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One-pot Synthesis of D-Glucosamine and Chitobiosyl Building Blocks Catalyzed by Triflic Acid on Molecular Sieves

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Supporting Information

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General information

Unless otherwise stated, all reactions were carried out under argon. Dry dichloromethane and acetonitrile were dried from a safe purification system containing activated Al_2O_3 (Glass Technology GT S100). Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F_{254} plates and visualized under UV (254 nm) and/or by staining with 5% sulfuric acid or orcinol. Silica gel SDS 60 ACC 35-70 mm was used for column chromatography. NMR spectra were recorded on Bruker DPX 250, AV300 and AV360 NMR spectrometers at 20ºC. Chemical shifts (in ppm) were determined relative to residual non-deuterated solvent as an internal reference. Coupling constant(s) in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: br (broad), s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). Mass spectra (Positive mode ESI) on a MicrOTOFq Mass Spectrometer were obtained by the analytical services of our Institute. Optical rotations were measured on a Perkin Elmer 341 Polarimeter (*c* in g / 100 mL).

General procedure for persilylation[1]

To a suspension of substrate in dry CH_2Cl_2 (c = 0.2 M) were successively added hexamethyldisilazane (2 equiv) and trimethylsilyl trifluoromethanesulfonate (10 mol%). The mixture was stirred at room temperature until completion and then diluted in hexanes. The organic phase was washed with water. The aqueous phase was extracted twice with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The persilylated compounds were used without further purification.

Phenyl 2-deoxy-2-trifluoroacetamido-3,4,6-tri-*O*-trimethylsilyl-1-thio-β-D-glucopyranoside 1a: From **1** (0.140 g, 0.381 mmol); reaction time: 1h30. **1a** (0.199 g, 89%) as a white amorphous solid; $[\alpha]^{22}_D$ -6.0 (*c* 1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.55-7.52 (m, 2H, 2H-Ar), 7.32-7.29 (m, 3H, 3H-Ar), 7.07 (d, J = 7.9 Hz, 1H, NH), 5.03 (d, $J_{1,2}$ = 7.3 Hz, 1H, H-1), 4.07 (dd, $J_{6a,6b}$ = 10.8 Hz, $J_{6a,5}$ = 5.1 Hz, 1H, H-6a), 3.98-3.75 (m, 4H, H-2, H-3, H-4 and H-6b), 3.61-3.54 (m, 1H, H-5), 0.20 (s, 9H, $Si(CH_3)_3$), 0.18 (s, 9H, $Si(CH_3)_3$), 0.17 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 134.8, 131.8, 128.9, 127.6

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(6C, 6C-Ar), 84.7 (C-1), 81.1 (C-5), 73.7 (C-3), 70.2 (C-4), 62.3 (C-6), 55.1 (C-2), 0.3 ($Si(\underline{C}H_3)_3$), 0.2 ($Si(\underline{C}H_3)_3$), -0.4 ($Si(\underline{C}H_3)_3$); ESI HRMS for $C_{23}H_{40}F_3NNaO_5Si_3$ $[M+Na]^+$: calcd 606.1779, found 606.1791.

Phenyl 2-deoxy-2-trichloroacetamido-3,4,6-tri-*O*-trimethylsilyl-1-thio-β-D-glucopyranoside 2a: From **2** (0.187 g, 0.449 mmol); reaction time: 2h. **2a** (0.252 g, 89%) as a white amorphous solid; $[\alpha]^{22}_D$ +51.6 (*c* 0.31, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2H, 2H-Ar), 7.43 (d, J = 8.2 Hz, 1H, NH), 7.35-7.29 (m, 3H, 3H-Ar), 5.09 (d, $J_{1,2}$ = 7.2 Hz, 1H, H-1), 4.08 (dd, $J_{6a,6b}$ = 10.4 Hz, $J_{6a,5}$ = 5.7 Hz, 1H, H-6a), 3.95-3.78 (m, 4H, H-2, H-3, H-4 and H-6b), 3.62-3.56 (m, 1H, H-5), 0.20 (s, 18H, $2Si(CH_3)_3$), 0.17 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 161.3 ($NH\underline{C}$=O), 134.9, 132.1, 129.0, 127.7 (6C, 6C-Ar), 84.7 (C-1), 81.2 (C-5), 73.5 (C-4), 70.2 (C-3), 62.5 (C-6), 56.3 (C-2), 0.4 (2C, $2Si(\underline{C}H_3)_3$), -0.4 ($Si(\underline{C}H_3)_3$); ESI HRMS for $C_{23}H_{40}Cl_3NNaO_5SSi_3$ $[M+Na]^+$: calcd 654.0893, found 654.0897.

Phenyl 2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-3,4,6-tri-*O*-trimethylsilyl-1-thio-β-D-glucopyranoside 3a: From **3** (0.109 g, 0.245 mmol); reaction time: 1h. **3a** (0.150 g, 93%) as a white foam; $[\alpha]^{22}_D$ -4.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.57-7.53 (m, 2H, 2H-Ar), 7.36-7.26 (m, 3H, 3H-Ar), 5.16 (d, J = 9.1 Hz, 1H, NH), 4.94 (d, $J_{1,2}$ = 9.9 Hz, 1H, H-1), 4.79 (d, J = 12.0 Hz, 1H, $CHCCl_3$), 4.75 (d, J = 12.0 Hz, 1H, $CHCCl_3$), 3.89 (dd, $J_{6a,6b}$ = 11.3 Hz, $J_{6a,5}$ = 2.8 Hz, 1H, H-6a), 3.82-3.75 (m, 2H, H-3 and H-6b), 3.67 (dd, $J_{4,3}$ = $J_{4,5}$ = 7.9 Hz, 1H, H-4), 3.47 (m, 1H, H-2), 3.36 (m, 1H, H-5), 0.20 (s, 9H, $Si(CH_3)_3$), 0.17 (s, 9H, $Si(CH_3)_3$), 0.14 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8 ($NH\underline{C}$=O), 133.9, 131.9, 128.8, 127.4 (6C, 6C-Ar), 95.3 ($CH_2\underline{C}Cl_3$), 86.2 (C-1), 80.9 (C-5), 76.7 (C-3), 74.7 ($\underline{C}H_2CCl_3$), 71.6 (C-4), 62.1 (C-6), 57.5 (C-2), 0.8 ($Si(\underline{C}H_3)_3$), 0.7 ($Si(\underline{C}H_3)_3$), -0.2 ($Si(\underline{C}H_3)_3$); ESI HRMS for $C_{24}H_{42}Cl_3NNaO_6SSi_3$ $[M+Na]^+$: calcd 684.0998, found 684.1004.

