 2H, H-5 and H-3), 2.45 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 0.99 (d, *J* = 6.3 Hz, 3H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.72 (C=O), 145.37 (ArC), 135.59 (ArC), 133.11 (ArC), 131.97 (ArC), 129.80 (ArC), 129.29 (ArC), 128.52 (ArC), 127.98 (ArC), 110.38 (O_2C), 83.69 (H-1), 77.99 (H-4), 76.63 (H-2), 75.04 (H-3), 65.35 (H-5), 27.81 (CH_3), 26.56 (CH_3), 21.84 (CH_3), 16.76 (H-6).

HRMS (MALDI+): Calculated for $C_{23}H_{27}S_2O_7Na^+$ 516.11211 m/z found 516.11245 m/z.

1-Adamantyl 2,3,4-tri-*O*-benzyl-1-α/β-L-rhamnopyranoside (SI4)



SI4

A mixture of **2** (0.114 g, 0.216 mmol), 1-adamantanol (0.05 g, 0.325 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled down to -78 °C, where N-iodosuccinimide (0.073 g, 0.325 mmol) was added. The reaction mixture was stirred and slowly allowed to reach rt. After 16 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and reaction was diluted with DCM. The organic phase was washed once with H_2O, brine and then dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 15% EtOAc in heptane) to give **SI4** as a mixture of anomers (0.092 g, 0.161 mmol, 74% α/β 0.78/1) as a clear syrup.

A mixture of **2** (0.22 g, 0.418 mmol), 1-adamantanol (0.086 g, 0.569 mmol) and molecular sieves (3 Å) in DCM (4 mL) was cooled down to -78 °C. N-iodosuccinimide (0.128 g, 0.569 mmol) and triflic acid (0.006 g, 0.038 mmol) was added to the reaction mixture. The reaction mixture was stirred and slowly reach rt. After 4 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and reaction was diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 15% EtOAc in heptane) to give **SI4** as a mixture of anomers (0. g, 0. mmol, 72% α/β 1/0.18) as clear syrup.

R_f (3/7 EtOAc/Heptane) = 0.69

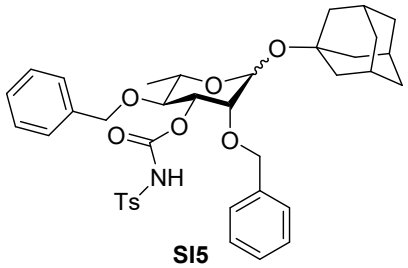
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 2H, ArH), 7.36 – 7.21 (m, 23H, ArH), 5.09 (d, *J* = 2.0 Hz, 0.5H, H-1(α)), 4.99 (d, *J* = 12.8 Hz, 1H, CH_2), 4.95 – 4.90 (m, 2.5H, CH_2), 4.76 (d, *J* = 12.5 Hz, 0.5H, CH_2), 4.67 (d, *J* = 12.6 Hz, 0.5H, CH_2), 4.62 (dd, *J* = 10.6, 4.8 Hz, 4H, CH_2, H-1(β)), 4.46 (d, *J* = 11.8 Hz, 1H, CH_2), 4.39 (d, *J* = 11.8 Hz, 1H, CH_2), 3.91 – 3.82 (m, 1H, H-3(α), H-5(α)), 3.72 (d, *J* = 3.1 Hz, 1H, H-2(α)), 3.61 – 3.53 (m, 2H, H-4, H-2(β)), 3.43 (dd, *J* = 9.4, 3.1 Hz, 1H, H-3(β)), 3.27 (dq, *J* = 9.2, 6.1 Hz, 1H, H-5(β)), 2.13 (p, *J* = 3.3 Hz, 3H, CH), 2.09 – 2.05

(m, 1.7H, CH), 1.84 (dq, *J* = 11.6, 2.4 Hz, 3H, CH_2), 1.78 – 1.72 (m, 3H, CH_2), 1.68 – 1.50 (m, 8H, CH_2), 1.33 (d, *J* = 6.1 Hz, 3H, H-6(β)), 1.28 (d, *J* = 6.2 Hz, 1.6H, H-6(α)).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.08 (ArC), 138.89 (ArC), 138.85 (ArC), 138.78 (ArC), 138.68 (ArC), 138.50 (ArC), 128.75 (ArC), 128.45 (ArC), 128.18 (ArC), 128.11 (ArC), 127.79 (ArC), 127.70 (ArC), 127.60 (ArC), 127.56 (ArC), 127.40 (ArC), 94.26 (C-1(β)), 91.07 (C-1(α)), 82.76 (C-3(β)), 81.16 (C-4), 80.26 (C-3(α)), 76.35 (C-2(β)), 75.54 (CH_2), 75.45 (CH_2), 75.08 (H-2(α)), 74.86 (C), 74.23 (C), 73.82 (CH_2), 72.77 (CH_2), 72.25 (CH_2), 71.57 (H-5(β)), 71.40 (CH_2), 67.55 (C-5(α)),42.58 (CH_2), 42.36 (CH_2), 36.42 (CH_2), 36.37 (CH_2), 30.75 (CH), 30.67 (CH), 18.41 (C-6 (β)), 18.13 (C-6 (α)).

HRMS (MALDI+): Calculated for $C_{37}H_{44}O_5Na^+$ 591.30809 m/z found 591.30776 m/z.

1-Adamantyl 2,4-di-*O*-benzyl-2-*O*-tosylcarbamate-α/β-L-rhamnopyranoside (SI5)



SI5

A mixture of **6** (0.151 g, 0.238 mmol), 1-adamantanol (0.057 g, 0.374 mmol) and molecular sieves (3 Å) in DCM (2.5 mL) was cooled to -78 °C where N-iodosuccinimide (0.080 g, 0.357 mmol) was added. The reaction mixture was stirred and slowly allowed to reach rt. After 23 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and reaction was diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 28% EtOAc in heptane) to give **SI5** as a mixture of anomers (0.089 g, 0.132 mmol, 55% α/β 1/0.1) as clear syrup.

A mixture of **6** (0.200 g, 0.316 mmol), 1-adamantanol (0.074 g, 0.486 mmol) and molecular sieves (3 Å) in DCM (4 mL) was down to -78 °C, where N-iodosuccinimide (0.107 g, 0.473 mmol) and triflic acid (0.005 g, 0.032 mmol) was added. The reaction mixture was stirred and slowly allowed to reach rt. After 3 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and reaction was diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic

phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 28% EtOAc in heptane) to give **SI5** as the α anomer (0.151 g, 0.224 mmol, 71% α/β 1/-) as clear syrup.

***R_f*-α** (4/6 EtOAc/Heptane) = 0.51

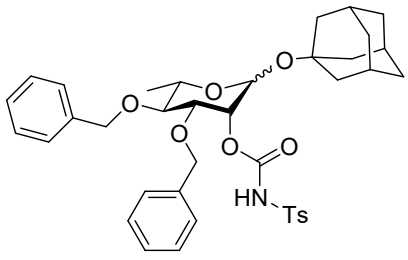
***R_f*-β** (4/6 EtOAc/Heptane) = 0.6

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H, ArH), 7.87 (d, *J* = 8.4 Hz, 0H, ArH), 7.32 (m, 10H, ArH), 7.21 – 7.15 (m, 2H, ArH), 5.14 (dd, *J* = 9.6, 3.3 Hz, 1H, H-3), 5.03 (d, *J* = 2.1 Hz, 1H, H-1(α)), 4.89 (d, *J* = 12.4 Hz, 0.1H, CH_2(β)), 4.70 – 4.67 (m, 0.16H, H-1(β)), 4.65 (dd, *J* = 12.5, 3.65 Hz, 0.2H, CH_2(β)), 4.58 – 4.50 (m, 2H, CH_2(α)), 4.45 (d, *J* = 11.0 Hz, 1H, CH_2(α)), 4.38 (d, *J* = 11.2 Hz, 1H, CH_2(α)), 3.90 (dq, *J* = 9.4, 6.3 Hz, 1H, H-5), 3.67 (dd, *J* = 3.4, 2.0 Hz, 1H, H-2), 3.49 (t, *J* = 9.5 Hz, 1H, H-4), 2.41 (s, 3H, CH_3), 2.15 (s, 1.8H, CH_2 (β)),2.08 (s,3H, CH_2(α)), 1.70 – 1.58 (m, 9H, CH_2), 1.58 – 1.51 (m, 3H, CH_2), 1.28 (d, *J* = 6.3 Hz, 3H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.89 (C=O), 145.08 (ArC), 138.15 (ArC), 138.05 (ArC), 135.67 (ArC), 129.70 (ArC), 128.53 (ArC), 128.51 (ArC), 128.45 (ArC), 128.20 (ArC), 128.15 (ArC), 128.04 (ArC), 127.86 (ArC), 93.37 (C-1(β)), 90.97 (C-1(α)), 79.45 (C-4), 77.67 (C-2), 76.56 (C-3), 74.93 (CH_2), 74.66 (C), 73.39 (CH_2), 67.29 (C-5), 42.46 (CH_2), 42.22 (CH_2), 36.28 (CH_2), 36.16 (CH_2), 30.82 (CH), 30.62 (CH), 21.75 (CH_3), 17.96 (C-6).

HRMS (MALDI+): Calculated for $C_{38}H_{45}NSO_8Na^+$ 698.27581 m/z found 698.27575 m/z.

1-Adamantyl 3,4-di-*O*-benzyl-2-*O*-tosylcarbamate-α/β-L-rhamnopyranoside (SI6)



SI6

A mixture of **8** (0.100 g, 0.158 mmol), 1-adamantanol (0.040 g, 0.263 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C where N-iodosuccinimide (0.053 g, 0.237 mmol) was

added. The reaction mixture was stirred and slowly allowed to reach rt. After 20 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 39% EtOAc in heptane) to give **SI6** as a mixture of anomers (0.062 g, 0.092 mmol, 58% α/β 1/0.6) as a white solid.

A mixture of **8** (0.206 g, 0.325 mmol), 1-adamantanol (0.082 g, 0.539 mmol) and molecular sieves (3 Å) in DCM (4 mL) was cooled to -78 °C, where N-iodosuccinimide (0.110 g, 0.488 mmol) and triflic acid (0.005 g, 0.033 mmol) was added to the reaction mixture. The reaction mixture was stirred and slowly warmed to rt. After 3 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 39% EtOAc in heptane) to give **SI6** as a mixture of anomers (0.135 g, 0.200 mmol, 61% α/β 1/0.13) as a white solid.

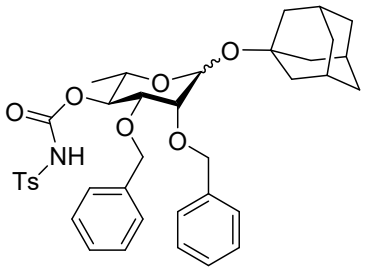
R_f (3/7 EtOAc/Heptane) = 0.5

^{1}H NMR (500 MHz, CDCl3) δ 8.09 – 7.95 (m, 3H, ArH), 7.38 – 7.24 (m, 11H, ArH), 5.15 (d, *J* = 2.0 Hz, 1H, H-1(α)), 5.06 (dd, *J* = 3.2, 2.0 Hz, 1H, H-2), 4.84 (d, *J* = 10.8 Hz, 1H, CH_2), 4.76 – 4.71 (m, 0.19H, H-1(β)), 4.65 (d, *J* = 11.1 Hz, 1H, CH_2), 4.56 (d, *J* = 10.8 Hz, 1H, CH_2), 4.48 (d, *J* = 11.1 Hz, 1H, CH_2), 3.98 (m, 2H, H-3, H-5), 3.37 (t, *J* = 9.5 Hz, 1H, H-4), 2.44 (s, 3H, CH_3), 2.15 (q, *J* = 3.2 Hz, 3H, CH), 1.82 – 1.71 (m, 6H, CH_2), 1.67 – 1.56 (m, 6H, CH_2), 1.31 (d, *J* = 6.2 Hz, 1H).

^{13}C NMR (126 MHz, CDCl3) δ 150.08 (C=O), 145.00 (ArC), 138.44 (ArC), 138.02 (ArC), 135.76 (ArC), 129.69 (ArC), 128.48 (ArC), 128.45 (ArC), 128.38 (ArC), 128.12 (ArC), 127.78 (ArC), 127.68 (ArC), 90.98 (C-1(β)), 90.38 (C-1(α)), 80.33 (C-4), 77.99 (C-3), 75.42 (CH_2), 75.05 (C), 73.39 (H-2), 71.92 (CH_2), 67.29 (C-5), 42.18 (CH_2), 36.30 (CH_2), 30.67 (CH), 21.76 (CH_2), 17.95 (C-6).

HRMS (MALDI+): Calculated for $C_{38}H_{45}NSO_8Na^+$ 698.27581 m/z found 698.27812 m/z.

1-Adamantyl 2,3-di-*O*-benzyl-4-*O*-tosylcarbamate-α/β-L-rhamnopyranoside (SI7)



SI7

A reaction mixture of **10** (0.180 g, 0.284 mmol), 1-adamantanol (0.067 g, 0.440 mmol) and molecular sieves (3 Å) in DCM (2.5 mL) was cooled to -78 °C, where N-iodosuccinimide (0.096 g, 0.426 mmol) was added. The reaction mixture was stirred and slowly warmed to rt. After 20 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 29% EtOAc in heptane) to give **SI7** as a mixture of anomers (0.160 g, 0.237 mmol, 83% α/β 0.6/1) as a white solid.

A mixture of **10** (0.210 g, 0.331 mmol), 1-adamantanol (0.080 g, 0.526 mmol) and molecular sieves (3 Å) in DCM (4 mL) was cooled to -78 °C, where N-iodosuccinimide (0.112 g, 0.497 mmol) and triflic acid (0.005 g, 0.033 mmol) was added. The reaction mixture was stirred and slowly warmed to rt and after 4 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and reaction was diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 29% EtOAc in heptane) to give **SI7** as a mixture of anomers (0.138 g, 0.204 mmol, 62% α/β 1/0.57) as a white solid

$\boldsymbol{R_f}$ (1/1 EtOAc/Heptane) = 0.52

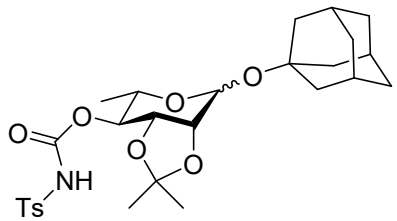
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.3, 5.8 Hz, 4H, ArH), 7.43 (dd, *J* = 7.5, 2.1 Hz, 2H, ArH), 7.31 (dt, *J* = 6.4, 2.0 Hz, 10H, ArH), 7.27 – 7.20 (m, 7H, ArH), 7.12 (dd, *J* = 6.6, 3.0 Hz, 2H, ArH), 5.09 (d, *J* = 2.0 Hz, 0.7H, H-1(α)), 4.98 – 4.92 (m, 3H, CH_2, H-4), 4.88 (d, *J* = 12.8 Hz, 1H, CH_2), 4.74 (d, *J* = 12.5 Hz, 1H, CH_2), 4.64 (s, 1H, H-1(β)), 4.61 (d, *J* = 12.5 Hz, 1H, CH_2), 4.43 (d, *J* = 11.8 Hz, 1H, CH_2), 4.30 (dd, *J* = 14.8, 11.9 Hz, 2H, CH_2), 4.09 (d, *J* = 12.0 Hz, 1H,

CH_2), 3.79 (dd, *J* = 9.7, 6.3 Hz, 0.8H, H-5(β)), 3.71 (dd, *J* = 11.6, 2.9 Hz, 1.8H, H-3), 3.55 – 3.53 (m, 0.75H, H-5(α)), 3.33 – 3.26 (m, 2H, H-5(β), H-2), 2.44 (s, 2H, CH_3(α)), 2.43 (s, 3H, CH_3(β)), 2.16 (t, *J* = 10.1 Hz, 9H, CH), 1.89 – 1.83 (m, 4H, CH_2), 1.78 – 1.73 (m, 10H, CH_2), 1.71 – 1.56 (m, 10H, CH_2), 1.14 (d, *J* = 6.2 Hz, 3H, H-6(β)), 1.05 (d, *J* = 6.3 Hz, 2.2H, H-6(α)).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.71 (C=O), 149.95 (C=O), 145.00 (ArC), 144.94 (ArC), 138.62 (ArC), 138.28 (ArC), 137.92 (ArC), 135.85 (ArC), 135.81 (ArC), 135.67 (ArC), 129.66 (ArC), 128.59 (ArC), 128.40 (ArC), 128.37 (ArC), 128.33 (ArC), 128.30 (ArC), 128.28 (ArC), 128.18 (ArC), 128.01 (ArC), 127.99 (ArC), 127.62 (ArC), 127.55 (ArC), 127.50 (ArC), 127.32 (ArC), 93.99 (C-1(β)), 91.19 (C-1(α)), 79.41 (C-2(β)), 77.07 (C-3 (α)), 76.33 (C-4), 75.83 (C), 75.06 (C-2(α)), 74.60 (C-3(β)), 73.66 (CH_2), 72.81 (CH_2), 71.96 (CH_2), 71.17 (CH_2), 69.75 (C-5(α)), 65.98 (C-5(β)), 42.40 (CH_2), 42.26 (CH_2), 36.28 (CH), 36.24 (CH), 30.66 (CH_2), 30.58 (CH_2), 21.70 (CH_3(β)), 21.68 (CH_3(α)), 17.69 (C-6(β)), 17.33 (C-6(α)).

HRMS (MALDI+): Calculated for $C_{38}H_{45}NSO_8Na^+$ 698.27581 m/z found 698.27733 m/z.

1-Adamantyl 2,3-*O*-isopropylidene-4-*O*-tosylcarbamate-α/β-L-rhamnopyranoside (SI8)



SI8

A mixture of **11** (0.111 g, 0.225 mmol), 1-adamantanol (0.051 g, 0.337 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.060 g, 0.267 mmol) was added. The reaction mixture was stirred and slowly allowed to reach rt. After 20 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 43% EtOAc in heptane) to give **SI8-α** and a mixture of **SI8-α** and **SI8-β** (0.069 g, 0.128 mmol, 57% α/β 1/0.3) as an off white solid.

A mixture of **11** (0.200 g, 0.405 mmol), 1-adamantanol (0.093 g, 0.607 mmol) and molecular sieves (3 Å) in DCM (4 mL) was cooled to -78 °C, where N-iodosuccinimide (0.143 g, 0.636

mmol) and triflic acid (0.004 g, 0.041 mmol) was added. The reaction mixture was stirred and slowly warmed to rt. After 4 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 43% EtOAc in heptane) to give **SI8-α** and a mixture of **SI8-α** and **SI8-β** (0.083 g, 0.154 mmol, 38% α/β 1/0.4) as an off white solid

R_f -α (4/6 EtOAc/Heptane) = 0.3

R_f -β (4/6 EtOAc/Heptane) = 0.26

^{1}H NMR (α) (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H, ArH), 7.38 – 7.30 (d, *J* = 8.4 Hz, ArH), 5.36 (s, 1H, H-1(α)), 4.61 (dd, *J* = 10.1, 7.7 Hz, 1H, H-4), 4.08 (dd, *J* = 7.7, 5.3 Hz, 1H, H-3), 3.98 (dd, *J* = 5.3, 0.9 Hz, 1H, H-2), 3.83 (dq, *J* = 10.1, 6.3 Hz, 1H, H-5), 2.44 (s, 3H, CH_3), 2.17 – 2.12 (m, 3H, CH), 1.85 – 1.74 (m, 6H, CH_2), 1.67 – 1.57 (m, 6H, CH_2), 1.47 (s, 3H CH_3), 1.30 (s, 3H CH_3), 0.98 (d, *J* = 6.3 Hz, 3H, H-6).

^{13}C NMR (α) (126 MHz, $CDCl_3$) δ 150.16 (C=O), 145.20 (ArC), 135.60 (ArC), 129.75 (ArC), 128.42 (ArC), 109.85 (C), 90.33 (C-1(α)), 78.33 (C-4), 77.65 (C-2), 75.35 (C-3), 75.08 (C), 63.36 (C-5), 42.67 (CH_2), 36.24 (CH_2), 30.76 (CH), 27.81 (CH_3), 26.53 (CH_3), 21.80 (CH_3), 16.83 (C-6).

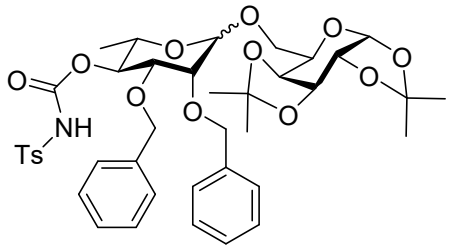
^{1}H NMR (α+β) (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4, 1.7 Hz, 3.7H, ArH), 7.53 – 7.47 (m, 3.8H, ArH), 7.36 – 7.27 (m, 2H, ArH), 5.36 (s, 1H, H-1(α)), 4.75 (d, *J* = 1.2 Hz, 0.6H, H-1(β)), 4.67 (t, *J* = 9.5 Hz, 0.7H, H-4(β)), 4.60 (dd, *J* = 10.1, 7.7 Hz, 1H, H-4(α)), 4.08 (dd, *J* = 7.7, 5.4 Hz, 1H, H-3(α)), 3.99 – 3.95 (m, 1H, H-2(α)), 3.87 – 3.79 (m, 2H, H-5(α), H-2(β)), 3.49 (dd, *J* = 9.6, 3.5 Hz, 0.6H, H-3(β)), 3.35 – 3.28 (m, 0.6H, H-5(β)), 2.44 (d, *J* = 2.0 Hz, 6H, CH_3), 2.17 – 2.11 (m, 7H, CH), 1.82 – 1.74 (m, 10H, CH_2), 1.68 – 1.56 (m, 11H, CH_2), 1.47 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.15 (d, *J* = 6.2 Hz, 1.8H, H-6(β)), 0.99 (d, *J* = 6.3 Hz, 3H, H-6(α)).

^{13}C NMR (α+β) (126 MHz, $CDCl_3$) δ 150.45 (C=O), 149.94 (C=O), 145.29 (ArC), 145.19 (ArC), 129.018 (ArC), 129.09 (ArC), 128.17 (ArC), 127.65 (ArC), 127.44 (ArC), 109.85 (C), 92.44 (C-1(β)), 90.23 (C-1(α)), 78.33 (C-4(α)), 77.76 (C-4(β)), 77.16 (C-2(α)), 75.94 (C), 75.36 (C-3 (α)), 75.14 (C), 72.87 (C-2(β)), 72.05 (C-3(β)), 69.22 (C-5 (β)), 63.19 (C-5 (α)), 42.63 (CH_2), 42.52

(CH_2), 36.34 (CH_2), 36.21 (CH_2), 27.78 (CH_3), 27.28 (CH_3), 21.84 (CH_3), 21.81 (CH_3), 17.72 (C-6(β)), 16.74 (C-6(α)).

HRMS (MALDI+): Calculated for $C_{23}H_{27}S_2O_7Na^+$ 558.21321 m/z found 558.21269 m/z.

1,2:3,4-di-*O*-isopropylidene-β-D-galactopyranose-(6-1)-2,3-di-*O*-benzyl-4-*O*-tosylcarbamate-α/β-L-rhamnopyranoside (SI9)



SI9

A mixture of **10** (0.100 g, 0.158 mmol), 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose (0.063 g, 0.242 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.053 g, 0.237 mmol) was added. The reaction mixture was stirred and slowly warmed to rt. After 16 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 39% EtOAc in heptane) to give **SI9-α** (0.053 g, 0.068 mmol, 43%) as a white solid and **SI9-β** (0.047 g, 0.060 mmol, 48%) as a white solid. total yield 81% (α/β 0.8/1).

A mixture of **10** (0.103 g, 0.162 mmol), 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose (0.061 g, 0.234 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.055 g, 0.244 mmol) and triflic acid (0.002 g, 0.016 mmol) was added. The reaction mixture was stirred and slowly warmed rt. After 3 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO2, 0% to 39% EtOAc in heptane) to give **SI9-α** (0.024 g, 0.030 mmol, 19%) as a white solid and **SI9-β** (0.027 g, 0.034 mmol, 21%) as a white solid. total yield 40% (α/β 1/0.84).

R_f-α (1/1 EtOAc/Heptane) = 0.55

R_f-β (1/1 EtOAc/Heptane) = 0.45

^{1}H NMR (α) (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H, ArH), 7.31 – 7.22 (m, 10H, ArH), 7.14 – 7.11 (m, 2H, ArH), 5.53 (d, *J* = 5.0 Hz, 1H, H-1(G)), 4.97 (t, *J* = 9.8 Hz, 1H, H-4(R)), 4.85 (d, *J* = 1.9 Hz, 1H, H-1(R)), 4.69 – 4.62 (m, 2H, CH_2), 4.61 (dd, *J* = 5.6, 2.3 Hz, 1H, H-3(G)), 4.36 (d, *J* = 11.9 Hz, 1H, CH_2), 4.33 (dd, *J* = 5.0, 2.4 Hz, 1H, H-2(g)), 4.19 – 4.13 (m, 2H, CH_2, H-4(G)), 3.92 (ddd, *J* = 7.2, 5.3, 2.0 Hz, 1H, H-5(G)), 3.81 – 3.76 (m, 2H, H-6(G), H-2(R)), 3.74 (dd, *J* = 9.8, 6.3 Hz, 1H, H-5(R)), 3.64 (dd, *J* = 9.8, 3.1 Hz, 1H, H-3(R)), 3.58 (dd, *J* = 10.5, 7.2 Hz, 1H, H-6(G)), 2.40 (s, 3H, CH_3(R)), 1.54 (s, 3H, CH_3(G)), 1.44 (s, 3H, CH_3(G)), 1.35 (s, 3H, CH_3(G)), 1.33 (s, 3H, CH_3(G)), 1.11 (d, *J* = 6.2 Hz, 3H, H-6(R)).

^{13}C NMR (α) (126 MHz, $CDCl_3$) δ 149.66 (C=O), 145.17 (ArC), 138.21 (ArC), 138.14 (ArC), 135.78 (ArC), 128.27 (ArC), 127.96 (ArC), 127.51 (ArC) 109.57 (C), 108.74 (C), 98.32 (C-1(R)), 96.39 (C-1(G)), 76.36 (C-3(R)) 76.14 (C-4(R)), 74.18 (C-2(R)), 72.83 (CH_2), 71.61 (CH_2), 71.26 (C-4(G)), 70.80 (C-3(G)), 70.61 (C-2(G)), 67.20 (C-5(R)), 66.55 (C-6(G)), 66.11 (C-5(G)), 26.21 (CH_3), 26.00 (CH_3), 25.01 (CH_3), 24.51 (CH_3), 21.74 (CH_3), 17.32 (H-6(R)).

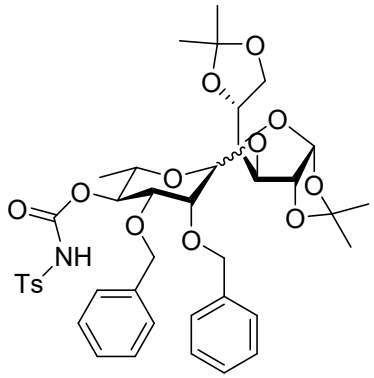
^{1}H NMR (β) (500 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H, ArH), 7.40 – 7.36 (m, 2H, ArH), 7.30 – 7.22 (m, 8H, ArH), 7.14 – 7.10 (m, 2H, ArH), 5.50 (d, *J* = 5.0 Hz, 1H, H-1(G)), 4.94 (t, *J* = 9.6 Hz, 1H, H-4(R)), 4.83 (q, *J* = 12.5 Hz, 2H, CH_2), 4.58 (dd, *J* = 8.0, 2.4 Hz, 1H, H-3(G)), 4.37 (s, 1H, H-1(R)), 4.34 – 4.29 (m, 2H, CH_2, H-2(G)), 4.18 (dd, *J* = 8.0, 1.9 Hz, 1H, H-4(G)), 4.15 (d, *J* = 12.1 Hz, 1H, CH_2), 4.03 (ddd, *J* = 8.1, 5.7, 1.8 Hz, 1H, H-5(G)), 3.92 (dd, *J* = 9.4, 5.8 Hz, 1H, H-6(G)), 3.86 (d, *J* = 3.0 Hz, 1H, H-2(R)), 3.72 – 3.65 (m, 1H, H-6(G)), 3.29 (dd, *J* = 9.8, 3.0 Hz, 1H, H-3(R)), 3.25 (dd, *J* = 9.6, 6.2 Hz, 1H, H-5(R)), 2.42 (s, 3H, CH_3(R)), 1.53 (s, 3H, CH_3(G)), 1.44 (s, 3H, CH_3(G)), 1.33 (s, 3H, CH_3(G)), 1.32 (s, 3H, CH_3(G)), 1.09 (d, *J* = 6.2 Hz, 3H, H-6(R)).

^{13}C NMR (β) (126 MHz, $CDCl_3$) δ 149.55 (C=O), 145.26 (ArC), 138.48 (ArC), 137.79 (ArC), 135.77 (ArC), 129.76 (ArC), 128.47 (ArC), 128.41 (ArC), 128.39 (ArC), 128.00 (ArC), 127.72 (ArC), 127.70 (ArC), 127.63 (ArC), 109.18 (C), 108.72 (C), 101.84 (C-1(R)), 96.16 (C-1(G)), 78.92 (C-3(R)), 76.20 (C-4 (R)), 73.92 (CH_2), 73.08 (H-2(R)), 71.33 (CH_2), 70.69 (C-4(G)),70.65

(C-3(G)), 70.54 (C-2(G)), 72.24 (C-5(R)), 68.02 (C-6(G)), 65.75 (C-5(g)), 26.48 (CH_3), 26.05 (CH_3), 25.54 (CH_3), 24.54 (CH_3), 17.44 (H-6(R)).

HRMS (MALDI+): Calculated for $C_{40}H_{49}SNO_{13}Na^+$ 806.28168 m/z found 806.28105 m/z.

1,2:3,4-di-*O*-isopropylidene-α-D-glucofuranose-(3-1)-2,3-di-*O*-benzyl-4-*O*-tosylcarbamate-α/β-L-rhamnopyranoside (SI10)



SI10

A mixture of **10** (0.100 g, 0.158 mmol), 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.061 g, 0.237 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.053 g, 0.237 mmol) was added. The reaction mixture was stirred and slowly warmed to rt. After 18 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 30% EtOAc in heptane) to give **SI10-α** (0.040 g, 0.052 mmol, 33%) as a white solid and **SI10-β** (0.028 g, 0.035 mmol, 22%) as a white solid. total yield 55% (α/β 1/0.4).

A mixture of **10** (0.101 g, 0.159 mmol), 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.062 g, 0.239 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.054 g, 0.239 mmol) and triflic acid (0.002 g, 0.016 mmol) were added. The reaction mixture was stirred and slowly warmed to rt. After 5 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 30% EtOAc in heptane) to give

SI10-α (0.070 g, 0.090 mmol, 56%) as a white solid and **SI10-β** (0.022 g, 0.028 mmol, 18%) as a white solid. total yield 74% (α/β 1/0.29).

R_f-α (3/7 EtOAc/Heptane) = 0.72

R_f-β (3/7 EtOAc/Heptane) = 0.64

^{1}H NMR (α) (500 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H, ArH), 7.34 – 7.27 (m, 10H, ArH), 7.18 – 7.15 (m, 2H, ArH), 5.79 (d, *J* = 3.7 Hz, 1H, H-1(G)), 4.99 (t, *J* = 9.8 Hz, 1H, H-4(R)), 4.79 (d, *J* = 12.4 Hz, 1H, CH_2), 4.75 (s, 1H, H-1(R)), 4.56 (dd, *J* = 12.3, 1.1 Hz, 1H, CH_2), 4.41 (d, *J* = 11.9 Hz, 1H, CH_2), 4.27 – 4.21 (m, 2H, CH_2, H-3(R)), 4.18 – 4.10 (m, 3H, H-2(G), H-5(G), H-6(G)), 4.10 – 4.06 (m, 1H, H-4(G)), 4.02 – 3.96 (m, 2H, H-5(R), H-6(G)), 3.65 (m, 1H, H-2(R)), 3.59 (dd, *J* = 12.6, 2.8 Hz, 1H, H-3(R)), 2.43 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.13 (d, *J* = 6.2 Hz, 3H, H-6(R)).

^{13}C NMR (α) (126 MHz, $CDCl_3$) δ 145.18 (C=O), 137.97 (C), 137.85 (ArC), 137.85 (ArC), 135.75 (ArC), 129.75 (ArC), 128.55 (ArC), 128.50 (ArC), 128.46 (ArC), 128.32 (ArC), 128.00 (ArC), 127.97 (ArC), 127.86 (ArC), 112.19 (C), 109.42(C), 105.26 (C-1(G)), 95.91 (H-1(R)), 81.77 (C-2(G)), 80.81 (C-4(G)), 76.97 (C-3(G)), 76.79 (C-3(R)), 75.94 (C-4(R)), 74.54 (C-2(R)), 73.44 (CH_2), 72.23 (C-5(G)), 72.03 (CH_2), 67.78 (C-6(G)), 67.00 (C-5(R)), 26.95 (CH_3), 26.86 (CH_3), 26.29 (CH_3), 25.55 (CH_3), 21.81 (CH_3), 17.21 (C-6(R)).

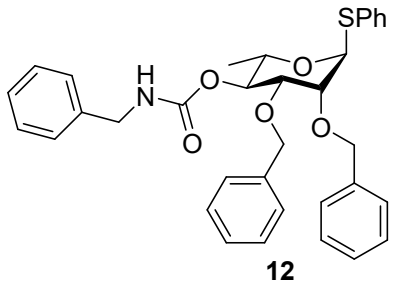
^{1}H NMR (β) (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H, ArH), 7.37 – 7.32 (m, 2H, ArH), 7.32 – 7.28 (m, 3H, ArH), 7.28 – 7.23 (m, 5H, ArH), 7.15 – 7.13 (m, 2H, ArH), 5.86 (d, *J* = 3.6 Hz, 1H, H-1(G)), 4.97 (d, *J* = 9.7 Hz, 1H, H-4(R)), 4.78 (dd, *J* = 16.7, 3.3 Hz, 3H, H-2(G), CH_2), 4.46 (s, 1H, H-1(R)), 4.38 (d, *J* = 12.0 Hz, 1H, CH_2), 4.20 (d, *J* = 12.1 Hz, 1H, CH_2), 4.11 (d, *J* = 3.0 Hz, 1H, H-3(G)), 4.06 – 3.99 (m, 2H, H-4(G), H-6(G)), 3.93 (dd, *J* = 8.4, 5.4 Hz, 1H, H-6(G)), 3.89 – 3.86 (m, 1H, H-5(G)), 3.81 (d, *J* = 2.9 Hz, 1H, H-2(R)), 3.31 – 3.25 (m, 2H, H-5(R), H-3(R)), 2.43 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.10 (d, *J* = 6.2 Hz, 3H, H-6(R)).

^{13}C NMR (β) (126 MHz, $CDCl_3$) δ 145.35 (C=O), 138.06 (ArC), 137.87 (ArC), 137.59 (ArC), 129.62 (ArC), 128.41 (ArC), 128.35 (ArC), 128.18 (ArC), 127.85 (ArC), 127.65 (ArC), 112.05 (C), 109.17 (C), 105.47 (C-1(G)), 102.52(C-1(R)), 84.06 (C-2(G)), 83.05 (C-3(G)), 80.94 (C-

4(G)), 78.80 (C-3(R)), 74.03 (CH_2), 72.97 (C-2(R)), 72.43 (C-5(G)), 71.54 (CH_2), 70.42 (C-5(R)), 67.97 (C-6(G)), 27.02 (CH_3), 26.92 (CH_3), 26.29 (CH_3), 25.52 (CH_3), 21.83 (CH_3), 17.45 (C-6(R)).

HRMS (MALDI+): Calculated for $C_{40}H_{49}SNO_{13}Na^+$ 806.28168 m/z found 806.28152 m/z.

Phenyl 2,3-di-*O*-benzyl-4-*O*-benzylcarbamoyl-1-thio-α-L-rhamnopyranoside (12)



12

Compound **9** (0.65 g, 1.49 mmol) was dissolved in toluene (10 mL). 4-Dimethylaminopyridine (0.04 g, 0.29 mmol) and benzyl isocyanate (0.595 g, 4.47 mmol) were added to the reaction mixture, which was stirred at reflux for 2 hours whereupon reaction mixture was cooled to rt. and diluted with toluene. The organic phase was washed twice with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0 % to 24 % EtOAc in heptane) to give **12** (0.62 g, 1.09 mmol, 73 %) as a white solid.

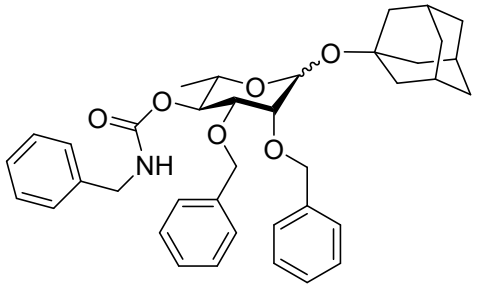
R_f (3/7 EtOAc/Heptane) = 0.38

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H, ArH), 7.35 – 7.26 (m, 13H, ArH), 5.51 (d, *J* = 1.9 Hz, 1H, H-1), 5.16 (t, *J* = 9.6 Hz, 1H, H-4), 4.89 (t, *J* = 6.0 Hz, 1H, N-H), 4.69 (d, *J* = 4.0 Hz, 2H, CH_2), 4.57 (d, *J* = 12.2 Hz, 1H, CH_2), 4.48 (d, *J* = 12.7 Hz, 1H, CH_2), 4.43 (dd, *J* =15.1, 6.2 Hz, 1H, CH_2), 4.37 (dd, *J* = 14.9, 5.7 Hz, 1H, CH_2), 4.14 (dq, *J* = 9.7, 6.2 Hz, 1H, H-5), 4.00 (s, Hz, 1H, H-2), 3.72 (dd, *J* = 9.6, 3.0 Hz, 1H, H-3), 1.30 (d, *J* = 6.3 Hz, 3H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.94 (C=O), 138.64 (Ar), 138.27 (Ar), 138.03 (Ar), 134.65 (Ar), 131.22 (Ar), 129.21 (Ar), 128.85 v, 128.49 (Ar), 128.45 (Ar), 128.10 (Ar), 127.86 (Ar), 127.82 (Ar), 127.76 (Ar), 127.67 (Ar), 127.45 (Ar), 86.14 (C-1), 77.35 (C-3), 76.28 (C-2), 74.11 (C-4), 72.49 (CH_2), 71.88 (CH_2), 68.58 (C-5), 45.36 (CH_2), 17.67 (C-6).

HRMS (MALDI+): Calculated for $C_{34}H_{35}SNO_5Na^+$ 592.21281 m/z found 592.21239 m/z.

1-Adamantyl 2,3-di-*O*-benzyl-4-*O*-benzylcarbamoyl-1-thio-α/β-L-rhamnopyranoside (SI11)



SI11

A mixture of **12** (0.100 g, 0.176 mmol), 1-adamantanol (0.040 g, 0.263 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.059 g, 0.263 mmol) was added. The reaction mixture was stirred and slowly allowed to reach rt. After 21 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 30% EtOAc in heptane) to give **SI11-α** (0.018 g, 0.029 mmol, 16%) as a clear syrup and **SI11-β** (0.083 g, 0.136 mmol, 77%) as a clear syrup. Total yield 93% (α/β 0.28/1).

A mixture of **12** (0.100 g, 0. mmol), 1-adamantanol (0.040 g, 0.263 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.059 g, 0.263 mmol) and triflic acid (0.003 g, 0.018 mmol) were added. The reaction mixture was stirred and slowly warmed to rt. After 4.5 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 30% EtOAc in heptane) to give **SI11** as a mixture of anomers (0.040 g, 0.065 mmol, 37% α/β 1/0.24) as a clear syrup.

R_f-β (1/1 EtOAc/Heptane) = 0.5

R_f-α (1/1 EtOAc/Heptane) = 0.45

^{1}H NMR (α) (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 2H, ArH), 7.42 (dd, *J* = 8.7, 7.2 Hz, 2H, ArH), 7.37 – 7.27 (m, 11H, ArH), 5.13 (d, *J* = 2.1 Hz, 1H, H-1), 5.07 (d, *J* = 9.6 Hz, 1H, H-4),

4.86 (t, *J* = 5.9 Hz, 1H, N-H), 4.80 (d, *J* = 12.5 Hz, 1H, CH_2), 4.67 (d, *J* = 12.5 Hz, 1H, CH_2), 4.59 (d, *J* = 11.4 Hz, 1H, CH_2), 4.51 (d, *J* = 12.0 Hz, 1H, CH_2), 4.43 (dd, *J* = 14.8, 6.0 Hz, 1H, CH_2), 4.35 (dd, *J* = 14.4, 5.5 Hz, 1H, CH_2), 3.86 (dd, *J* = 9.5, 6.2 Hz, 1H, H-5), 3.80 (dd, *J* = 9.7, 3.0 Hz, 1H, H-3), 3.59 (t, *J* = 2.6 Hz, 1H, H-2), 2.15 – 2.07 (m, 3H, CH), 1.69 (d, *J* = 2.7 Hz, 6H, CH_2), 1.66 – 1.52 (m, 6H, CH_2), 1.23 (d, *J* = 6.4 Hz, 3H, H-6).

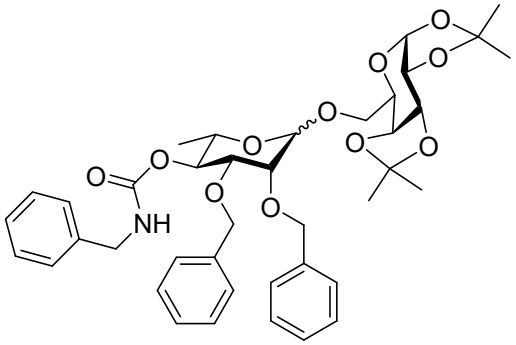
^{13}C NMR (α) (126 MHz, $CDCl_3$) δ 156.15 (C=O), 138.82 (ArC), 138.77 (ArC), 138.74 (ArC), 136.75 (ArC), 133.74 (ArC), 131.53 (ArC), 129.57 (ArC), 128.93 (ArC), 128.128 (ArC), 128.33 (ArC), 128.10 (ArC), 127.70 (ArC), 91.34 (C-1), 77.57 (C-3), 75.86 (C-2), 74.72 (C-4), 74.43 (C), 72.93 (CH_2), 71.96 (CH_2), 66.68 (C-5), 45.30 (CH_2), 42.41 (CH_2), 36.38 (CH_2), 30.64 (CH), 17.73 (C-6).

^{1}H NMR (β) (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 2H, ArH), 7.26 (ddt, *J* = 11.7, 8.4, 4.1 Hz, 13H, ArH), 5.04 (t, *J* = 9.7 Hz, 1H, H-4), 4.99 (d, *J* = 13.0 Hz, 1H, CH_2), 4.91 (d, *J* = 12.9 Hz, 1H, CH_2), 4.87 (t, *J* = 6.0 Hz, 1H, N-H), 4.64 (s, 1H, H-1), 4.47 – 4.41 (m, 2H, CH_2), 4.34 (dd, *J* = 14.9, 5.5 Hz, 1H, CH_2), 4.29 (d, *J* = 12.3 Hz, 1H, CH_2), 3.73 (d, *J* = 3.0 Hz, 1H, H-2), 3.38 (dd, *J* = 9.8, 3.0 Hz, 1H, H-3), 3.32 (dt, *J* = 9.5, 6.2 Hz, 1H, H-5), 2.17 – 2.13 (m, 3H, CH), 1.81 (ddt, *J* = 45.8, 11.9, 3.3 Hz, 6H, CH_2), 1.69 – 1.59 (m, 6H, CH_2), 1.30 (d, *J* = 6.1 Hz, 3H, H-6).

^{13}C NMR (β) (126 MHz, $CDCl_3$) δ 155.09 (C=O), 139.01 (ArC), 138.69 (ArC), 138.43 (ArC), 128.83 (ArC), 128.70 (ArC), 128.33 (ArC), 128.08 (ArC), 127.71 (ArC), 127.64 (ArC), 127.55 (ArC), 127.52 (ArC), 127.35 (ArC), 94.15 (C-1), 79.90 (C-3), 74.86 (C-2), 74.93 (C), 74.26 (C-4), 73.80 (CH_2), 71.01 (CH_2), 70.59 (C-5), 45.36 (CH_2), 43.52 (CH_2), 36.33 (CH_2), 30.78 (CH), 18.03 (C-6).

HRMS (MALDI+): Calculated for $C_{38}H_{45}NO_6Na^+$ 634.31391 m/z found 634.31408 m/z.

1,2:3,4-di-*O*-isopropylidene-β-D-galactopyranose-(6-1)-2,3-di-*O*-benzyl-4-*O*-benzylcarbamoyl-α/β-L-rhamnopyranoside (SI12)



SI12

A mixture of **12** (0.100 g, 0.175 mmol), 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose (0.068 g, 0.263 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.059 g, 0.263 mmol) was added to the reaction mixture. The reaction mixture was stirred and slowly allowed to reach rt. After 23 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 42% EtOAc in heptane) to give **SI12** as a mixture of anomers (0.113 g, 0.157 mmol, 89% α/β 0.26/1) as an amorphous solid.

A mixture of **12** (0.100 g, 0.175 mmol), 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose (0.069 g, 0.263 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.059 g, 0.263 mmol) and triflic acid (0.002 g, 0.018 mmol) were added to the reaction mixture. The reaction mixture was stirred and slowly warmed to rt. After 4 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 42% EtOAc in heptane) to give **SI12-α** (0.061 g, 0.085 mmol, 49%) as an amorphous solid and **SI12-β** (0.023 g, 0.031 mmol, 18%) as a clear syrup. total yield 67% (α/β 1/0.3).