Phenyl 2-allyloxycarbonylamino-2-deoxy-3,4,6-tri-*O*-trimethylsilyl-1-thio-β-D-glucopyranoside 4a: From **4** (0.059 g, 0.166 mmol); reaction time: 2h. **4a** (0.085 g, 90%) as a white foam; $[\alpha]^{22}_D$ -7.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H, 2H-Ar), 7.39-7.27 (m, 3H, 3H-Ar), 5.99-5.88 (m, 1H, $CH_2C\underline{H}$=CH_2), 5.35 (dd, J_{trans} = 17.4 Hz, J = 1.4 Hz, 1H, CH_2CH=$C\underline{H}_2$), 5.23 (d, J_{cis} = 10.5 Hz, 1H, CH_2CH=$C\underline{H}_2$), 4.95 (d, $J_{1,2}$ = 10.0 Hz, 1H, H-1), 4.85 (d, J = 9.1 Hz, 1H, NH), 4.60 (m, 2H, $C\underline{H}_2CH$=CH_2), 3.87-3.72 (m, 3H, H-3, H-6a and H-6b), 3.61 (dd, $J_{4,3}$ = $J_{4,5}$ = 8.2 Hz, 1H, H-4), 3.38-3.29 (m, 1H, H-5),

0.17 (s, 9H, $Si(CH_3)_3$), 0.15 (s, 9H, $Si(CH_3)_3$), 0.14 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 155.4 ($NH\underline{C}=O$), 132.8 ($CH_2\underline{C}H=CH_2$), 131.9, 128.8, 127.3 (6C, 6C-Ar), 117.8 ($CH_2CH=\underline{C}H_2$), 89.1 (C-1), 80.9 (C-5), 77.2 (C-3), 71.8 (C-4), 65.7 ($\underline{C}H_2CH=CH_2$), 62.1 (C-6), 57.5 (C-2), 0.8 ($Si(\underline{C}H_3)_3$), 0.7 ($Si(\underline{C}H_3)_3$), -0.2 ($Si(\underline{C}H_3)_3$); ESI HRMS for $C_{25}H_{45}NNaO_6SSi_3$ $[M+Na]^+$: calcd 594.2168, found 594.2164.

(2-Methyl-5-*tert*-butylphenyl) 2-deoxy-2-trifluoroacetamido-3,4,6-tri-*O*-trimethylsilyl-1-thio-β-D-glucopyranoside 5a: From **5** (1.16 g, 2.65 mmol); reaction time: 17h. **5a** (1.68 g, 97%) as a white amorphous solid; $[\alpha]^{22}_D$ -14.2 (*c* 1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.9 Hz, 1H, H-Ar), 7.22 (dd, *J* = 1.9 Hz, *J* = 7.9 Hz, 1H, H-Ar), 7.13 (d, *J* = 7.9 Hz, 1H, H-Ar), 6.87 (d, *J* = 8.3 Hz, 1H, NH), 4.95 (d, $J_{1,2}$ = 8.4 Hz, 1H, H-1), 4.05-3.76 (m, 5H, H-2, H-3, H-4, H-6a and H-6b), 3.53-3.50 (m, 1H, H-5), 2.35 (s, 3H, CH_3), 1.32 (s, 9H, $C(\underline{C}H_3)_3$), 0.20 (s, 9H, $Si(CH_3)_3$), 0.18 (s, 9H, $Si(CH_3)_3$), 0.16 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 135.8, 132.9, 129.9, 128.7, 124.7 (6C, 6C-Ar), 85.8 (C-1), 81.0 (C-5), 74.5 (C-3 or C-4), 70.5 (C-3 or C-4), 62.3 (C-6), 55.8 (C-2), 31.3 ($C(\underline{C}H_3)_3$), 20.2 (CH_3), 0.5 ($Si(\underline{C}H_3)_3$), 0.3 ($Si(\underline{C}H_3)_3$), 0.2 ($Si(\underline{C}H_3)_3$); ESI HRMS for $C_{28}H_{50}F_3NNaO_5Si_3$ $[M+Na]^+$: calcd 676.2562, found 676.2574.

(2-Methyl-5-*tert*-butylphenyl) 2-deoxy-2-trichloroacetamido-3,4,6-tri-*O*-trimethylsilyl-1-thio-β-D-glucopyranoside 6a: From **6** (2.05 g, 4.21 mmol); reaction time: 2h. **6a** (2.86 g, 97%) as a white amorphous solid; $[\alpha]^{22}_D$ -12.7 (*c* 1, $CHCl_3$); ^1H NMR (360 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.3 Hz, 1H, H-Ar), 7.37 (d, *J* = 8.6 Hz, 1H, NH), 7.23 (dd, *J* = 2.3 Hz, *J* = 8.2 Hz, 1H, H-Ar), 7.14 (d, *J* = 8.2 Hz, 1H, H-Ar), 5.02 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1), 4.06 (dd, $J_{6a,6b}$ = 10.9 Hz, $J_{6a,5}$ = 5.9 Hz, 1H, H-6a), 4.03-3.97 (m, 1H, H-2), 3.93-3.84 (m, 3H, H-3, H-4 and H-6b), 3.61 (dd, $J_{5,4}$ = 9.6 Hz, 1H, H-5), 2.40 (s, 3H, CH_3), 1.35 (s, 9H, $C(\underline{C}H_3)_3$), 0.23 (s, 9H, $Si(CH_3)_3$), 0.22 (s, 9H, $Si(CH_3)_3$), 0.17 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 161.7 ($NH\underline{C}=O$), 149.9, 136.6, 134.5, 130.2, 129.1, 124.9 (6C, 6C-Ar), 85.7 (C-1), 81.6 (C-5), 74.6 (C-3 or C-4), 70.6 (C-3 or C-4), 62.9 (C-6), 57.1 (C-2), 34.8 ($\underline{C}(CH_3)_3$), 31.7 ($C(\underline{C}H_3)_3$), 20.7 (CH_3), 0.9 ($Si(\underline{C}H_3)_3$), 0.7 ($Si(\underline{C}H_3)_3$), 0.0 ($Si(\underline{C}H_3)_3$); ESI HRMS for $C_{28}H_{50}Cl_3NNaO_5SSi_3$ $[M+Na]^+$: calcd 724.1675, found 724.1672.

(2-Methyl-5-*tert*-butylphenyl) 2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-3,4,6-tri-*O*-trimethylsilyl-1-thio-β-D-glucopyranoside 7a: From **7** (0.450 g, 0.872 mmol); reaction time: 2h. **7a** (0.614 g, 96%) as a white foam; $[\alpha]^{22}_D$ +3.2 (*c* 1, $CHCl_3$); ^1H NMR (300

MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.9 Hz, 1H, H-Ar), 7.20 (dd, *J* = 1.9 Hz, *J* = 7.9 Hz, 1H, H-Ar), 7.11 (d, *J* = 7.9 Hz, 1H, H-Ar), 5.06 (d, *J* = 9.0 Hz, 1H, NH), 4.87 (d, $J_{1,2}$ = 10.1 Hz, 1H, H-1), 4.80 (d, *J* = 12.1 Hz, 1H, $CHCCl_3$), 4.70 (d, *J* = 12.1 Hz, 1H, $CHCCl_3$), 3.86-3.70 (m, 4H, H-3, H-4, H-6a and H-6b), 3.54-3.45 (m, 1H, H-2), 3.33 – 3.28 (m, 1H, H-5), 2.35 (s, 3H, CH_3), 1.32 (s, 9H, $C(C\underline{H}_3)_3$), 0.20 (s, 9H, $Si(CH_3)_3$), 0.17 (s, 9H, $Si(CH_3)_3$), 0.14 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8 ($NH\underline{C}$=O), 149.5, 136.1, 133.8, 129.8, 128.5, 124.4 (6C, 6C-Ar), 95.2 ($CH_2\underline{C}Cl_3$), 87.1 (C-1), 80.8 (C-5), 76.7 (C-3), 74.8 ($\underline{C}H_2CCl_3$), 71.4 (C-4), 62.0 (C-6), 57.7 (C-2), 34.5 ($\underline{C}(CH_3)_3$), 31.4 ($C(\underline{C}H_3)_3$), 20.3 (CH_3), 0.9 ($Si(\underline{C}H_3)_3$), 0.7 ($Si(\underline{C}H_3)_3$), -0.1 ($Si(\underline{C}H_3)_3$); ESI HRMS for $C_{29}H_{52}Cl_3NNaO_6SSi_3$ $[M+Na]^+$: calcd 754.1781, found 754.1808.

(2-Methyl-5-*tert*-butylphenyl) 2-allyloxycarbonylamino-2-deoxy-3,4,6-tri-*O*-trimethylsilyl-1-thio-β-D-glucopyranoside 8a: From **8** (1.29 g, 3.03 mmol); reaction time: 1h30. **8a** (1.89 g, 97%) as a white foam; $[\alpha]^{22}_D$ +3.0 (*c* 1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.63 (d, *J* = 1.9 Hz, 1H, H-Ar), 7.20 (dd, *J* = 1.9 Hz, *J* = 7.9 Hz, 1H, H-Ar), 7.12 (d, *J* = 7.9 Hz, 1H, H-Ar), 6.02-5.87 (m, 1H, $CH_2C\underline{H}=CH_2$), 5.32 (dd, J_{trans} = 17.3 Hz, *J* = 1.3 Hz, 1H, $CH_2CH=C\underline{H}_2$), 5.20 (dd, J_{cis} = 10.3 Hz, *J* = 1.3 Hz, 1H, $CH_2CH=C\underline{H}_2$), 4.89 (d, $J_{1,2}$ = 10.1 Hz, 1H, H-1), 4.83 (d, *J* = 9.1 Hz, 1H, NH), 4.67-4.54 (m, 2H, $C\underline{H}_2CH=CH_2$), 4.05-3.76 (m, 5H, H-2, H-3, H-4, H-6a and H-6b), 3.53-3.50 (m, 1H, H-5), 2.35 (s, 3H, CH_3), 1.32 (s, 9H, $C(C\underline{H}_3)_3$), 0.20 (s, 9H, $Si(CH_3)_3$), 0.18 (s, 9H, $Si(CH_3)_3$), 0.16 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 155.5 ($NH\underline{C}$=O), 149.5, 136.3 (2C, C-Ar), 134.0 ($CH_2\underline{C}H=CH_2$), 132.9, 129.8, 129.0, 124.5 (4C, C Ar), 117.9 ($CH_2CH=\underline{C}H_2$), 87.3 (C-1), 80.7 (C-5), 77.0 (C-3), 71.6 (C-4), 65.7 ($\underline{C}H_2CH=CH_2$), 62.1 (C-6), 57.7 (C-2), 31.4 ($C(\underline{C}H_3)_3$), 20.3 (CH_3), 0.9 ($Si(\underline{C}H_3)_3$), 0.7 ($Si(\underline{C}H_3)_3$), -0.1 ($Si(\underline{C}H_3)_3$); ESI HRMS for $C_{30}H_{55}NNaO_6SSi_3$ $[M+Na]^+$: calcd 664.2950, found 664.2934.