$\boldsymbol{R_f}$-β (3/7 EtOAc/Heptane) = 0.43

$\boldsymbol{R_f}$-α (3/7 EtOAc/Heptane) = 0.29

^{1}H NMR (α) (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.0 Hz, 2H; ArH), 7.27 (m, 13H, ArH), 5.52 (d, *J* = 5.0 Hz, 1H, H-1(G)), 5.11 (t, *J* = 9.7 Hz, 1H, H-4(R)), 4.89 (d, *J* = 2.0 Hz, 1H, H-1(R)), 4.83 (t, *J* = 6.0 Hz, 1H, N-H), 4.74 (q, *J* = 12.5 Hz, 2H, CH_2), 4.61 – 4.55 (m, 2H, CH_2, H-3(G)), 4.47 – 4.39 (m, 2H, CH_2), 4.37 – 4.29 (m, 2H, H-2(G), CH_2), 4.15 (dd, *J* = 7.9, 1.9 Hz, 1H, H-4(G)), 3.92 (ddd, *J* = 7.2, 5.4, 1.9 Hz, 1H, H-5(G)), 3.85 (s, 2H, H-2(R)), 3.81 (dd, *J* = 10.6, 5.6 Hz, 1H, H-6(G)), 3.75 (m, 2H, H-5(R), H-3(R)), 3.58 (dd, *J* = 10.4, 7.0 Hz, 1H, H-6(G)), 1.52 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.27 (d, *J* = 5.8 Hz, 3H, H-6(R)).

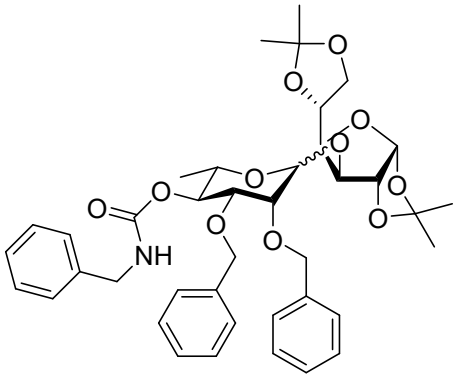
^{13}C NMR (α) (126 MHz, $CDCl_3$) δ 156.05 (C=O), 138.70 (ArC), 138.65 (ArC), 138.53 (ArC), 128.80 (ArC), 128.38 (ArC), 128.31 (ArC), 128.04 (ArC), 127.67 (ArC), 127.65 (ArC), 127.62 (ArC), 127.51 (ArC), 109.45 (C), 108.68 (C), 98.50 (C-1(R)), 96.38 (C-1(G)), 77.50 (C-3(R)), 74.47 (C-2(R)), 74.20 (C-4(R)), 72.88 (CH_2), 71.74 (CH_2), 71.22 (C-4(R)), 70.75 (C-2(G)), 70.68 (C-3(G)), 67.35 (C-5(G)), 67.17 (C-5(R)), 66.02 (C-6(G)), 45.32 (CH_2), 26.26 (CH_3), 26.09 (CH_3), 25.11 (CH_3), 24.55 (CH_3), 17.67 (C-6(R)).

^{1}H NMR (β) (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H, ArH), 7.30 – 7.22 (m, 13H, ArH), 5.51 (d, *J* = 5.0 Hz, 1H, H-1(G)), 5.07 (t, *J* = 9.6 Hz, 1H, H-4(R)), 4.93 (d, *J* = 12.7 Hz, 1H, CH_2), 4.89 – 4.84 (m, 2H, N-H, CH_2), 4.59 (dd, *J* = 8.0, 2.3 Hz, 1H, H-3(G)), 4.48 (d, *J* = 12.3 Hz, 1H, CH_2), 4.42 (d, *J* = 11.1 Hz, 2H, H-1(R), CH_2), 4.36 (d, *J* = 15.6 Hz, 1H, CH_2), 4.31 (dd, *J* = 5.0, 2.3 Hz, 2H, H-2(G), CH_2), 4.23 (dd, *J* = 8.0, 1.9 Hz, 1H, H-4(G)), 4.07 (ddd, *J* = 8.0, 5.6, 1.9 Hz, 1H, H-5(G)), 3.95 – 3.90 (m, 2H, H-2(R), H-6(G)), 3.72 (t, *J* = 9.1 Hz, 1H, H-6(G)), 3.35 (ddd, *J* = 19.6, 9.6, 4.5 Hz, 2H, H-3(R), H-5(R)), 1.55 (s, 1H, CH_3), 1.45 (s, 3H, CH_3), 1.34 – 1.30 (m, 9H, CH_3, H-6(R)).

^{13}C NMR (β) (126 MHz, $CDCl_3$) δ 155.90 (C=O), 138.81 (ArC), 138.64 (ArC), 138.28 (ArC), 128.84 (ArC), 128.61 (ArC), 128.38 (ArC), 128.16 (ArC), 127.67 (ArC), 127.62 (ArC), 127.47 (ArC), 109.13 (C), 108.72 (C), 101.84 (C-1(R)), 96.42 (C-1(G)), 79.43 (C-3(R)), 74.05 (C-4(R)), 73.95 (CH_2), 73.60 (C-2(R)), 71.27 (C-3(G)), 71.19 (CH_2), 70.95 (C-5(R)), 70.70 (C-2(G)), 70.64 (C-4(G)), 67.90 (C-6(G)), 65.90 (C-5(G)), 45.36 (CH_2), 26.31 (CH_3), 26.15 (CH_3), 25.09 (CH_3), 24.57 (CH_3), 17.70 (C-6(R)).

HRMS (MALDI+): Calculated for $C_{40}H_{49}NO_{11}Na^+$ 742.31978 m/z found 742.31918 m/z.

1,2:3,4-di-*O*-isopropylidene-α-D-glucofuranose-(3-1)-2,3-di-*O*-benzyl-4-*O*-benzylcarbamoyl-α/β-L-rhamnopyranoside (SI13)



SI13

A reaction mixture of **12** (0.103 g, 0.181 mmol), 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.069 g, 0.263 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.059 g, 0.263 mmol) was added. The reaction mixture was stirred and slowly warmed to rt. After 26 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 45% EtOAc in heptane) to give **SI13** as a mixture of anomers (0.085 g, 0.118 mmol, 67% α/β 0.6/1) as a clear syrup.

A mixture of **12** (0.090 g, 0.158 mmol), 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.062 g, 0.237 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.053 g, 0.237 mmol) and triflic acid (0.002 g, 0.016 mmol) were added. The reaction mixture was stirred and slowly warmed to rt. After 3 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and reaction was diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 45% EtOAc in heptane) to give **SI13** as a mixture of anomers (0.083 g, 0.115 mmol, 73% α/β 1/0.2) as a clear syrup.

$\boldsymbol{R_f}$ (3/7 EtOAc/Heptane) = 0.53

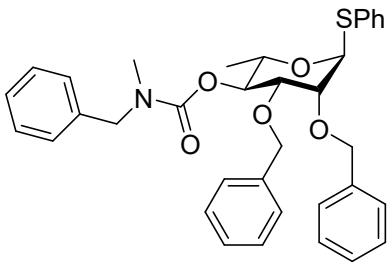
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 6.8 Hz, 2H, ArH), 7.23 – 7.16 (m, 13H, ArH), 5.82 (d, J = 3.5 Hz, 1H, H-1(G)), 5.02 (t, J = 9.6 Hz, 1H, H-4(R)), 4.80 (dd, J = 15.3, 7.9 Hz, 2H, CH_2),

4.74 (d, J = 3.7 Hz, 1H, H-2(G)), 4.72 (d, J = 1.9 Hz, 0.18H, H-1(α)(R)), 4.44 (d, J = 14.7 Hz, 2H, H-1(β)(R), CH_2), 4.40 – 4.34 (m, 1H, CH_2), 4.32 – 4.26 (m, 2H, CH_2), 4.07 (d, J = 3.0 Hz, 1H, H-3(G)), 4.02 – 3.94 (m, 2H, H-6(G), H-4(G)), 3.90 – 3.85 (m, 2H, H-6(G), H-5(G)), 3.80 (d, J = 2.9 Hz, 1H, H-2(R)), 3.30 (m, 2H, H-3(R), H-5(R)), 1.42 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.28 (d, J = 6.0 Hz, 3H, H-6(R)), 1.23 (s, 3H, CH_3), 1.15 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.86 (C=O), 138.57 (ArC), 138.45 (ArC), 138.14 (ArC), 128.87 (ArC), 128.58 (ArC), 128.41 (ArC), 128.29 (ArC), 127.80 (ArC), 127.63 (ArC), 127.62 (ArC), 112.01 (C), 109.14 (C), 105.60 (C-1(G)), 102.60 (C-1(β)(R)), 96.18 (C-1(α)(R)), 84.31 (C-2(G)), 82.96 (C-3(G)), 81.10 (C-4(G)), 79.19 (C-3(R)), 74.08 (CH_2), 73.92 (C-4(R)), 73.47 (C-2(R)), 72.56 (H-5(G)), 71.55 (CH_2), 71.28 (C-5(R)), 68.01 (C-6(G)), 45.37 (CH_2), 26.99 (CH_3), 26.97 (CH_3), 26.34 (CH_3), 25.55 (CH_3), 17.75 (C-6(R)).

HRMS (MALDI+): Calculated for $C_{40}H_{49}NO_{11}Na^+$ 743.31978 m/z found 742.31917 m/z.

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*N*-benzyl-*N*-methylcarbamoyl)-1-thio-α-L-rhamnopyranoside (13)



13

Compound **12** (0.103 g, 0.181 mmol) was dissolved in DMF (1.5 mL) and the reaction mixture was cooled to 0 °C. NaH (0.011 g, 0.271 mmol) was added and the reaction mixture was stirred at 0 °C for 30 minutes whereupon MeI (0.039 g, 0.271 mmol) was added. The cooling was removed and the reaction mixture was stirred for 23 hours. The reaction was quenched with MeOH. The reaction mixture was then extracted with EtOAc and the organic phase washed with brine and dried over $MgSO_4$ and concentrated in vacuo. The product was purified with flash column chromatography, (SiO_2, 0% to 29% EtOAc in heptane) to give **13** (0.09 g, 0.154 mmol, 85%) as a clear syrup.

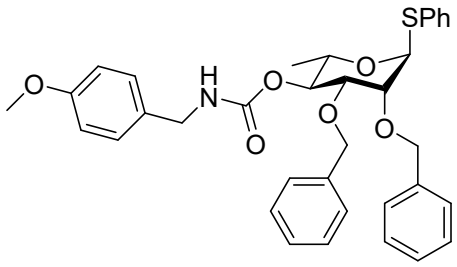
R_f (3/7 EtOAc/Heptane) = 0.5

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.17 (m, 15H, ArH), 5.57 (d, *J* = 12.7 Hz, 1H, H-1), 5.31 (t, *J* = 9.5 Hz, 1H, H-4), 4.75 (s, 1H, CH_2), 4.73 – 4.61 (m, 2H, CH_2), 4.56 – 4.42 (m, 3H, CH_2), 4.27 – 4.14 (m, 1H, H-5), 4.04 (d, *J* = 28.5 Hz, 1H, H-2), 3.87 – 3.74 (m, 1H, H-3), 2.99 (s, 1.5H, CH_3), 2.80 (s, 1.5H, CH_3), 1.38 – 1.30 (m, 3H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.27 (C=O), 155.82 (C=O), 138.21 (ArC), 137.98 (ArC), 137.60, (ArC) 134.59 (ArC), 131.19 (ArC), 129.17 (ArC), 128.71 (ArC), 128.45 (ArC), 128.06 (ArC), 127.74 (ArC), 127.41 (ArC), 127.08 (ArC), 86.09 (C-1), 77.68 (C-3), 76.12 (C-2), 74.38 (C-4), 72.42 (CH_2), 71.70 (CH_2), 68.74 (C-5), 52.82 (CH_2), 52.32 (CH_2), 34.95 (CH_3), 33.52 (CH_3), 17.68 (C-6).

HRMS (MALDI+): Calculated for $C_{35}H_{37}NSO_5Na^+$ 606.22846 m/z found 606.22834 m/z.

Phenyl 2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzylcarbamoyl)-1-thio-α-L-rhamnopyranoside (14)



14

Compound **9** (0.201 g, 0.460 mmol) was dissolved in toluene (4 mL). 4-Dimethylaminopyridine (0.019 g, 0.156 mmol) and 4-methoxybenzyl isocyanate (0.225 g, 1.38 mmol) were added to the reaction mixture, which was stirred at reflux for 24 hours, whereupon it was cooled to rt. and diluted with toluene. The organic phase was washed twice with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0 % to 40 % EtOAc in heptane) to give **14** (0.173 g, 0.289 mmol, 63%) as a white solid

R_f-β (3/7 EtOAc/Heptane) = 0.25

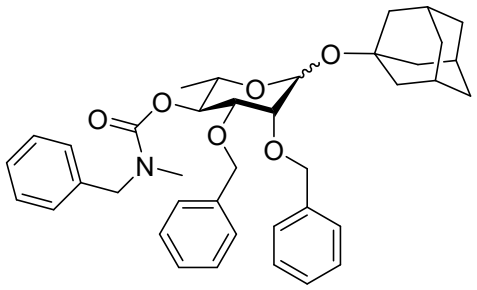
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dt, *J* = 6.4, 1.5 Hz, 2H, ArH), 7.35 – 7.27 (m, 13H, ArH), 7.19 (d, *J* = 8.3 Hz, 2H, ArH), 6.82 (d, *J* = 8.2 Hz, 2H, ArJ), 5.51 (d, *J* = 1.9 Hz, 1H, H-1), 5.15 (t,

J = 9.6 Hz, 1H, H-4), 4.83 (t, *J* = 5.9 Hz, 1H, N-H), 4.72 – 4.65 (m, 2H, CH_2), 4.57 (d, *J* = 12.2 Hz, 1H, CH_2), 4.48 (d, *J* = 12.1 Hz, 1H, CH_2), 4.38 (dd, *J* = 14.6, 6.2 Hz, 1H, CH_2), 4.29 (dd, *J* = 14.5, 5.6 Hz, 1H, CH_2), 4.13 (dq, *J* = 9.7, 6.3 Hz, 1H, H-5), 3.99 (t, *J* = 2.5 Hz, 1H, H-2), 3.79 (s, 3H, OCH_3), 3.73 – 3.70 (m, 1H, H-3), 1.29 (d, *J* = 6.2 Hz, 3H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.02 (C=O),138.31 (ArC), 138.05 (ArC), 134.67 (ArC), 131.21 (ArC), 129.21 (ArC), 129.04 (ArC), 128.49 (ArC), 128.45 (ArC), 128.10 (ArC), 127.82 (ArC), 127.74 (ArC), 127.44 (ArC), 114.21 (ArC), 86.15 (C-1), 77.56 (C-3), 76.19 (C-2), 74.05 (C-4), 72.49 (CH_2), 71.87 (CH_2), 68.59 (C-5), 55.45 (CH_3), 44.71 (CH_2), 17.68 (C-6).

HRMS (MALDI+): Calculated for $C_{35}H_{37}NSO_6Na^+$ 622.22338 m/z found 622.22352 m/z.

1-Adamantyl 2,3-di-*O*-benzyl-4-*O*-(*N*-benzyl-*N*-methylcarbamoyl)-1-thio-α/β-L-rhamnopyranoside (SI14)



SI14

A mixture of **13** (0.065 g, 0.111 mmol), 1-adamantanol (0.025 g, 0.166 mmol) and molecular sieves (3 Å) in DCM (1.5 mL) was cooled to -78 °C, where N-iodosuccinimide (0.037 g, 0.166 mmol) was added. The reaction mixture was stirred and slowly warmed to rt. After 21 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 30% EtOAc in heptane) to give **SI14** as a mixture of anomers (0.063 g, 0.101 mmol, 91% α/β 0.26/1) as a clear syrup.

A mixture of **13** (0.090 g, 0.154 mmol), 1-adamantanol (0.035 g, 0.231 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.052 g, 0.231 mmol) and triflic acid (0.002 g, 0.015 mmol) were added. The reaction mixture was stirred and

slowly warmed rt. After 4 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 30% EtOAc in heptane) to give **SI14** as a mixture of anomers (0.08 g, 0.128 mmol, 83% α/β 1/0.15) as a clear syrup.

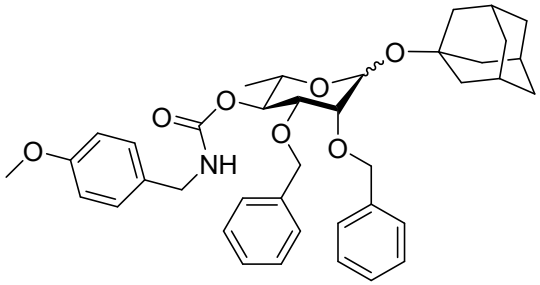
R_f-β (3/7 EtOAc/Heptane) = 0.46

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, J = 14.9, 7.1 Hz, 2H, ArH), 7.25 (qt, *J* = 13.3, 8.4 Hz, 20H, ArH), 5.15 (dq, *J* = 17.2, 9.6 Hz, 1.2H, H-1(α), H-4), 5.05 – 4.87 (m, 2H, CH_2), 4.67 (d, *J* = 16.5 Hz, 1H, H-1(β)), 4.61 (d, *J* = 15.1 Hz, 1H, CH_2), 4.52 – 4.38 (m, 2H, CH_2), 4.34 – 4.20 (m, 1H, CH_2), 3.92 – 3.70 (m, 1H, H-2), 3.41 (td, *J* = 26.4, 8.0 Hz, 2H, H-3, H-5), 2.93 (s, 2H, CH_3), 2.72 (s, 2H, CH_3), 2.13 (d, *J* = 21.2 Hz, 5H, CH), 1.87 – 1.74 (m, 6H, CH_2), 1.63 (q, *J* = 15.5 Hz, 6H, CH_2), 1.32 (d, *J* = 6.4 Hz, 1.5H, H-6(α)), 1.27 (d, *J* = 4.4 Hz, 3H, H-6(β)).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.86 (C=O), 155.31 (C=O), 138.98 (ArC), 138.79 (ArC), 138.71 (ArC), 138.42 (ArC), 137.72 (ArC), 137.64 (ArC), 128.67 (ArC), 128.34 (ArC), 128.05 (ArC), 127.43 (ArC), 127.32 (ArC), 94.12 (C-1(β)), 91.59 (C-1(α)), 80.06 (C-3), 79.85 (C-3), 77.92 (C-2), 75.96, 74.91 (C), 74.66 (C-4), 73.72 (CH_2), 70.87 (CH_2), 70.67 (C-5), 52.76 (CH_2), 52.25 (CH_2), 42.46 (CH_2), 36.31 (CH_2), 34.91 (CH_3), 33.43 (CH_3), 30.75 (CH), 30.68 (CH), 18.05 (C-6(β)), 17.77 (C-6(α)).

HRMS (MALDI+): Calculated for $C_{39}H_{47}NO_6Na^+$ 648.32956 m/z found 648.32956 m/z.

1-Adamantyl 2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzylcarbamoyl)-1-thio-α/β-L-rhamnopyranoside (SI15)



SI15

A mixture of **14** (0.100 g, 0.167 mmol), 1-adamantanol (0.038 g, 0.250 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.056 g, 0.250 mmol) was added. The reaction mixture was stirred and slowly warmed to rt. After 17 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 35% EtOAc in heptane) to give **SI15** as a mixture of anomers (0.069 g, 0.107 mmol, 64% α/β 0.2/1) as a clear syrup.

A mixture of **14** (0.102 g, 0.170 mmol), 1-adamantanol (0.039 g, 0.255 mmol) and molecular sieves (3 Å) in DCM (2 mL) was cooled to -78 °C, where N-iodosuccinimide (0.057 g, 0.255 mmol) and triflic acid (0.003 g, 0.017 mmol) were added. The reaction mixture was stirred and slowly warmed to rt. After 3 hours the reaction was quenched with saturated $Na_2S_2O_3$ (aq.) and diluted with DCM. The organic phase was washed once with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated. The product was purified with flash column chromatography, (SiO_2, 0% to 35% EtOAc in heptane) to give **SI15** as a mixture of anomers (0.092 g, 0.143 mmol, 84% α/β 1/0.11) as a clear syrup.

R_f-β (3/7 EtOAc/Heptane) = 0.23

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.8 Hz, 2H, ArH), 7.41 – 7.17 (m, 13H, ArH), 6.82 (d, *J* = 3.1 Hz, 2H, ArH), 5.16 (d, *J* = 2.1 Hz, 0.27H, H-1(α)), 5.06 (t, *J* = 9.6 Hz, 1H, H-4), 5.02 (d, *J* = 12.9 Hz, 1H, CH_2), 4.94 (d, *J* = 12.9 Hz, 1H, CH_2), 4.89 (t, *J* = 5.9 Hz, 1H, N-H), 4.67 (s, 1H, H-1(β)), 4.48 (d, *J* = 12.3 Hz, 1H, CH_2), 4.40 (dd, *J* = 14.7, 5.9 Hz, 1H, CH_2), 4.30 (dd, *J* = 14.4, 10.7 Hz, 2H, CH_2), 3.80 (s, 3H, OCH_3), 3.76 (d, *J* = 2.9 Hz ,H-2), 3.38 (m, 2H, H-5, H-3), 2.18 (q, *J* = 3.2 Hz, 3H, CH), 2.15 – 2.11 (m, 1H, CH), 1.91 – 1.85 (m, 3H, CH_2), 1.82 – 1.78 (m, 3H, CH_2), 1.75 – 1.59 (m, 6H, CH_2), 1.33 (d, *J* = 6.2 Hz, 3H, H-6(β)), 1.25 (d, *J* = 6.3 Hz, 1H, H-6(α)).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.03 (C=O), 155.91 (C=O), 138.96 (ArC), 138.80 (ArC), 138.69 (ArC), 138.42 (ArC), 129.01 (ArC), 128.66 (ArC), 128.36 (ArC), 128.28 (ArC), 128.04 (ArC), 127.58 (ArC), 127.49 (ArC), 127.31 (ArC), 114.14 (ArC), 94.10 (C-1(β)), 91.50 (C-1(α)), 79.90 (C-3), 74.91 (C), 74.85 (C-2), 74.13 (C-4), 73.38 (CH_2), 71.09 (CH_2), 70.56 (C-5), 55.39 (OCH_3), 44.78 (CH_2), 42.53 (CH_2), 42.36 (CH_2), 36.40 (CH_2), 36.34 (CH_2), 30.74 (CH), 30.66 (CH), 17.99 (C-6(β)), 17.70 (C-6(α)).

HRMS (MALDI+): Calculated for $C_{39}H_{47}NO_7Na^+$ 664.32447 m/z found 664.32471 m/z.

SI.3 Check of anomerization

To check whether triflic acid promoted anomerization under the reaction conditions a model experiment was carried out: Pure **SI12**-β (0.01 g, 0.016 mmol) was dissolved in DCM (0.3 mL) to which 1-adamantanol (0.003 g, 0.024 mmol), NIS (0.005 g, 0.024 mmol) and tifilic acid (0.001 g, 0.004 mmol) were added. The reaction was stirred at rt. for 2 hours and monitored by TLC. The TLC of the reaction mixture showed two spots, one spot with a R_f corresponding to **SI12**-β and a spot at the baseline (R_f of 0) (Figure SI.1). No spot corresponding to **SI12**-α could be observed in the reaction mixture. This suggests that anomerization of the β-product is not significant under the reaction conditions.

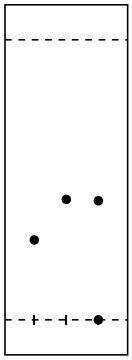
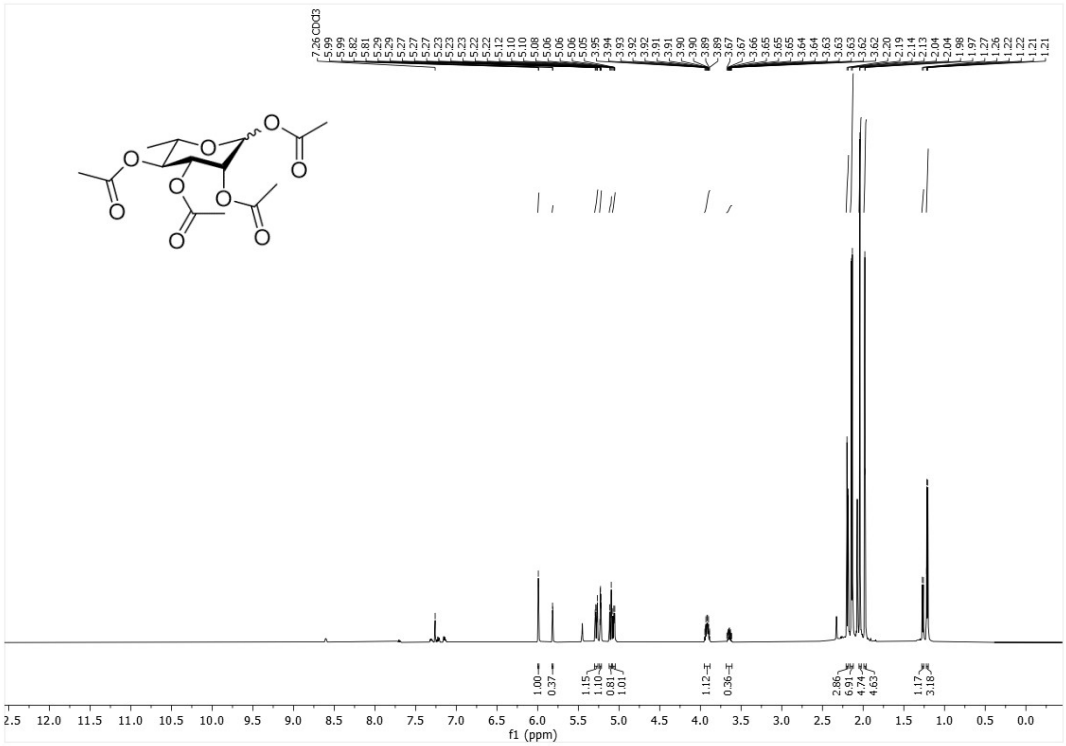
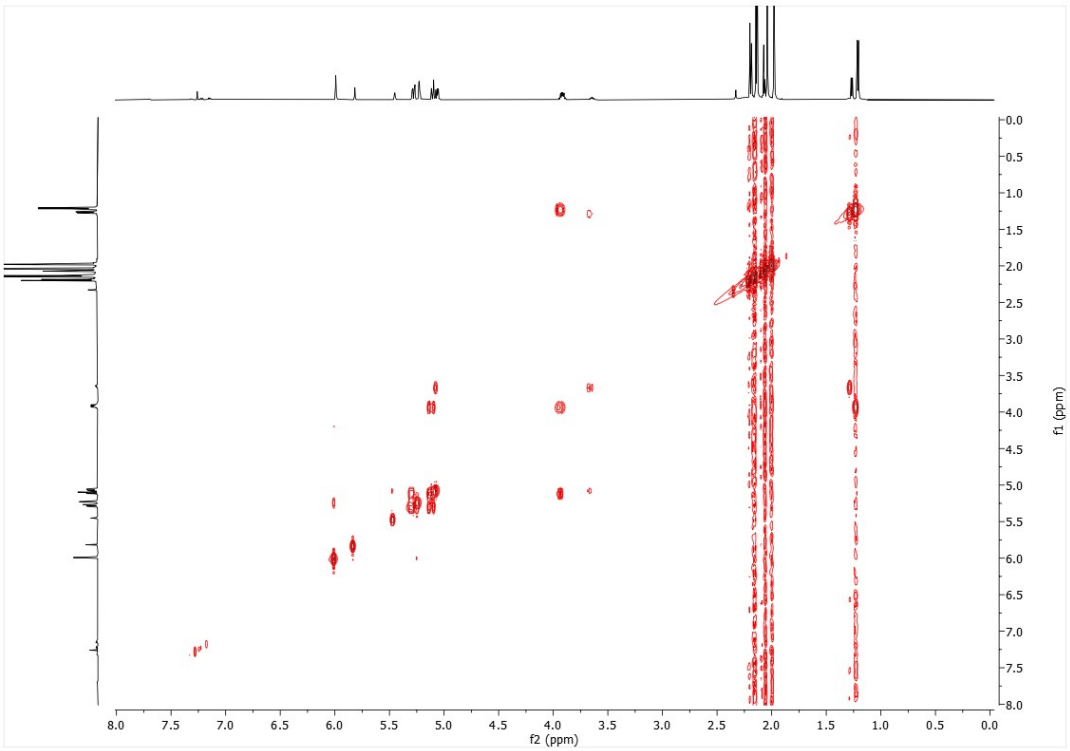


Figure SI.1: Illustration of the TLC of the reaction after 2 hours. Left spot: **SI12**-α, middle spot: **SI12**-β and right spot: reaction mixture.

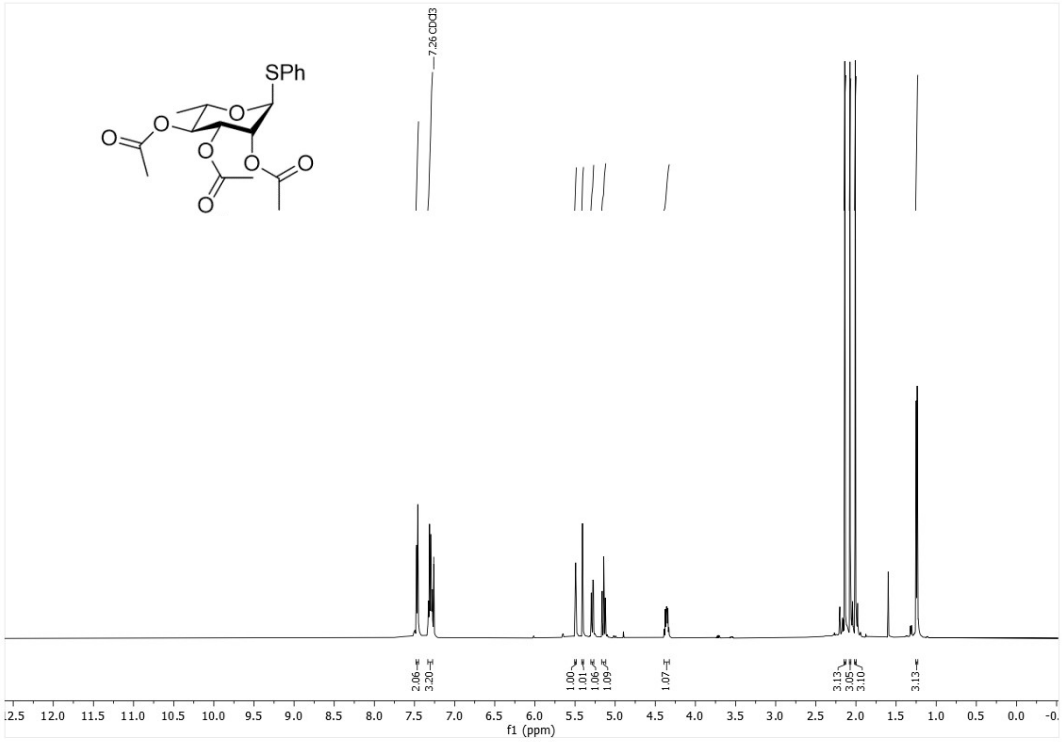
SI.4 NMR data

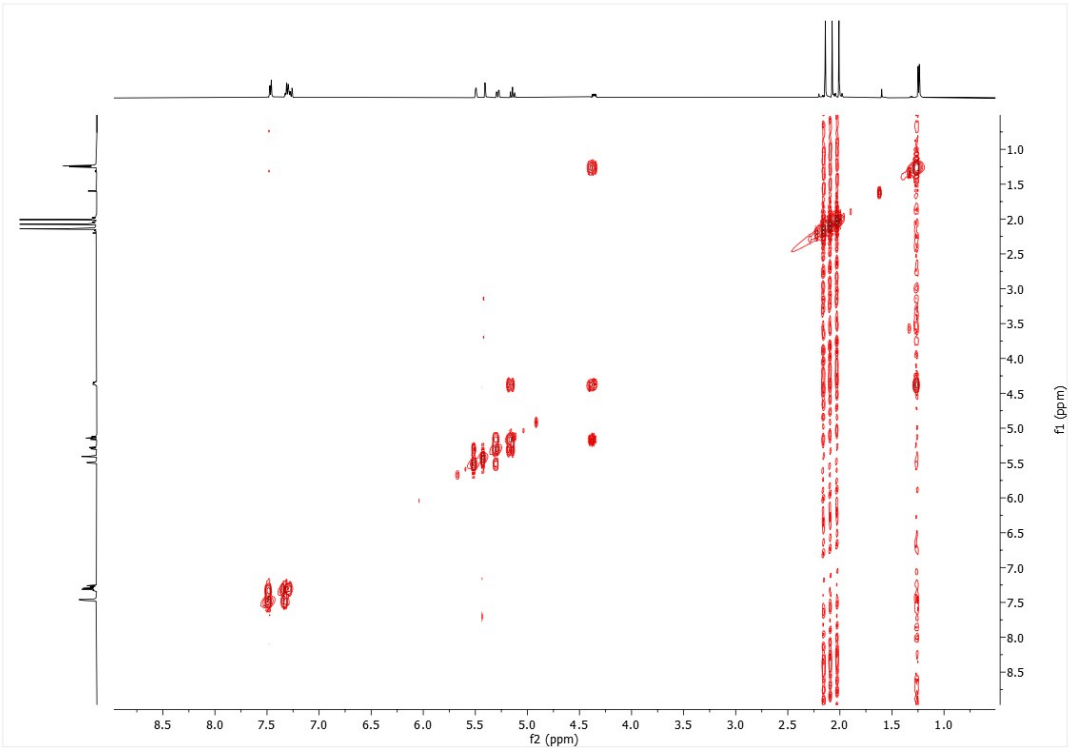
1,2,3,4-tetra-*O*-acetyl-L-rhamnopyranose (SI1) ($CDCl_3$)



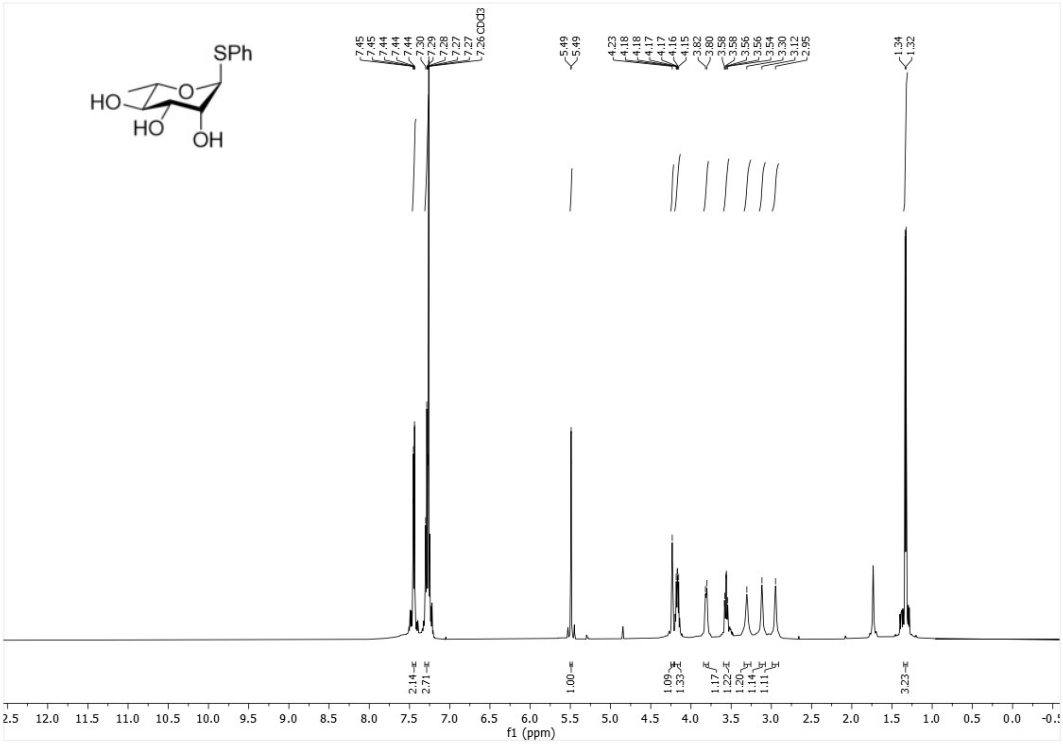


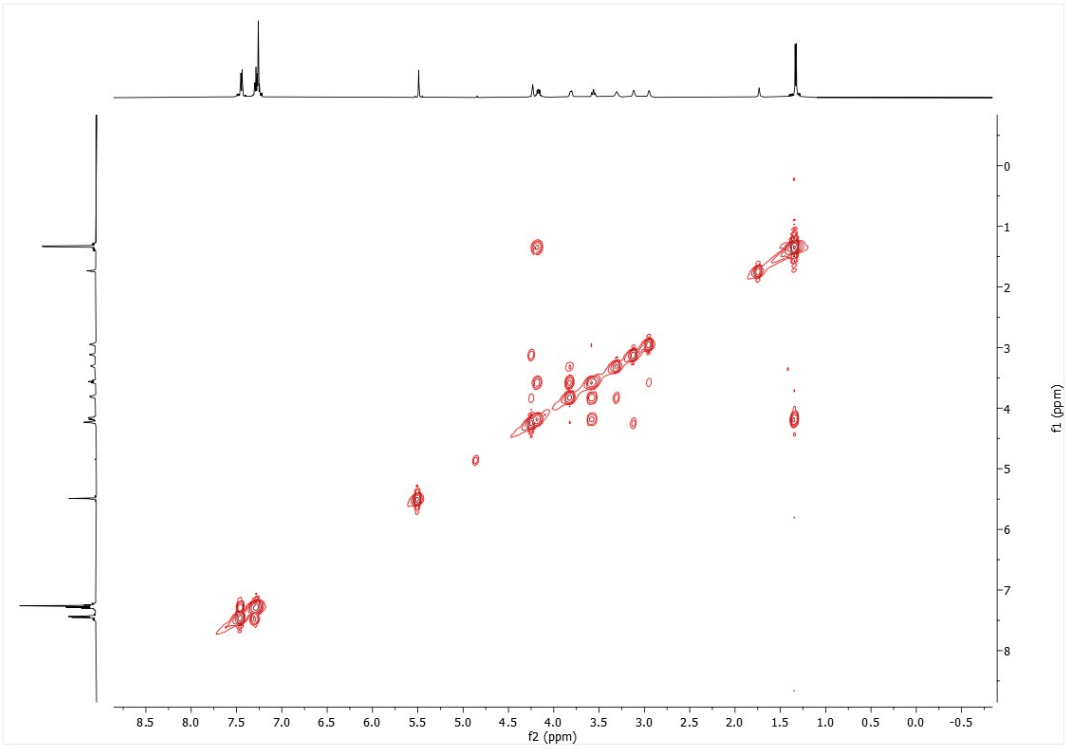
Phenyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (SI2) ($CDCl_3$)



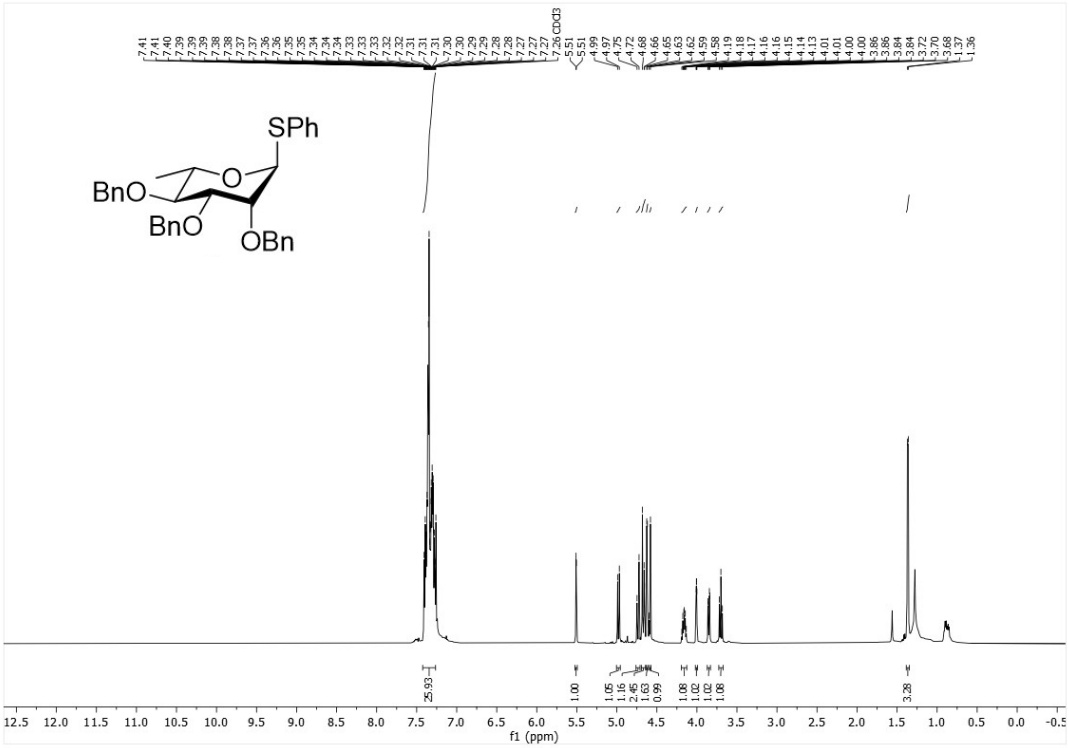


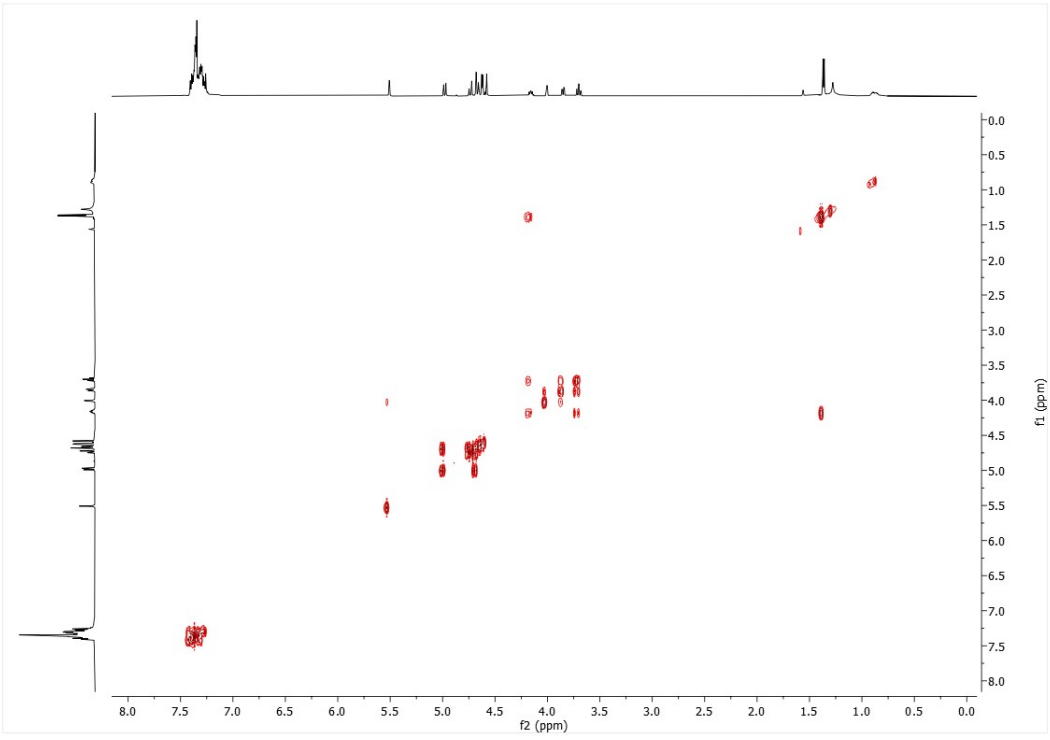
Phenyl 1-thio-α-L-rhamnopyranose (1) ($CDCl_3$)