(2-Methyl-5-*tert*-butylphenyl) 2-deoxy-2-methoxycarbonylamino-3,4,6-tri-*O*-trimethylsilyl-1-thio-β-D-glucopyranoside 9a: From **9** (1.10 g, 2.75 mmol) with 3 equiv of HMDS; reaction time: 6h30. **9a** (1.65 g, 97%) as a white foam; $[\alpha]^{22}_D$ +4.0 (*c* 1, $CHCl_3$); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.65 (d, *J* = 1.9 Hz, 1H, H-Ar), 7.24 (dd, *J* = 1.9 Hz, *J* = 7.9 Hz, 1H, H-Ar), 7.15 (d, *J* = 7.9 Hz, 1H, H-Ar), 6.55 (d, *J* = 9.8 Hz, 1H, NH), 4.86 (d, $J_{1,2}$ = 10.5 Hz, 1H, H-1), 3.90 (m, 2H, H-6a and H-6b), 3.83-3.71 (m, 2H, H-3 and H-4), 3.67 (s, 3H, CH_3), 3.63-3.53 (m, 1H, H-2), 3.29-3.24 (m, 1H, H-5), 2.33 (s, 3H, CH_3), 1.35 (s, 9H, $C(C\underline{H}_3)_3$), 0.23 (s, 9H, $Si(CH_3)_3$), 0.18 (s, 9H, $Si(CH_3)_3$), 0.17 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (90

MHz, $(CD_3)_2CO$) δ 158.3 (NH<u>C</u>=O), 151.0, 137.0 , 136.1, 131.3, 129.4, 125.6 (6C, 6C-Ar), 89.8 (C-1), 82.0 (C-5), 79.6 (C-3), 73.3 (C-4), 63.6 (C-6), 59.2 (C-2), 52.8 (CH_3), 35.8 ($\underline{C}(CH_3)_3$), 32.5 ($C(\underline{C}H_3)_3$), 21.0 (CH_3), 1.9 ($Si(\underline{C}H_3)_3$), 1.8 ($Si(\underline{C}H_3)_3$), 1.0 ($Si(\underline{C}H_3)_3$); ESI HRMS for $C_{28}H_{53}NNaO_6SSi_3$ $[M+Na]^+$: calcd 638.2794, found 638.2828.

Methyl 2-deoxy-2-trifluoroacetamido-3,4,6-tri-*O*-trimethylsilyl-α-D-glucopyranoside 10a: From **10** (0.400 g, 1.39 mmol) with 3.5 equiv of HMDS; reaction time: 24h. **10a** (0.668 g, 95%) as a white amorphous solid; $[\alpha]^{22}_D$ +56.2 (*c* 0.45, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.40 (d, J = 8.3 Hz, 1H, NH), 4.64 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-1), 4.08 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H-2), 3.77-3.72 (m, 3H, H-3, H-6a and H-6b), 3.62 (dd, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.54-3.50 (m, 1H, H-5), 3.37 (s, 3H, CH_3), 0.19 (s, 9H, $Si(CH_3)_3$), 0.14 (s, 9H, $Si(CH_3)_3$), 0.13 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 97.7 (C-1), 73.5 (C-3), 73.2 (C-5), 71.8 (C-4), 61.7 (C-6), 54.9 (C-2), 54.4 (CH_3), 0.8 (2C, $2Si(\underline{C}H_3)_3$), -0.3 ($Si(\underline{C}H_3)_3$); ESI HRMS for $C_{18}H_{38}F_3NNaO_6Si_3$ $[M+Na]^+$: calcd 528.1851, found 528.1845.

***tert*-Butyldimethylsilyl 2-deoxy-2-trifluoroacetamido-3,4,6-tri-*O*-trimethylsilyl-β-D-glucopyranoside 11a:** From **11** (1.07 g, 2.75 mmol); reaction time: 3h30. **11a** (1.60 g, 96%) as a white amorphous solid; $[\alpha]^{22}_D$ -2.4 (*c* 0.38, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.72 (d, J = 8.6 Hz, 1H, NH), 4.91 (d, $J_{1,2}$ = 5.5 Hz, 1H, H-1), 3.94 (dd, $J_{6a,6b}$ = 10.9 Hz, $J_{6a,5}$ = 4.5 Hz, 1H, H-6a), 3.82 (dd, $J_{3,2}$ = $J_{3,4}$ = 7.6 Hz, 1H, H-3), 3.76-3.72 (m, 2H, H-4 and H-6b), 3.63 (m,1, H-2), 3.39 (m, 1H, H-5), 0.91 (s, 9H, $C(C\underline{H}_3)_3$), 0.20 (s, 9H, $Si(CH_3)_3$), 0.16 (s, 9H, $Si(CH_3)_3$), 0.14 (s, 9H, $Si(CH_3)_3$), 0.13 (s, 3H, CH_3), 0.11 (s, 3H, CH_3); ^{13}C NMR (90 MHz, $CDCl_3$) δ 94.2 (C-1), 77.1 (C-5), 73.6 (C-3), 71.0 (C-4), 62.2 (C-6), 58.3 (C-2), 25.5 ($C(\underline{C}H_3)_3$), 17.8 ($\underline{C}(CH_3)_3$), 0.6 ($Si(\underline{C}H_3)_3$), 0.5 ($Si(\underline{C}H_3)_3$), -0.4 ($Si(\underline{C}H_3)_3$), -4.3 (CH_3), -5.4 (CH_3); ESI HRMS for $C_{23}H_{50}F_3NNaO_6Si_4$ $[M+Na]^+$: calcd 628.2560, found 628.2573.

***tert*-Butyldiphenylsilyl 2-deoxy-2-trifluoroacetamido-3,4,6-tri-*O*-trimethylsilyl-β-D-glucopyranoside 12a:** From **12** (0.960 g, 1.87 mmol); reaction time: 2h15. **12a** (1.32 g, 97%) as a white amorphous solid; $[\alpha]^{22}_D$ -14.3 (*c* 0.75, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.73-7.67 (m, 4H, 4H-Ar), 7.46-7.36 (m, 6H, 6H-Ar), 6.65 (d, J = 9.2 Hz, 1H, NH), 4.77 (d, $J_{1,2}$ = 5.7 Hz, 1H, H-1), 3.99-3.90 (m, 1H, H-2), 3.84-3.75 (m, 2H, H-4 and H-6a), 3.65-3.54 (m, 2H, H-3 and H-6b), 3.21-3.15 (m, 1H, H-5), 1.10 (s, 9H, $C(C\underline{H}_3)_3$), 0.15 (s, 18H, $Si(CH_3)_3$), 0.04 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 136.0, 133.3, 132.8, 130.1, 129.9, 127.8, 127.6 (12C, 12C-Ar), 94.4 (C-1), 77.2 (C-5), 73.7 (C-3), 70.4 (C-4), 62.0 (C-6),

56.8 (C-2), 26.8 (C(<u>C</u>H$_3$)$_3$), 19.1 (<u>C</u>(CH$_3$)$_3$), 0.5 (Si(<u>C</u>H$_3$)$_3$), 0.3 (Si(<u>C</u>H$_3$)$_3$), -0.5 (Si(<u>C</u>H$_3$)$_3$); ESI HRMS for $C_{33}H_{54}F_3NNaO_6Si_4$ $[M+Na]^+$: calcd 752.2873, found 752.2859.

General procedure for tandem acetalation/benzylation

To a solution of persilylated substrate in dry CH_2Cl_2 (c = 0.2 M) were added benzaldehyde (3 equiv) and 3Å molecular sieves (1 g per g of substrate). The mixture was stirred at room temperature for 15 min. before adding trifluoromethanesulfonic acid (5 mol%) and triethylsilane (1.2 equiv). After stirring for 10-40 min., triethylamine was added and the solution was then diluted with CH_2Cl_2, filtered through a celite pad and washed with water. The aqueous layer was extracted with CH_2Cl_2 then the combined organic layers were dried over Na_2SO_4, filtered and concentrated. Compounds **11b** and **12b** were purified by silica gel chromatography. For the other products (**1b-10b**), the crude residue was taken up in a minimal amount of solvent then hexanes were added to precipitate the product. After triturating for 15 min. then cooling at -25°C for 1h, the precipitate was filtered off and washed with hexanes.

Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-trifluoroacetamido-1-thio-β-D-glucopyranoside 1b: From **1a** (0.080 g, 0.137 mmol); room temperature; reaction time: 15 min. **1b** (0.069 g, 92%) as a white amorphous solid; $[\alpha]^{22}_D$ -25.8 (*c* 0.5, CH_2Cl_2/MeOH 4:1); ^{1}H NMR (250 MHz, DMSO) δ 7.47-7.20 (m, 15H, 15H-Ar), 5.76 (s, 1H, CH-Ph), 5.10 (d, $J_{1,2}$ = 9.8 Hz, 1H, H-1), 4.77 (d, *J* = 11.7 Hz, 1H, CHPh), 4.60 (d, *J* = 11.7 Hz, 1H, CHPh), 4.30 (dd, $J_{6a,6b}$ = 10.1 Hz, $J_{6a,5}$ = 5.1 Hz, 1H, H-6a), 4.00-3.78 (m, 4H, H-2, H-3, H-4 and H-6b), 3.65-3.57 (m, 1H, H-5); ^{13}C NMR (63 MHz, DMSO) δ 138.6-126.4 (18C, 18C Ar), 100.6 (CH-Ph), 86.3 (C-1), 81.1 (C-4), 79.4 (C-3), 74.0 (CH_2Ph), 70.4 (C-5), 68.0 (C-6), 54.3 (C-2); ESI HRMS for $C_{28}H_{26}F_3NNaO_5S$ $[M+Na]^+$: calcd 568.1376, found 568.1368.

Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside 2b: From **2a** (0.158 g, 0.250 mmol) at 0°C; reaction time: 10 min.
2b (0.116 g, 78%) as a white amorphous solid; $[\alpha]^{22}_D$ -24.6 (*c* 0.5, CH_2Cl_2/MeOH 4:1); ^{1}H NMR (250 MHz, DMSO) δ 7.49-7.24 (m, 15H, 15H-Ar), 5.76 (s, 1H, CH-Ph), 5.19 (d, $J_{1,2}$ = 9.8 Hz, 1H, H-1), 4.75 (d, *J* = 11.7 Hz, 1H, CHPh), 4.65 (d, *J* = 11.7 Hz, 1H, CHPh), 4.31 (dd, $J_{6a,6b}$ = 10.1 Hz, $J_{6a,5}$ = 4.7 Hz, 1H, H-6a), 4.04-3.78 (m, 4H, H-2, H-3, H-4 and H-6b), 3.60-3.51 (m, 1H, H-5); ^{13}C NMR (63 MHz, DMSO) δ 161.7 (NH<u>C</u>=O), 138.2, 137.5, 133.4, 130.7, 129.1, 128.8, 128.1, 127.5, 125.9 (18C, 18C-Ar), 100.6 (CH-Ph), 87.0 (C-1), 81.0 (C-

4), 79.5 (C-3), 74.1 (CH_2Ph), 70.4 (C-5), 68.1 (C-6), 55.9 (C-2); ESI HRMS for $C_{28}H_{26}Cl_3NNaO_5S$ $[M+Na]^+$: calcd 616.0489, found 616.0486.

Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside 3b: From **3a** (0.143 g, 0.215 mmol); room temperature; reaction time: 10 min. **3b** (0.114 g, 85%) as a white amorphous solid; $[\alpha]^{22}_D$ -11.8 (*c* 0.5, CH_2Cl_2/MeOH 4:1); ^{1}H NMR (360 MHz, DMSO) δ 7.64 (d, J = 9.6 Hz, 1H, NH), 7.45-7.25 (m, 15H, 15H-Ar), 5.72 (s, 1H, CH-Ph), 5.01 (d, $J_{1,2}$ = 10.4 Hz, 1H, H-1), 4.88 (d, J = 12.8 Hz, 1H, CHPh or $CHCCl_3$), 4.83 (d, J = 12.8 Hz, 1H, CHPh or $CHCCl_3$), 4.76 (d, J = 11.8 Hz, 1H, CHPh or $CHCCl_3$), 4.65 (d, J = 11.8 Hz, 1H, CHPh or $CHCCl_3$), 4.27 (dd, $J_{6a,6b}$ = 10.0 Hz, $J_{6a,5}$ = 5.0 Hz, 1H, H-6a), 3.81-3.75 (m, 3H, H-3, H-4 and H-6b), 3.67-3.60 (m, 1H, H-2), 3.58-3.52 (m, 1H, H-5); ^{13}C NMR (63 MHz, DMSO) δ 154.3 (NH<u>C</u>=O), 138.1, 137.4, 132.8, 130.7, 129.1, 128.8, 128.1, 127.5, 127.4, 125.9 (18C, 18C-Ar), 100.0 (CH-Ph), 96.1 ($CH_2\underline{C}Cl_3$), 86.5 (C-1), 80.4 (C-3 or C-4), 79.6 (C-3 or C-4), 73.5 (2C, CH_2Ph, $\underline{C}H_2CCl_3$), 69.8 (C-5), 67.6 (C-6), 55.9 (C-2); ESI HRMS for $C_{29}H_{28}Cl_3NNaO_6S$ $[M+Na]^+$: calcd 646.0595, found 646.0585.

Phenyl 2-allyloxycarbonylamino-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside 4b: From **4a** (0.085 g, 0.149 mmol); room temperature; reaction time: 20 min. **4b** (0.066 g, 83%) as a white amorphous solid; $[\alpha]^{22}_D$ -17.4 (*c* 0.5, CH_2Cl_2/MeOH 4:1); ^{1}H NMR (300 MHz, DMSO) δ 7.62 (d, J = 9.4 Hz, 1H, NH), 7.45 – 7.26 (m, 15H, 15H-Ar), 5.98-5.85 (m, 1H, $CH_2\underline{C}H=CH_2$), 5.72 (s, 1H, CH-Ph), 5.34 (dd, J_{trans} = 17.3 Hz, J = 1.3 Hz, 1H, $CH_2CH=C\underline{H}_2$), 5.17 (d, J_{cis} = 10.5 Hz, 1H, $CH_2CH=C\underline{H}_2$), 5.00 (d, $J_{1,2}$ = 10.2 Hz, 1H, H-1), 4.75 (d, J = 11.9 Hz, 1H, CHPh), 4.63 (d, J = 11.9 Hz, 1H, CHPh), 4.52 (m, 2H, $C\underline{H}_2CH=CH_2$), 4.25 (dd, $J_{6a,6b}$ = 10.0 Hz, $J_{6a,5}$ = 4.7 Hz, 1H, H-6a), 3.80-3.73 (m, 3H, H-3, H-4 and H-6b), 3.65-3.50 (m, 2H, H-2 and H-5); ^{13}C NMR (63 MHz, DMSO) δ 155.7 (NH<u>C</u>=O), 138.6, 137.6, 133.8, 133.6, 129.9, 129.0, 128.7, 128.1, 128.0, 127.3, 126.9, 126.3, 125.9 (19C, 18C-Ar and $CH_2\underline{C}H=CH_2$), 116.8 ($CH_2CH=\underline{C}H_2$), 100.1 (CH-Ph), 86.5 (C-1), 80.5 (C-3 or C-4), 80.0 (C-3 or C-4), 73.5 (CH_2Ph), 69.7 (C-5), 67.6 (C-6), 64.4 ($\underline{C}H_2CH=CH_2$), 55.6 (C-2); ESI HRMS for $C_{30}H_{31}NNaO_6S$ $[M+Na]^+$: calcd 556.1764, found 556.1763.

(2-Methyl-5-*tert*-butylphenyl) 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-trifluoroacetamido-1-thio-β-D-glucopyranoside 5b: From **5a** (0.153 g, 0.234 mmol); 0°C; reaction time: 10 min. **5b** (0.122 g, 85%) as a white amorphous solid; $[\alpha]^{22}_{D}$ +18.1 (*c* 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 1H, NH), 7.56-7.10 (m, 13H, 13H-Ar), 5.60 (s, 1H, CH-Ph), 4.95 (d, $J_{1,2}$ = 10.2 Hz, 1H, H-1), 4.86 (d, *J* = 11.7 Hz, 1H, CHPh), 4.66 (d, *J* = 11.7 Hz, 1H, CHPh), 4.35 (dd, $J_{6a,6b}$ = 10.6 Hz, $J_{6a,5}$ = 4.9 Hz, 1H, H-6a), 3.99-3.74 (m, 4H, H-2, H-3, H-4 and H-6b), 3.55-3.47 (m, 1H, H-5), 2.32 (s, 3H, CH_3), 1.20 (s, 9H, $C(C\underline{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 137.6, 137.0, 131.6, 130.2, 130.0, 129.1, 128.4, 128.3, 128.0, 125.9, 125.4 (18C, 18C-Ar), 101.3 (CH-Ph), 86.7 (C-1), 82.3 (C-4), 77.2 (C-3), 74.5 (CH_2Ph), 70.2 (C-5), 68.6 (C-6), 55.2 (C-2), 31.2 ($C(\underline{C}H_3)_3$), 20.1 (CH_3); ESI HRMS for $C_{33}H_{36}F_3NNaO_5S$ $[M+Na]^+$: calcd 638.2158, found 638.2144.