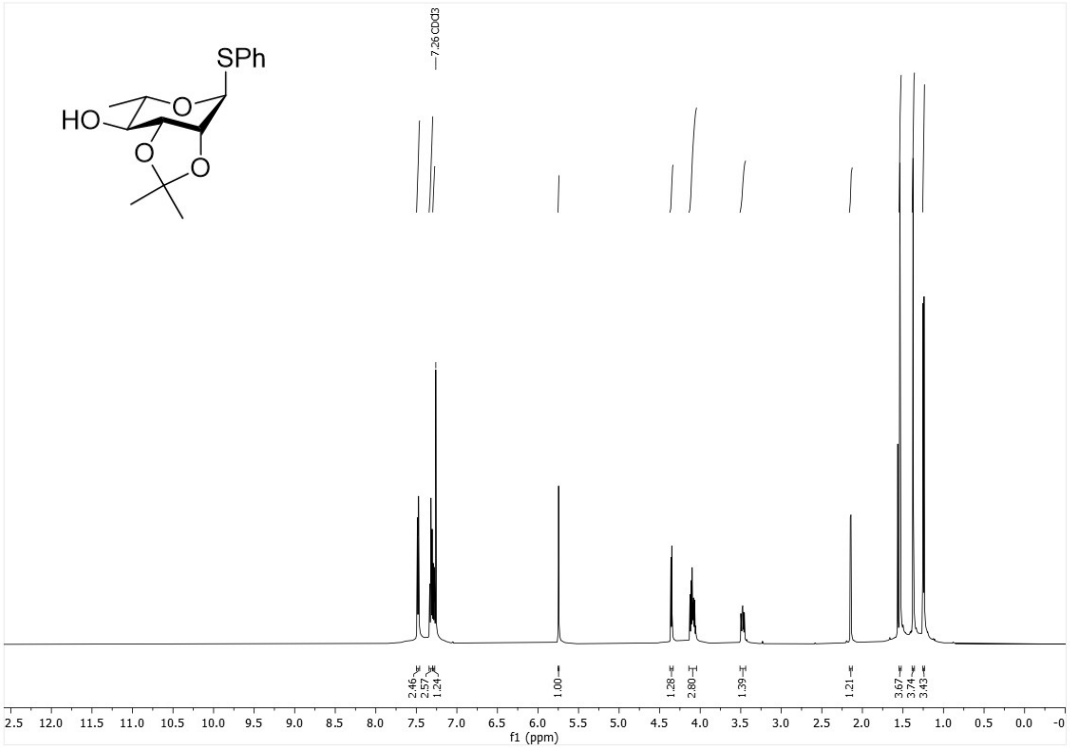


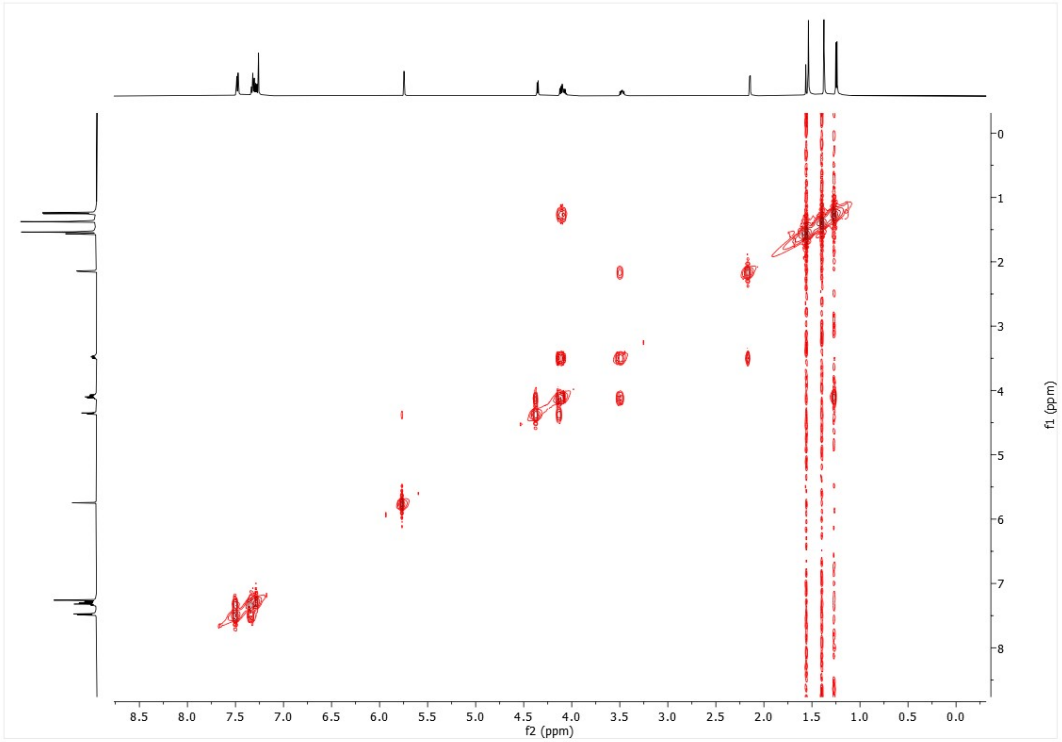
Phenyl 2,3,4-tri-*O*-benzyl-1-thio-α-L-rhamnopyranoside (2) ($CDCl_3$)



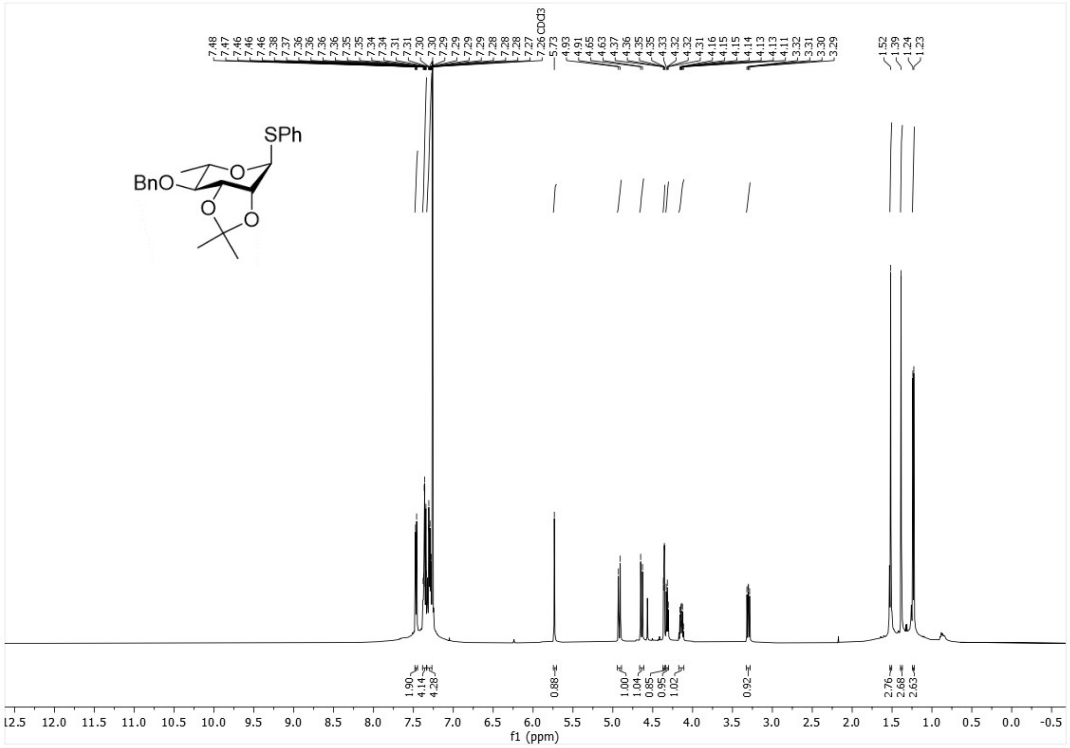


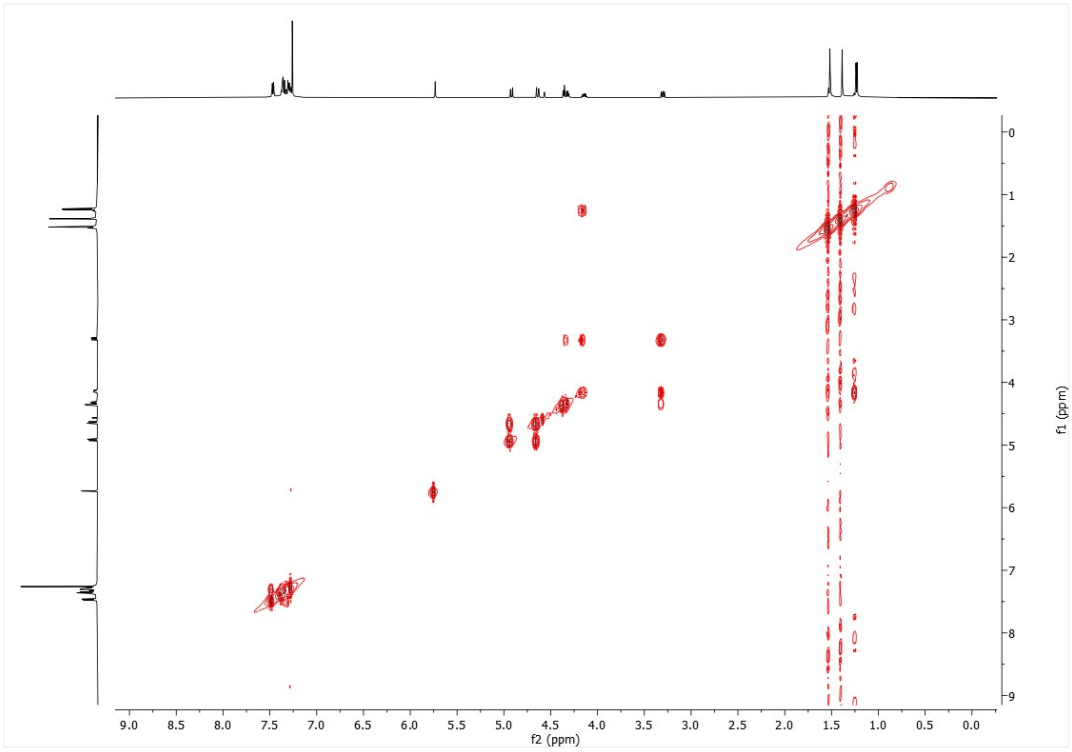
Phenyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (3) ($CDCl_3$)



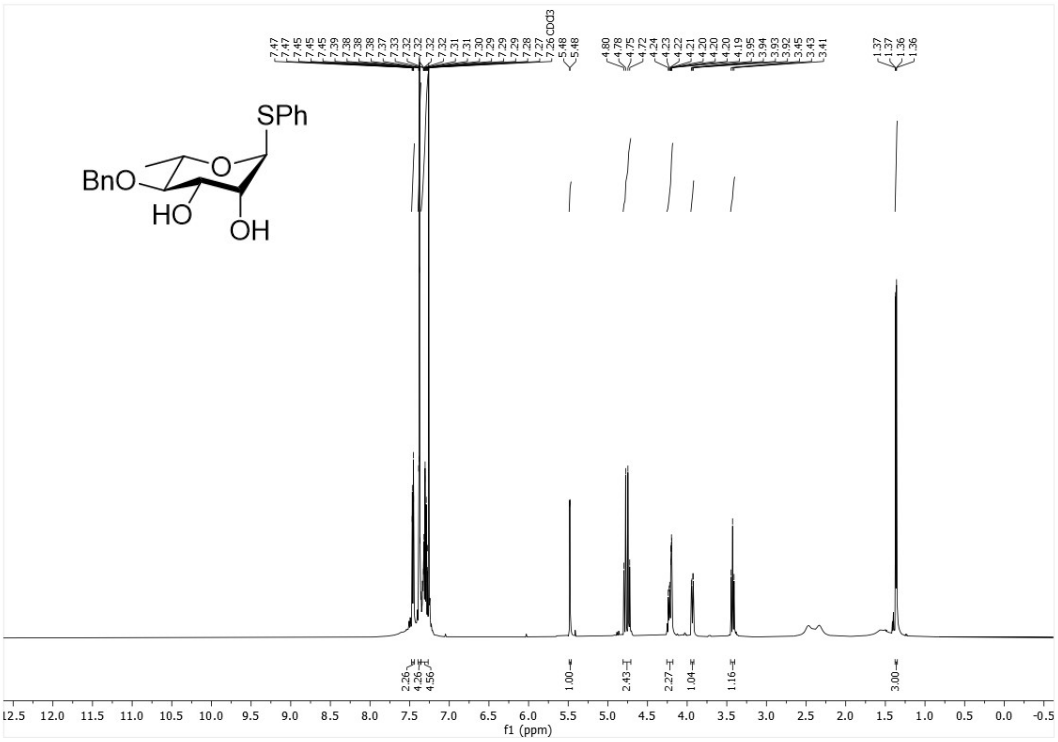


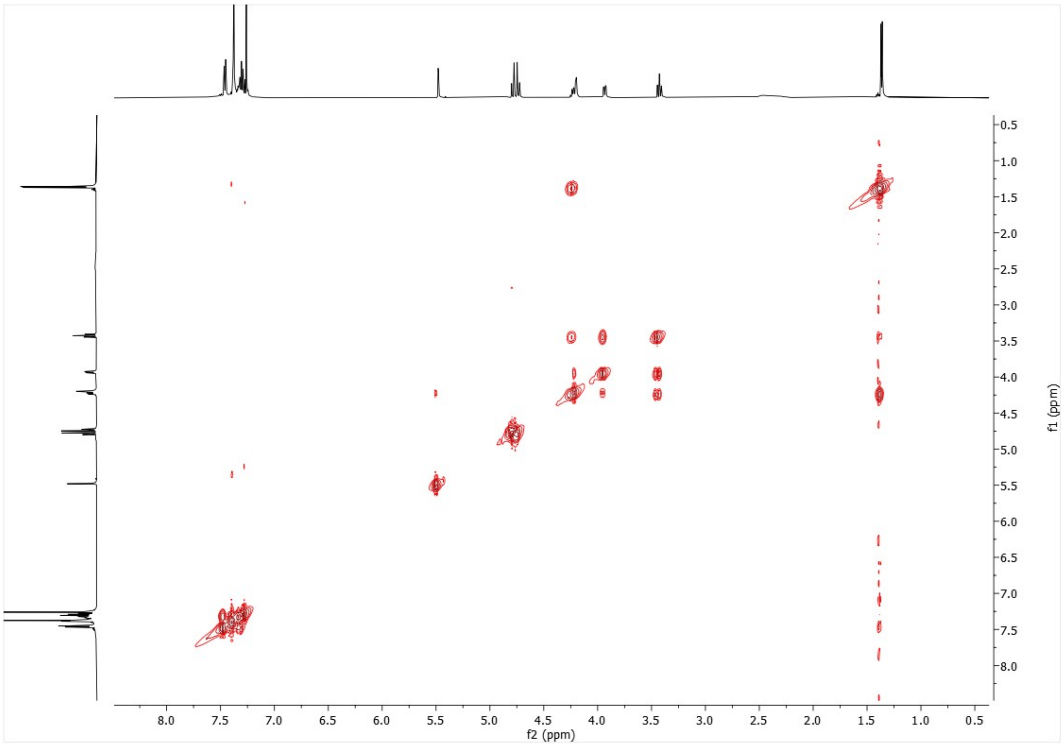
Phenyl 4-*O*-benzyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (SI3) ($CDCl_3$)



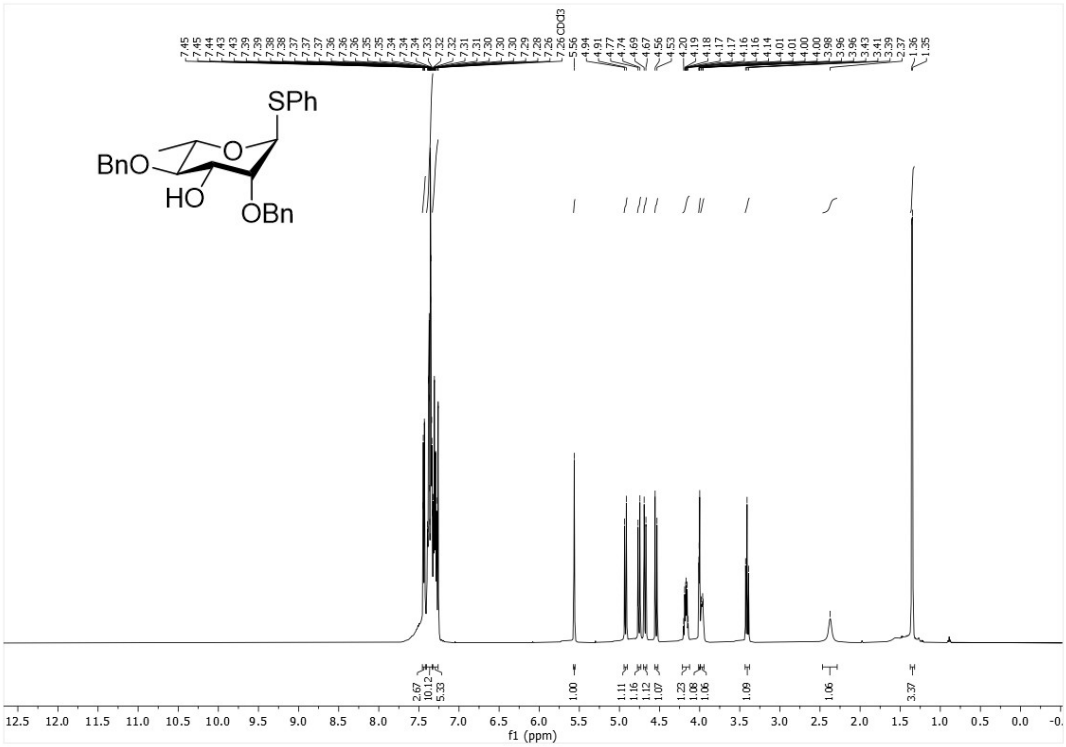


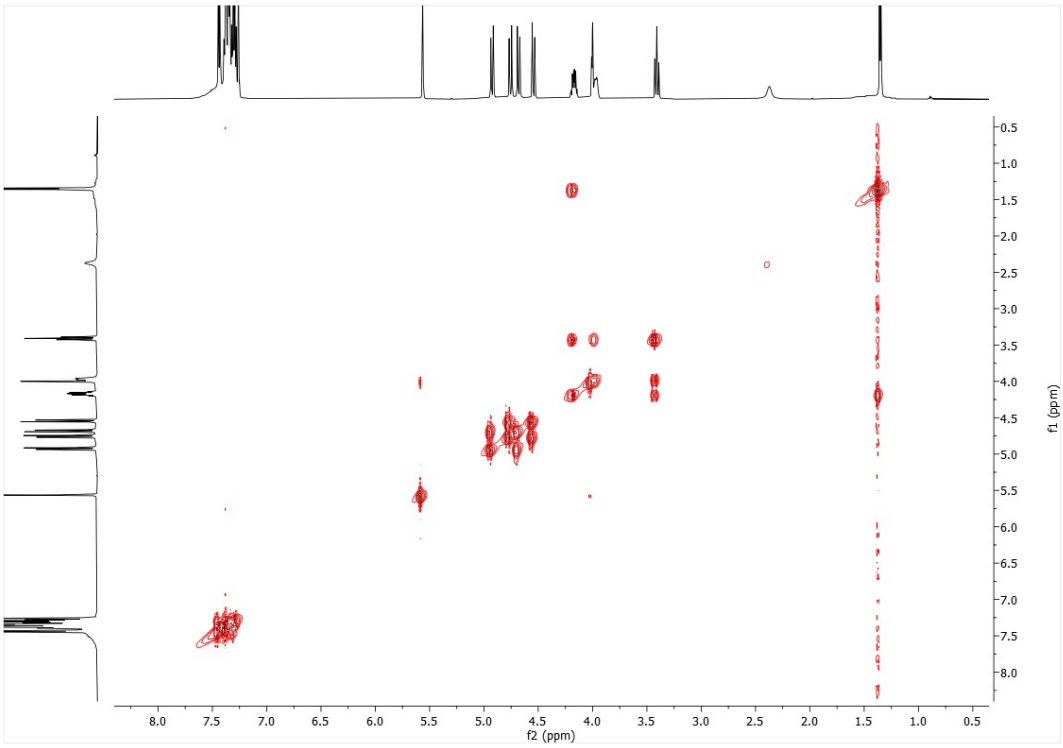
Phenyl 4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (4) ($CDCl_3$)



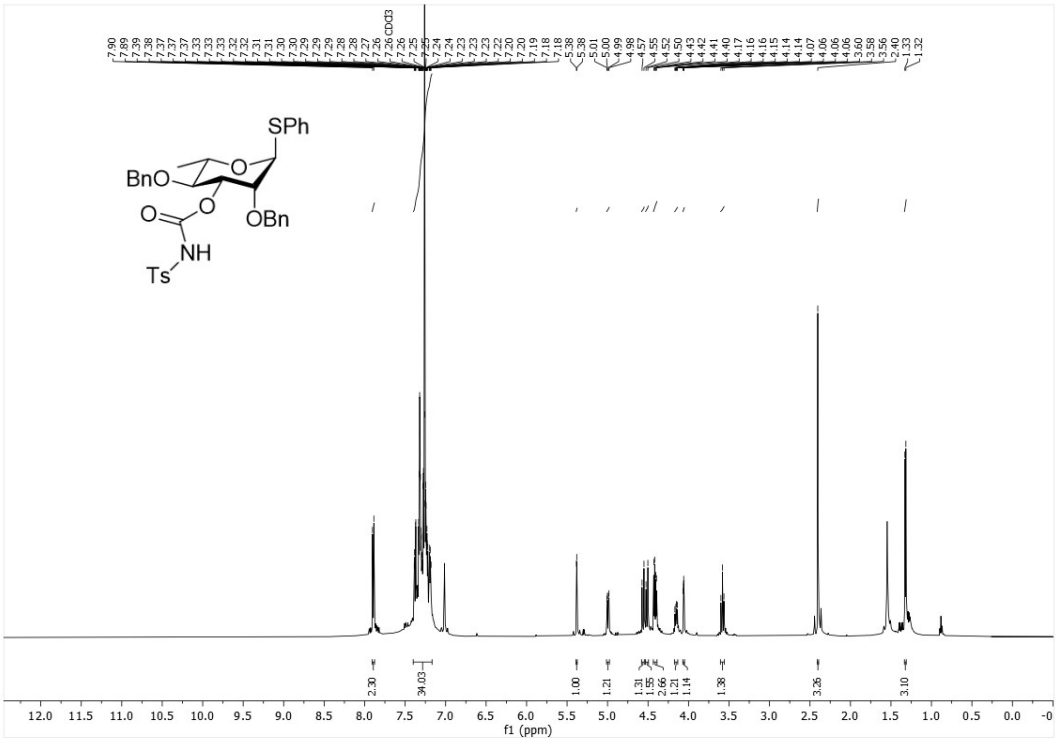


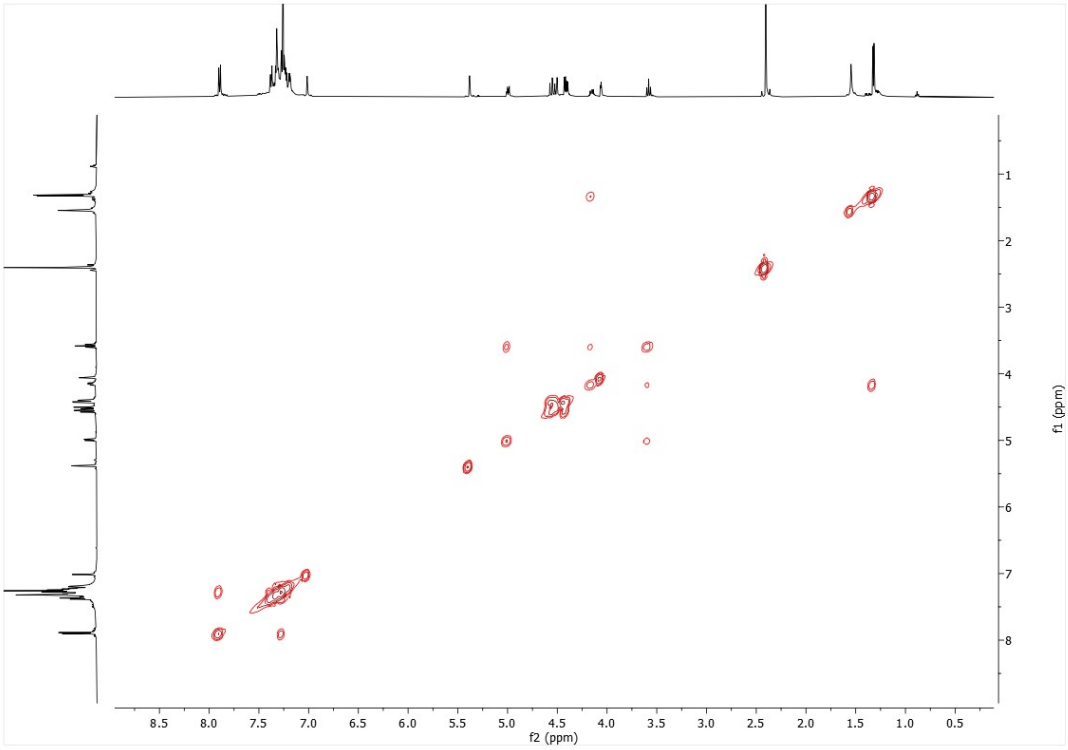
Phenyl 2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (5) ($CDCl_3$)

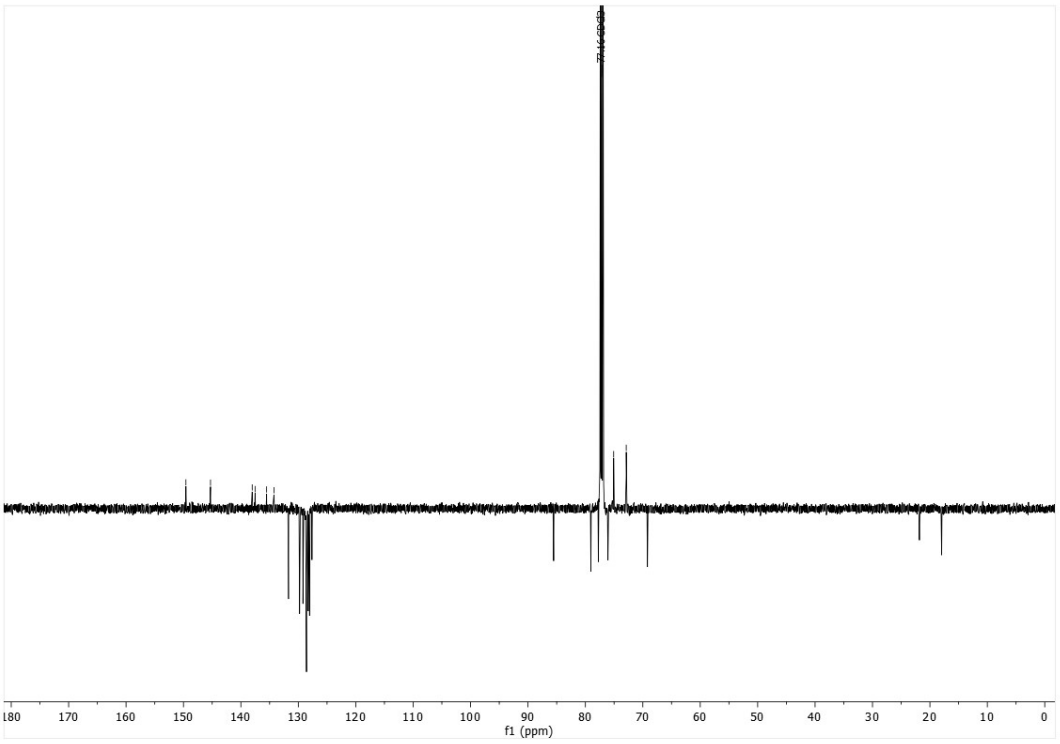


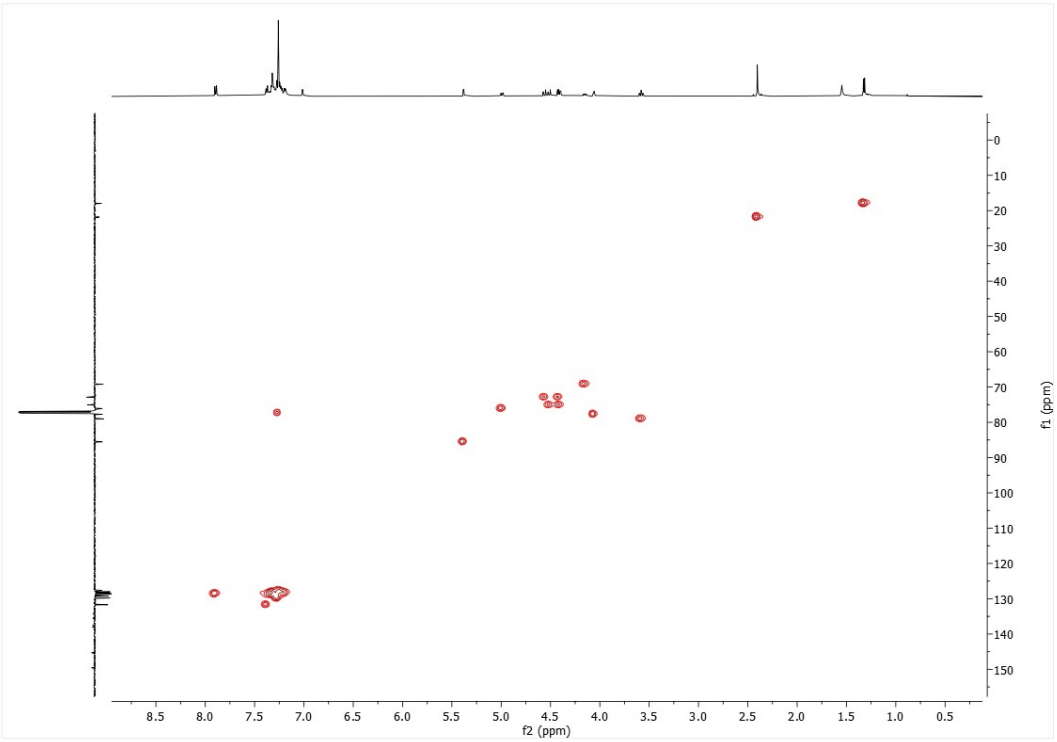


Phenyl 2,4-di-*O*-benzyl-3-*O*-tosylcarbamate-1-thio-α-L-rhamnopyranoside (6) ($CDCl_3$)

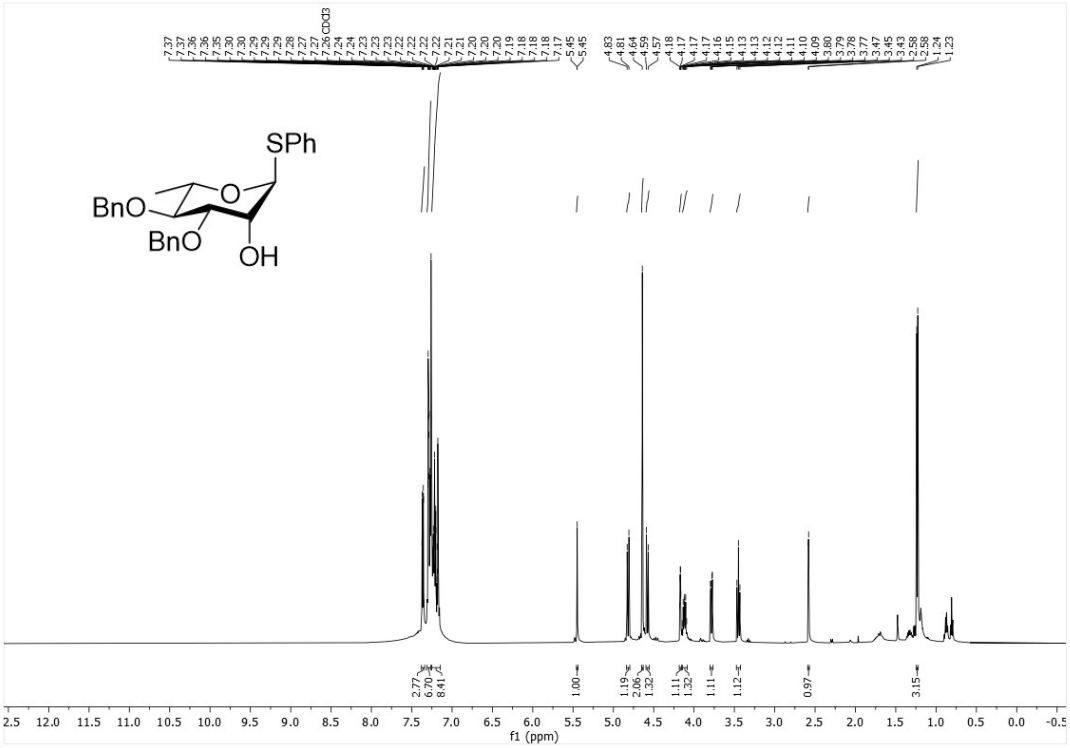


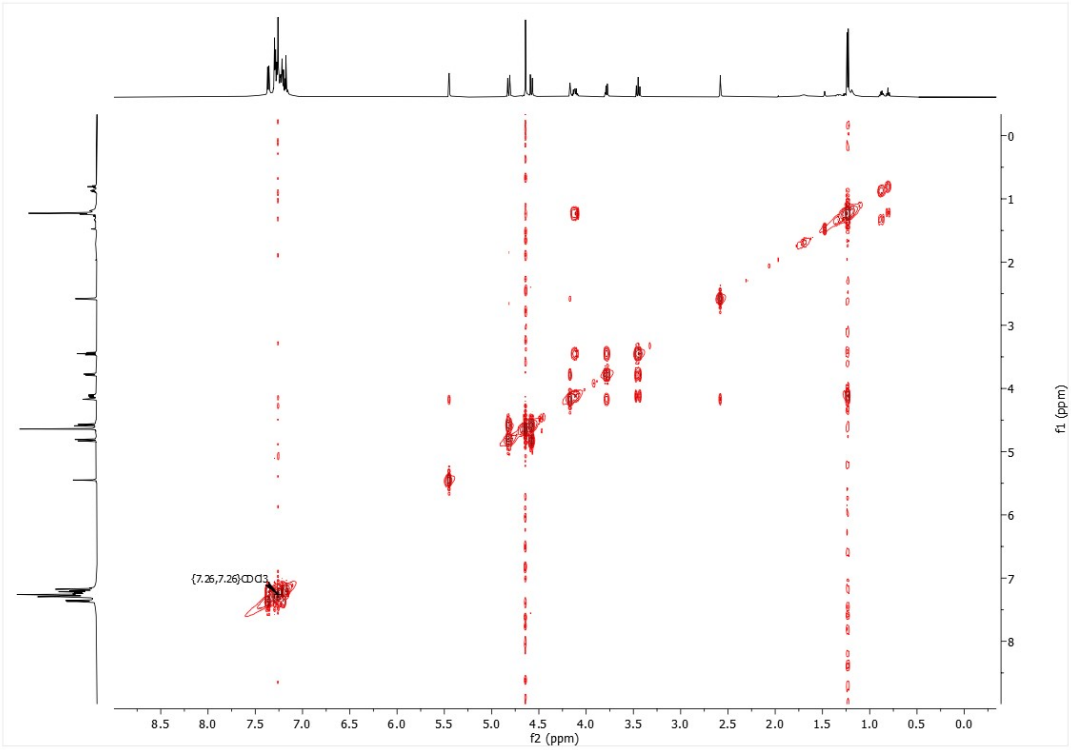



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

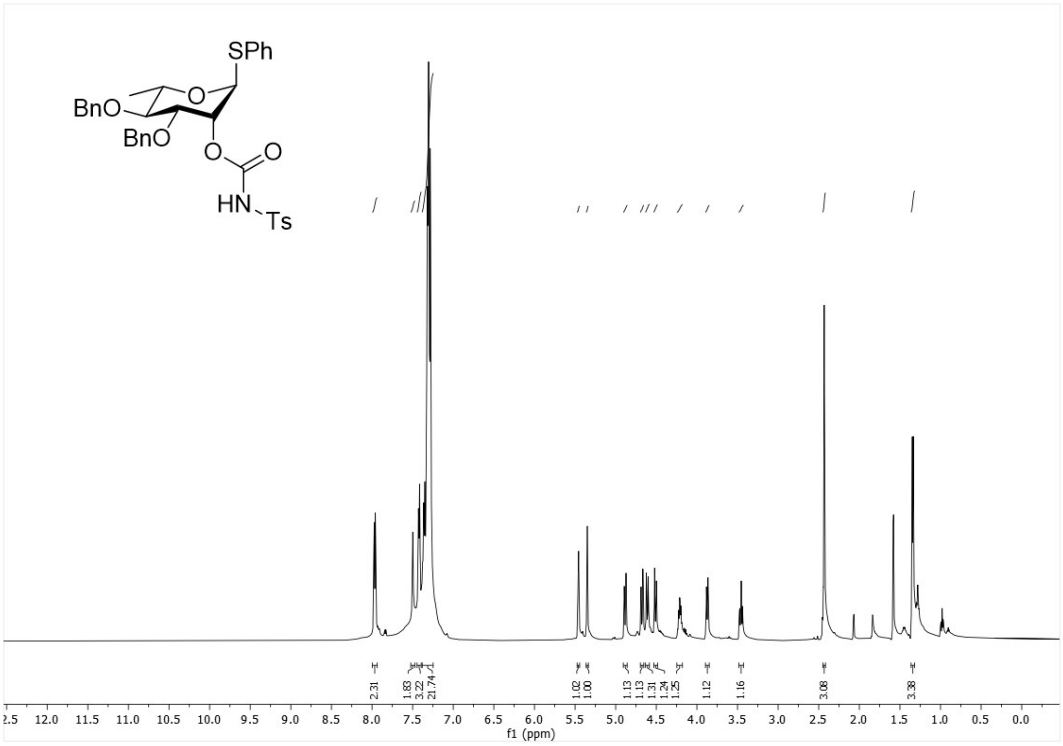

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)

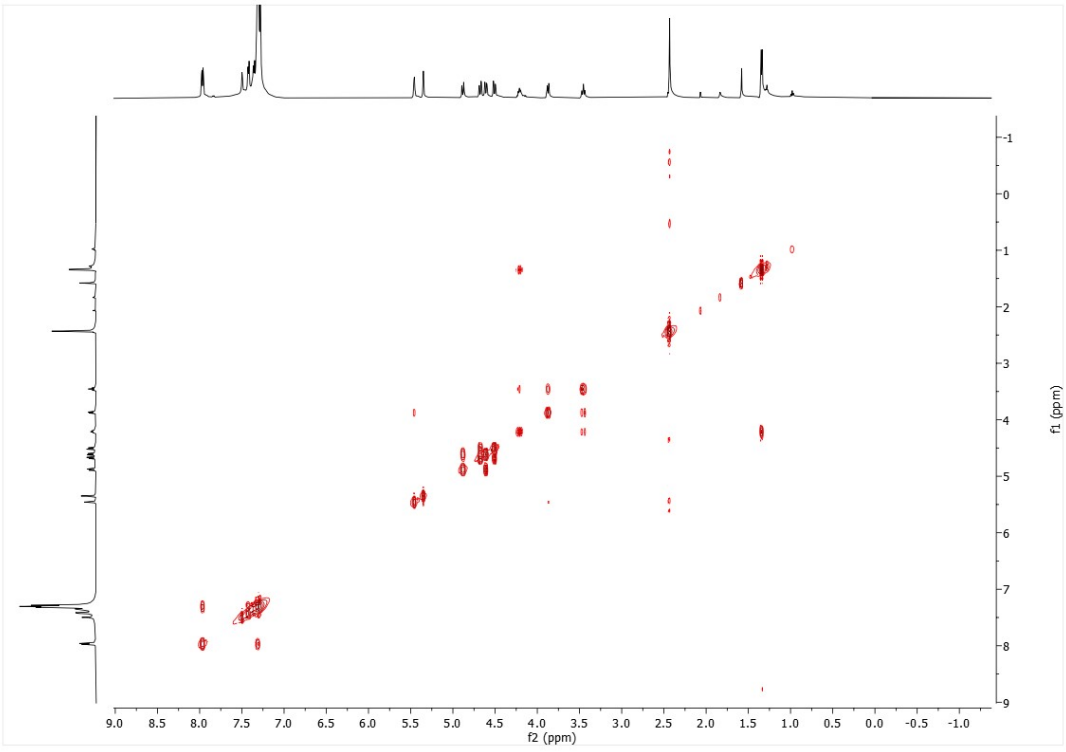
Phenyl 3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (7) ($CDCl_3$)

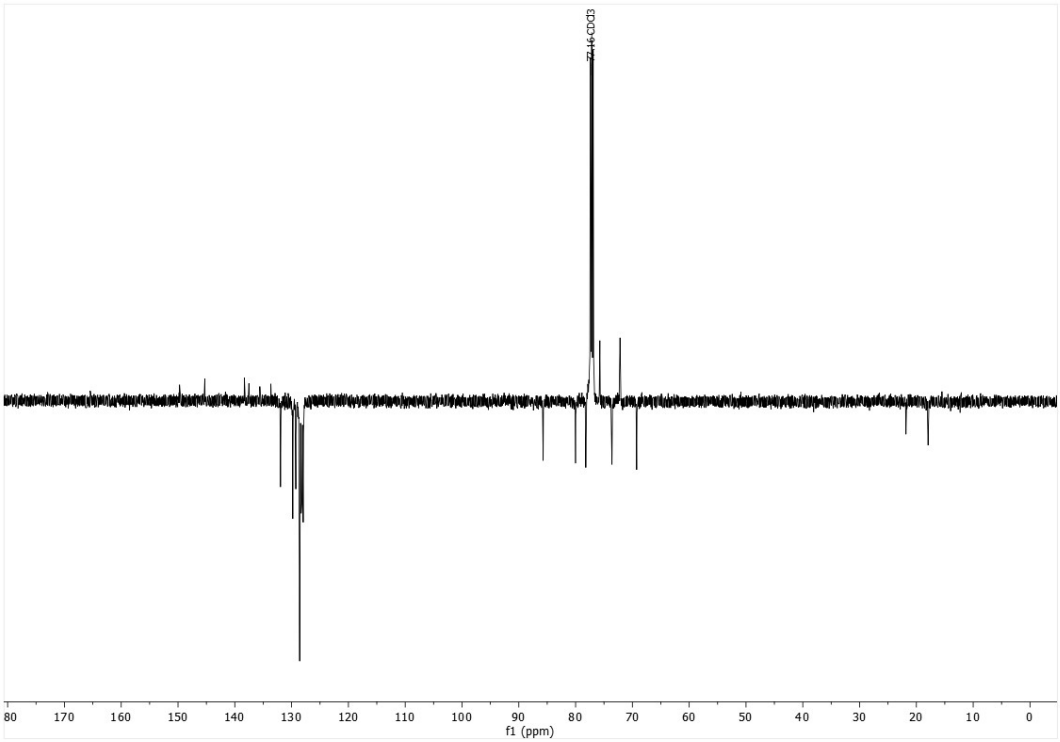


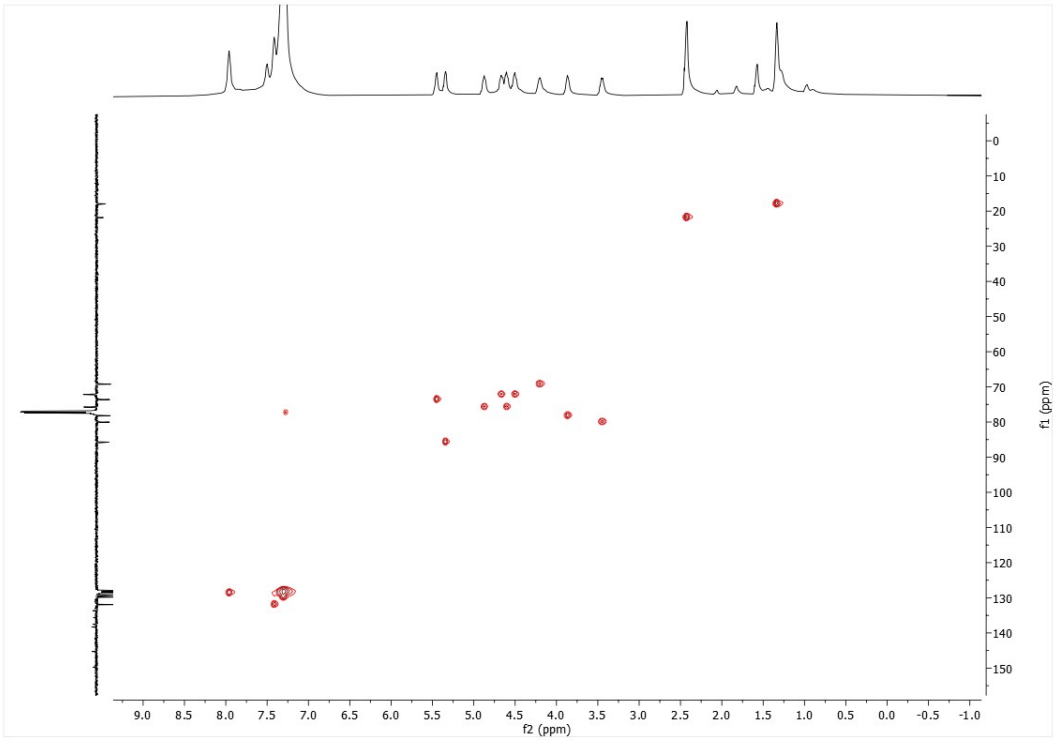


Phenyl 3,4-di-*O*-benzyl-2-*O*-tosylcarbamate-1-thio-α-L-rhamnopyranoside (8) ($CDCl_3$)

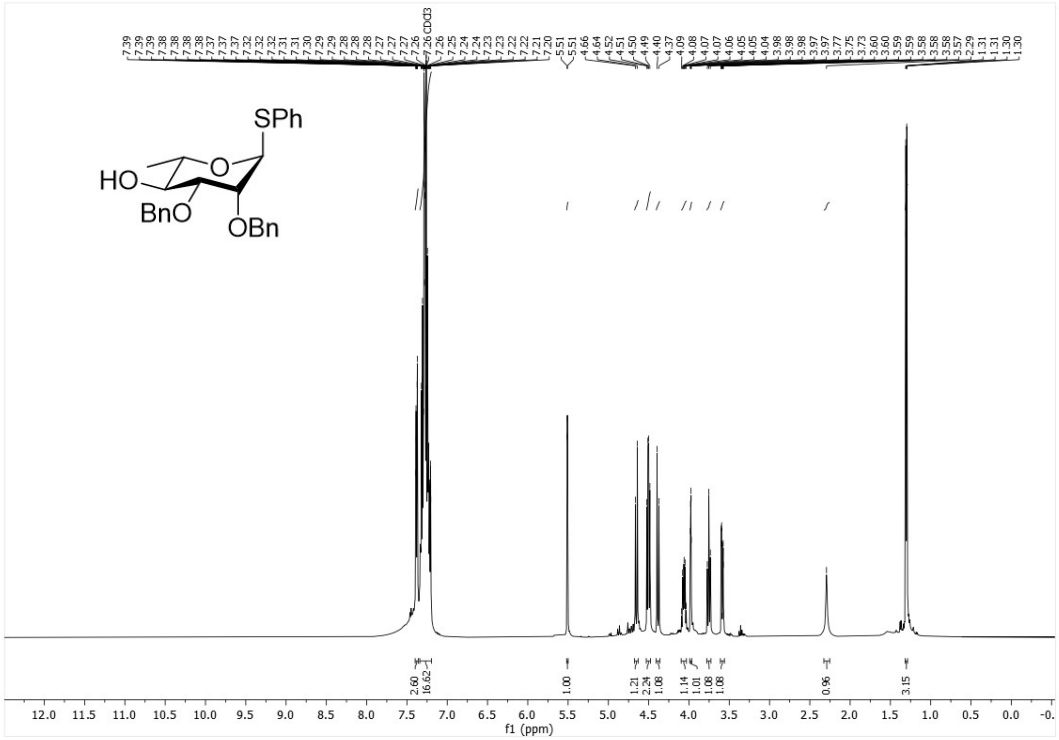


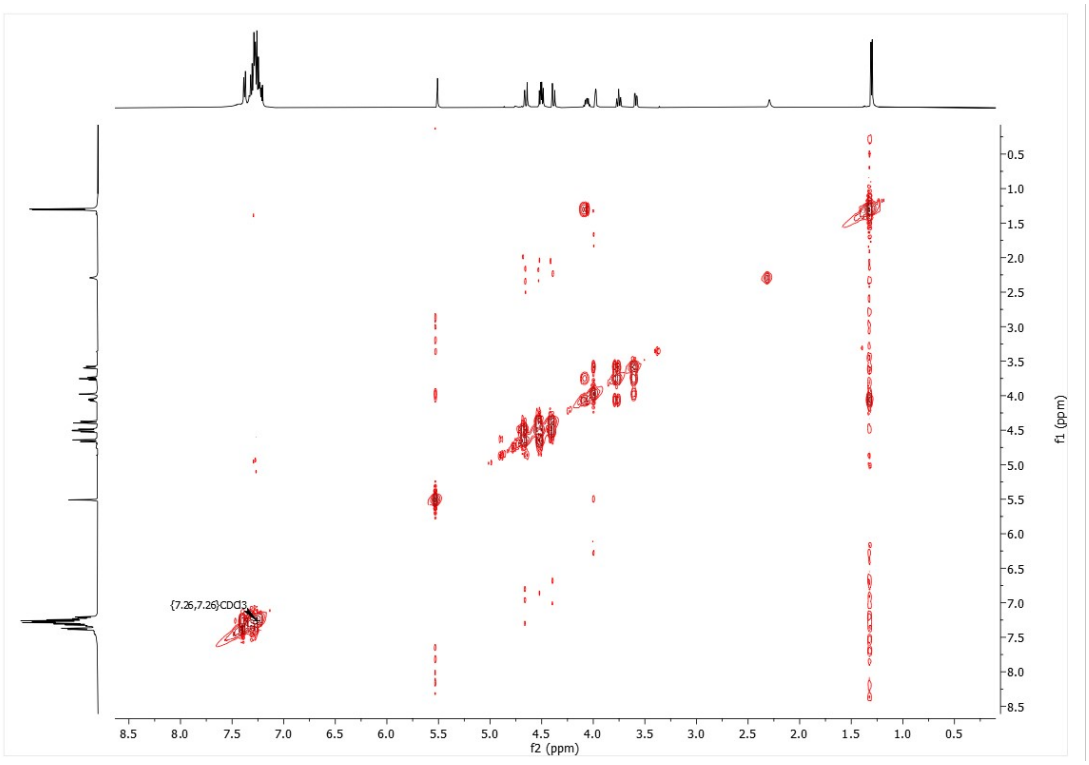



ZZ-16-CDCl3
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

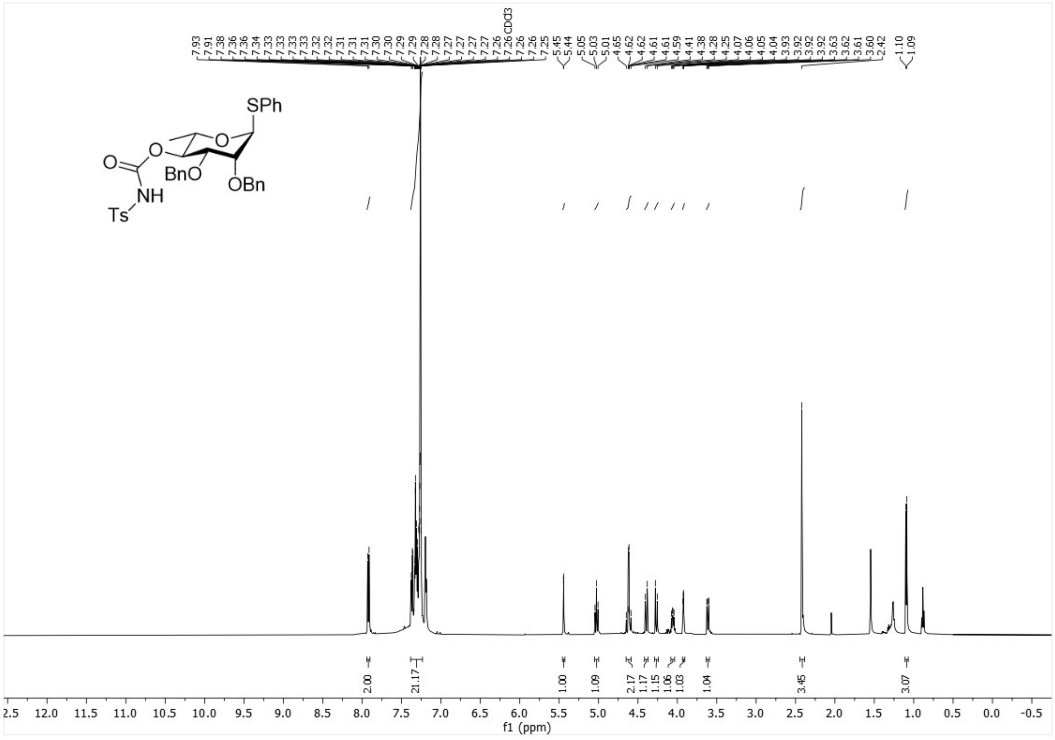

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)

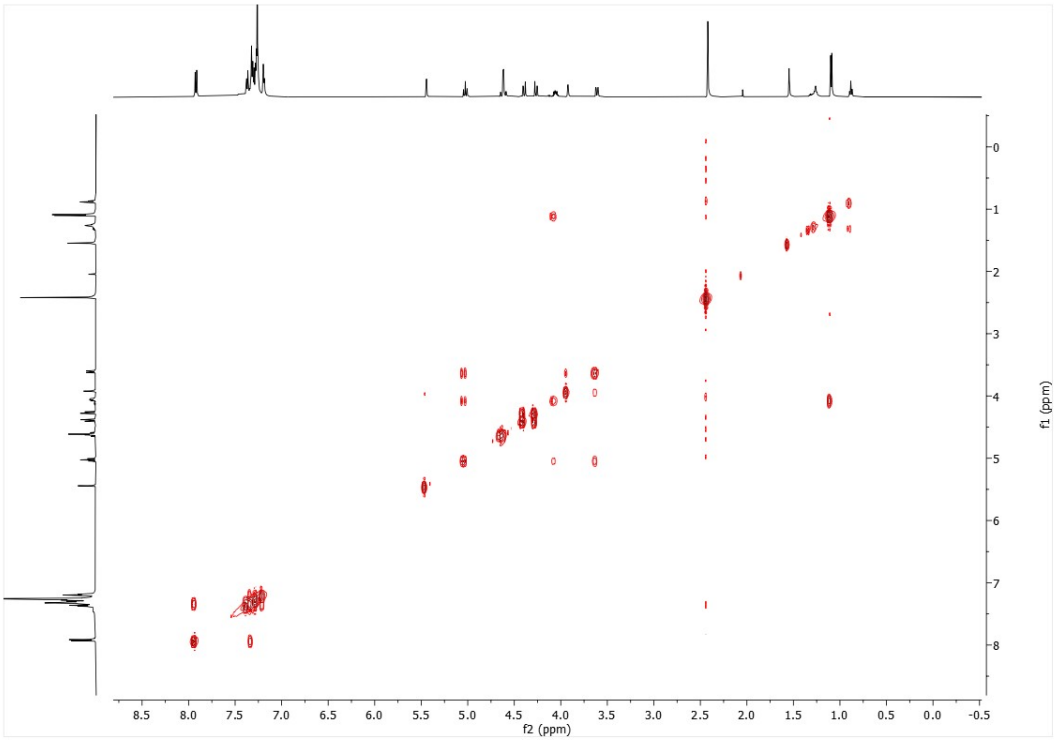
Phenyl 2,3-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (9) ($CDCl_3$)

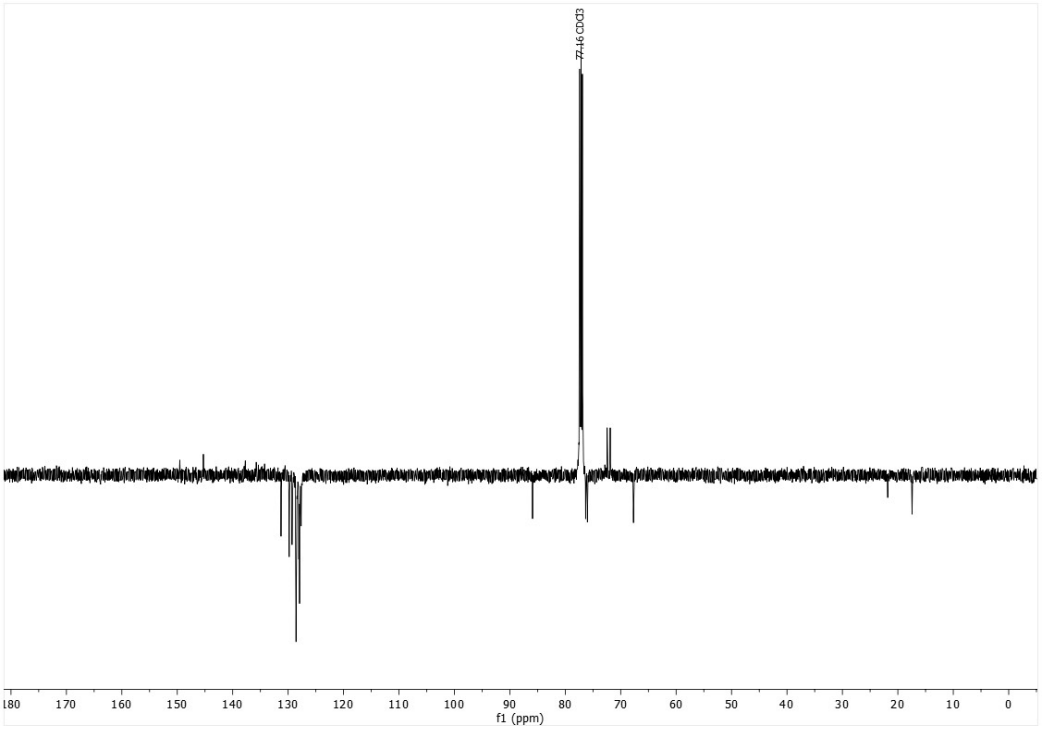


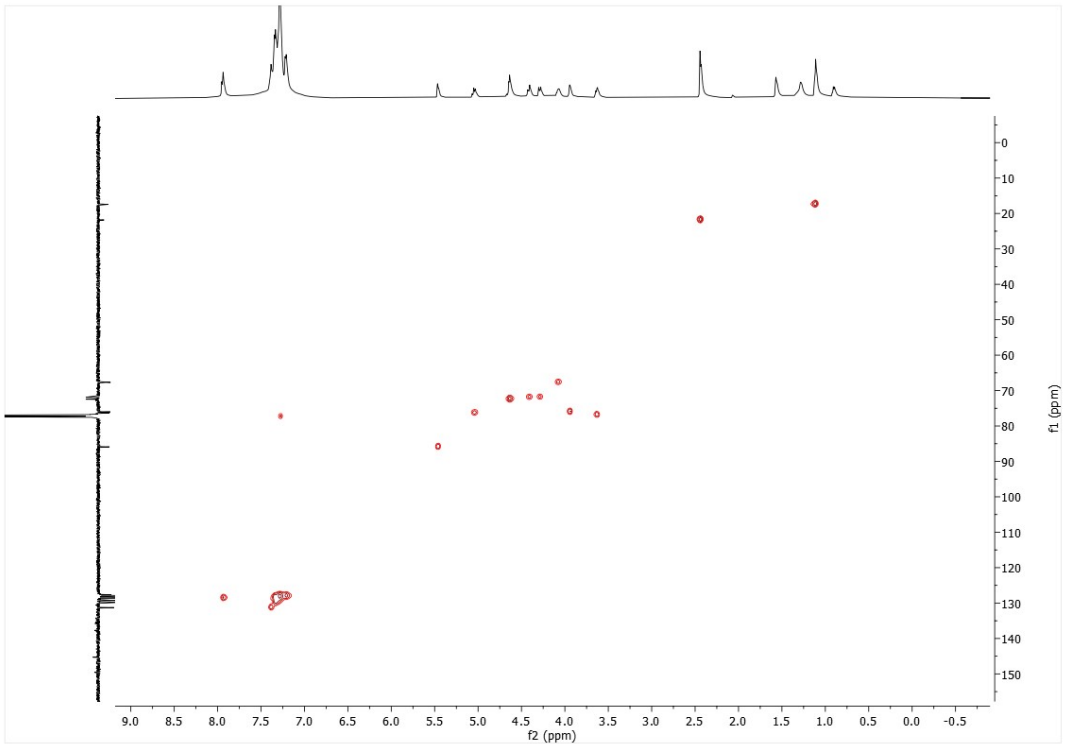


Phenyl 2,3-di-*O*-benzyl-4-*O*-tosylcarbamate-1-thio-α-L-rhamnopyranoside (10) ($CDCl_3$)

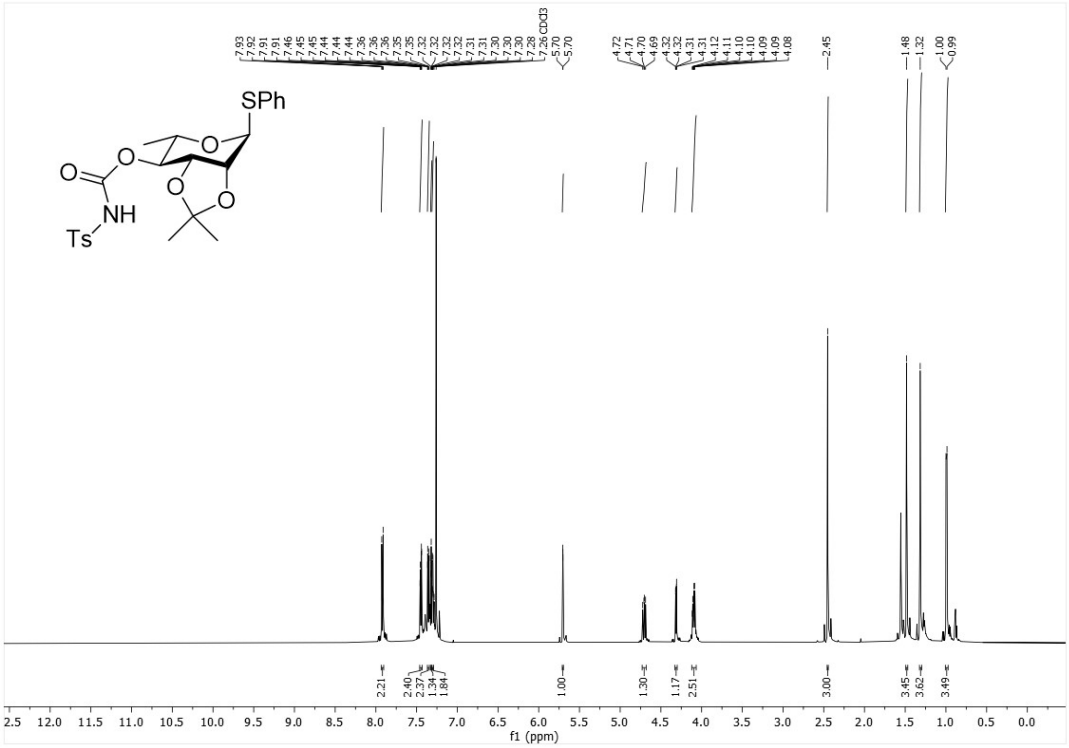


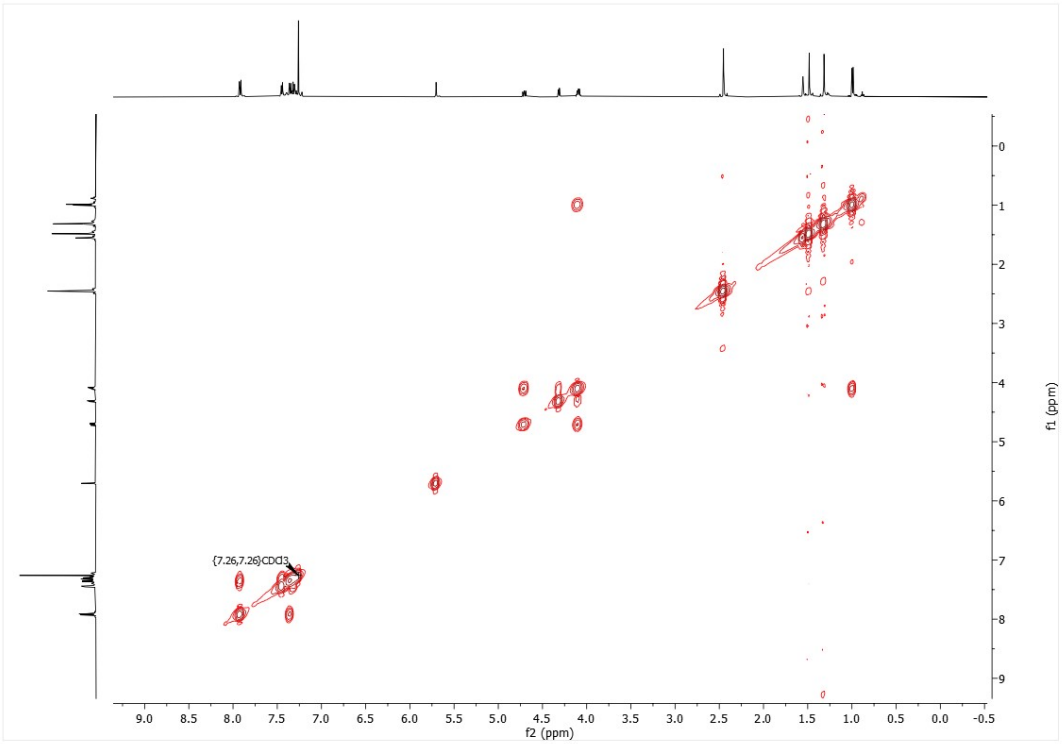


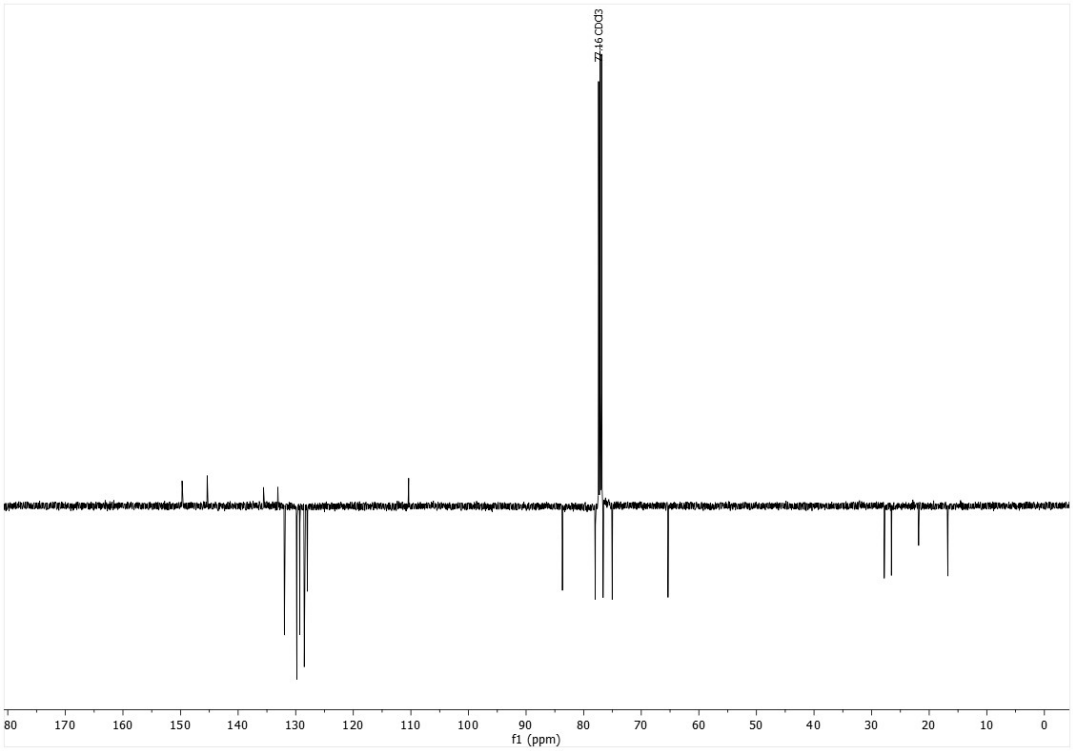

77.16 CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

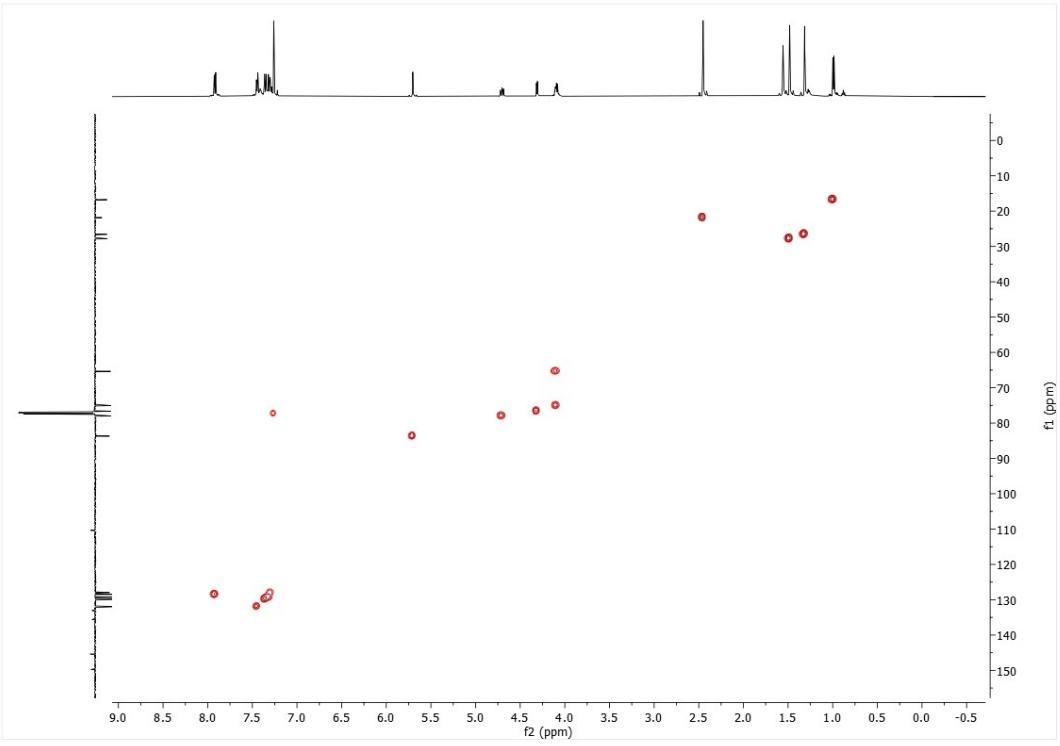

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)

Phenyl 2,3-*O*-isopropylidene-4-*O*-tosylcarbamate-1-thio-α-L-rhamnopyranoside (11) ($CDCl_3$)

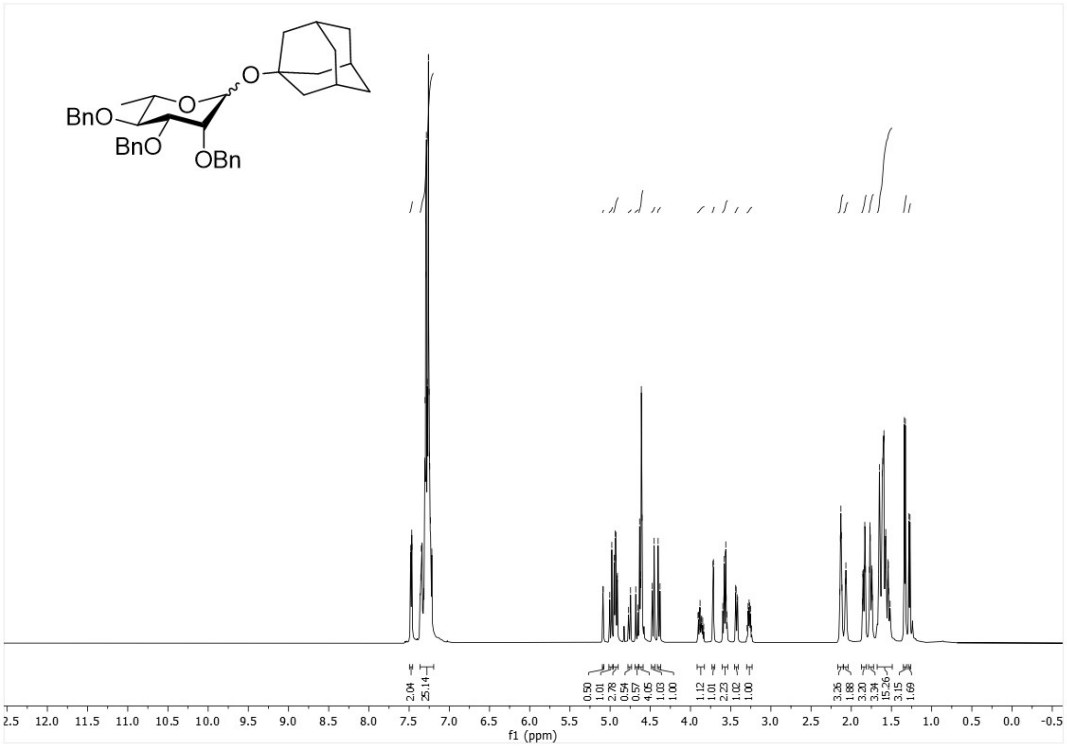


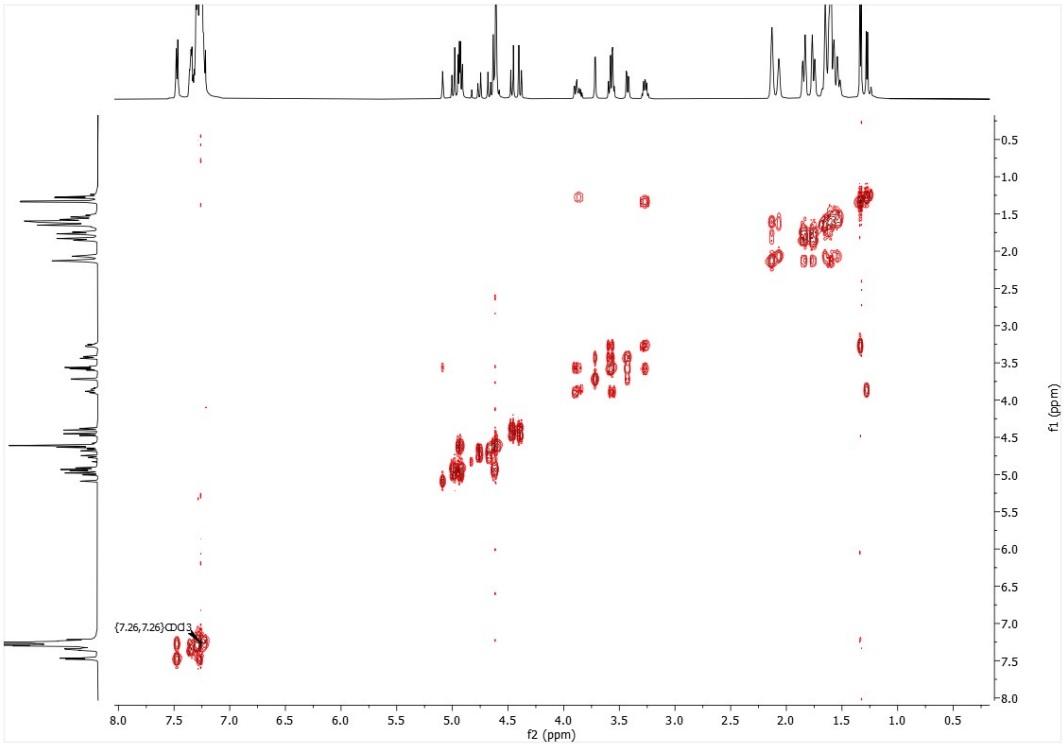


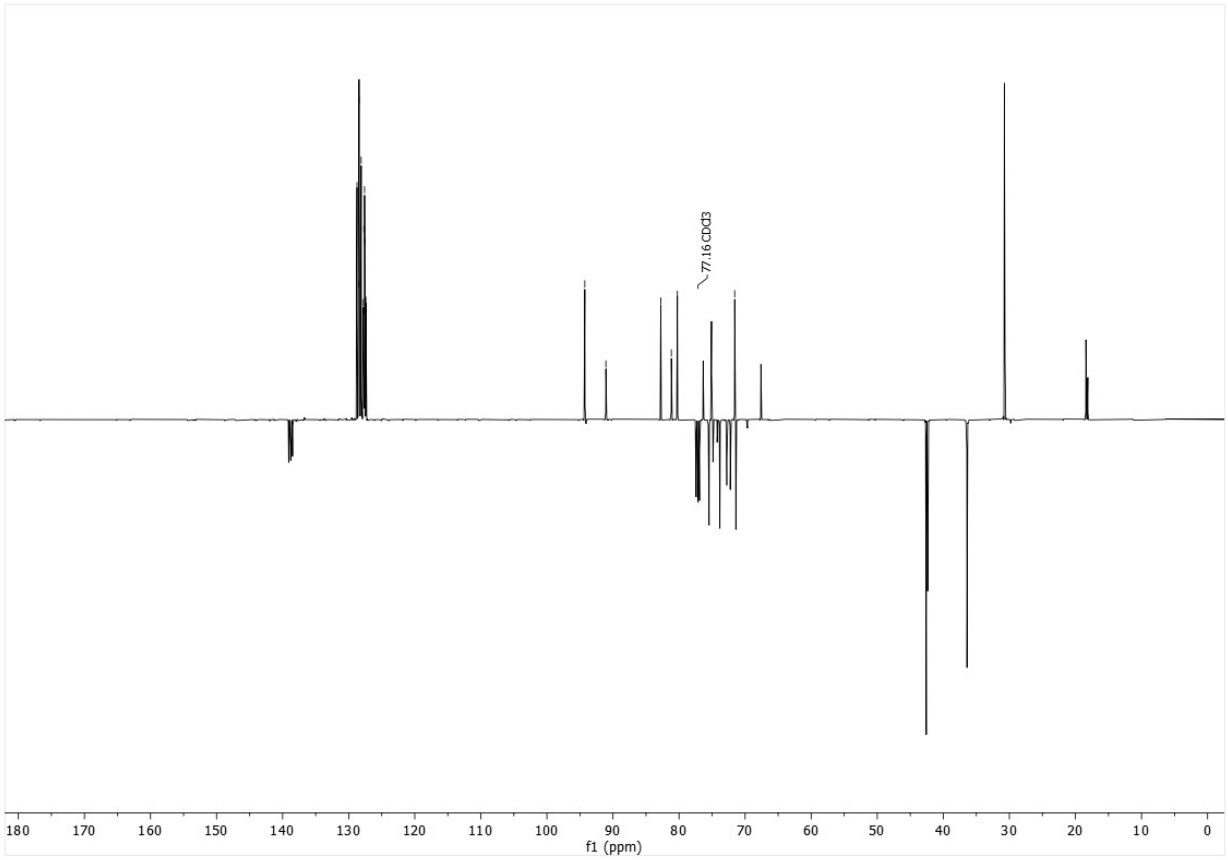

77.16 CDCl3
f1 (ppm)

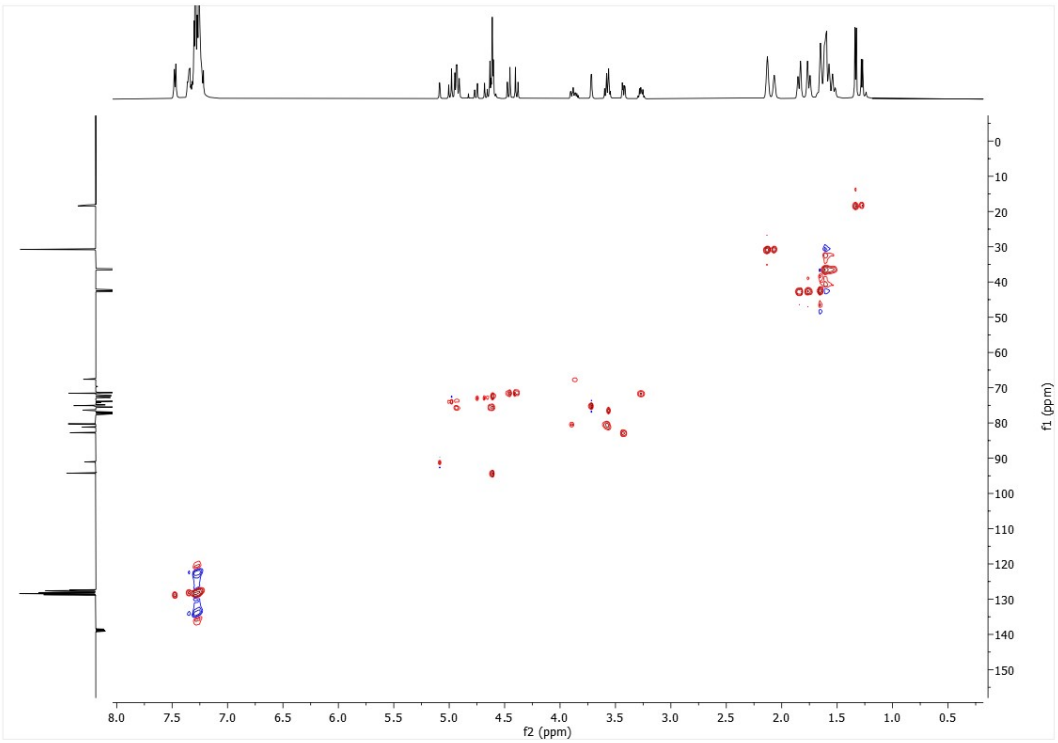

f1 (ppm)
f2 (ppm)

1-Adamantyl 2,3,4-tri-*O*-benzyl-1-α/β-L-rhamnopyranoside (SI4) ($CDCl_3$)

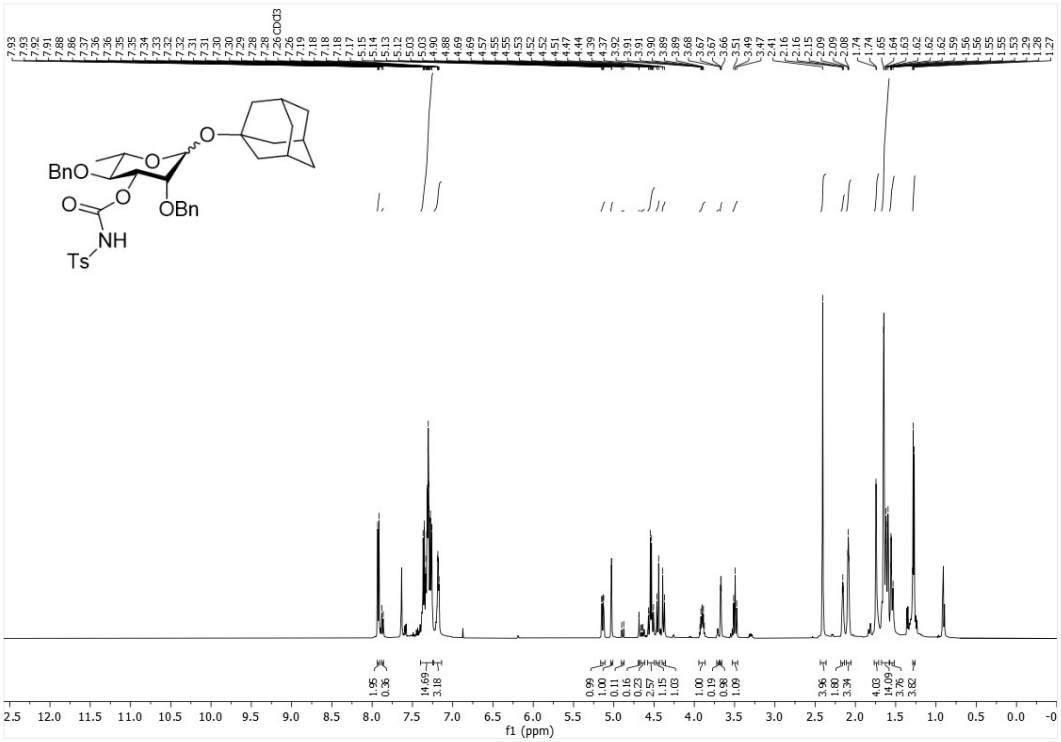


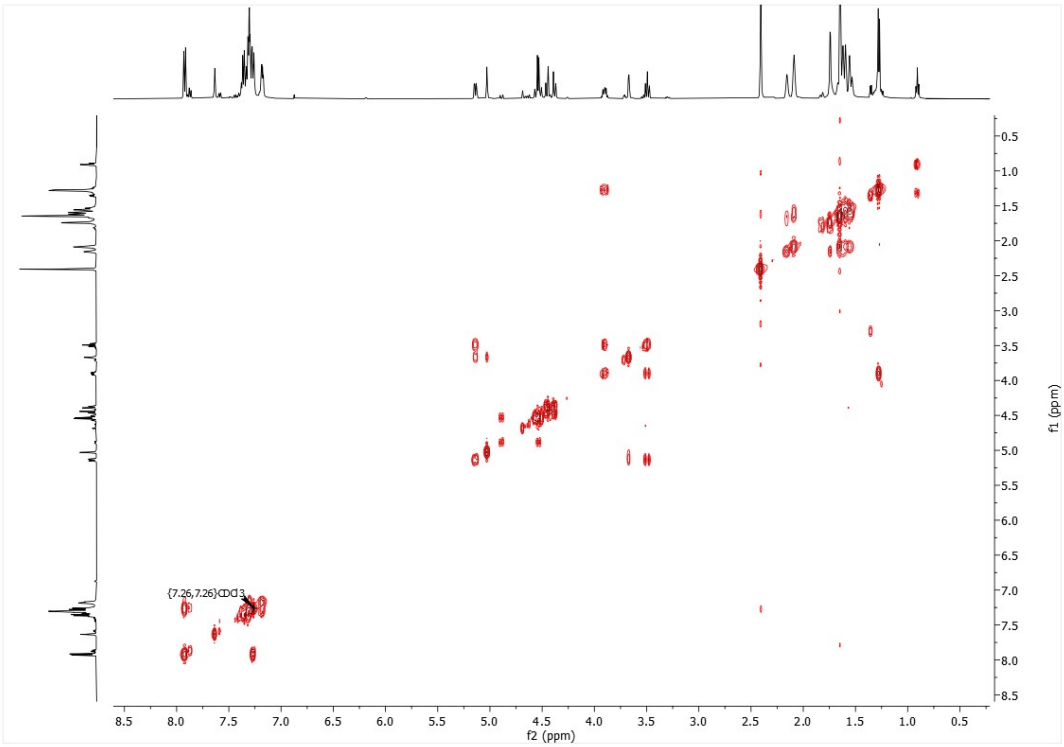


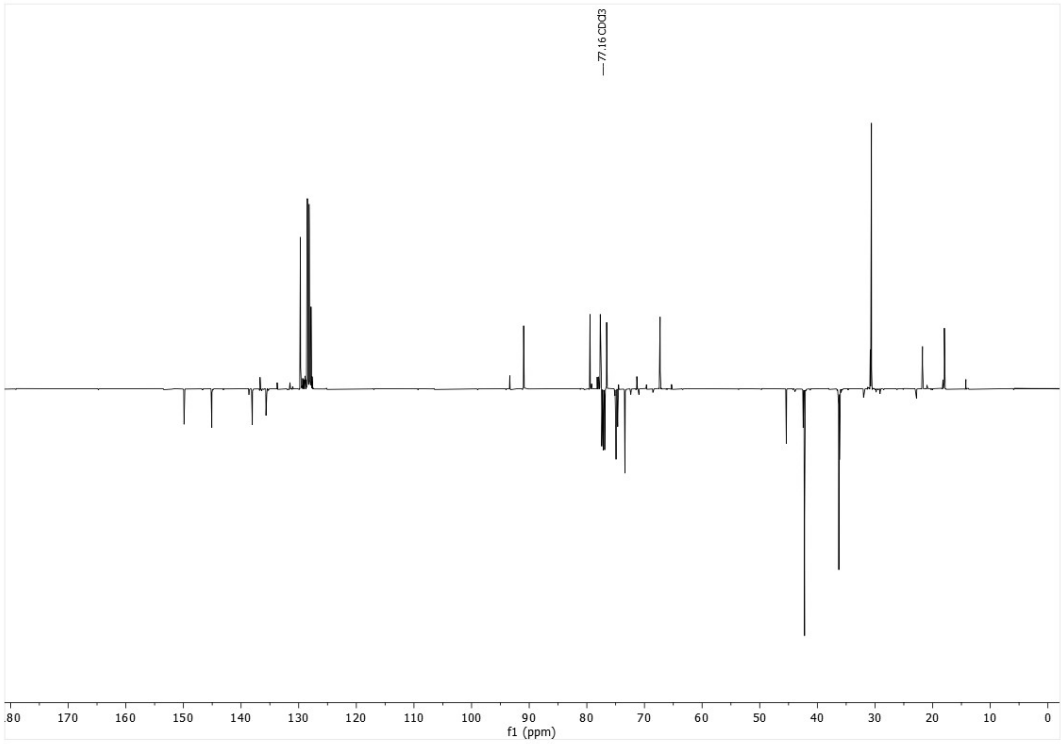

77.16 CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

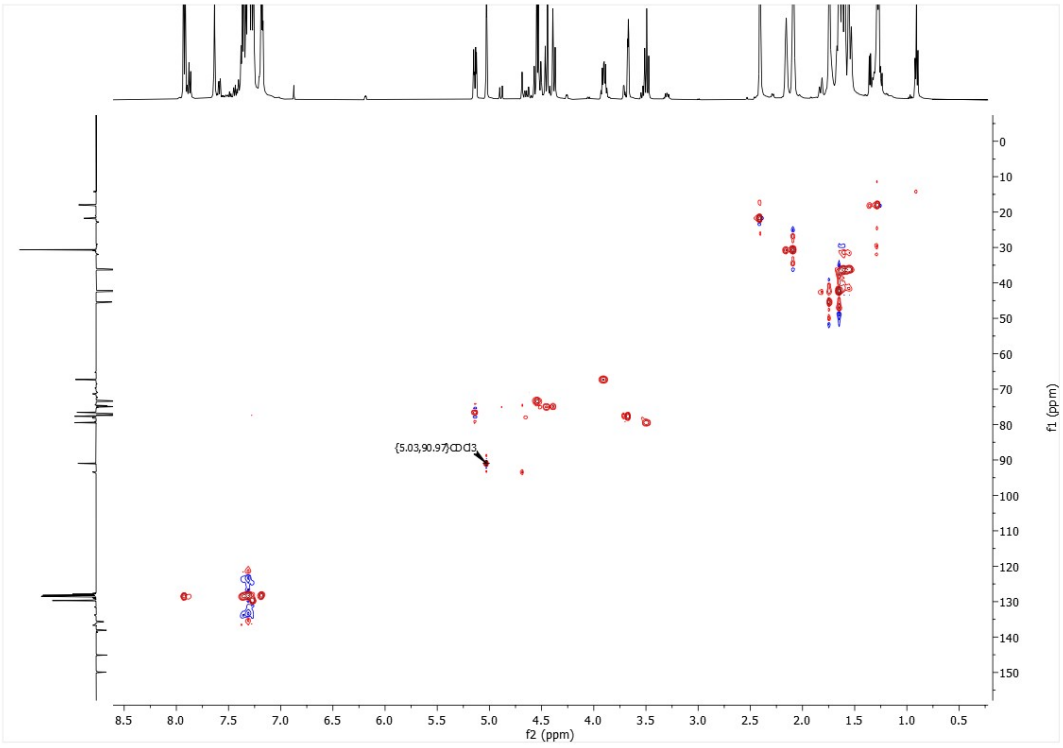

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)

1-Adamantyl 2,4-di-*O*-benzyl-2-*O*-tosylcarbamate-α/β-L-rhamnopyranoside (SI5) ($CDCl_3$)