(2-Methyl-5-*tert*-butylphenyl) 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside 6b: From **6a** (0.152 g, 0.216 mmol); room temperature; reaction time: 10 min. **6b** (0.120 g, 83%) as a white amorphous solid; $[\alpha]^{22}_{D}$ -0.8 (*c* 0.8, $CHCl_3$/MeOH 1:4); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.8 Hz, 1H, H-Ar), 7.53-7.25 (m, 11H, 11H-Ar), 7.15 (d, *J* = 8.2 Hz, 1H, H-Ar), 6.95 (d, *J* = 7.7 Hz, 1H, NH), 5.63 (s, 1H, CH-Ph), 5.26 (d, $J_{1,2}$ = 10.5 Hz, 1H, H-1), 4.93 (d, *J* = 11.4 Hz, 1H, CHPh), 4.72 (d, *J* = 11.4 Hz, 1H, CHPh), 4.41 (dd, $J_{6a,6b}$ = 10.4 Hz, $J_{6a,5}$ = 5.0 Hz, 1H, H-6a), 4.25 (dd, $J_{3,2}$ = $J_{3,4}$ = 9.4 Hz, 1H, H-3), 3.91-3.66 (m, 3H, H-2, H-4 and H-6b), 3.65-3.55 (m, 1H, H-5), 2.39 (s, 3H, CH_3), 1.33 (s, 9H, $C(C\underline{H}_3)_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 161.7 ($NH\underline{C}$=O), 149.6, 137.6, 137.1, 131.4, 130.3, 130.1, 129.1, 128.5, 128.3, 128.0, 126.à? 125.4 (18C, 18C-Ar), 101.3 (CH-Ph), 86.1 (C-1), 82.4 (C-4), 77.3 (C-3), 74.9 (CH_2Ph), 70.3 (C-5), 68.9 (C-6), 57.0 (C-2), 34.5 ($\underline{C}(CH_3)_3$), 31.3 ($C(\underline{C}H_3)_3$), 20.4 (CH_3); ESI HRMS for $C_{33}H_{36}Cl_3NNaO_5S$ $[M+Na]^+$: calcd 686.1272, found 686.1273.

(2-Methyl-5-*tert*-butylphenyl) 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside 7b: From **7a** (0.090 g, 0.123 mmol); room temperature; reaction time: 10 min. **7b** (0.077 g, 90%) was obtained as a white foam; $[\alpha]^{22}_{D}$ +2.2 (*c* 1, CH_2Cl_2/MeOH 4:1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.64 (d, *J* = 1.9 Hz, 1H, H-Ar), 7.55-7.51 (m, 2H, H-Ar and NH), 7.41-7.24 (m, 10H, 10H-Ar), 7.15 (d, *J* = 7.9 Hz, 1H, H-Ar), 5.76 (s, 1H, CH-Ph), 5.08 (d, $J_{1,2}$ = 10.5 Hz, 1H, H-1), 4.91 (d, *J* = 11.9 Hz, 1H, CHPh), 4.86 (s, 2H, CH_2CCl_3), 4.77 (d, *J* = 11.9 Hz, 1H, CHPh), 4.30 (dd, $J_{6a,6b}$ = 10.3 Hz, $J_{6a,5}$ = 5.1 Hz, 1H, H-6a), 4.01-3.80 (m, 4H, H-2, H-3, H-4 and H-6b), 3.63-3.55 (m,

1H, H-5), 2.33 (s, 3H, CH_3), 1.33 (s, 9H, C($C\underline{H}_3$)$_3$); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 154.4 (NH$\underline{C}$=O), 150.2, 139.8, 138.9, 136.8, 133.8, 130.7, 129.6, 128.9, 128.5, 128.2, 127.0, 125.4 (18C, 18C-Ar), 100.9 (CH-Ph), 96.1 ($CH_2\underline{C}Cl_3$), 87.8 (C-1), 81.8 (C-3 or C-4), 79.9 (C-3 or C-4), 74.1 (2C, CH_2Ph, $\underline{C}H_2CCl_3$), 70.2 (C-5), 68.2 (C-6), 56.6 (C-2), 34.1 ($\underline{C}(CH_3)_3$), 30.7 (C($\underline{C}H_3$)$_3$), 19.5 (CH_3); ESI HRMS for $C_{34}H_{38}Cl_3NNaO_6S$ $[M+Na]^+$: calcd 716.1378, found 716.1390.

(2-Methyl-5-*tert*-butylphenyl) 2-allyloxycarbonylamino-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside 8b: From **8a** (0.141 g, 0.220 mmol); room temperature; reaction time: 15 min. **8b** (0.123 g, 93%) as a white foam; $[\alpha]^{22}_D$ = +2.4 (*c* 1, $CHCl_3$/MeOH 1:1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.64 (d, *J* = 1.9 Hz, 1H, H-Ar), 7.55-7.23 (m, 11H, 11H-Ar), 7.15 (d, *J* = 7.9 Hz, 1H, H-Ar), 6.78 (d, *J* = 9.1 Hz, 1H, NH), 6.03-5.91 (m, 1H, $CH_2\underline{C}H$=CH_2), 5.74 (s, 1H, CH-Ph), 5.34 (dd, J_{trans} = 17.3 Hz, *J* = 1.5 Hz, 1H, CH_2CH=$C\underline{H}_2$), 5.17 (d, J_{cis} = 10.5 Hz, 1H, CH_2CH=$C\underline{H}_2$), 5.07 (d, $J_{1,2}$ = 10.2 Hz, 1H, H-1), 4.90 (d, *J* = 11.7 Hz, 1H, CHPh), 4.75 (d, *J* = 11.7 Hz, 1H, CHPh), 4.59 (m, 2H, $C\underline{H}_2CH$=CH_2), 4.28 (dd, $J_{6a,6b}$ = 10.2 Hz, $J_{6a,5}$ = 4.9 Hz, 1H, H-6a), 3.99-3.77 (m, 4H, H-2, H-3, H-4 and H-6b), 3.61-3.53 (m, 1H, H-5), 2.34 (s, 3H, CH_3), 1.33 (s, 9H, C($C\underline{H}_3$)$_3$); ^{13}C NMR (63 MHz, $(CD_3)_2CO$) δ 155.9 (NH$\underline{C}$=O), 150.1, 139.9, 139.0, 136.8, 134.6, 134.0, 130.6, 129.6, 129.5, 129.1, 128.9, 128.4, 128.1, 127.0, 125.3 (19C, 18C-Ar, $CH_2\underline{C}H$=CH_2), 116.3 (CH_2CH=$\underline{C}H_2$), 100.9 (CH-Ph), 87.9 (C-1), 81.8 (C-4), 80.1 (C-3), 74.1 (CH_2Ph), 70.2 (C-5), 68.3 (C-6), 65.8 ($\underline{C}H_2CH$=CH_2), 56.4 (C-2), 31.2 ($C(\underline{C}H_3)_3$), 20.1 (CH_3); ESI HRMS for $C_{35}H_{42}NO_6S$ $[M+H]^+$: calcd 604.2727, found 604.2724.