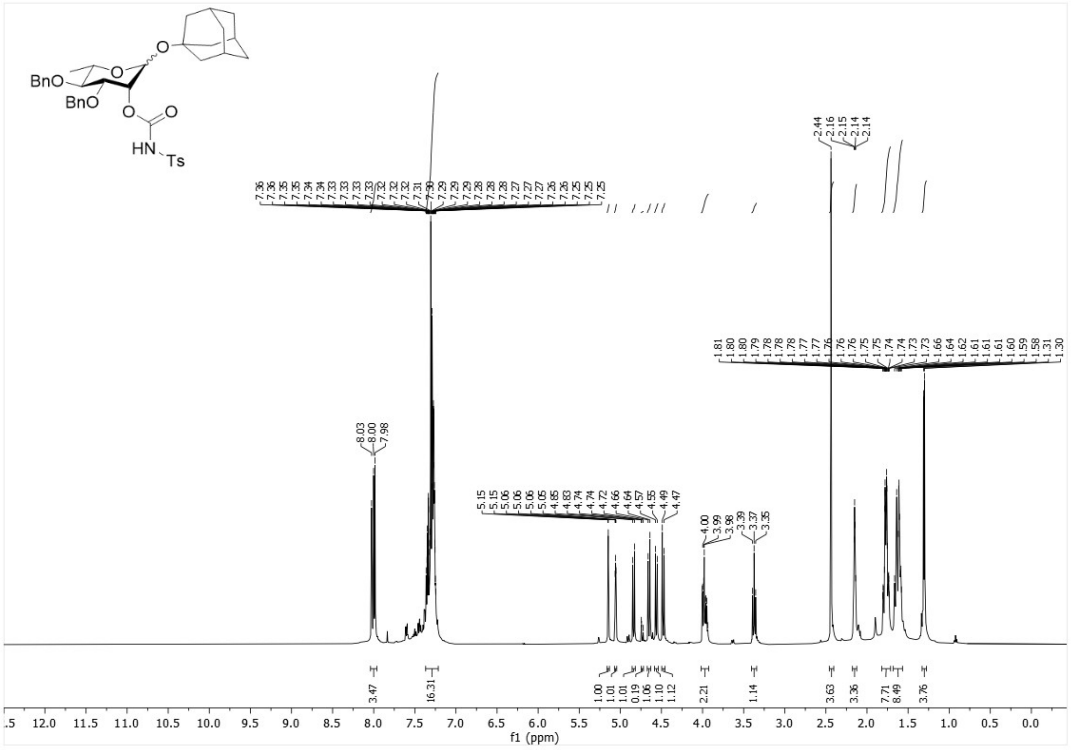


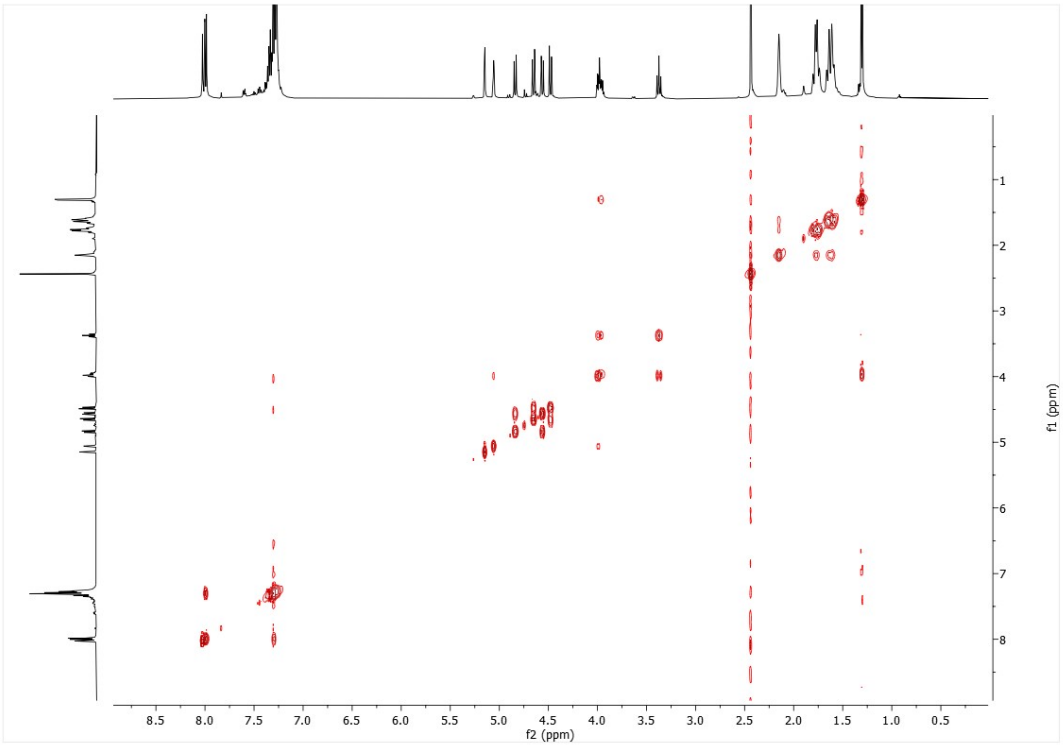


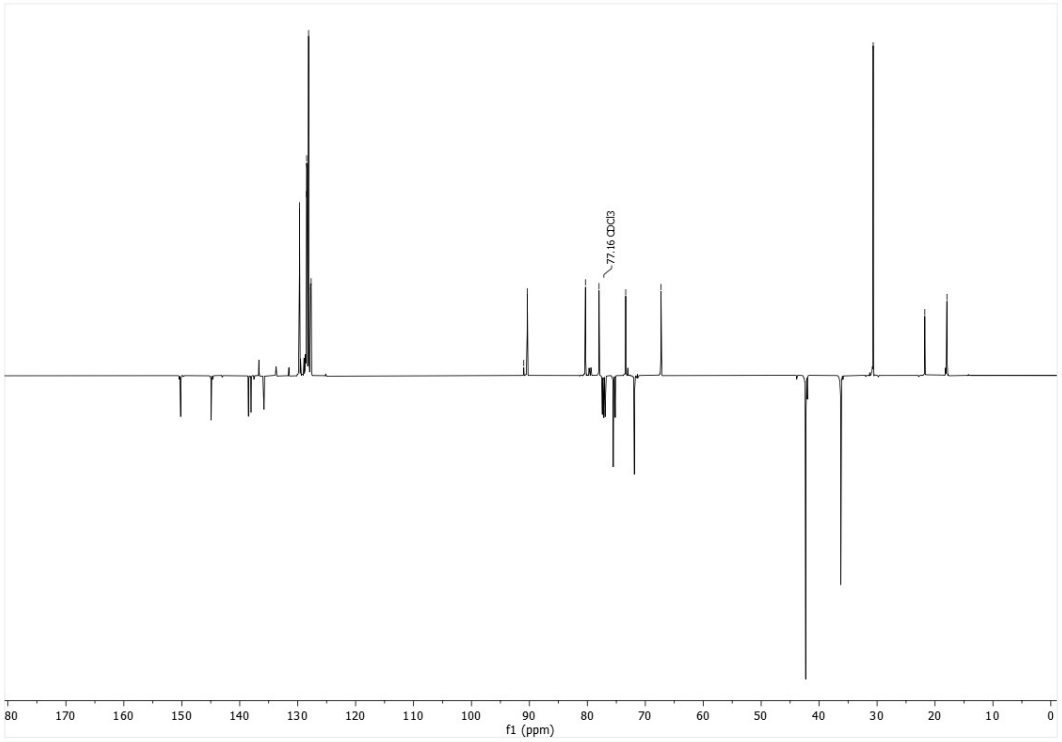

77.16 CDCl3
f1 (ppm)

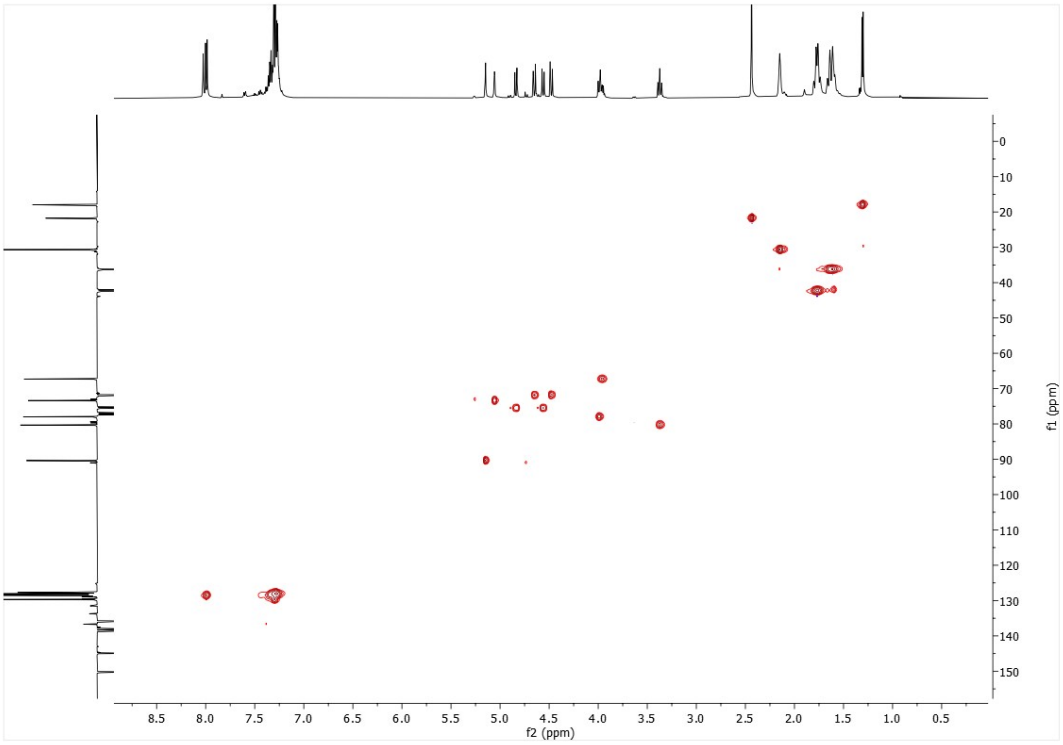

{5.03,90.97}CDCl3
f2 (ppm)
f1 (ppm)

1-Adamantyl 3,4-di-*O*-benzyl-2-*O*-tosylcarbamate-α/β-L-rhamnopyranoside (SI6) ($CDCl_3$)

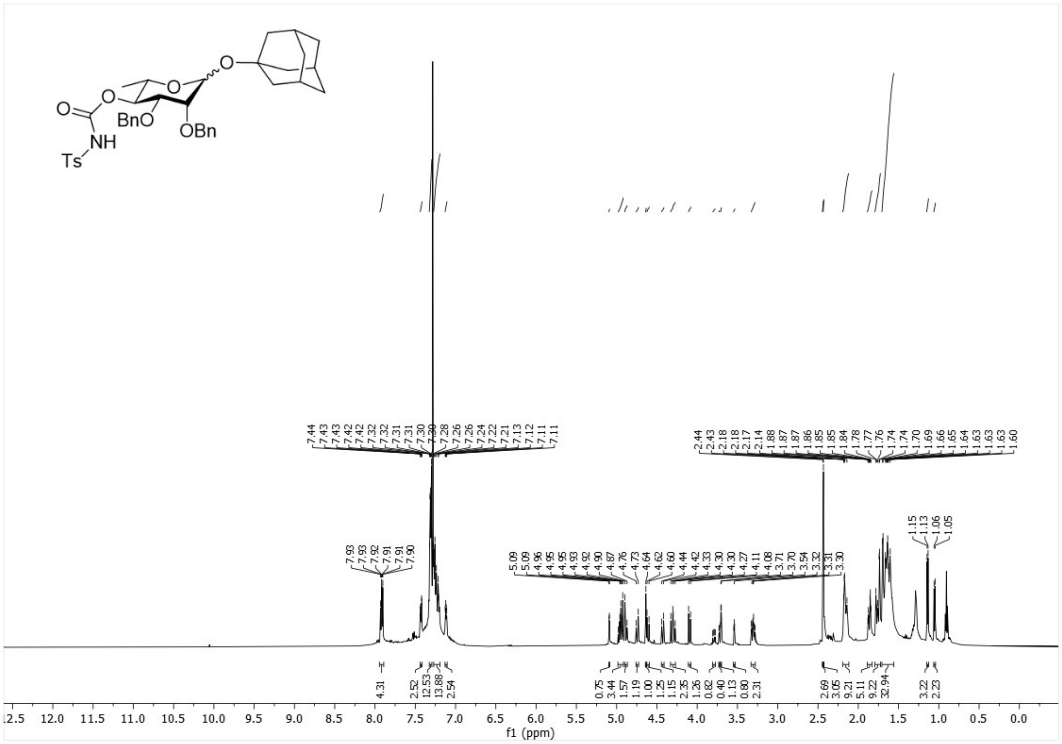


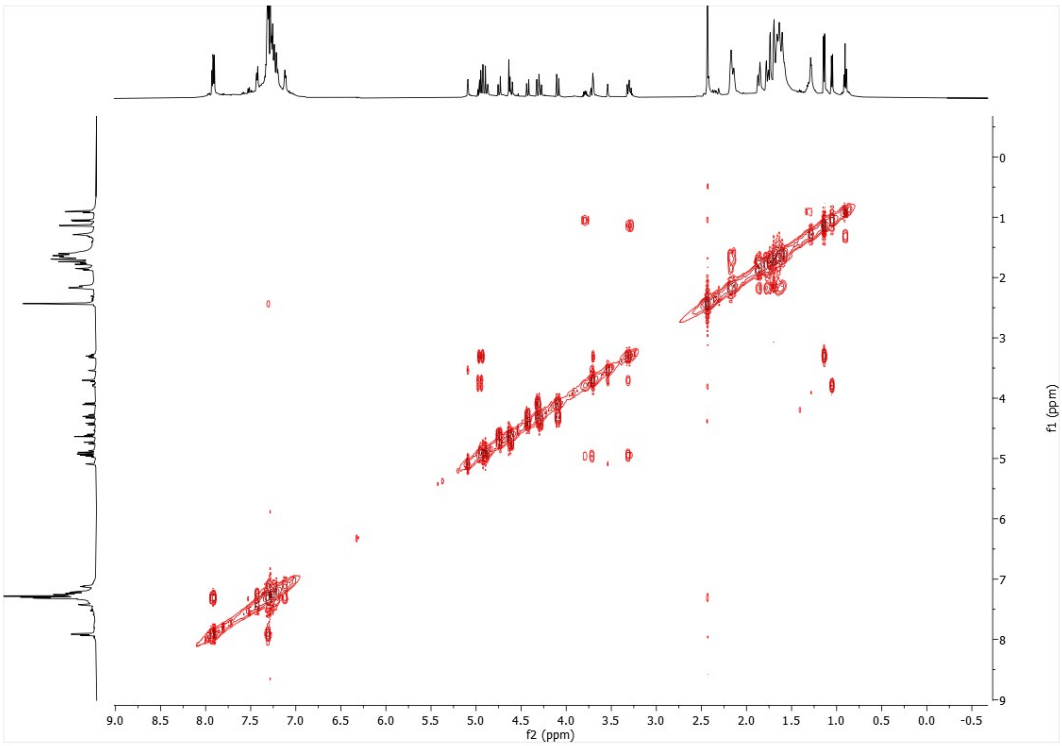


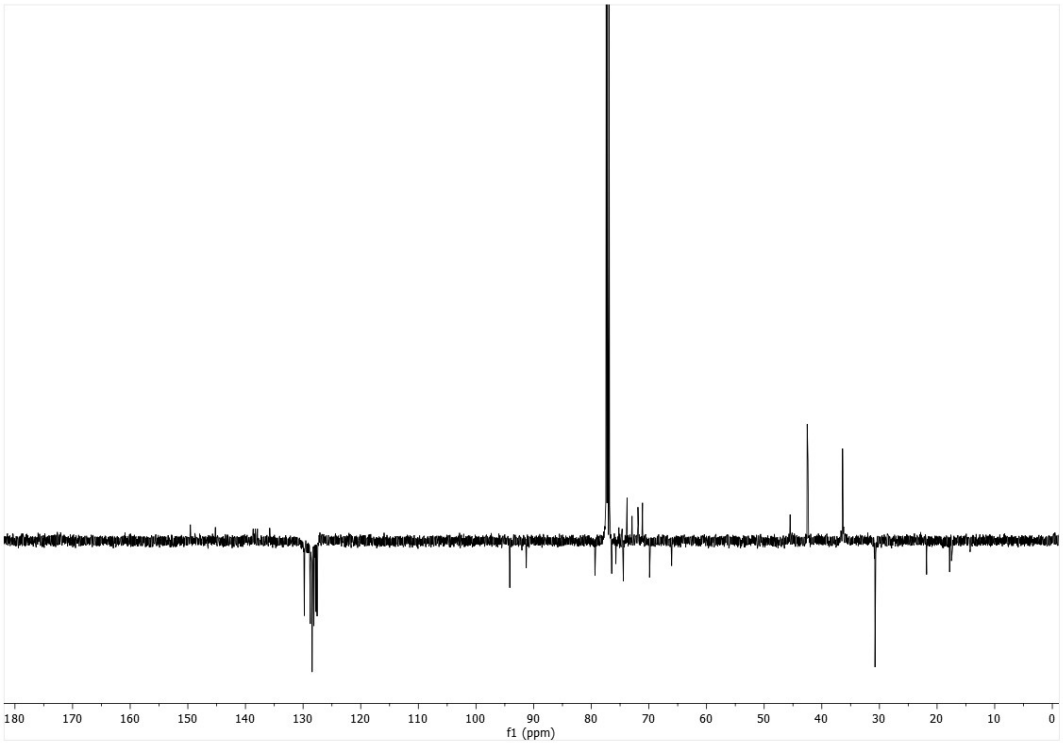

77.16 CDCl3
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

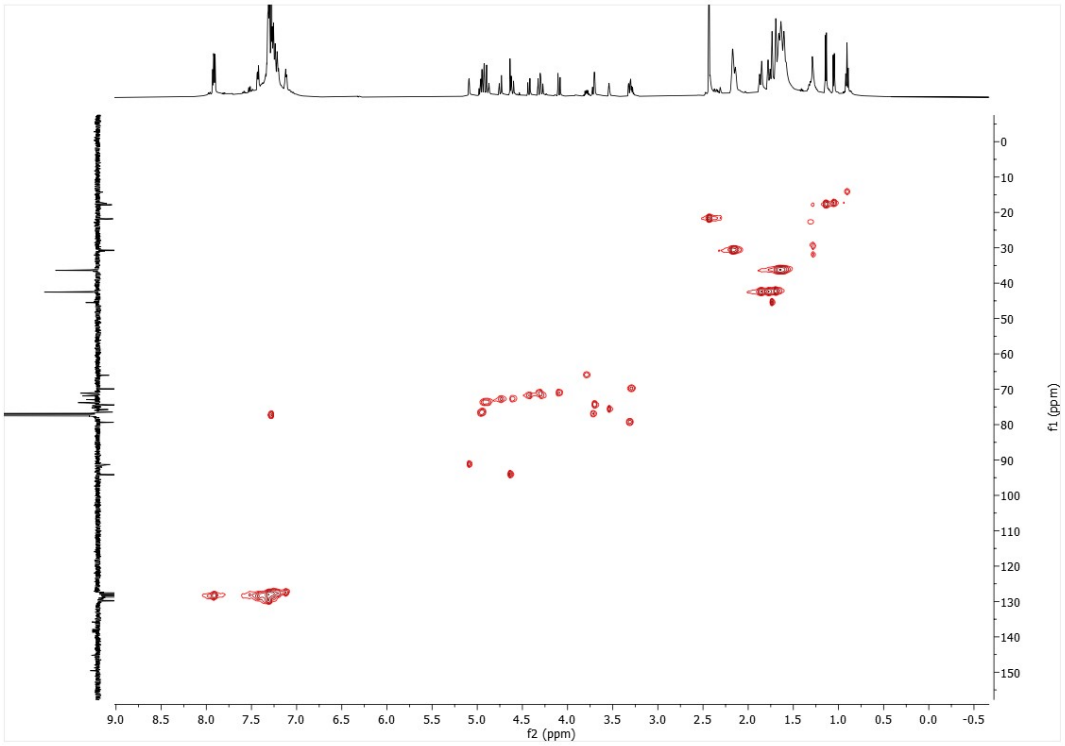

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)

1-Adamantyl 2,3-di-*O*-benzyl-4-*O*-tosylcarbamate-α/β-L-rhamnopyranoside (SI7) ($CDCl_3$)

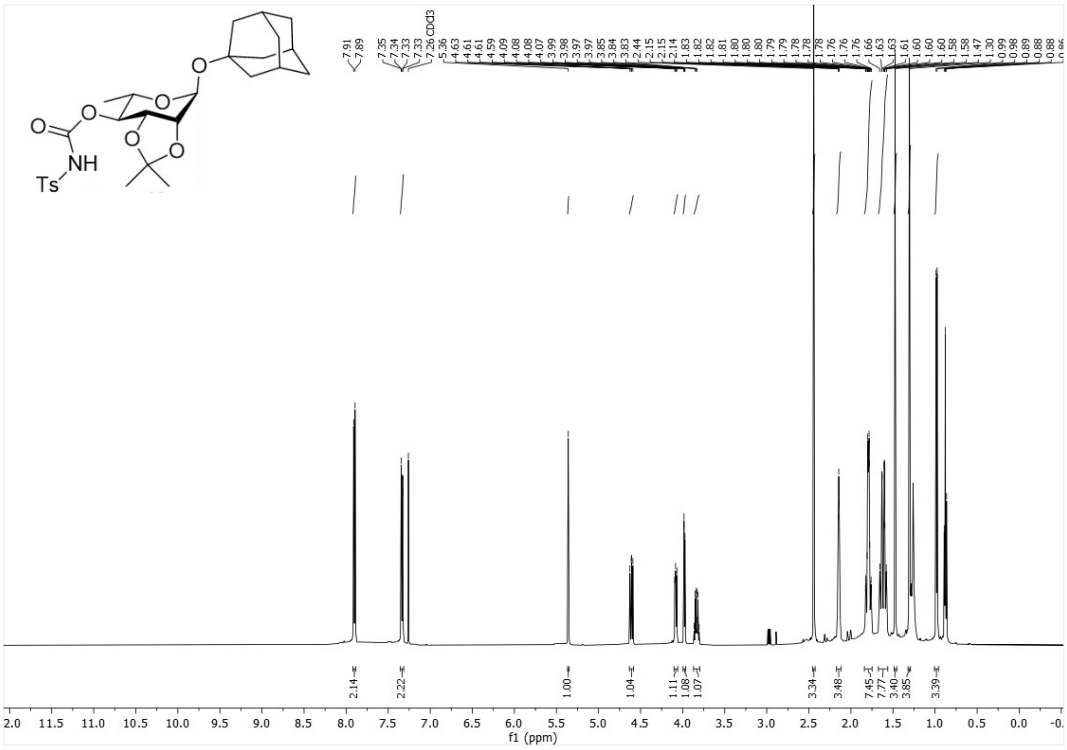


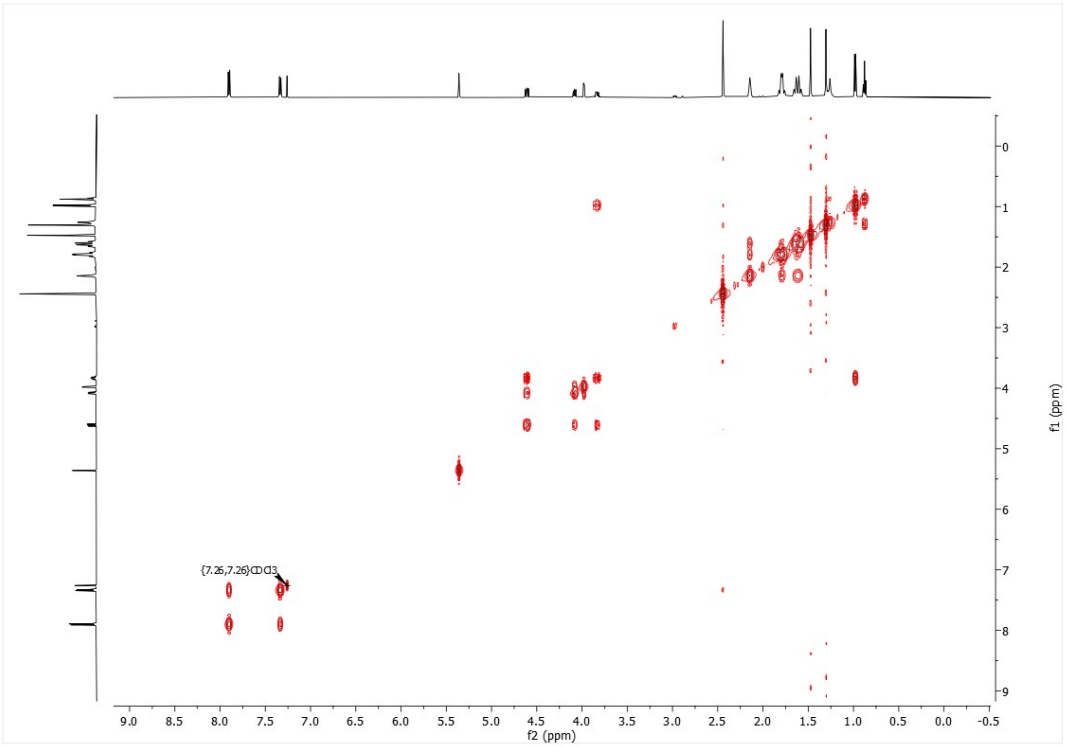


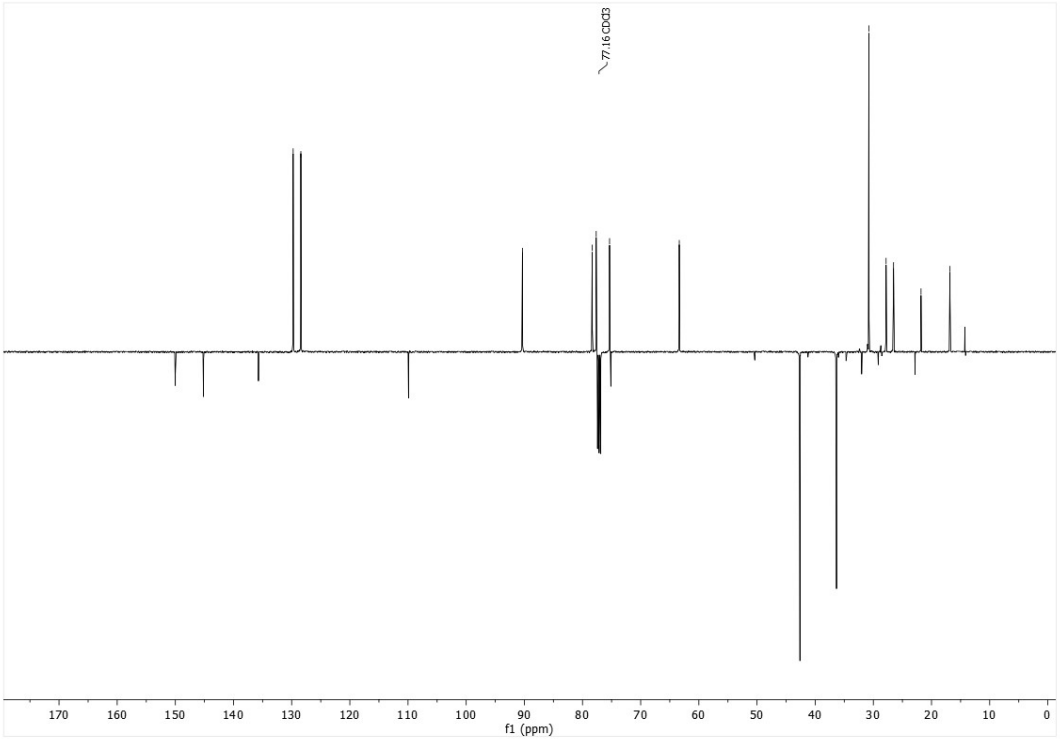

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

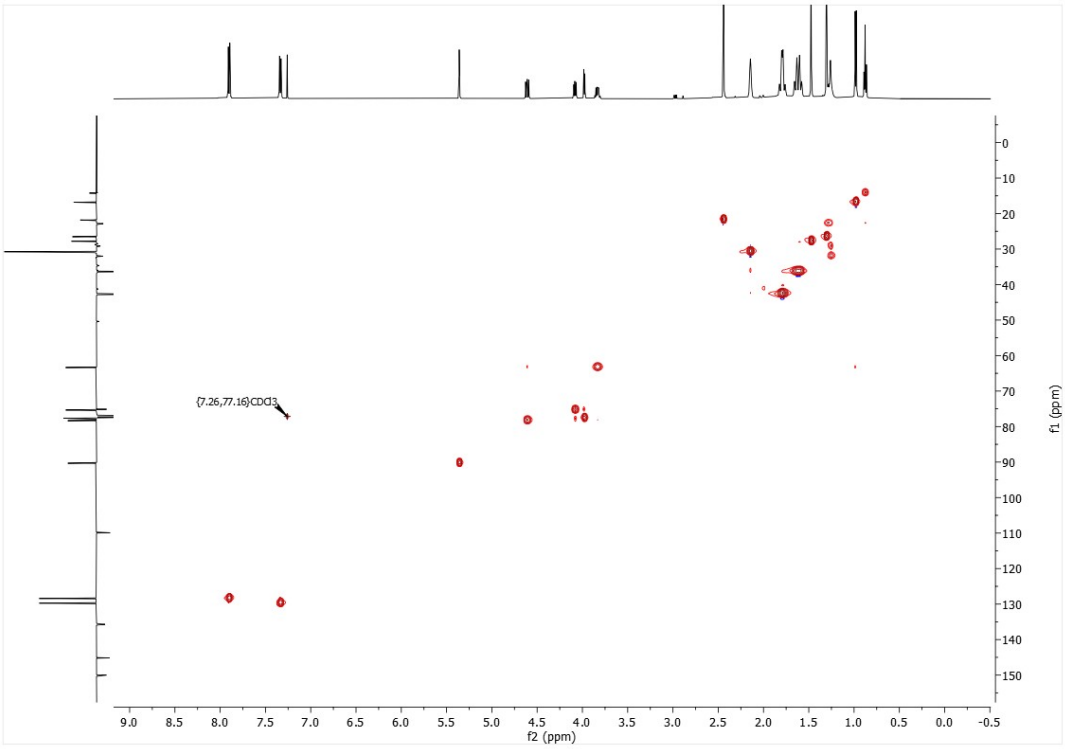

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)

1-Adamantyl 2,3-*O*-isopropylidene-4-*O*-tosylcarbamate-α-L-rhamnopyranoside (SI8-α) ($CDCl_3$)

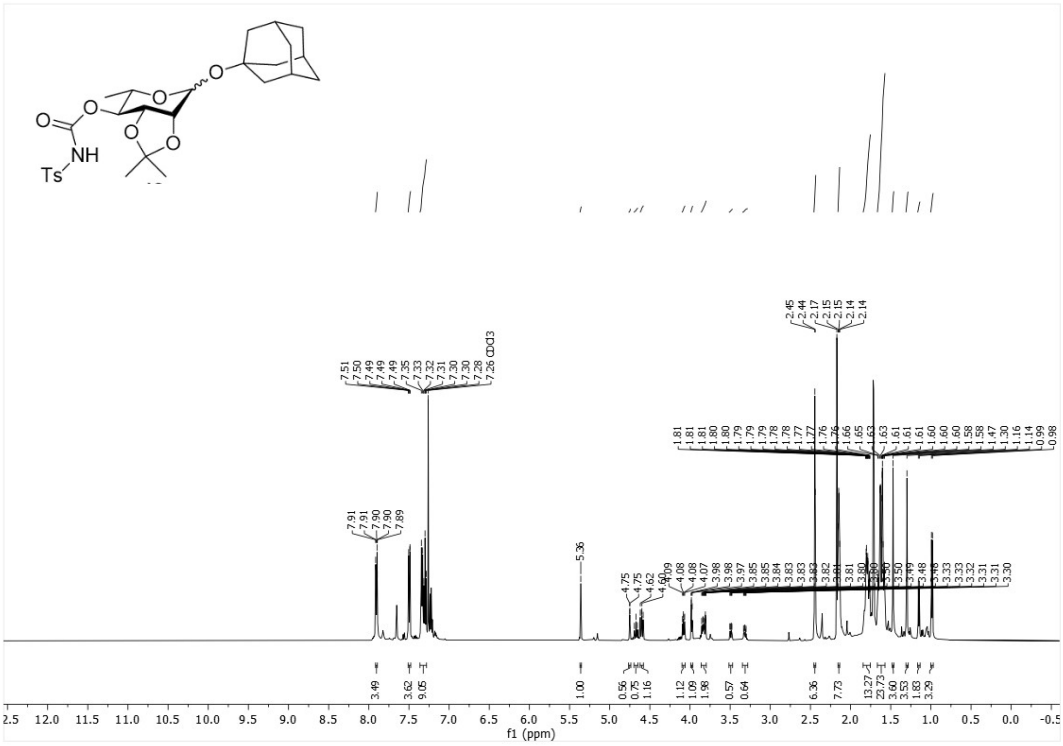


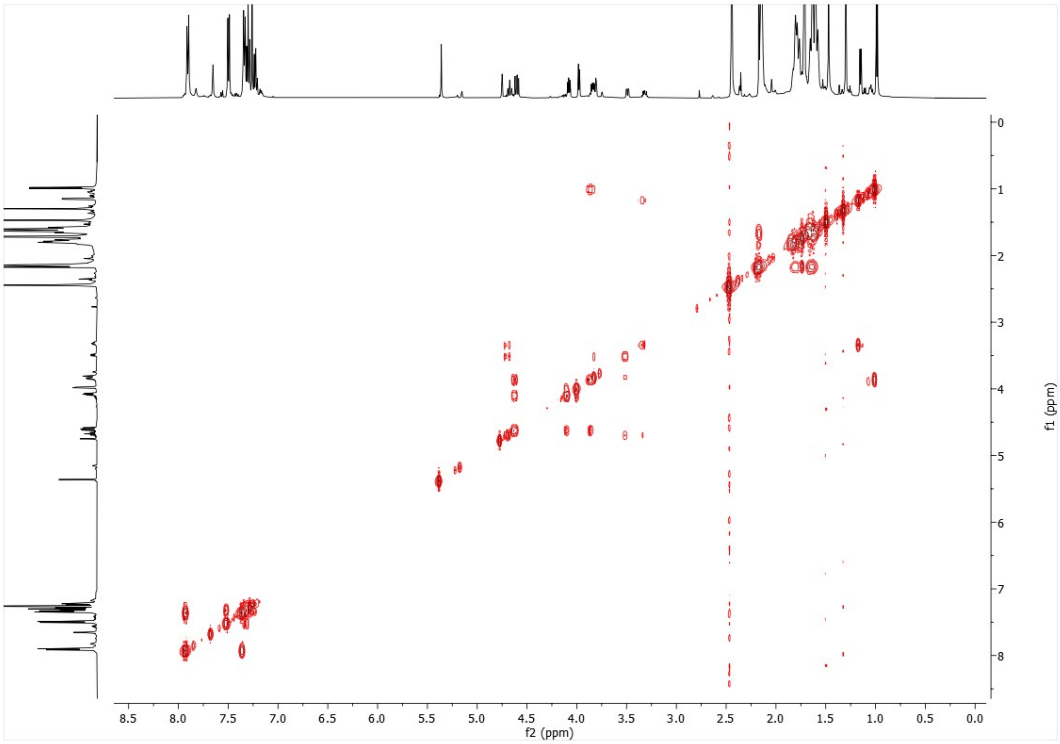


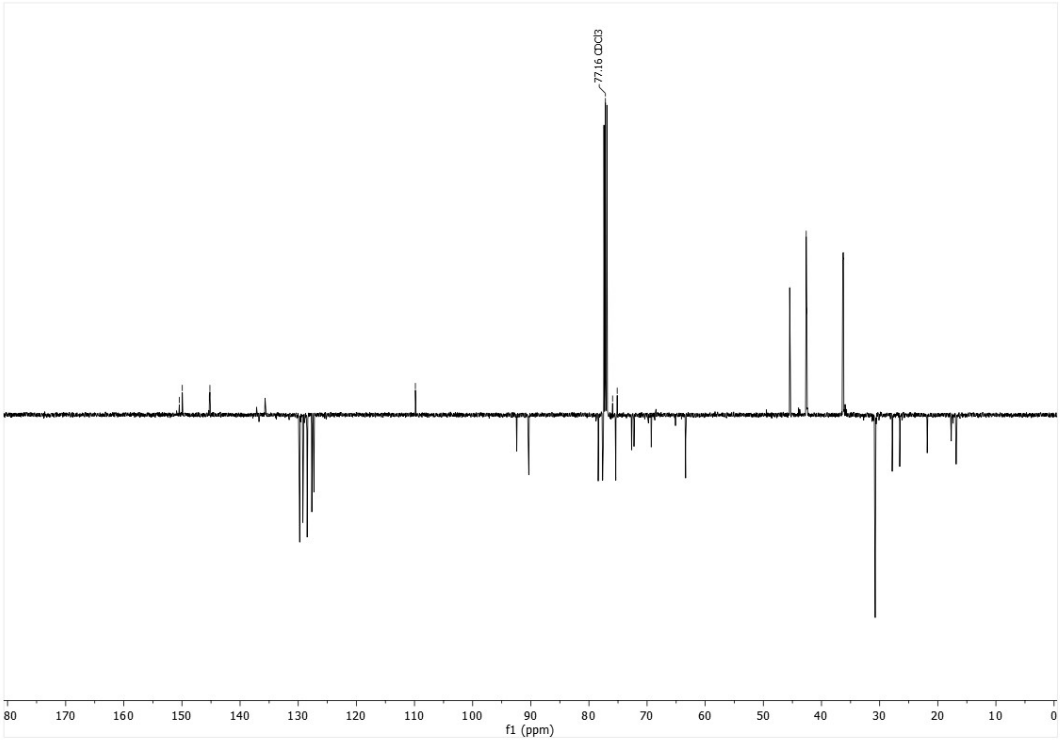

77.16 CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

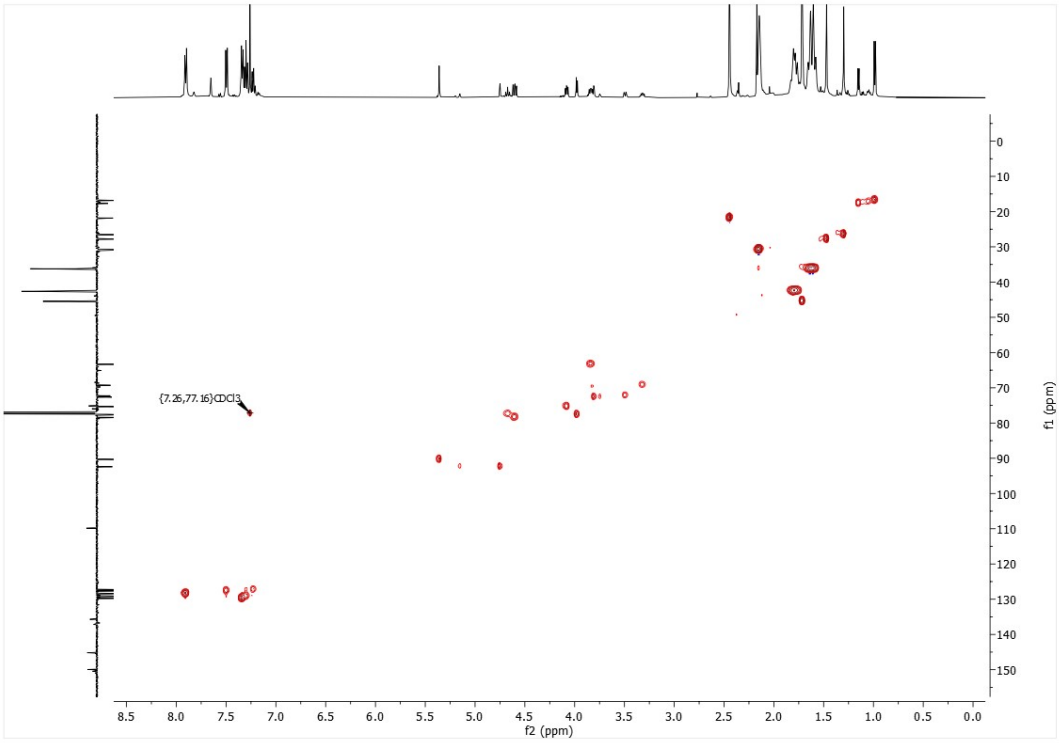

{7.26,77.16}CDCl3
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)

1-Adamantyl 2,3-*O*-isopropylidene-4-*O*-tosylcarbamate-α/β-L-rhamnopyranoside (SI8-α/β) ($CDCl_3$)

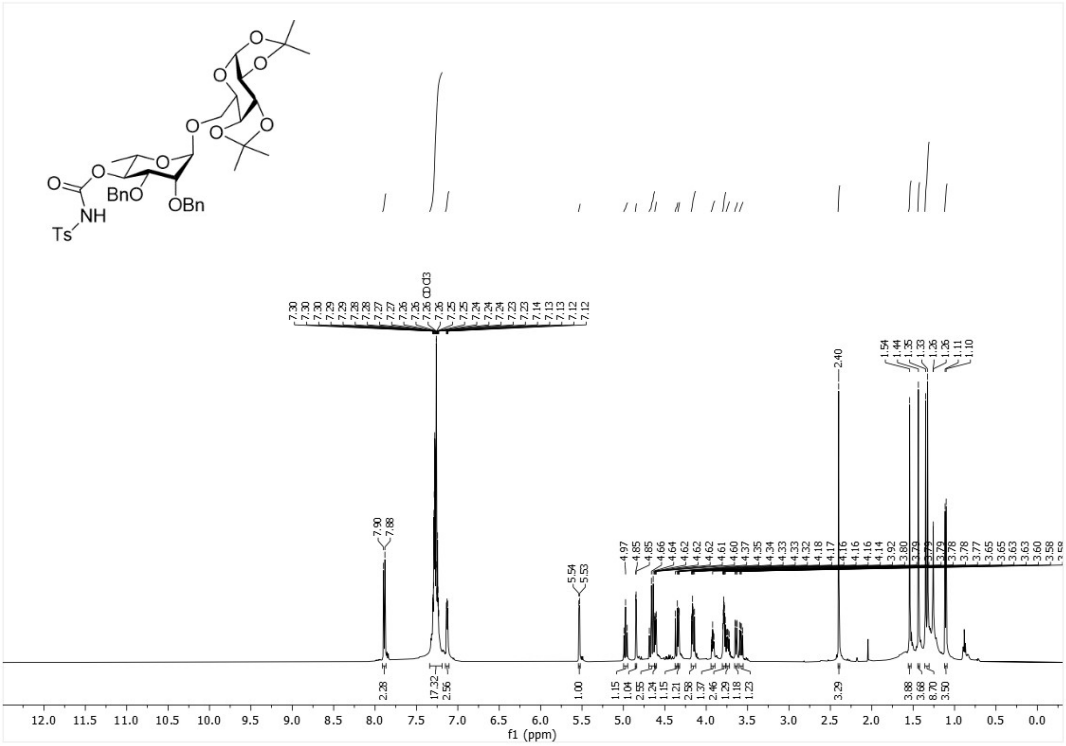


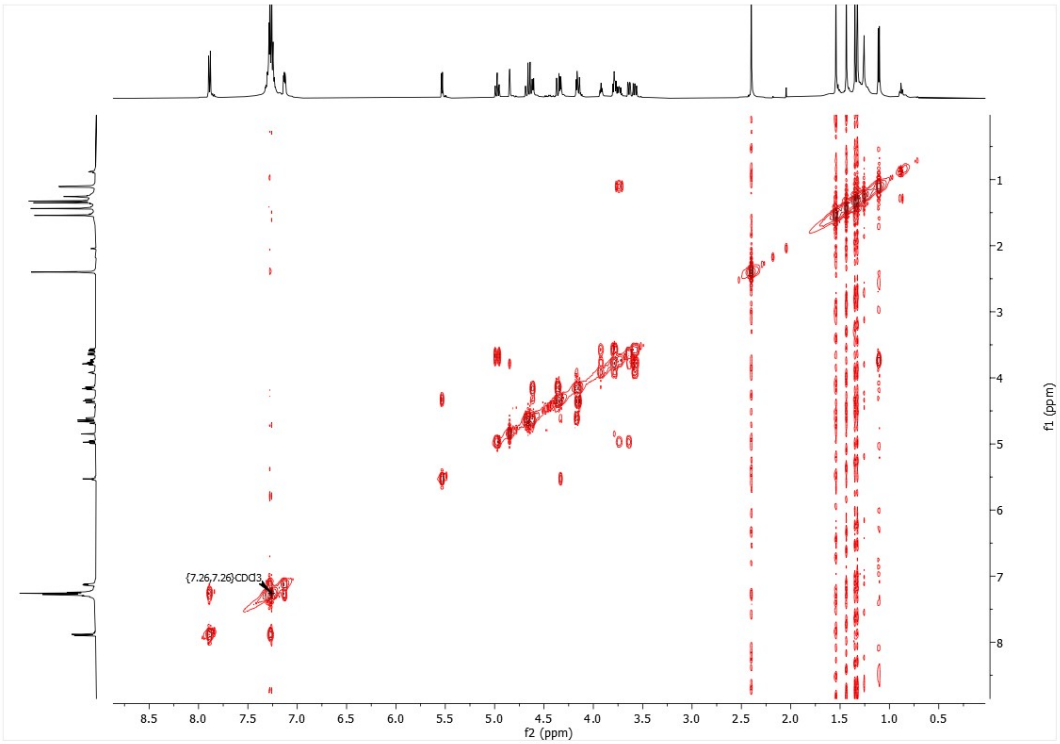


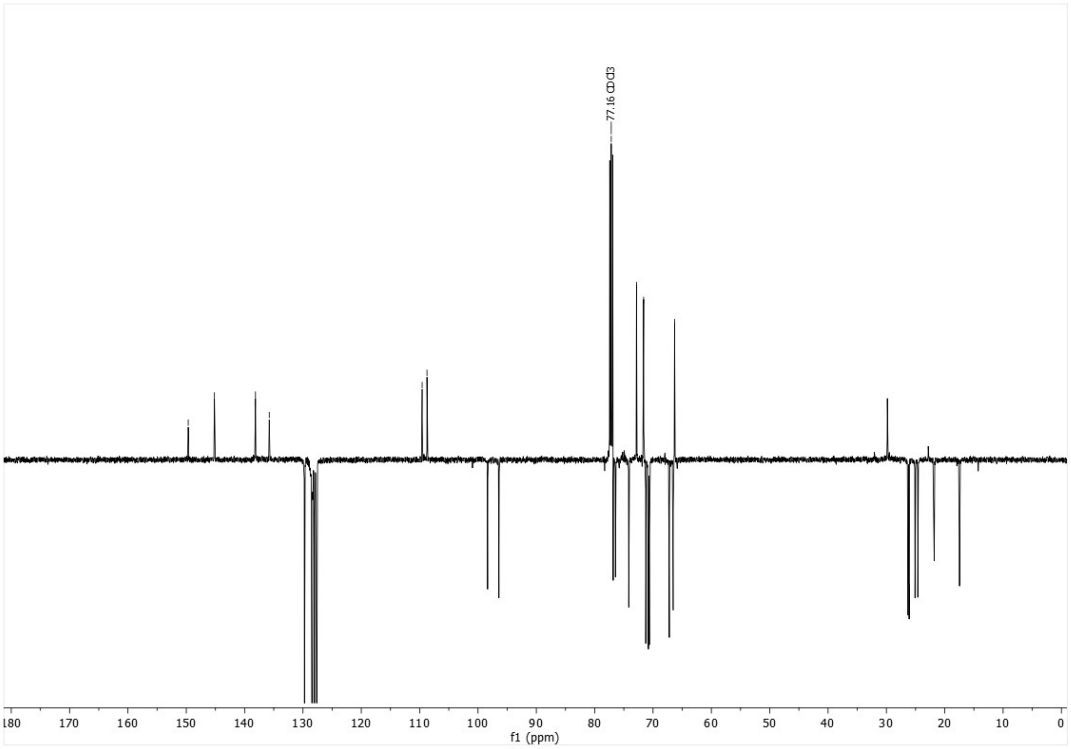

77.16 CDCl3
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

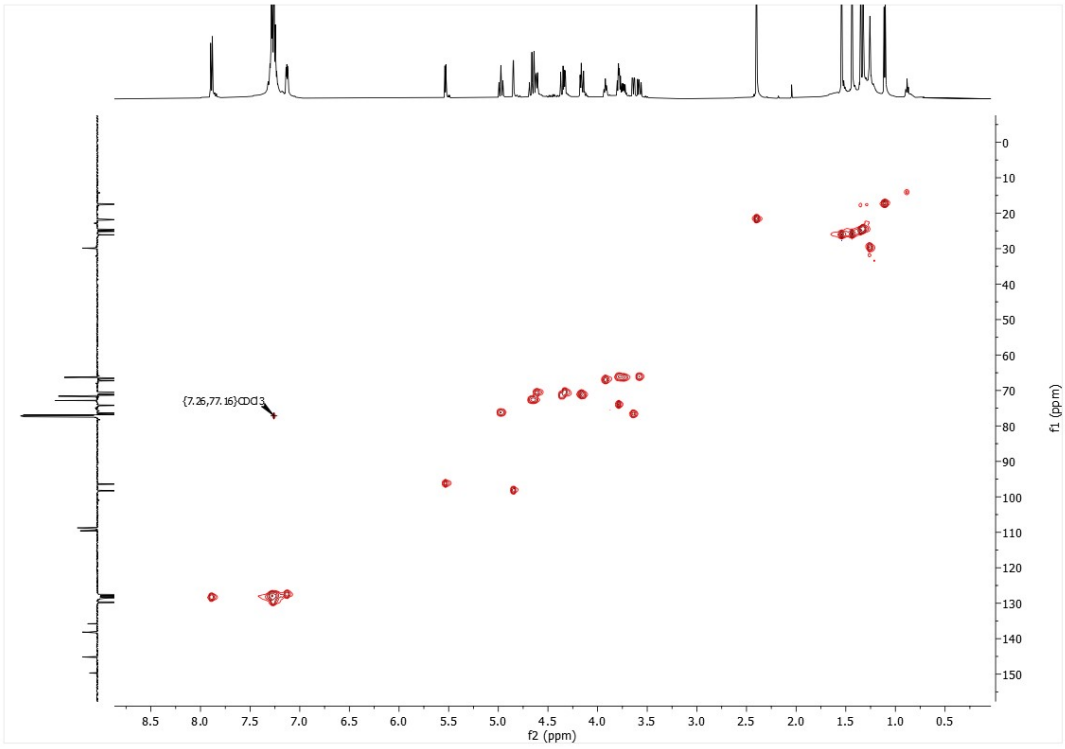

{7.26,77.16}CDCl3
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)

1,2:3,4-di-*O*-isopropylidene-β-D-galactopyranose-(6-1)-2,3-di-*O*-benzyl-4-*O*-tosylcarbamate-α-L-rhamnopyranoside (SI9-α) ($CDCl_3$)

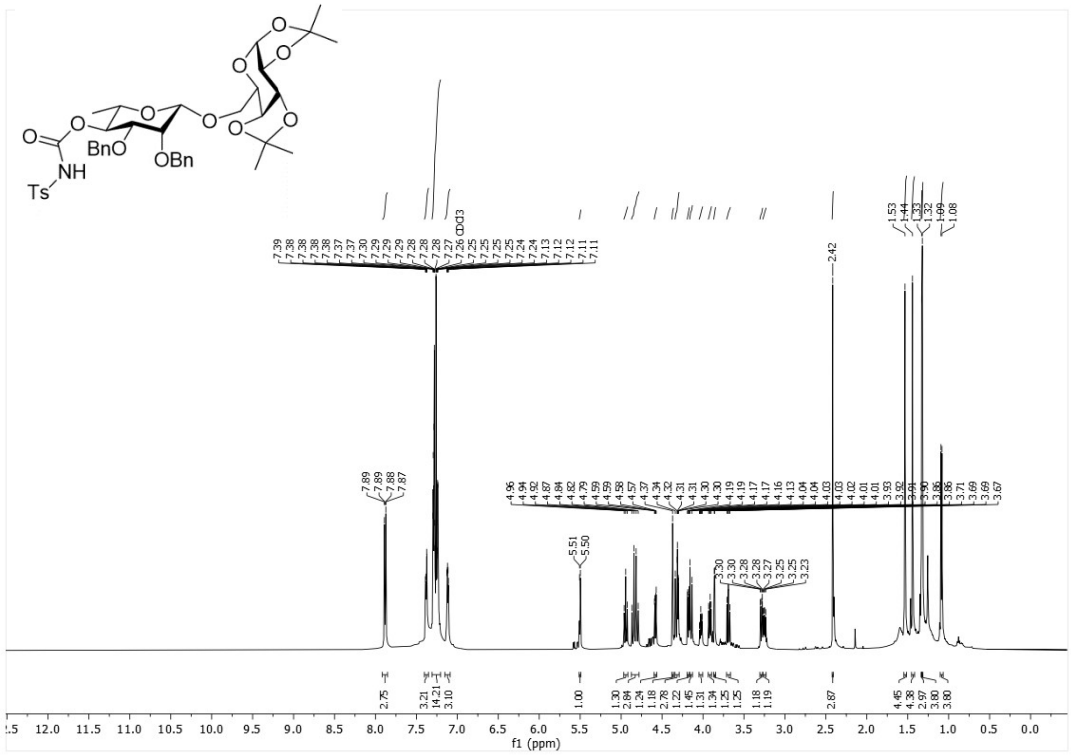


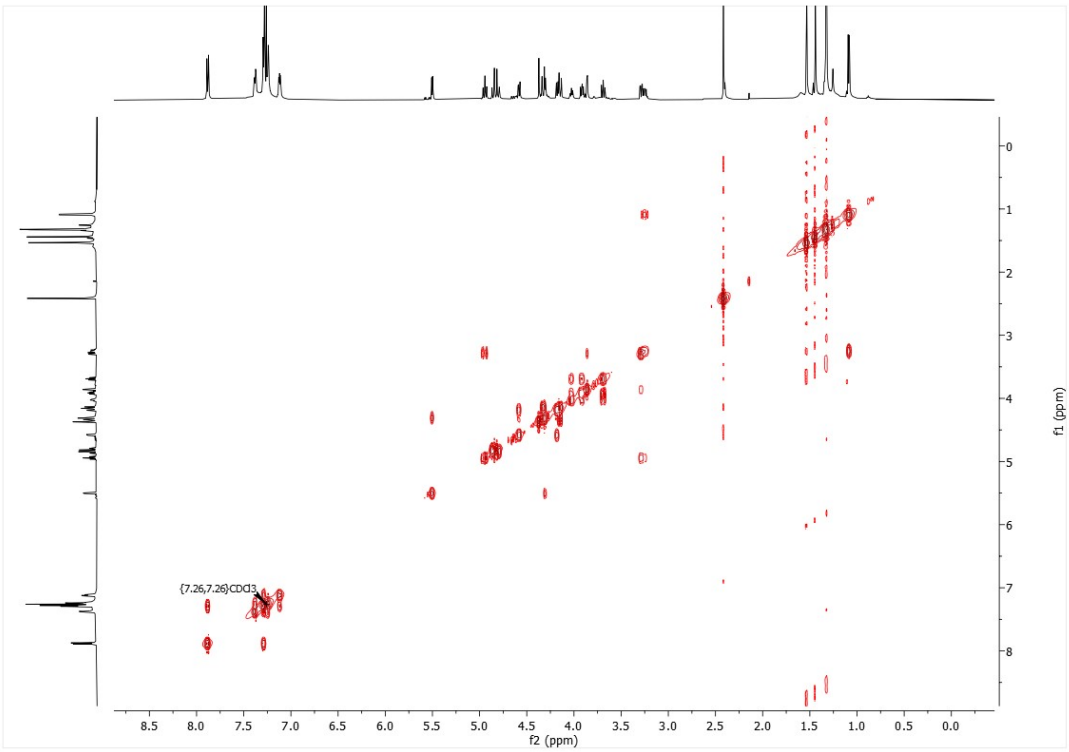


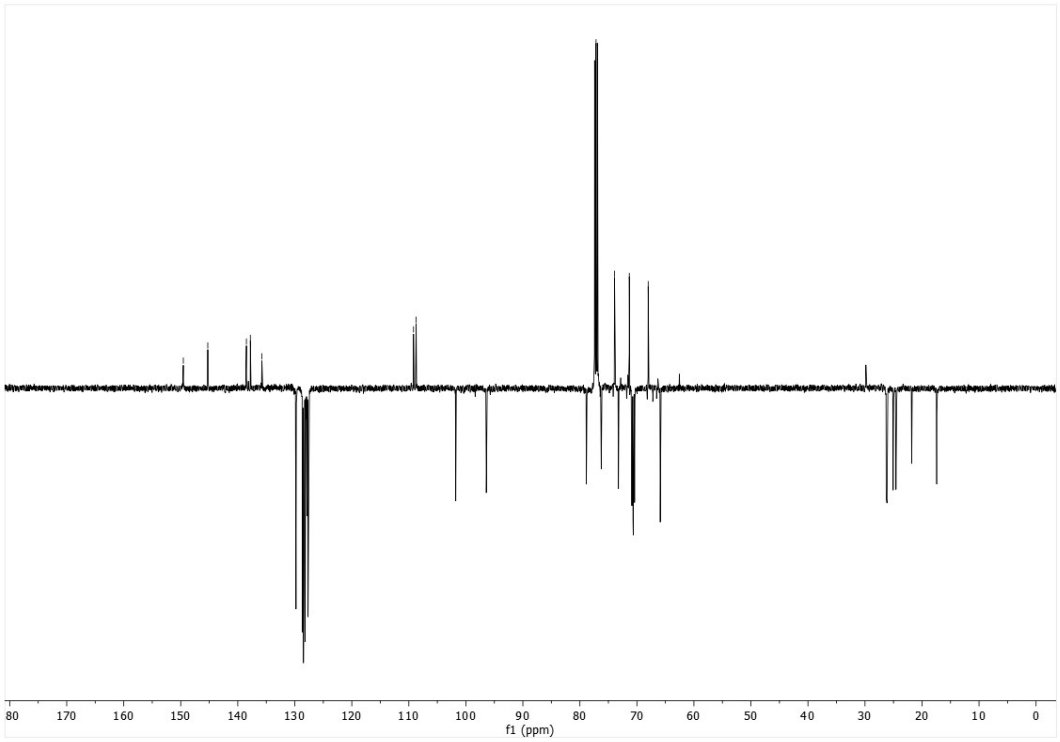

77.16 CDCl3
f1 (ppm)

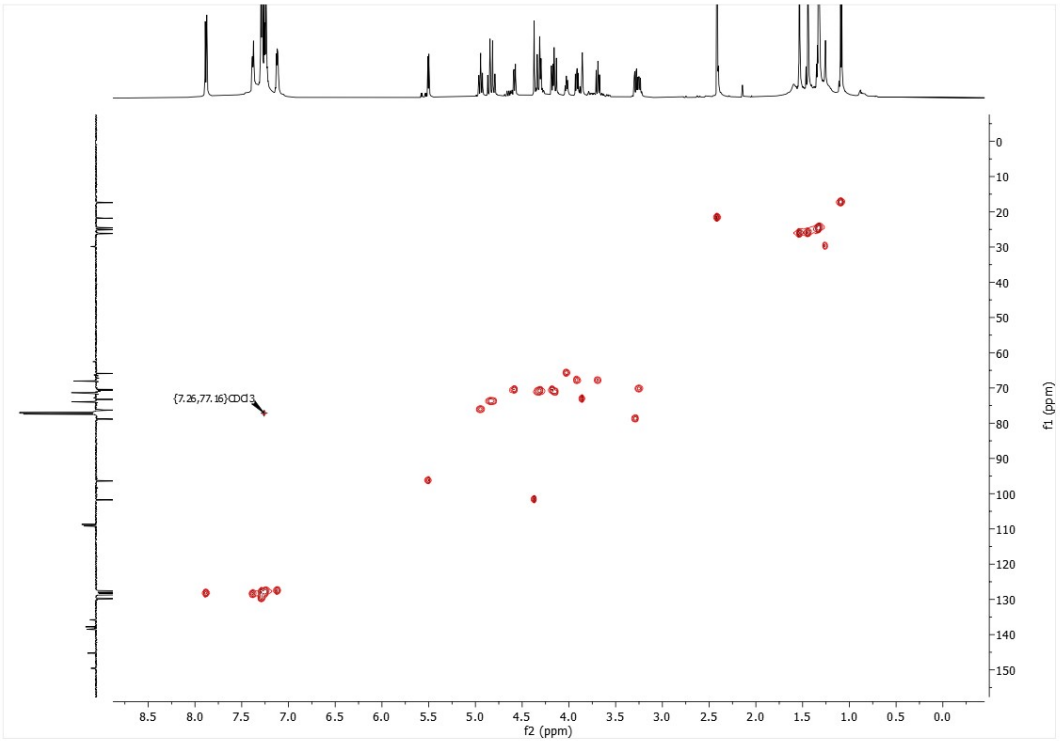

{7.26,77.16}CDCl3
f2 (ppm)
f1 (ppm)

1,2:3,4-di-*O*-isopropylidene-β-D-galactopyranose-(6-1)-2,3-di-*O*-benzyl-4-*O*-tosylcarbamate-β-L-rhamnopyranoside (SI9-β) ($CDCl_3$)

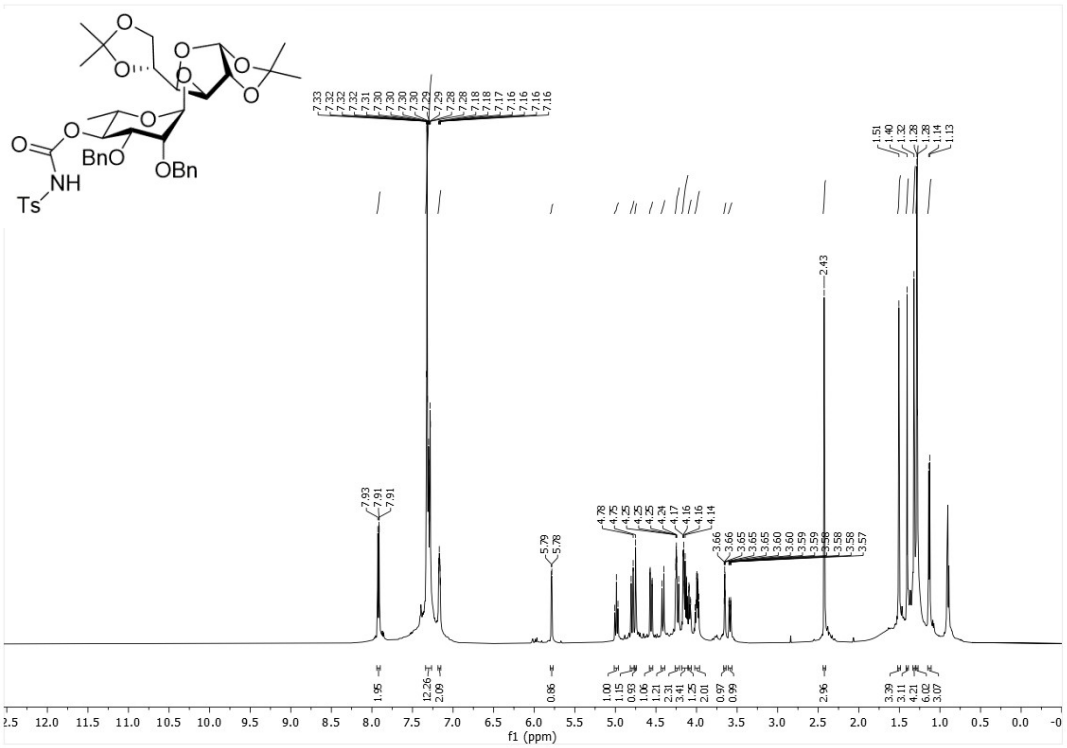


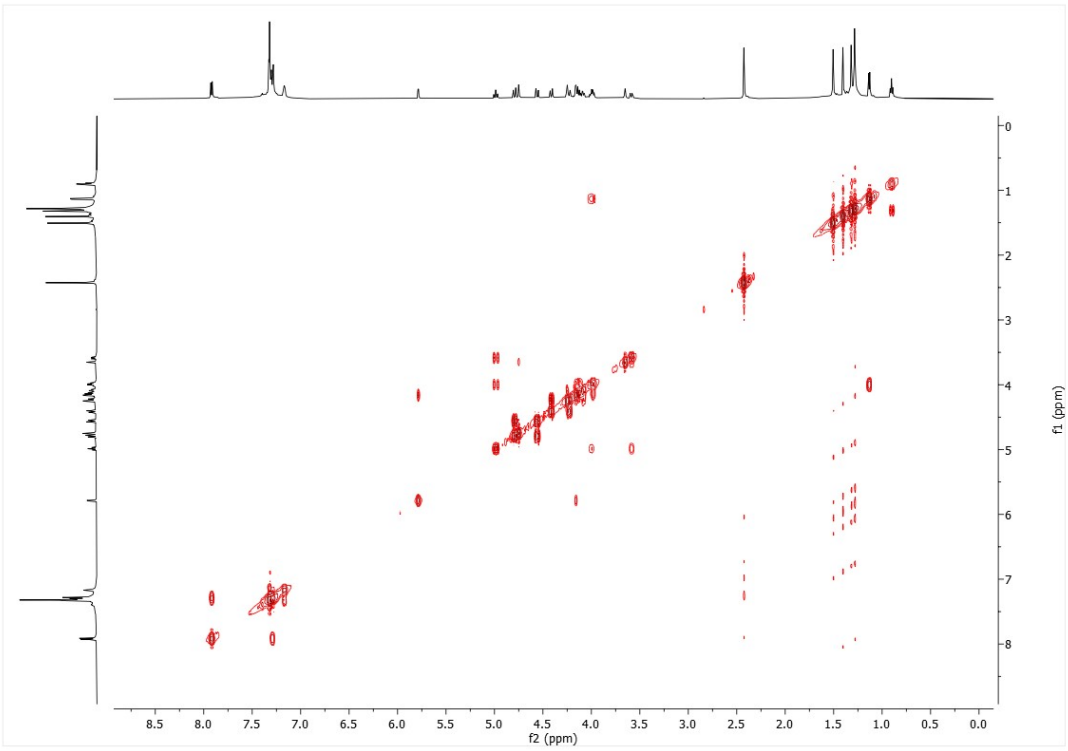


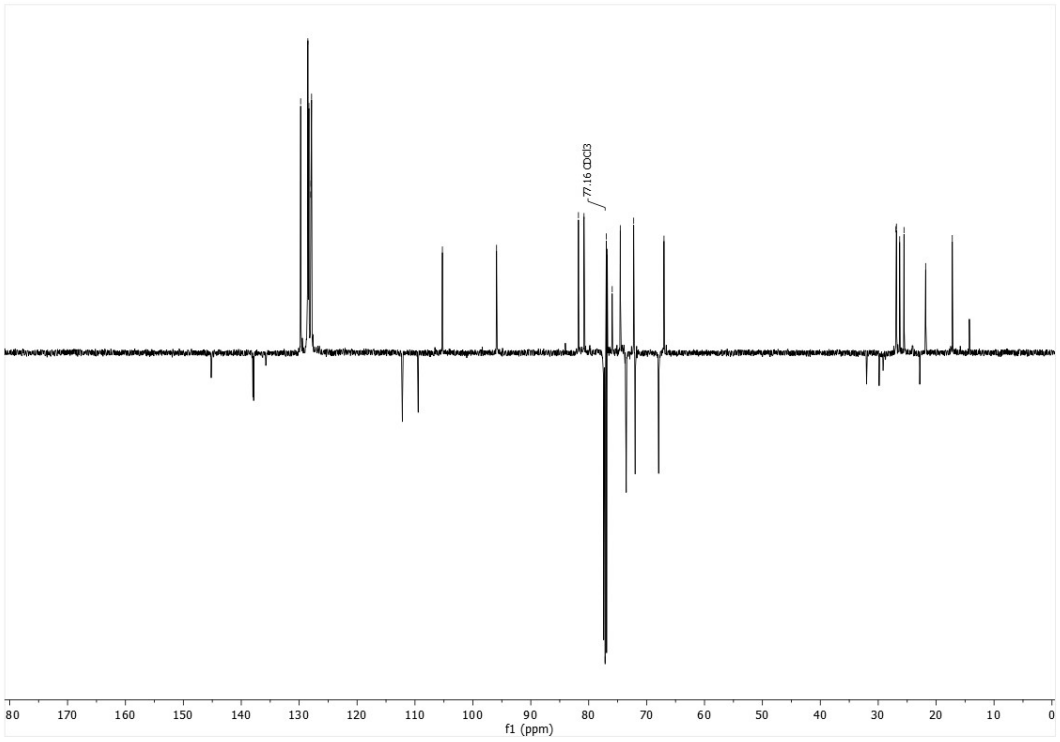

80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

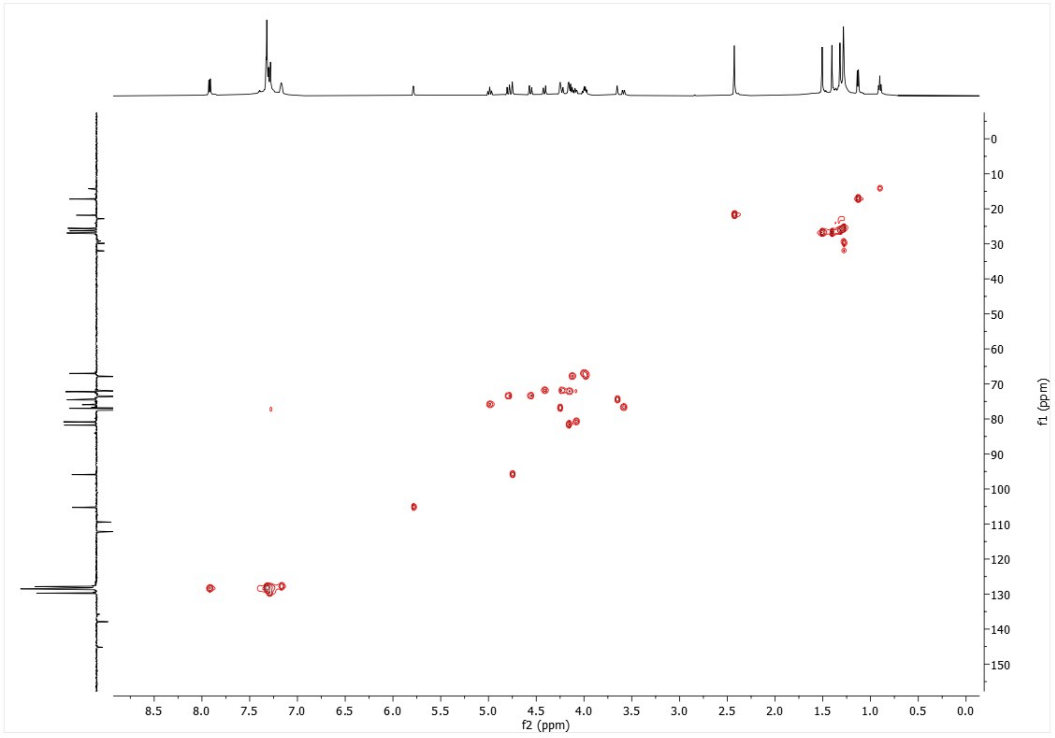

{7.26,77.16}CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)

1,2:3,4-di-*O*-isopropylidene-α-D-glucofuranose-(3-1)-2,3-di-*O*-benzyl-4-*O*-tosylcarbamate-α-L-rhamnopyranoside (SI10-α) ($CDCl_3$)

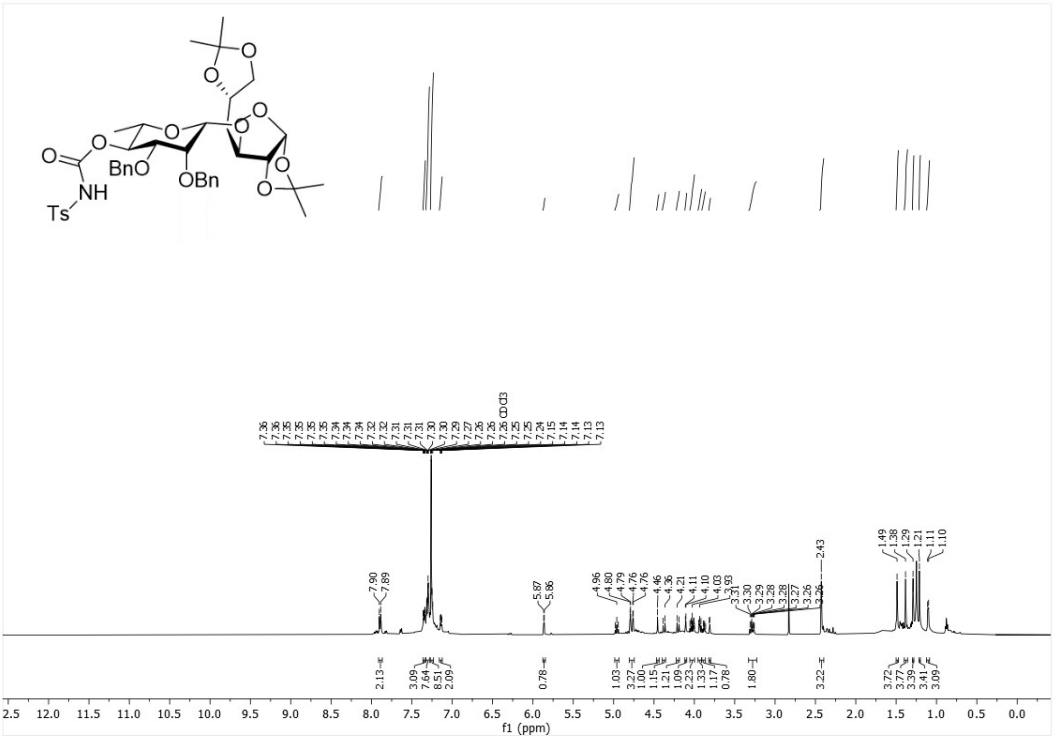


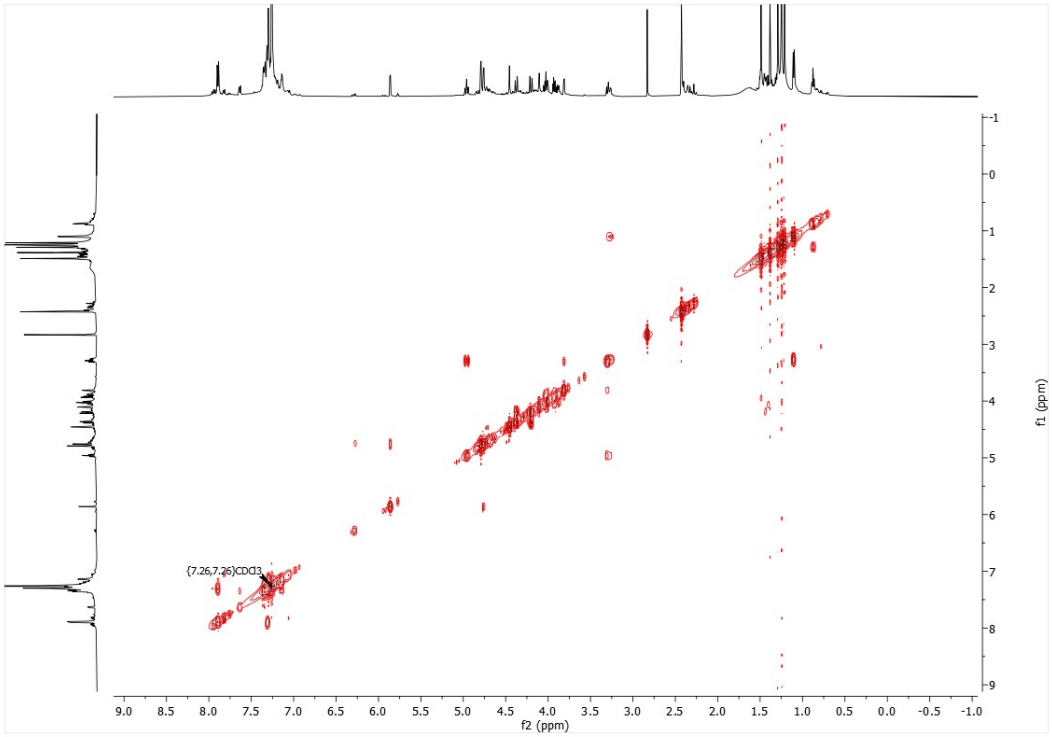


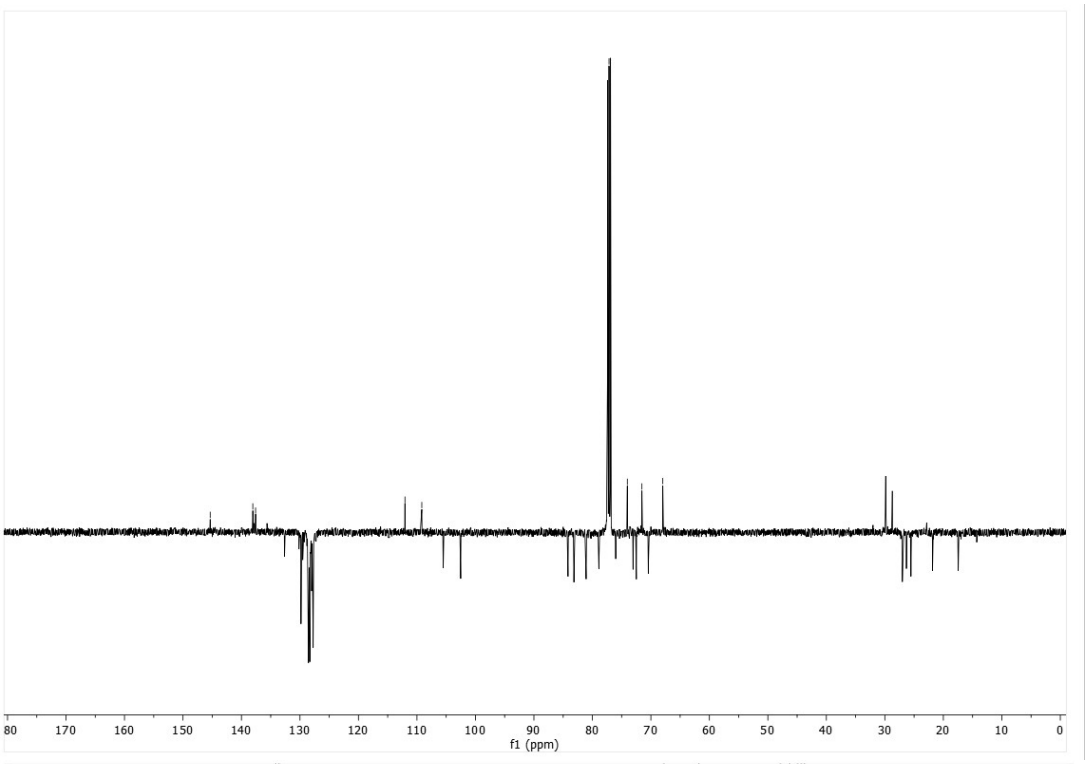

77.16 CDCl3
f1 (ppm)

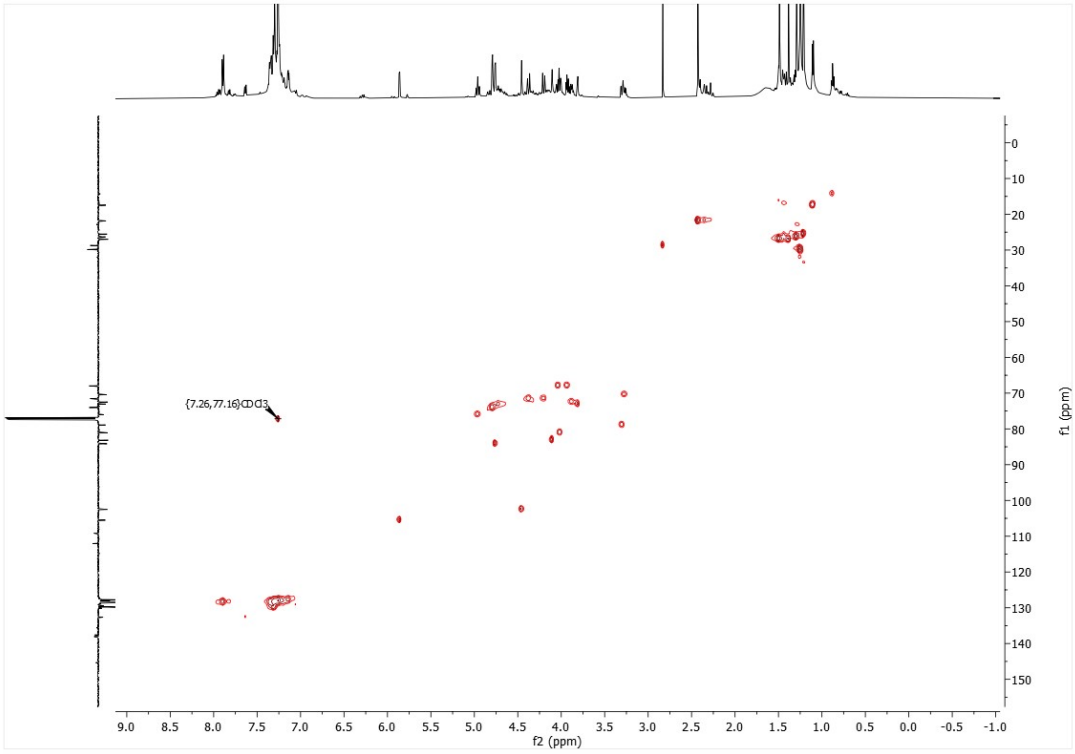

f2 (ppm)
f1 (ppm)

1,2:3,4-di-*O*-isopropylidene-α-D-glucofuranose-(3-1)-2,3-di-*O*-benzyl-4-*O*-tosylcarbamate-β-L-rhamnopyranoside (SI10-β) ($CDCl_3$)

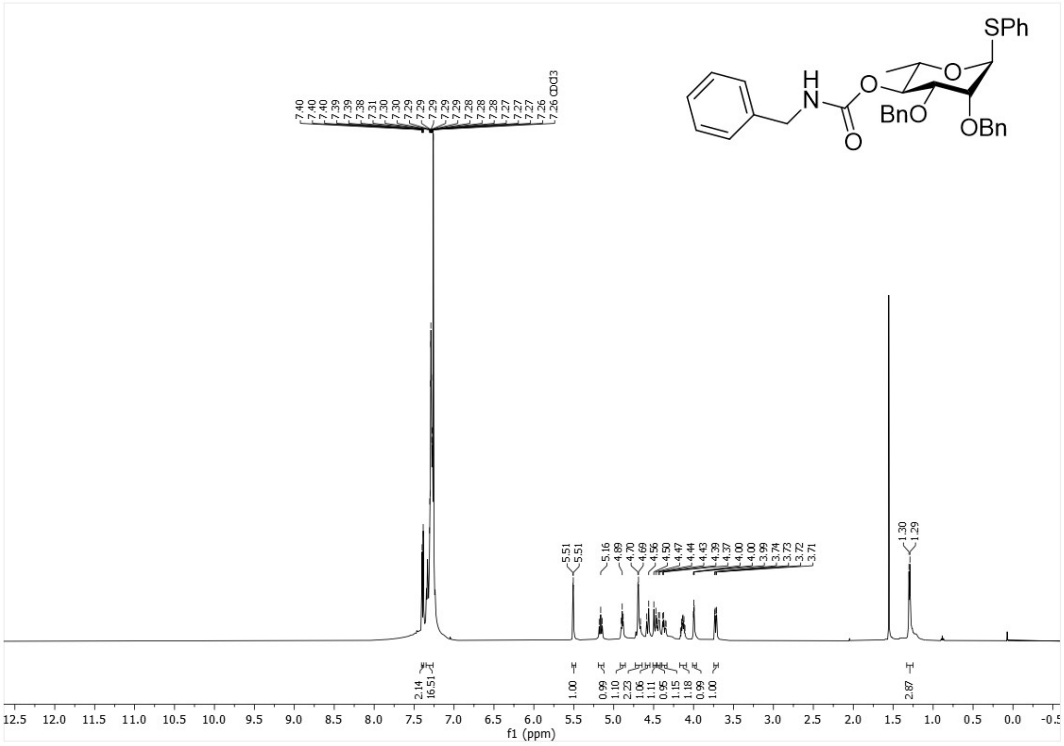


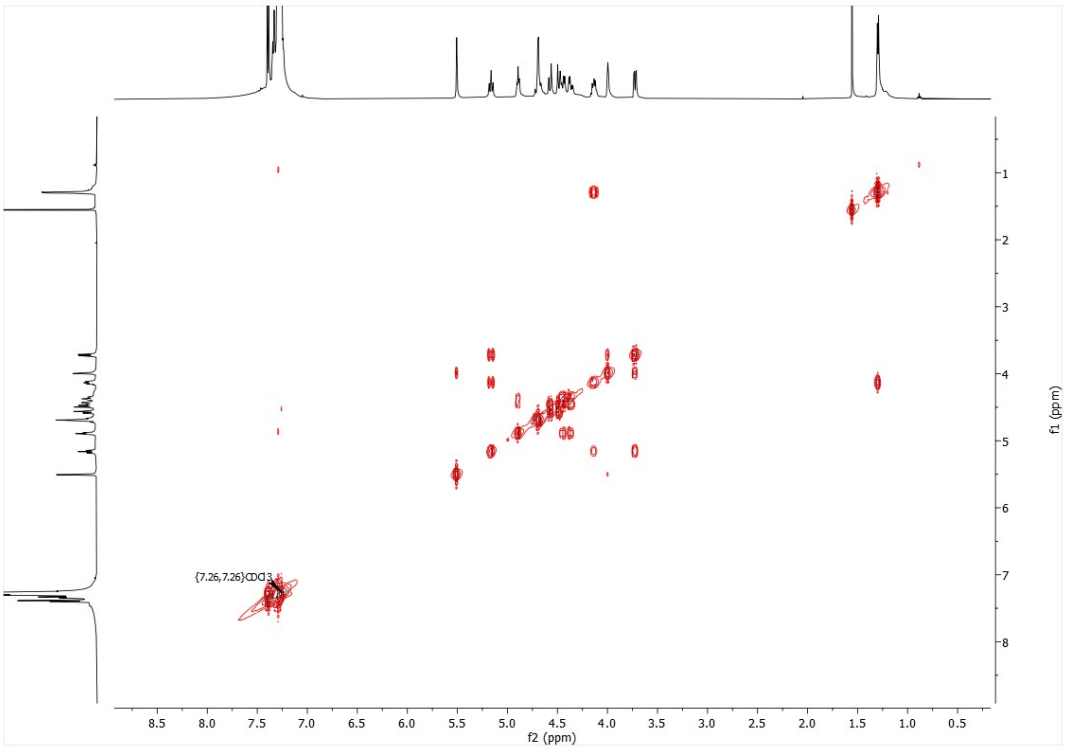


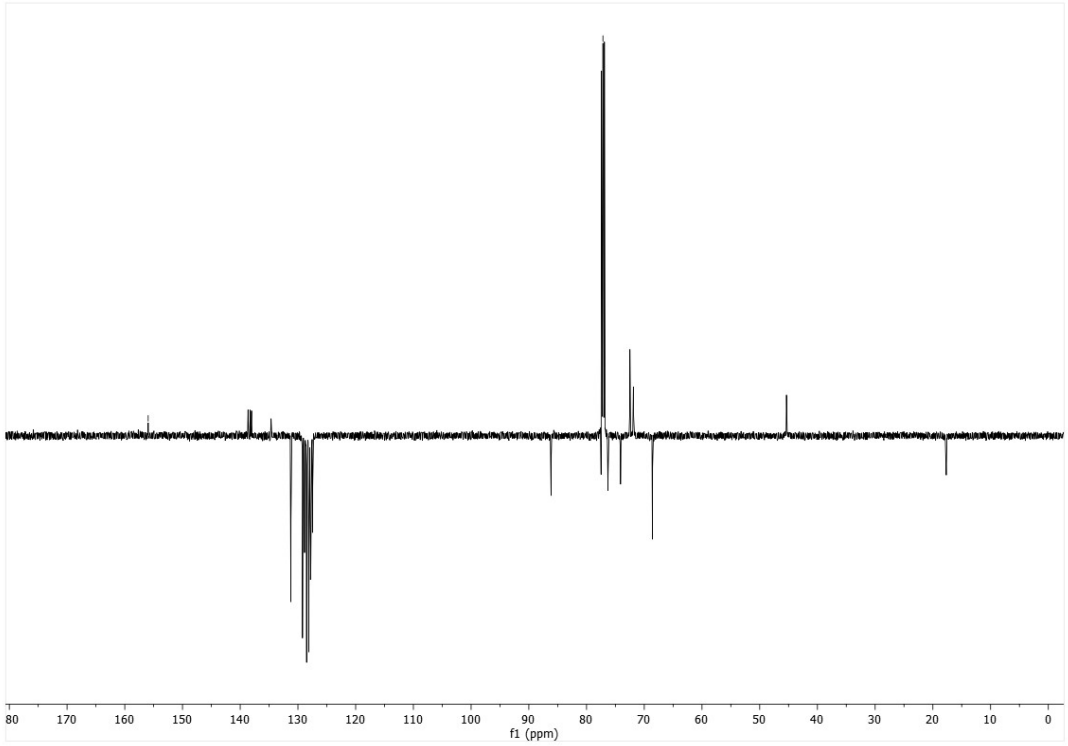

f1 (ppm)

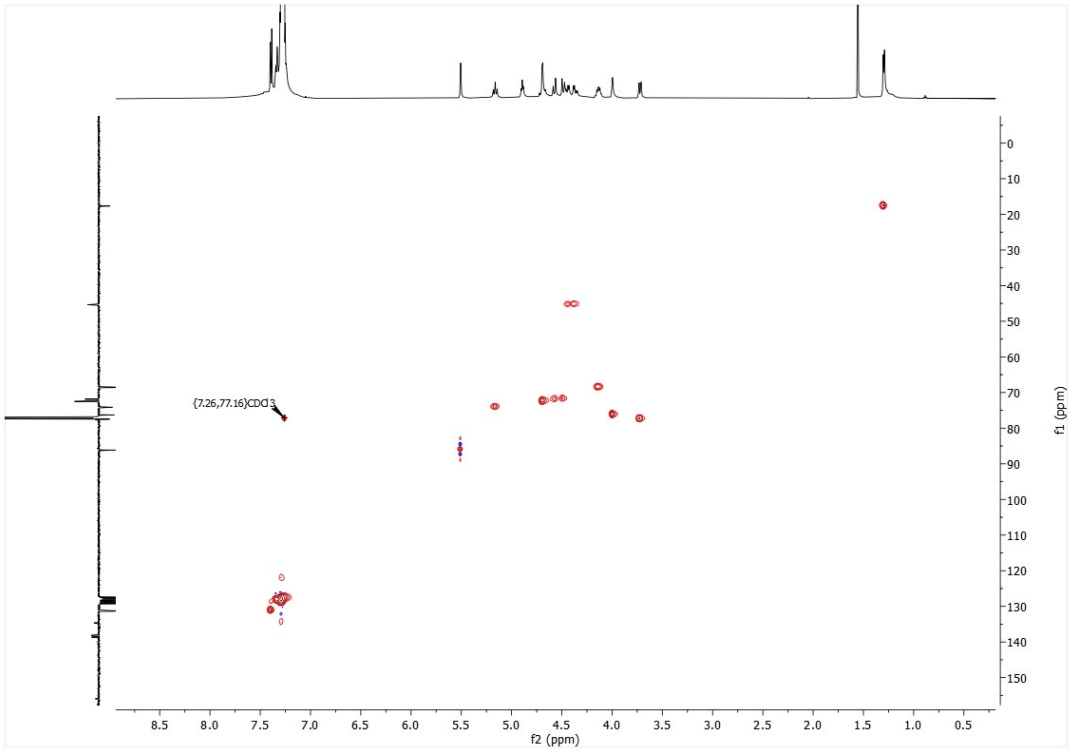

{7.26,77.16}CDCl3
f2 (ppm)
f1 (ppm)

Phenyl 2,3-di-*O*-benzyl-4-*O*-benzylcarbamoyl-1-thio-α-L-rhamnopyranoside (12) ($CDCl_3$)

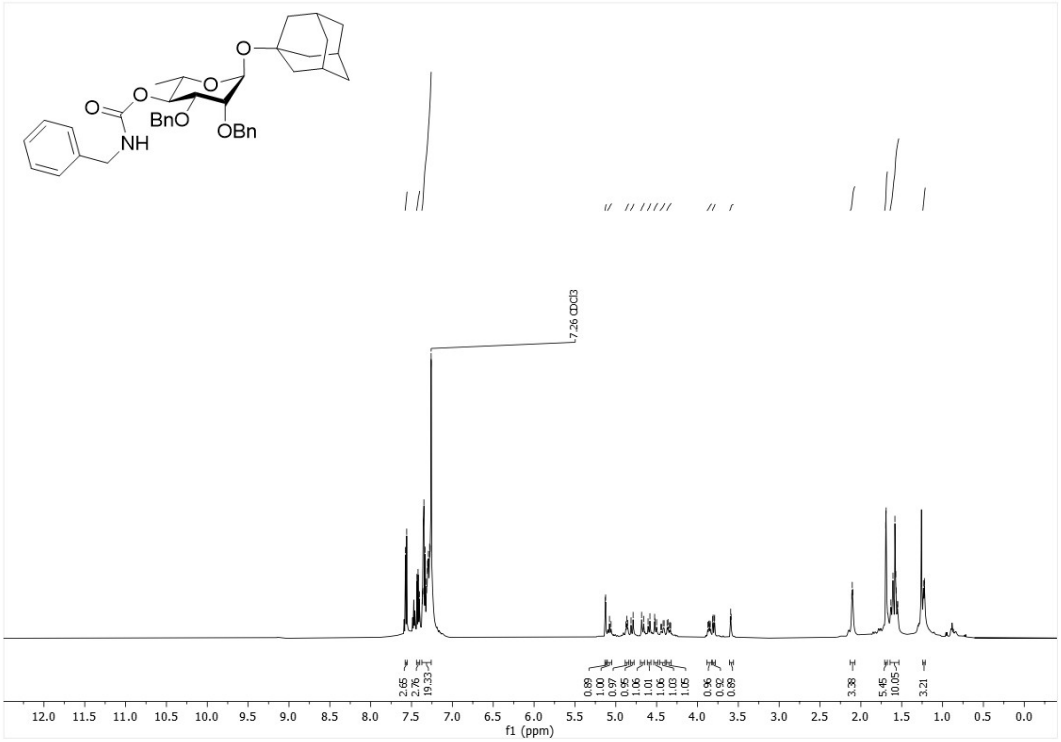


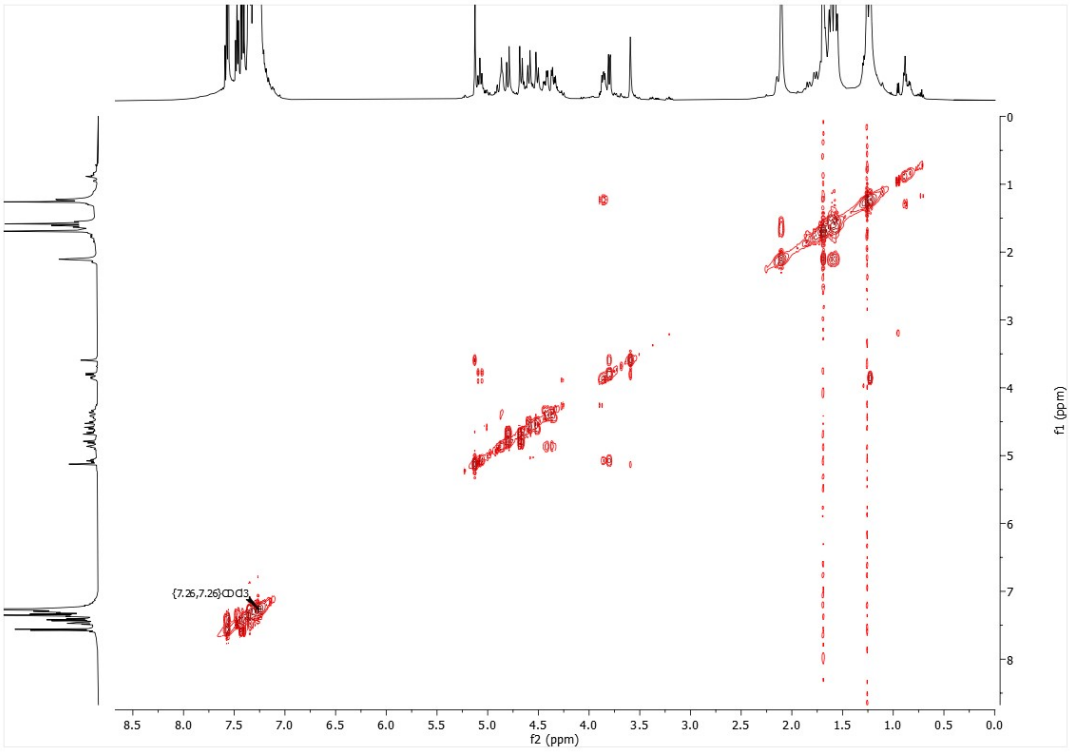


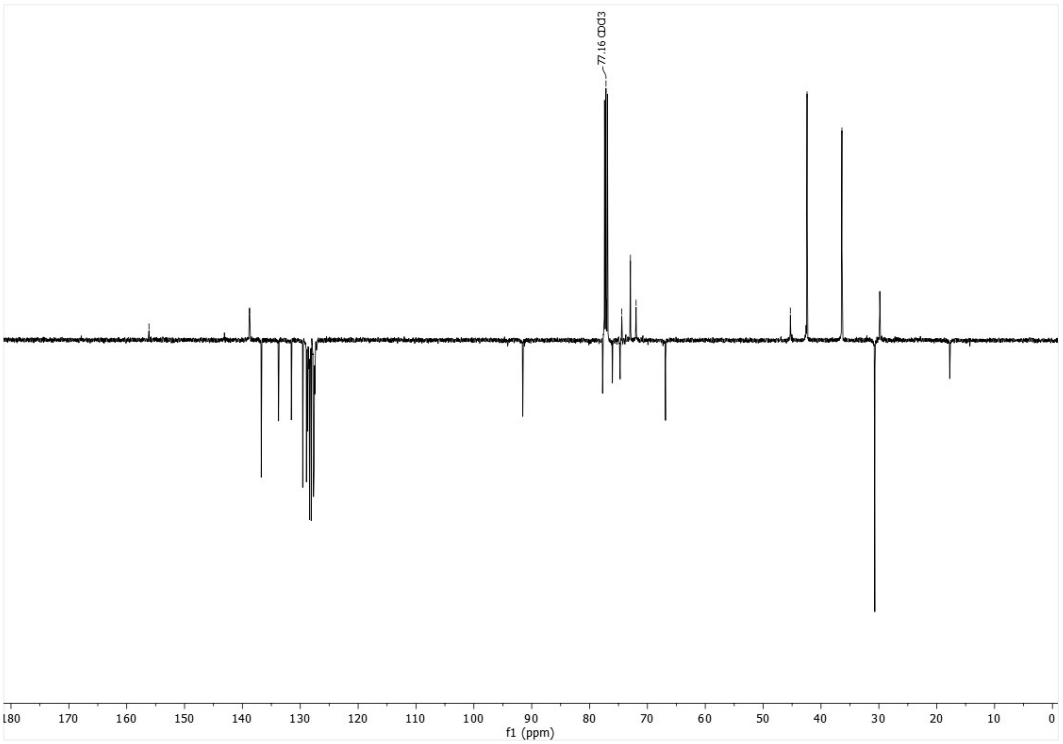

f1 (ppm)

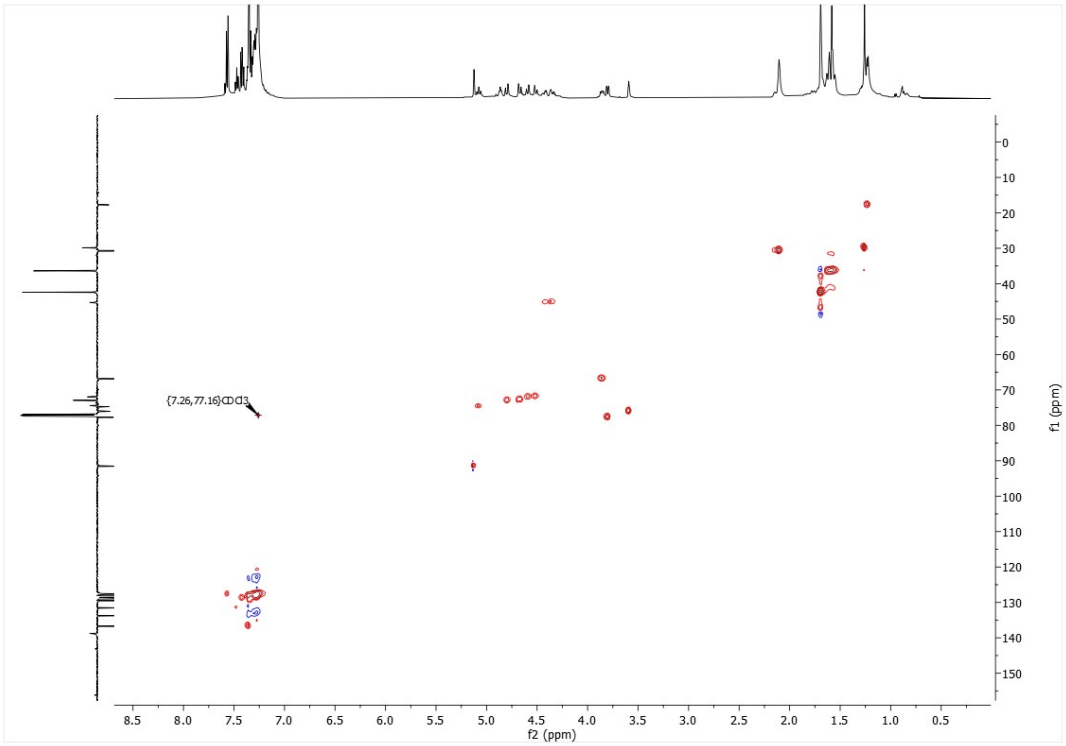

{7.26,77.16}CDCl3
f2 (ppm)
f1 (ppm)

1-Adamantyl 2,3-di-*O*-benzyl-4-*O*-benzylcarbamoyl-1-thio-α-L-rhamnopyranoside (SI11-α) ($CDCl_3$)

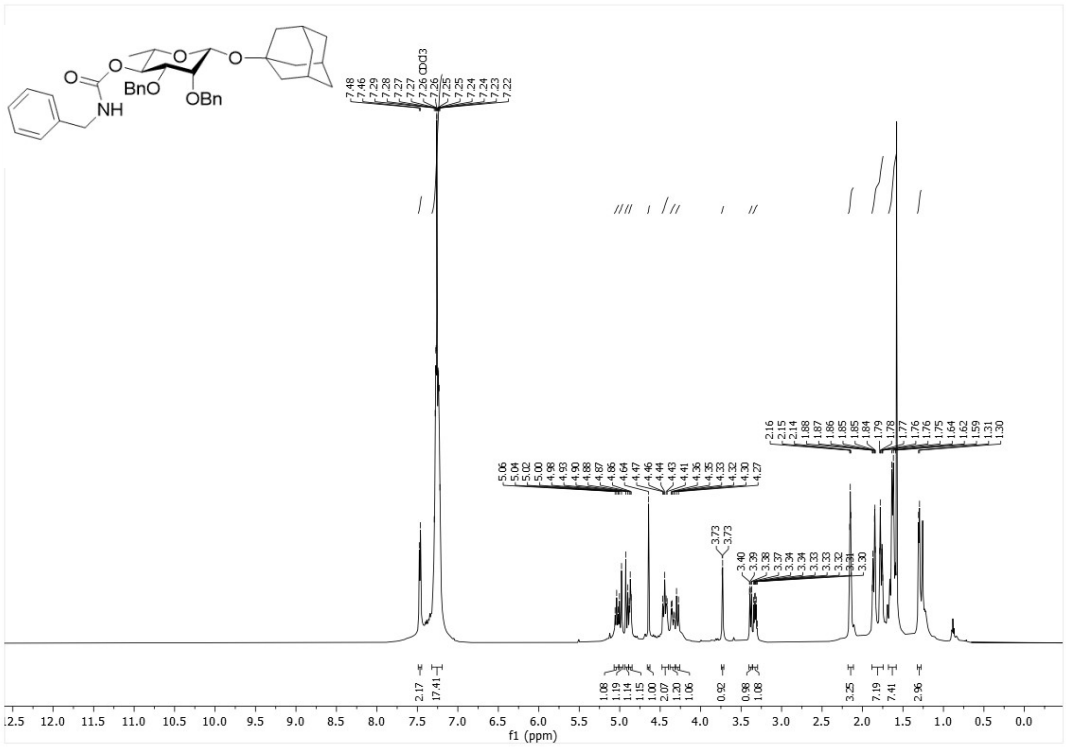


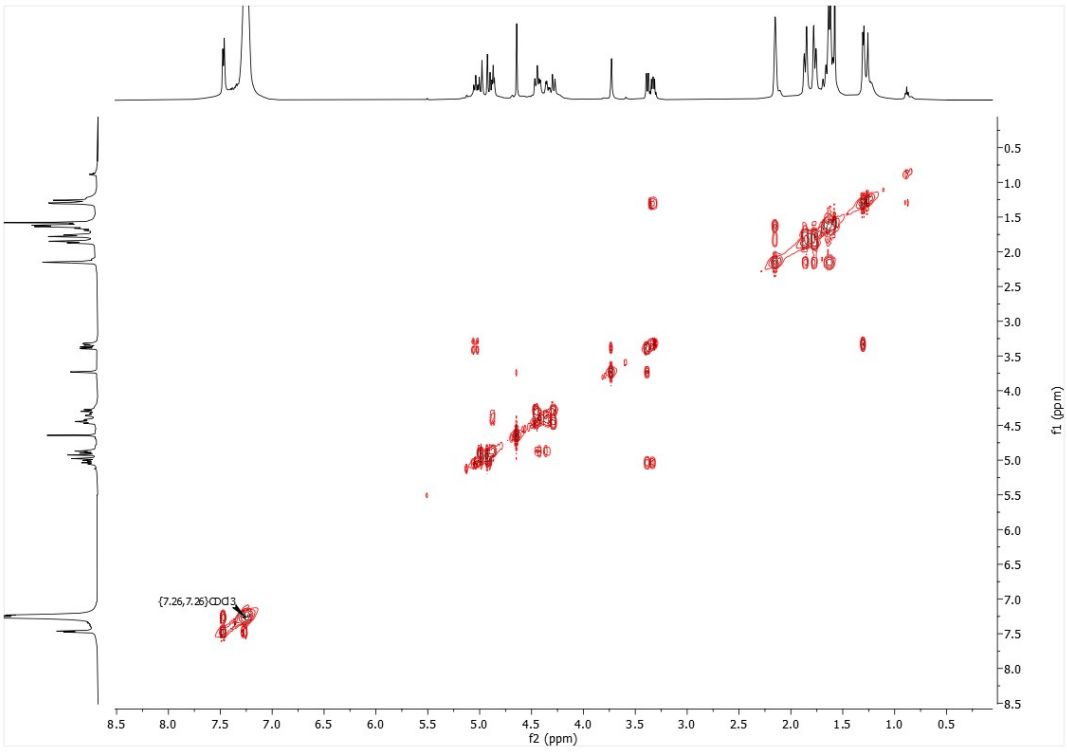


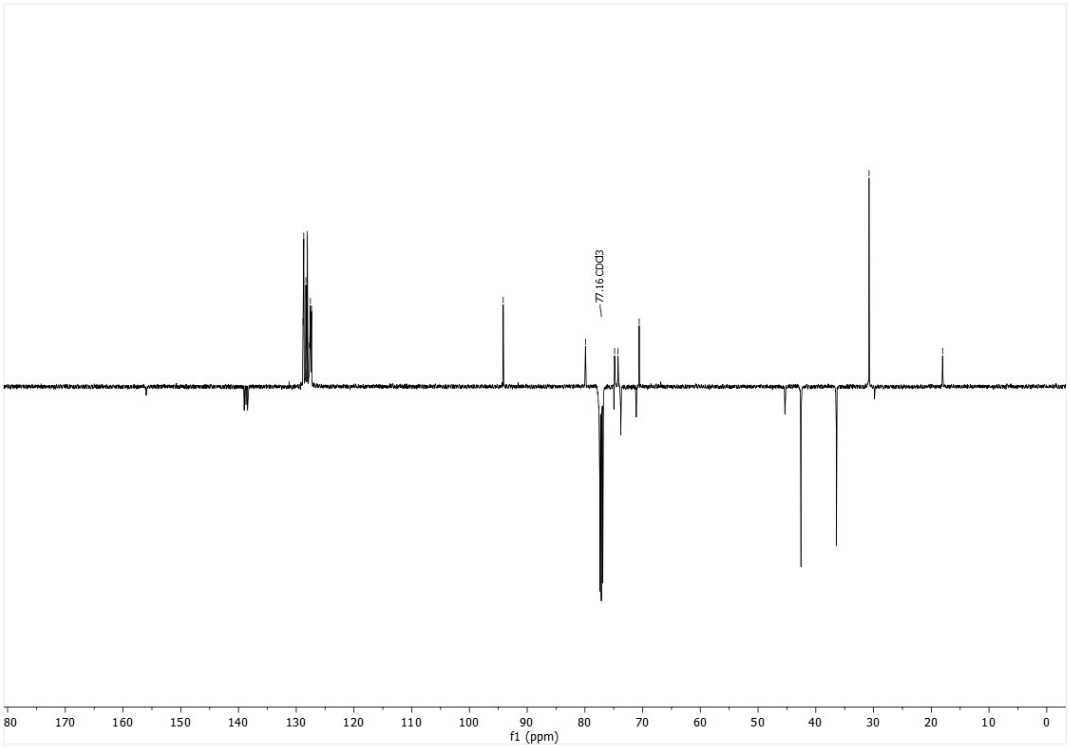

77.16 CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

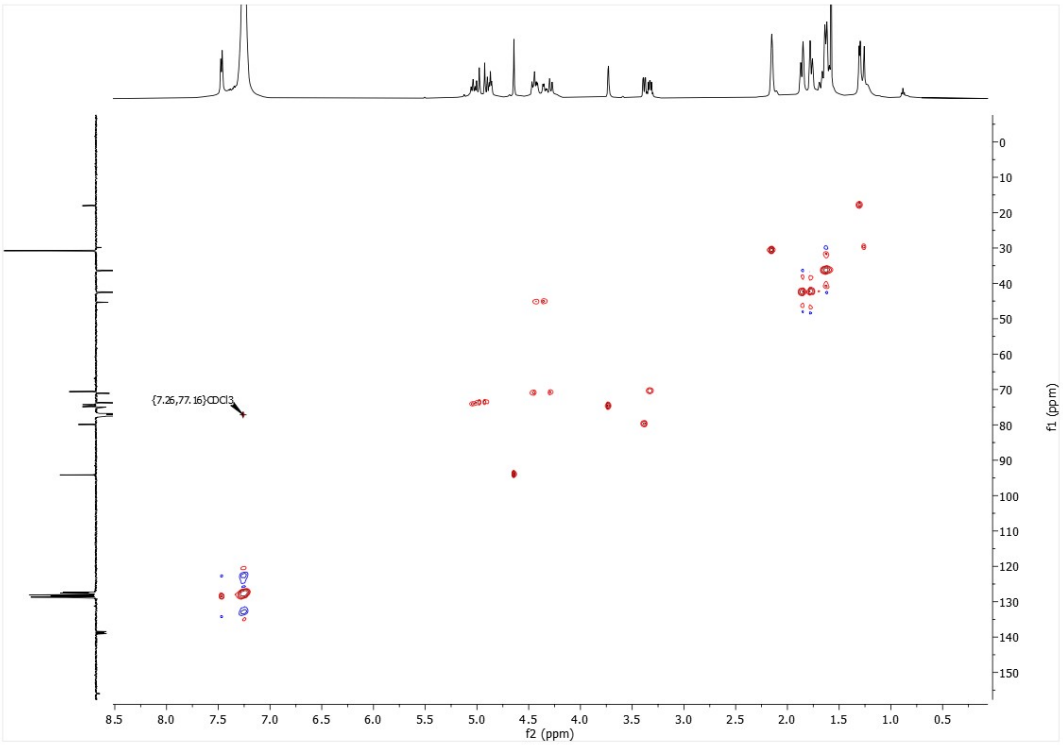

{7.26,77.16}CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)

1-Adamantyl 2,3-di-*O*-benzyl-4-*O*-benzylcarbamoyl-1-thio-β-L-rhamnopyranoside (SI11-β) ($CDCl_3$)

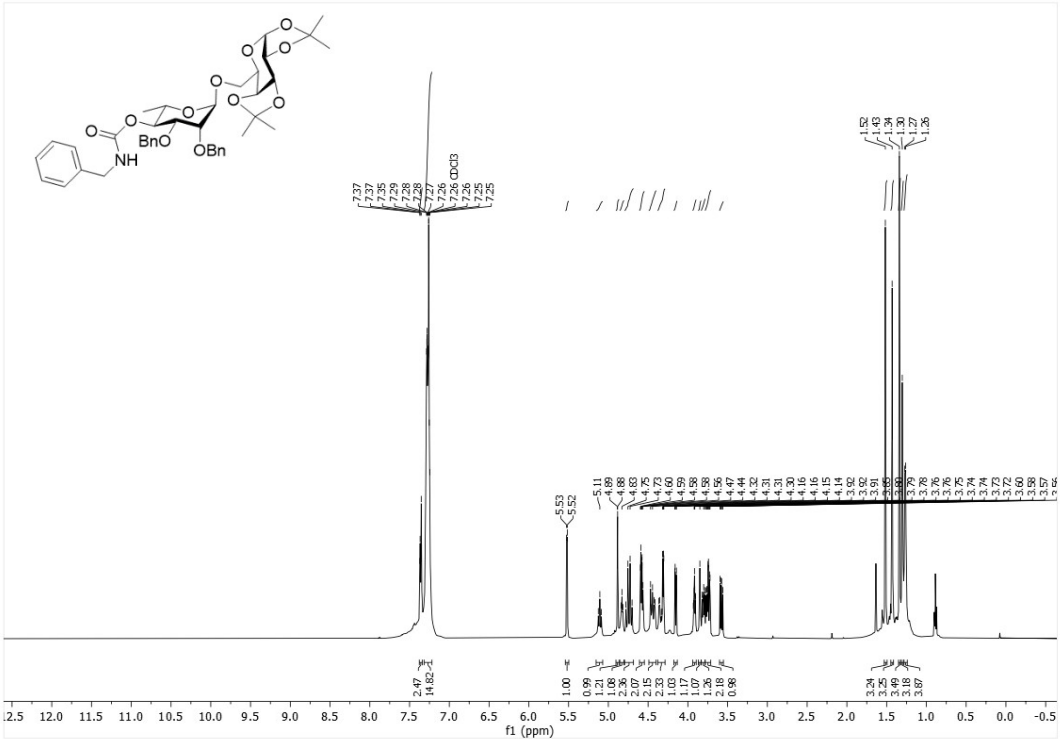


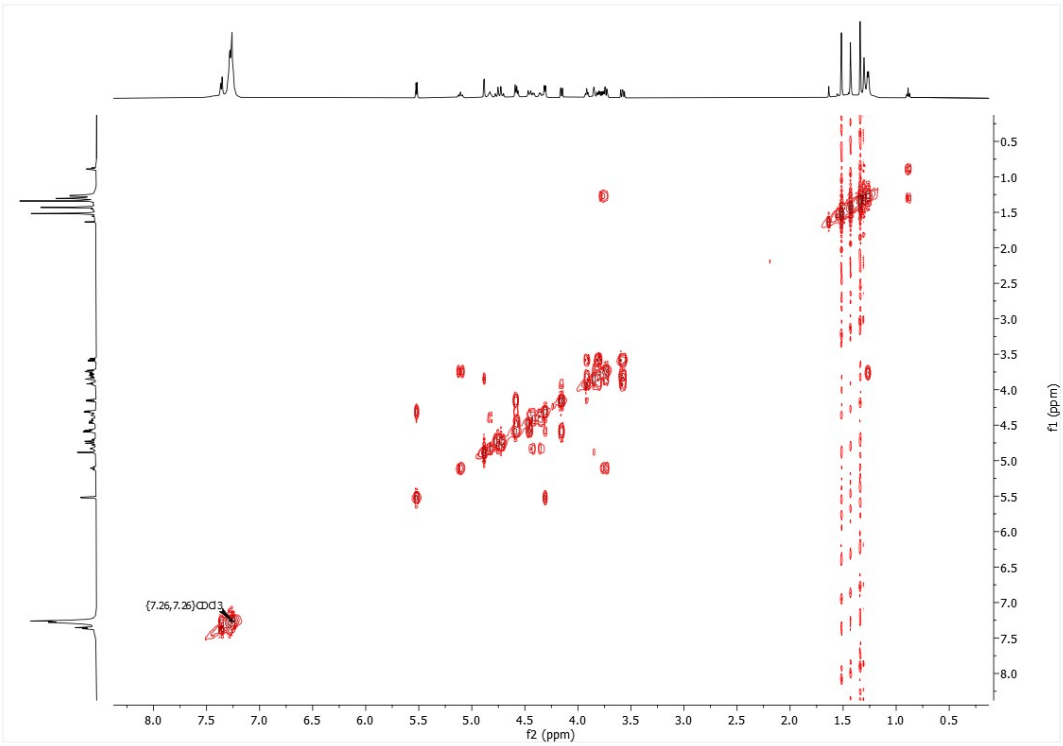


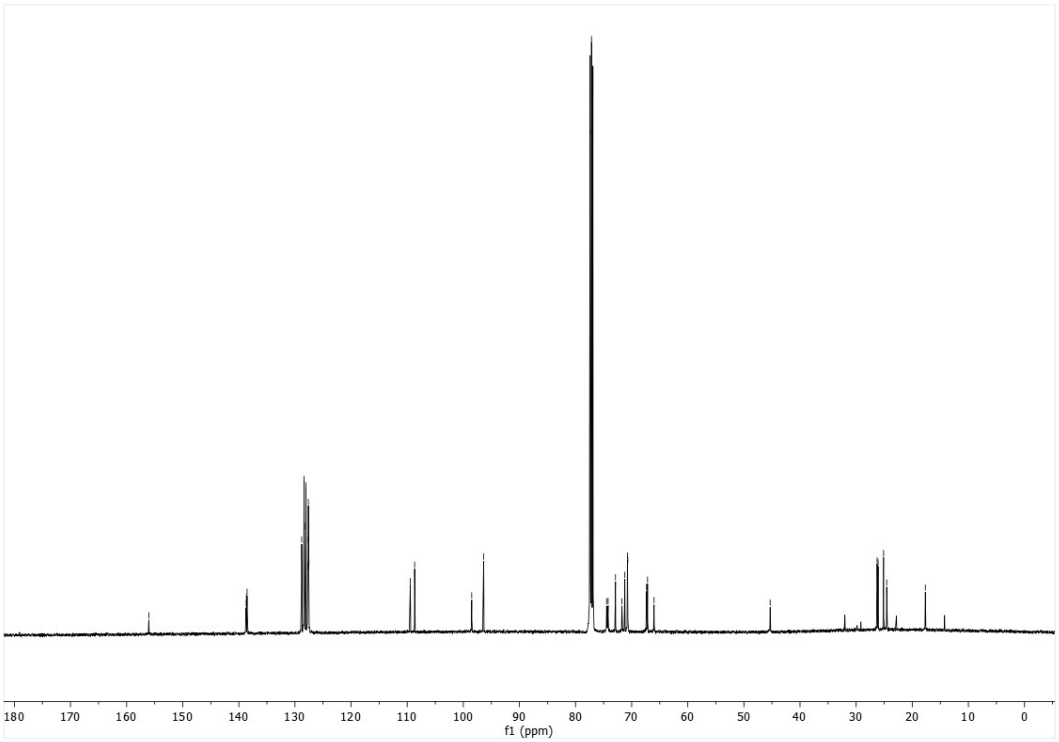

77.16 CDCl3
f1 (ppm)

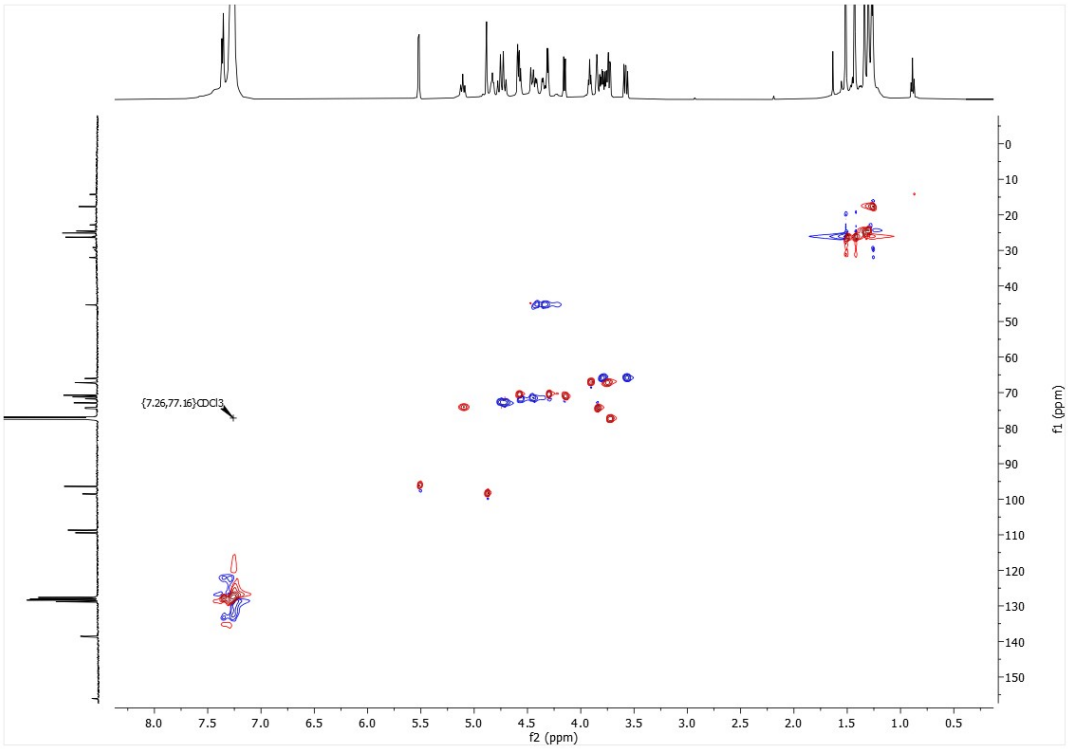

{7.26,77.16}CDCl3
f1 (ppm)
f2 (ppm)

1,2:3,4-di-*O*-isopropylidene-β-D-galactopyranose-(6-1)-2,3-di-*O*-benzyl-4-*O*-benzylcarbamoyl-α-L-rhamnopyranoside (SI12-α) ($CDCl_3$)

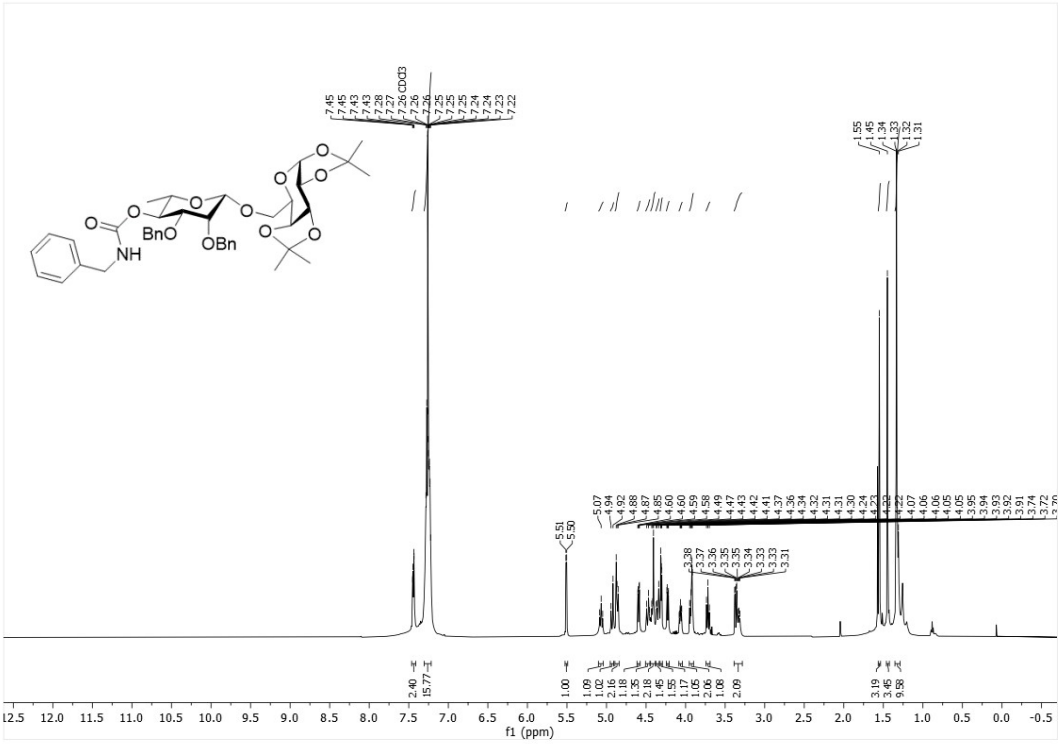


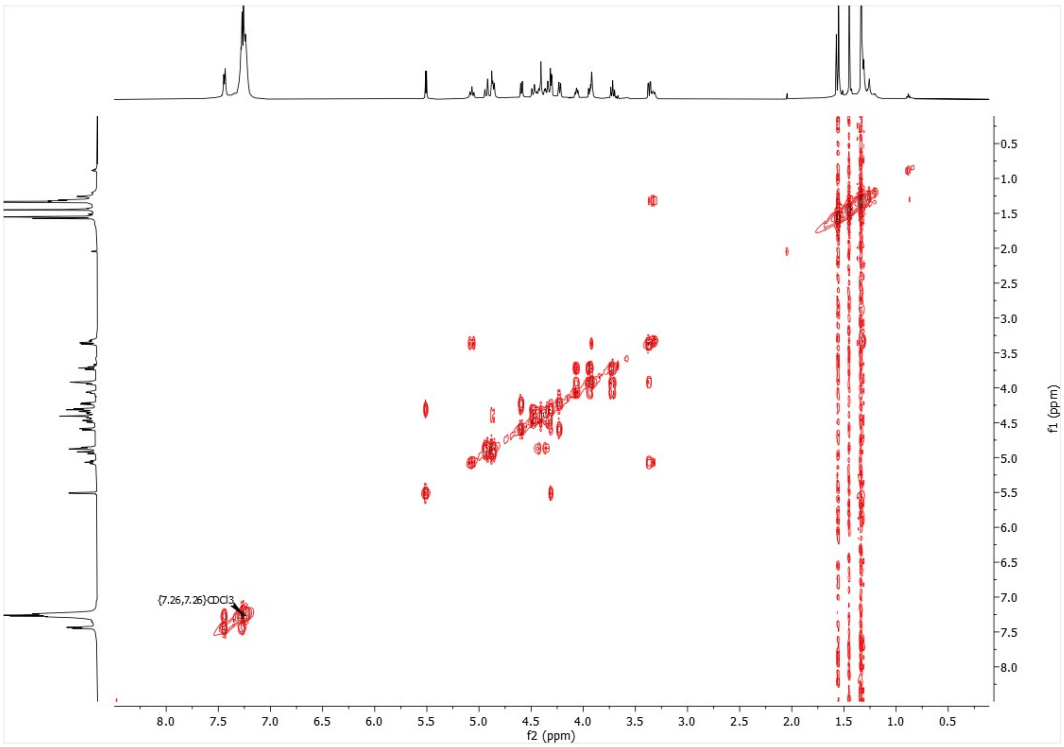


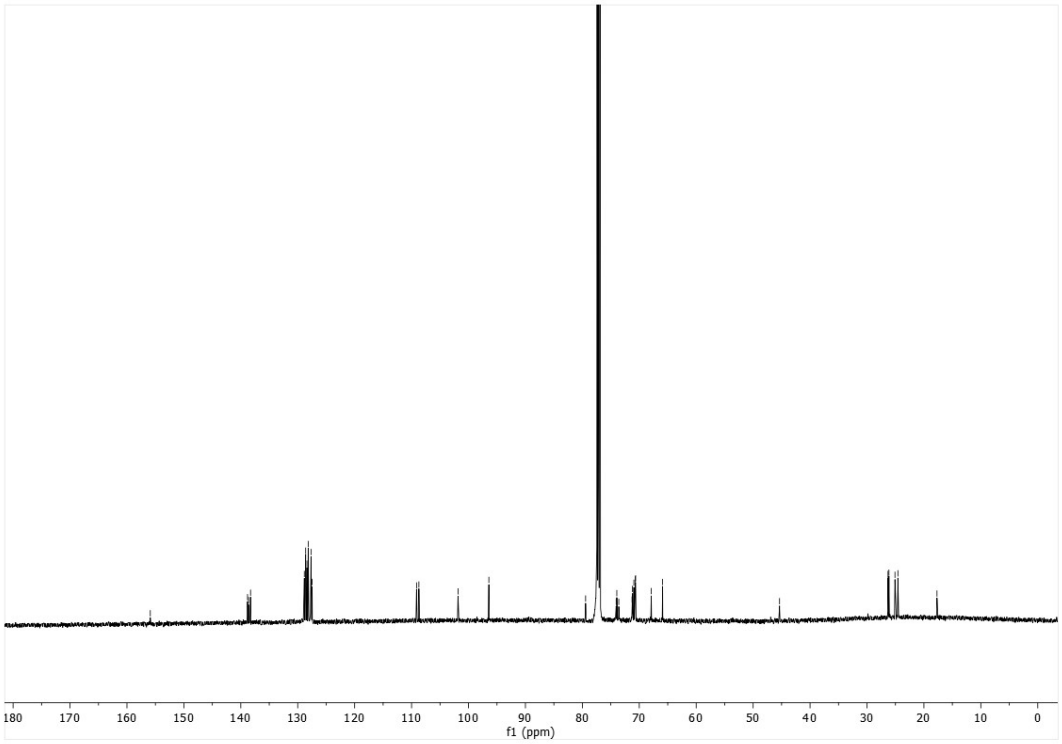

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

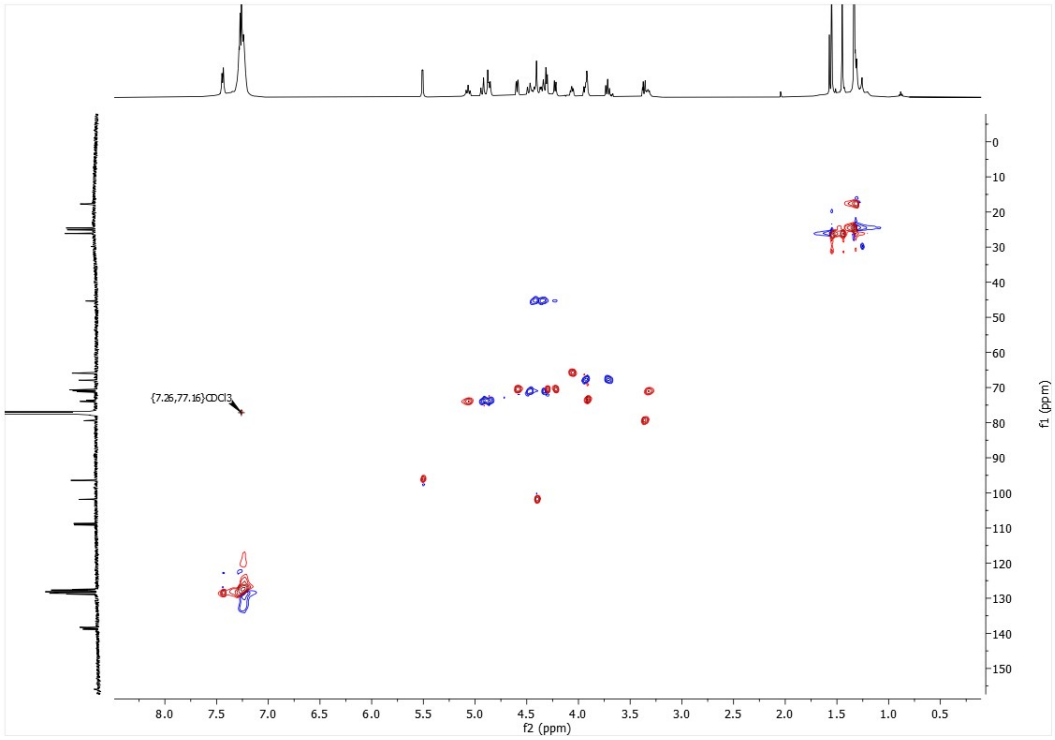

{7.26,77.16}CDCl3
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)

1,2:3,4-di-*O*-isopropylidene-β-D-galactopyranose-(6-1)-2,3-di-*O*-benzyl-4-*O*-benzylcarbamoyl-β-L-rhamnopyranoside (SI12-β) ($CDCl_3$)

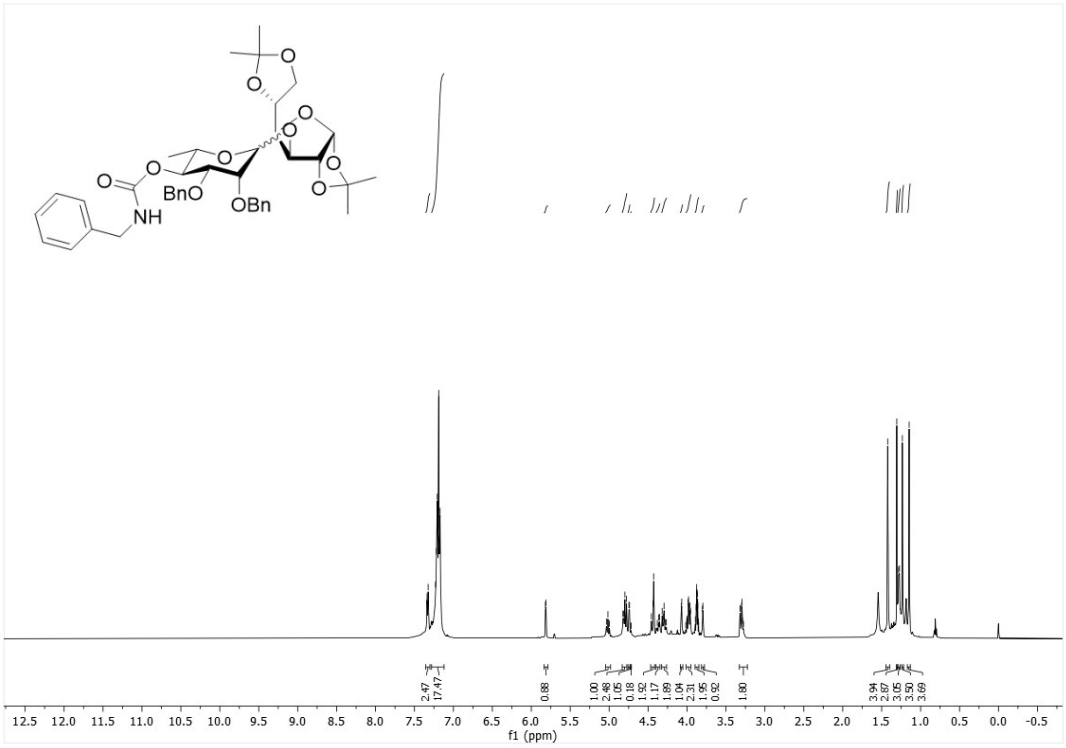


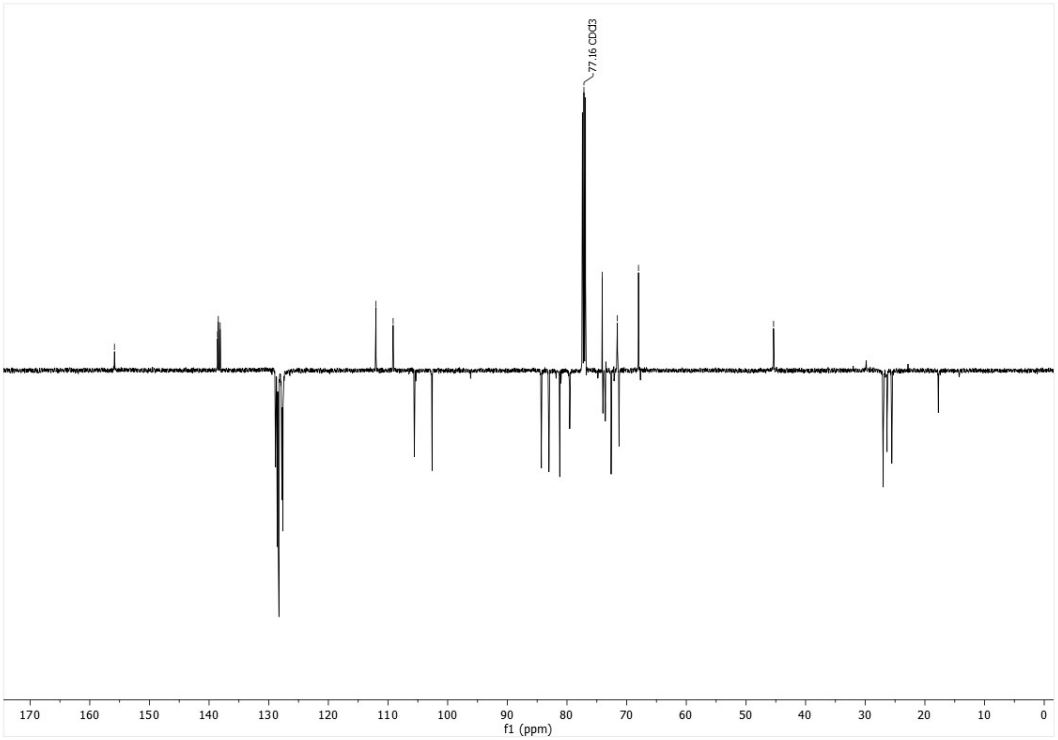


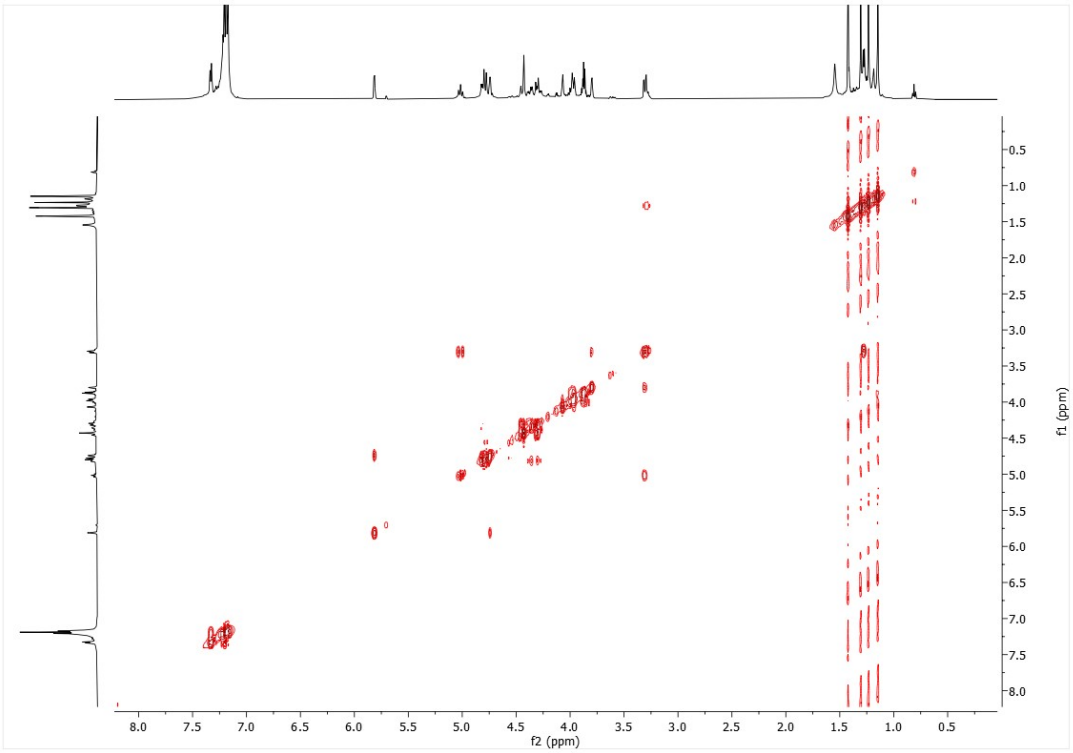

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

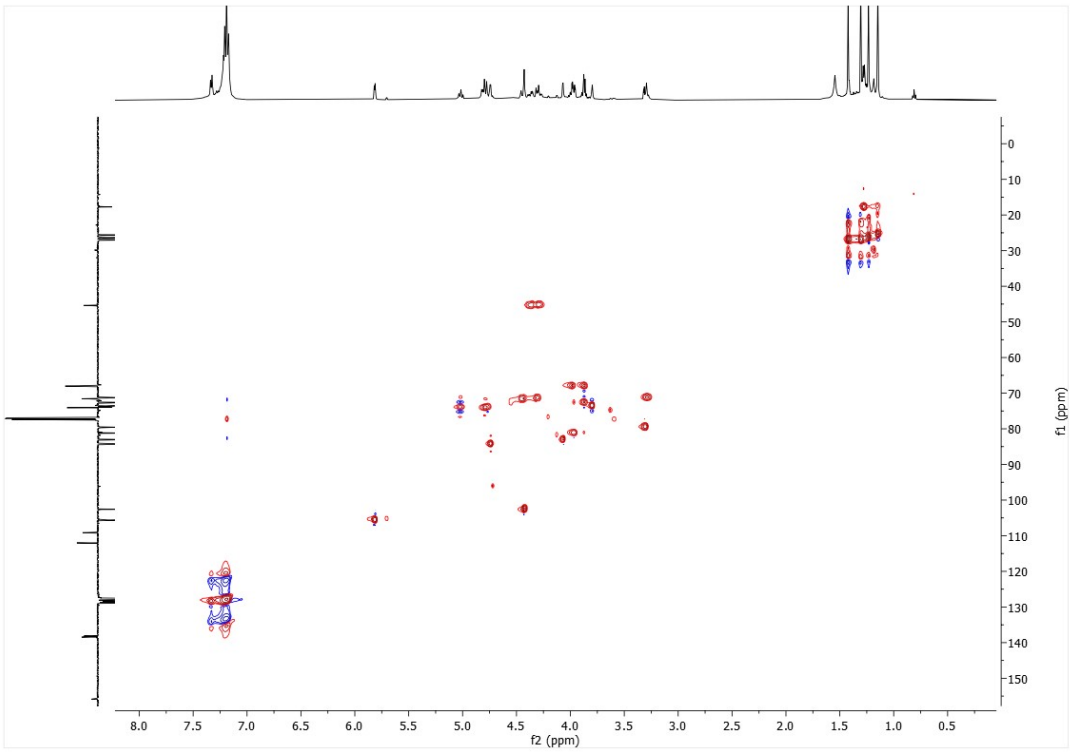

{7.26,77.16}CDCl3
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)

1,2:3,4-di-*O*-isopropylidene-α-D-glucofuranose-(3-1)-2,3-di-*O*-benzyl-4-*O*-benzylcarbamoyl-α/β-L-rhamnopyranoside (SI13) ($CDCl_3$)

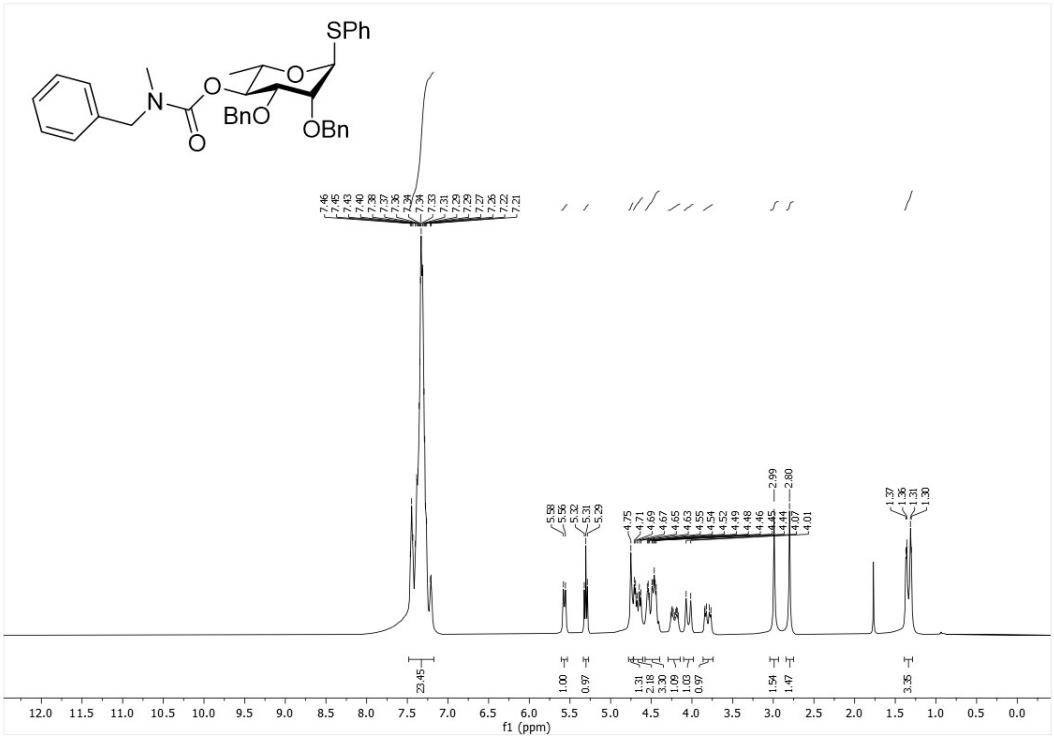


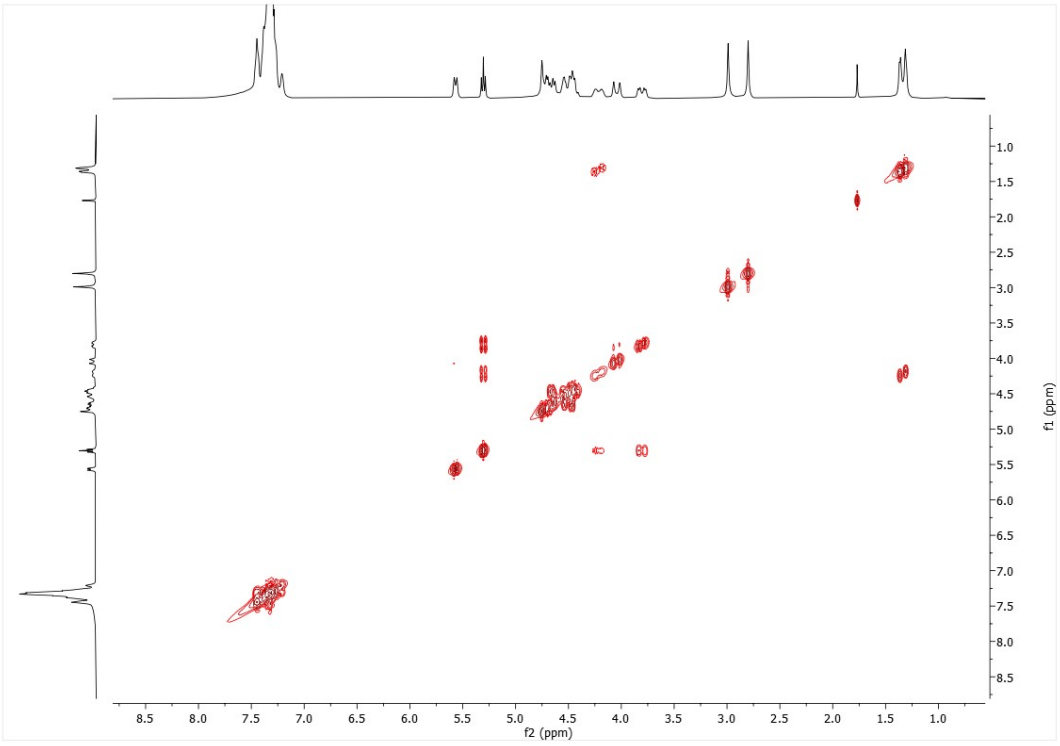


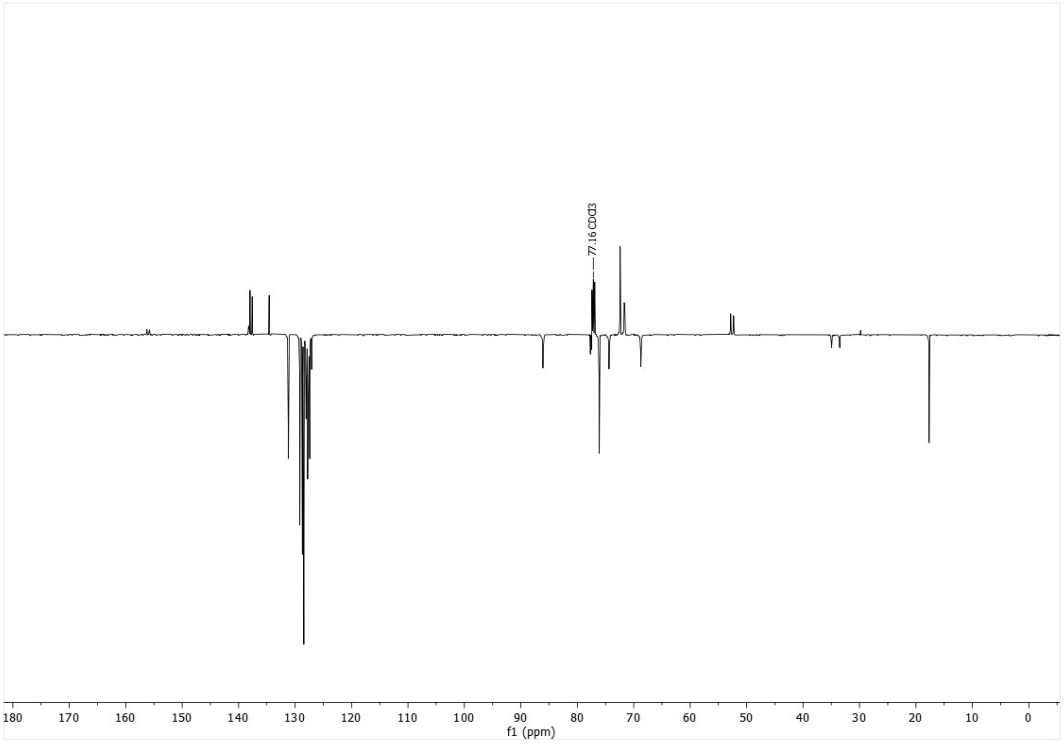

f2 (ppm)
f1 (ppm)

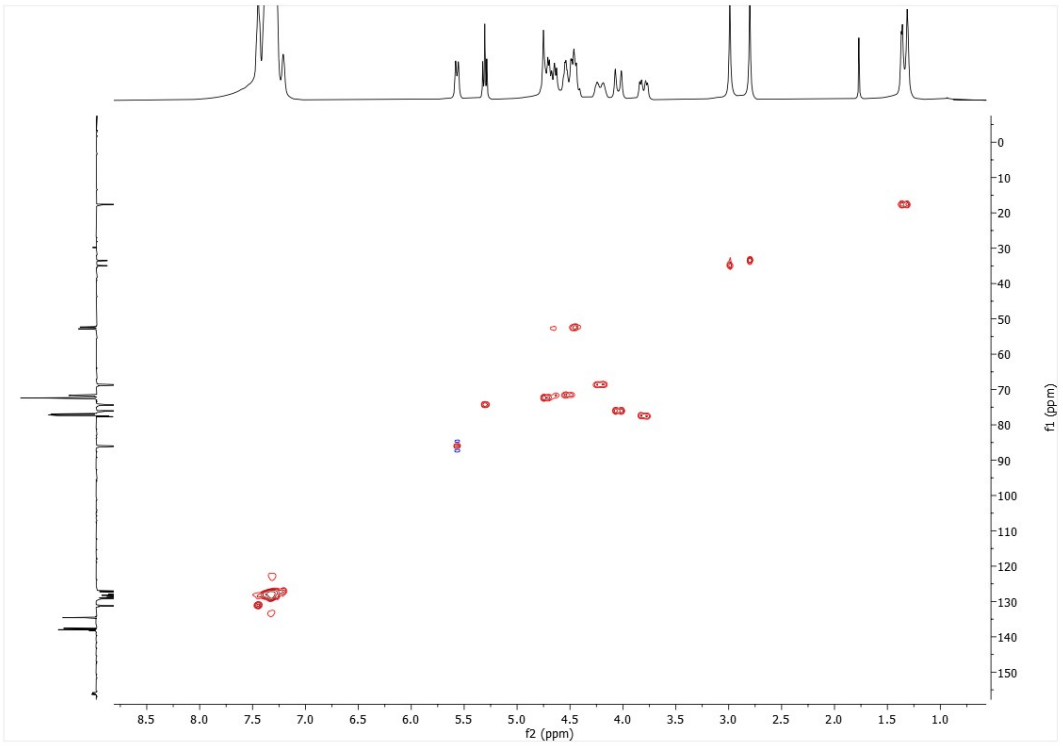

f2 (ppm)
f1 (ppm)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*N*-benzyl-*N*-methylcarbamoyl)-1-thio-α-L-rhamnopyranoside (13) ($CDCl_3$)

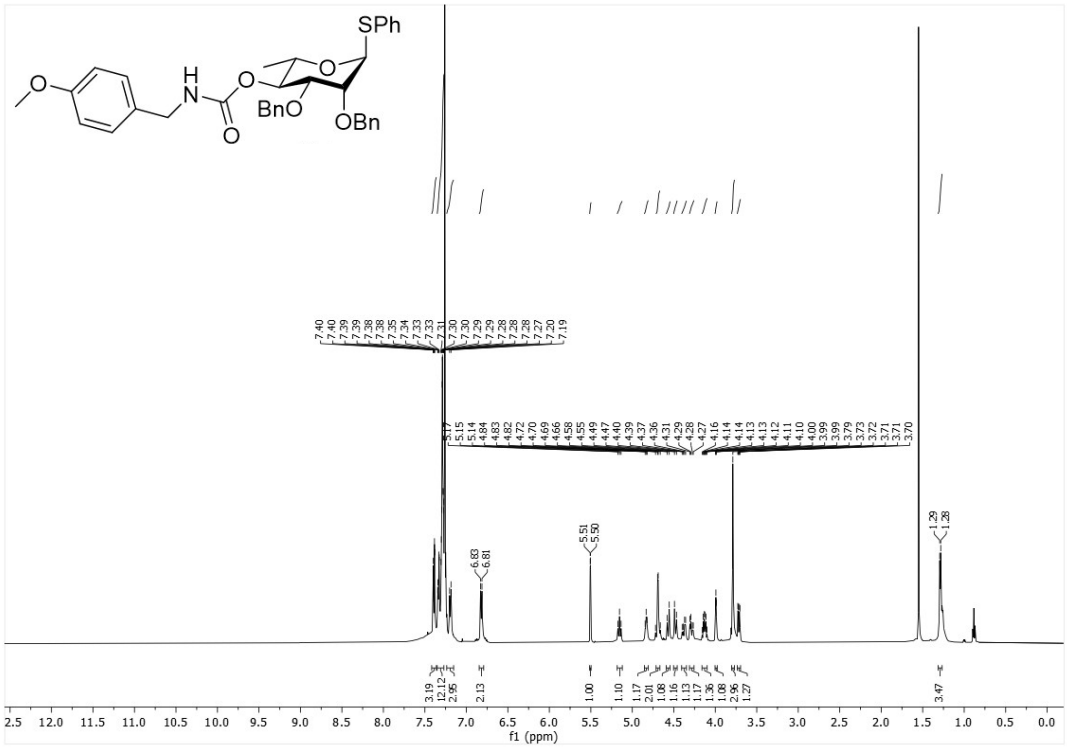


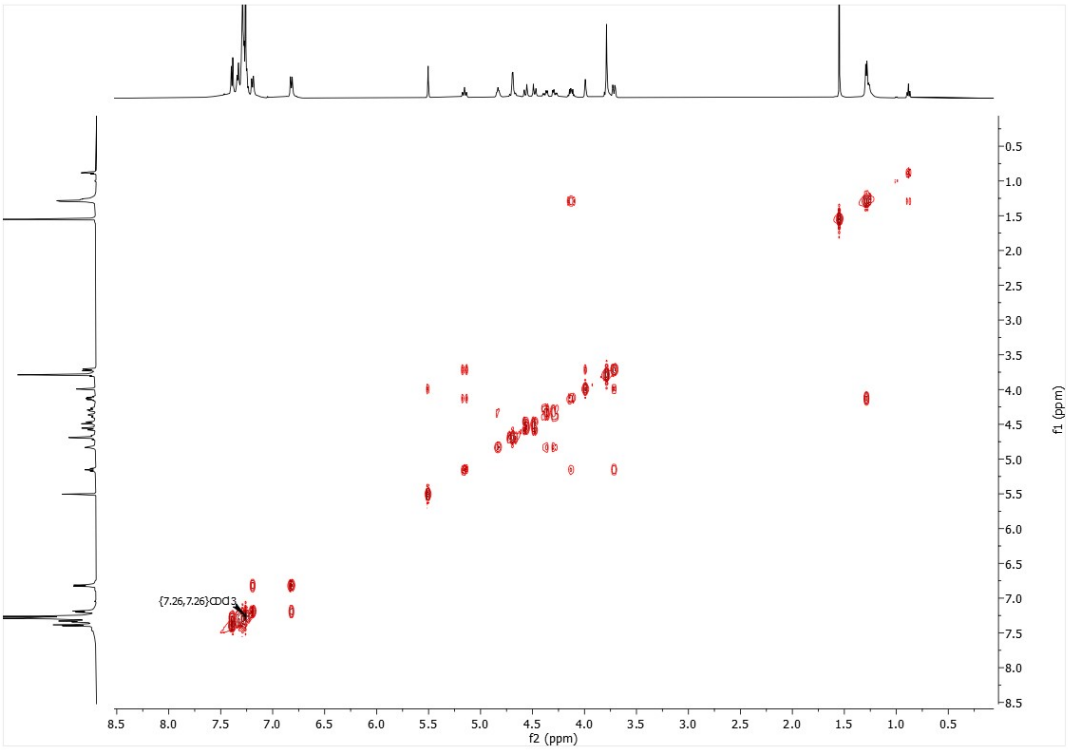


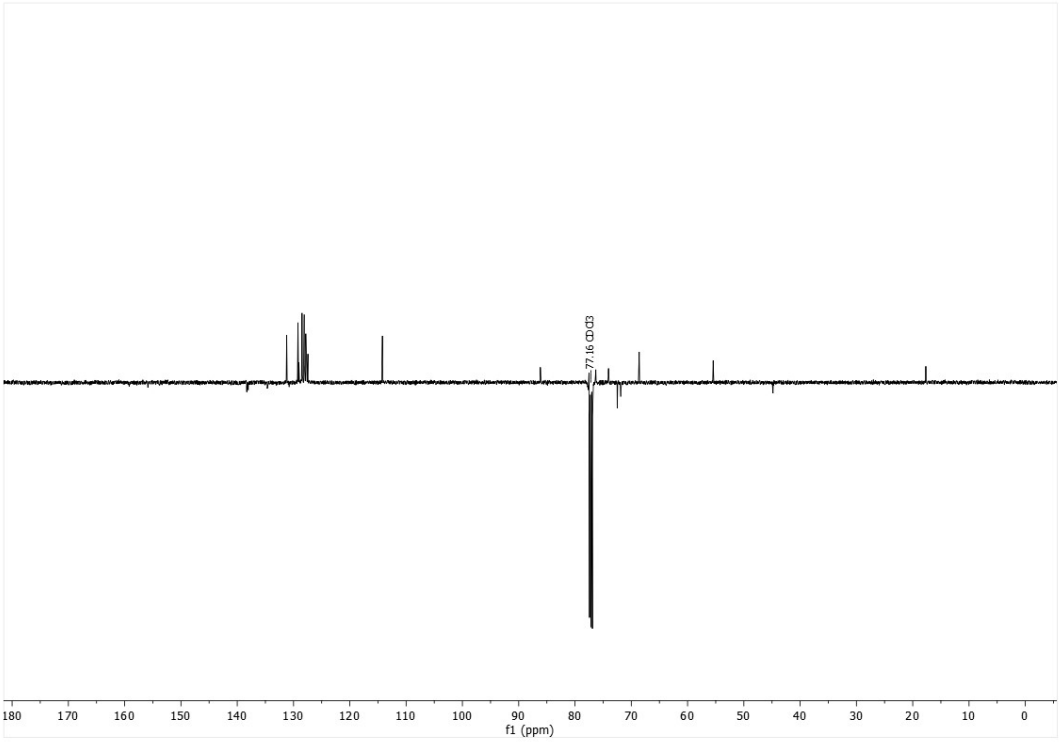

77.16 CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

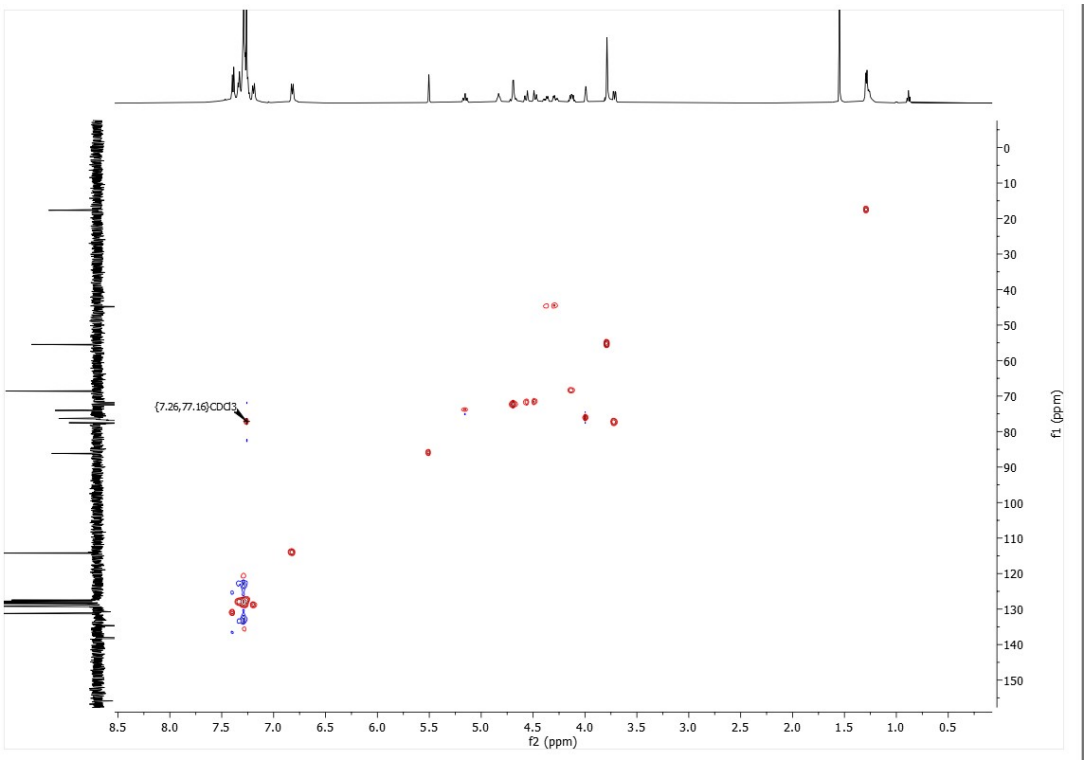

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f2 (ppm)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzylcarbamoyl)-1-thio-α-L-rhamnopyranoside (14) ($CDCl_3$)

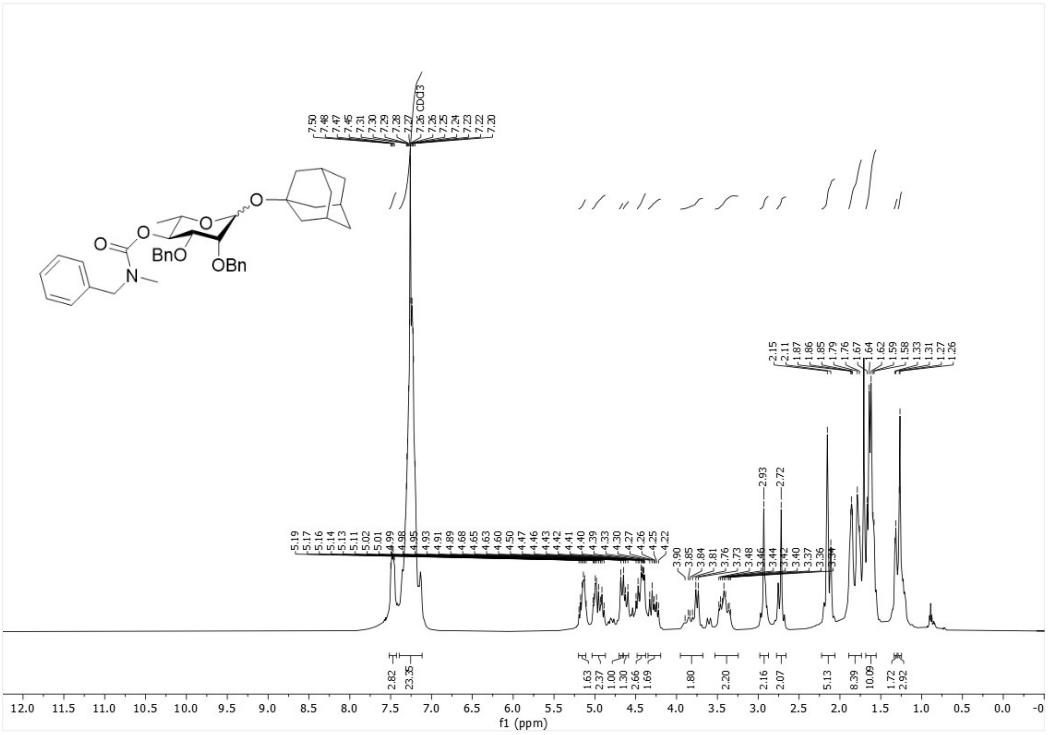


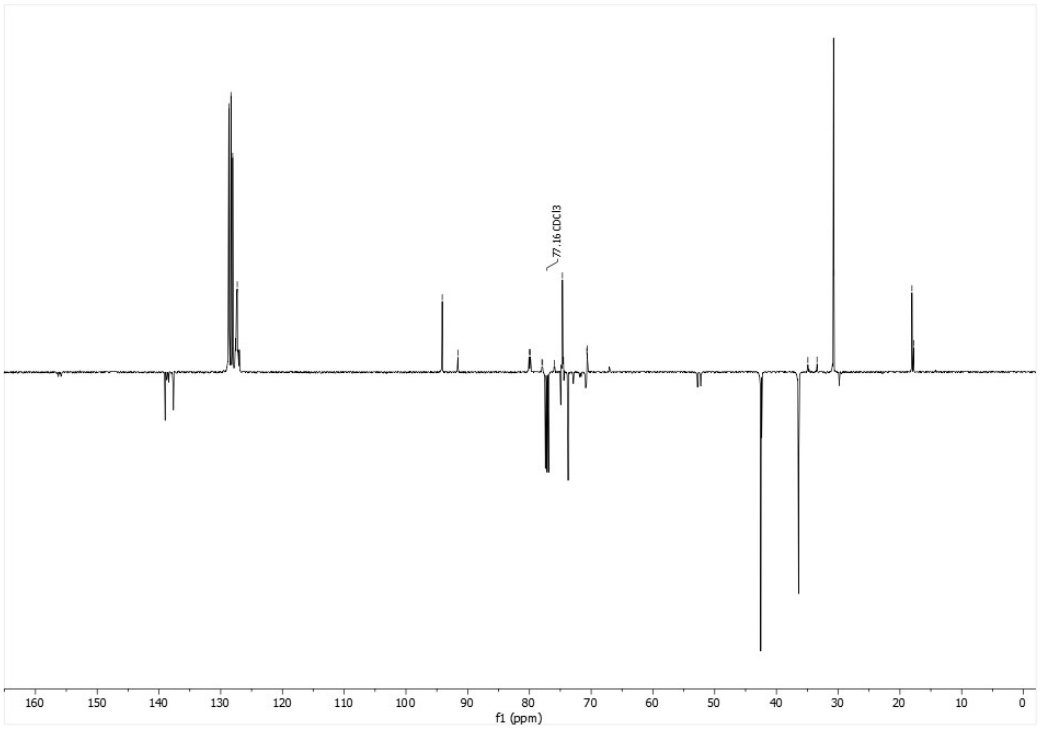


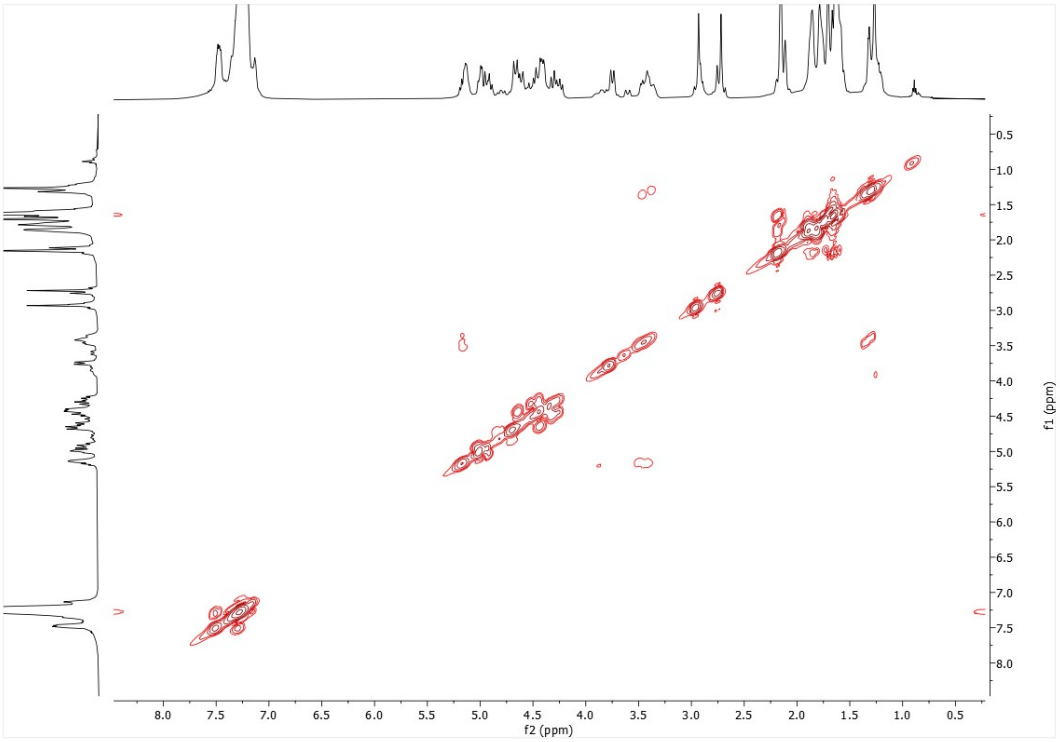

77.16 CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

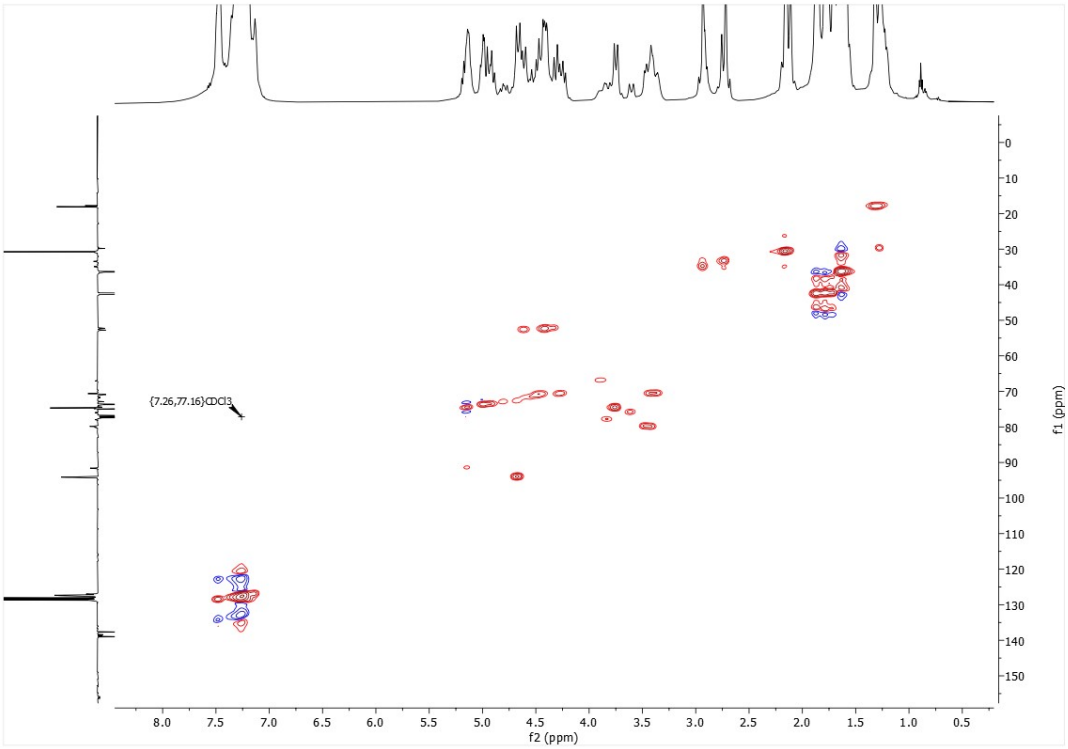

{7.26,77.16}CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)

1-Adamantyl 2,3-di-*O*-benzyl-4-*O*-(*N*-benzyl-*N*-methylcarbamoyl)-1-thio-α/β-L-rhamnopyranoside (SI14) ($CDCl_3$)

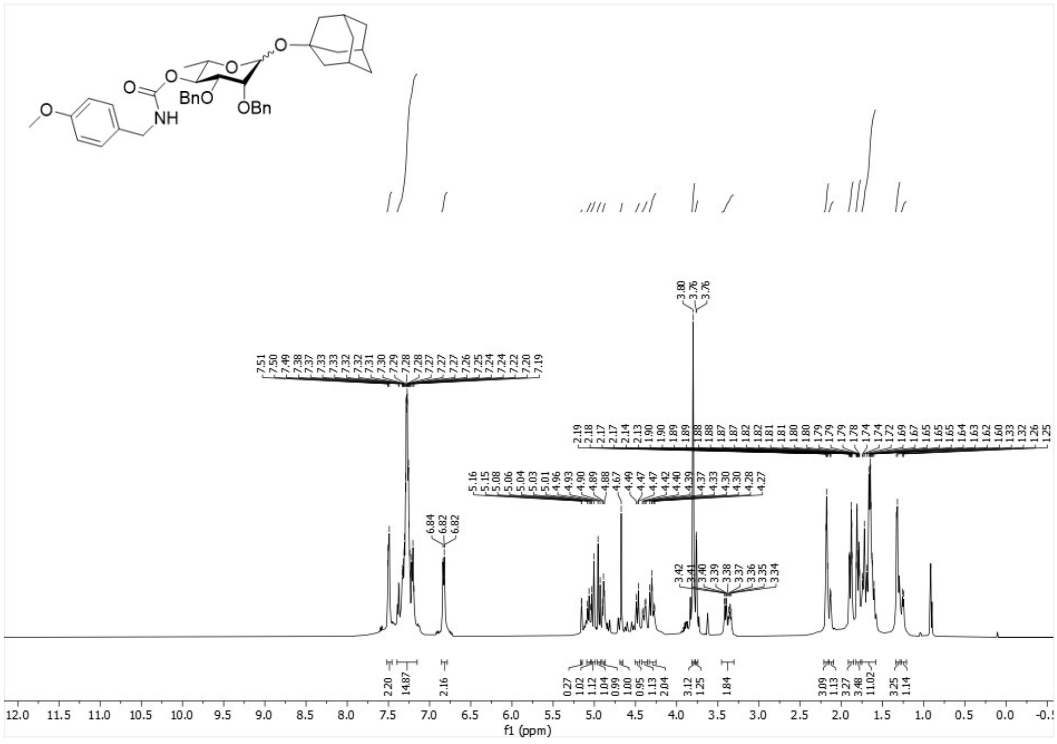


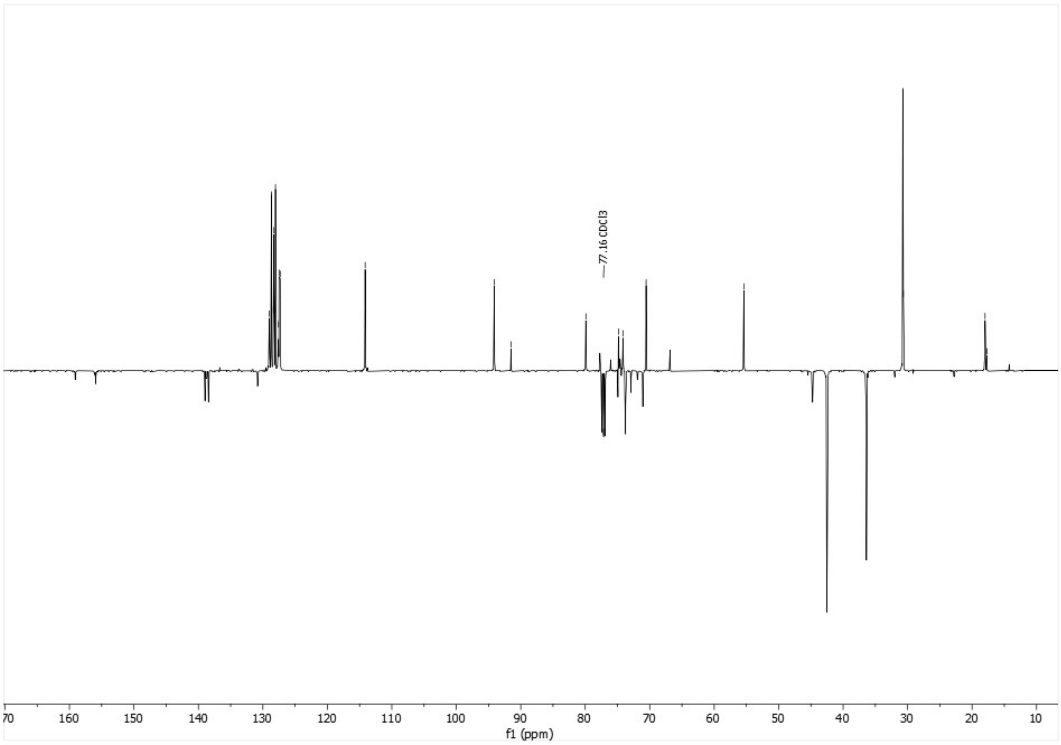


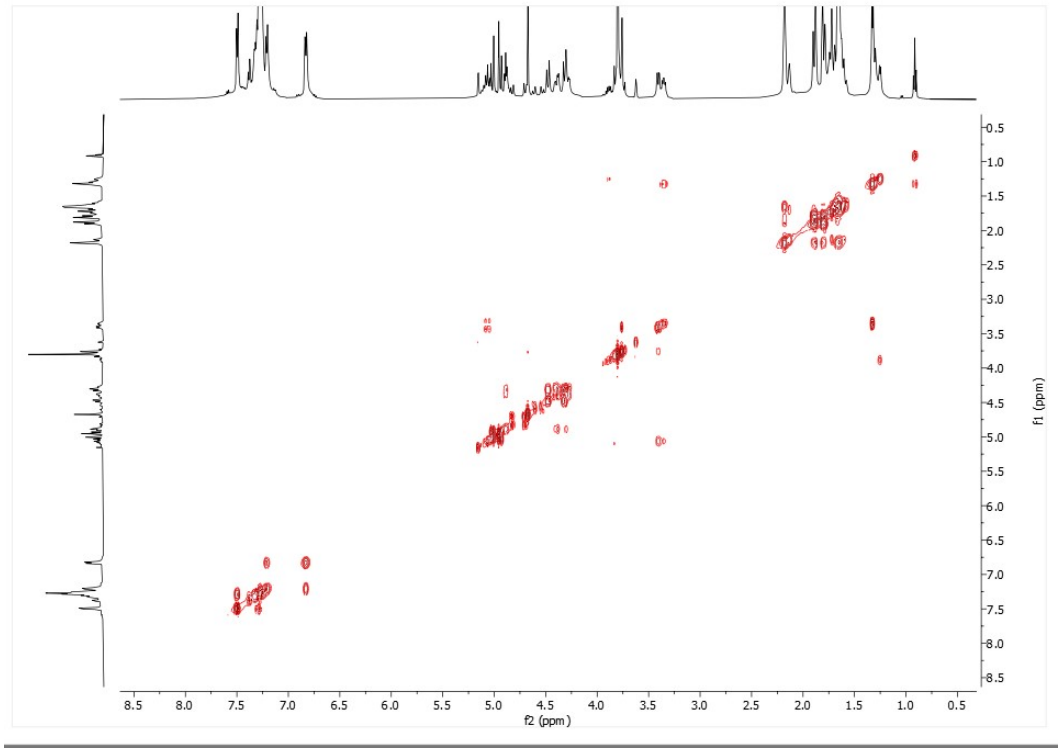

f2 (ppm)
f1 (ppm)

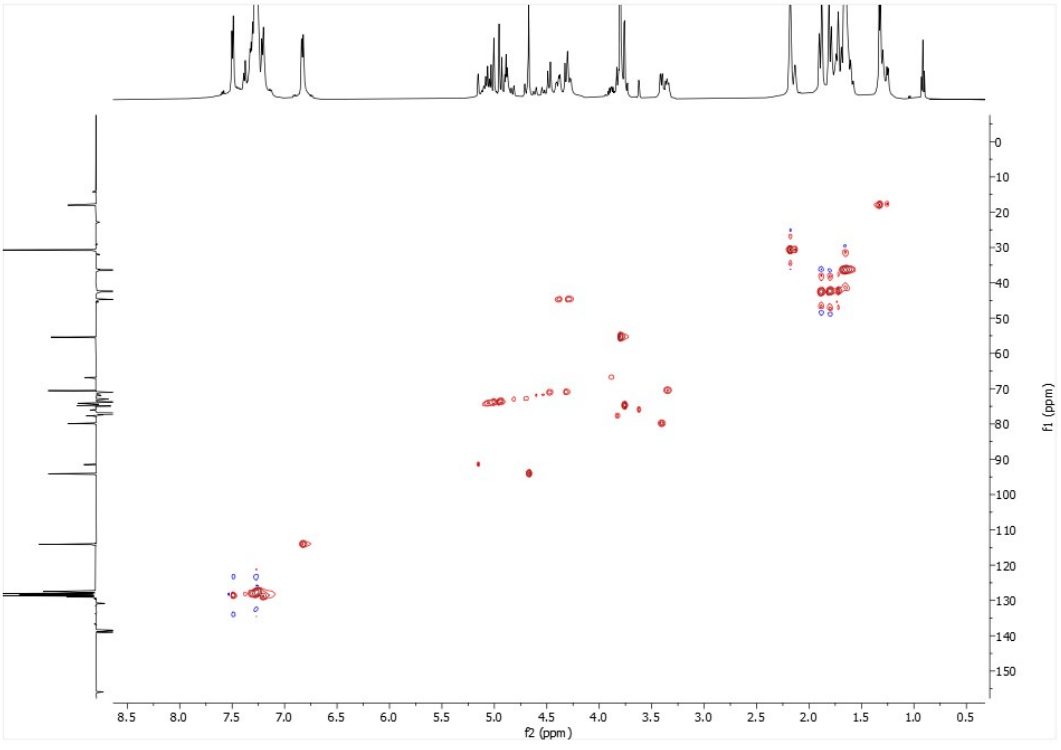

{7.26,77.16}CDCl3
f2 (ppm)
f1 (ppm)

1-Adamantyl 2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzylcarbamoyl)-1-thio-α/β-L-rhamnopyranoside (SI15) ($CDCl_3$)






f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)

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