(2-Methyl-5-*tert*-butylphenyl) 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-methoxycarbonylamino-1-thio-β-D-glucopyranoside 9b: From **9a** (0.183 g, 0.297 mmol); room temperature; reaction time: 30 min. **9b** (0.135 g, 79%) as a white foam; $[\alpha]^{22}_D$ -2.0 (*c* 0.35, MeOH); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.63 (d, *J* = 2.3 Hz, 1H, H-Ar), 7.54 -7.23 (m, 11H, 11H-Ar), 7.16 (d, *J* = 7.9 Hz, 1H, H-Ar), 6.68 (d, *J* = 8.7 Hz, 1H, NH), 5.75 (s, 1H, CH-Ph), 5.07 (d, $J_{1,2}$ = 10.6 Hz, 1H, H-1), 4.89 (d, *J* = 11.9 Hz, 1H, CHPh), 4.73 (d, *J* = 11.9 Hz, 1H, CHPh), 4.28 (dd, $J_{6a,6b}$ = 10.2 Hz, $J_{6a,5}$ = 5.3 Hz, 1H, H-6a), 3.98 -3.73 (m, 4H, H-2, H-3, H-4 and H-6b), 3.65 (s, 3H, CH_3), 3.60-3.52 (m, 1H, H-5), 2.33 (s, 3H, CH_3), 1.33 (s, 9H, C($C\underline{H}_3$)$_3$); ^{13}C NMR (63 MHz, $(CD_3)_2CO$) δ 156.5 (NH$\underline{C}$=O), 149.3, 139.0, 138.1, 135.9, 133.0, 129.8, 128.8, 128.7, 128.0, 127.5, 127.2, 126.2, 124.4 (18C, 18C-Ar), 100.9 (CH-Ph), 87.8 (C-1), 81.8 (C-4), 80.1 (C-3), 74.1 (CH_2Ph), 70.2 (C-5), 68.3 (C-6), 56.5 (C-2), 51.3

(CH_3), 34.1 ($\underline{C}(CH_3)_3$), 30.7 ($C(\underline{C}H_3)_3$), 19.4 (CH_3); ESI HRMS for $C_{33}H_{39}NNaO_6S$ $[M+Na]^+$: calcd 600.2390, found 600.2400.

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-trifluoroacetamido-α-D-glucopyranoside 10b: From **10a** (0.110 g, 0.217 mmol); 0°C; reaction time: 35 min. **10b** (0.081 g, 80%) as a white amorphous solid; $[\alpha]^{22}_D$ +60.4 (*c* 1, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.53-7.26 (m, 10H, 10H-Ar), 6.23 (d, J = 9.1 Hz, 1H, NH), 5.63 (s, 1H, CH-Ph), 4.91 (d, J = 11.7 Hz, 1H, CHPh), 4.77 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-1), 4.68 (d, J = 11.7 Hz, 1H, CHPh), 4.33-4.25 (m, 2H, H-2 and H-6a), 3.88-3.75 (m, 4H, H-3, H-4, H-5 and H-6b), 3.40 (s, 3H, CH_3); ^{13}C NMR (90 MHz, $CDCl_3$) δ 129.2, 128.6, 128.4, 128.2, 128.0, 126.1 (12C, C-Ar), 101.40 (CH-Ph), 98.26 (C-1), 82.74 (C-3), 75.00 (C-4 or C-5), 74.22 (CH_2Ph), 68.84 (C-6), 62.67 (C-4 or C-5), 55.34 (CH_3), 53.01 (C-2); ESI HRMS for $C_{23}H_{25}F_3NO_6$ $[M+H]^+$: calcd 468.1628, found 468.1612.

***tert*-Butyldimethylsilyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside 11b:** From **11a** (1.00 g, 1.65 mmol); 0°C; reaction time: 10 min. **11b** (0.866 g, 92%) as a white foam after flash chromatography (cyclohexane/EtOAc 9:1 to 4:1); $[\alpha]^{22}_D$ -63.0 (*c* 1, MeOH); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.54-7.23 (m, 10H, 10H-Ar), 6.56 (d, J = 8.3 Hz, 1H, NH), 5.56 (s, 1H, CH-Ph), 5.00 (d, $J_{1,2}$ = 7.8 Hz, 1H, H-1), 4.90 (d, J = 11.8 Hz, 1H, CHPh), 4.69 (d, J = 11.8 Hz, 1H, CHPh), 4.32 (dd, $J_{6a,6b}$ = 10.5 Hz, $J_{6a,5}$ = 5.0 Hz, 1H, H-6a), 4.02 (dd, $J_{3,2}$ = $J_{3,4}$ = 9.5 Hz, 1H, H-3), 3.82-3.67 (m, 3H, H-2, H-4 and H-6b), 3.56-3.48 (m, 1H, H-5), 0.99 (s, 9H, $C(C\underline{H}_3)_3$), 0.13 (s, 3H, CH_3), 0.11 (s, 3H, CH_3); ^{13}C NMR (90 MHz, $CDCl_3$) δ 157.4 (q, J = 37.7 Hz, $CF_3\underline{C}$=O), 137.9, 137.4, 129.1, 128.6, 128.4, 128.1, 126.2 (12C, 12C-Ar), 101.3 (CH-Ph), 95.5 (C-1), 82.7 (C-4), 75.9 (C-3), 74.3 (CH_2Ph), 68.7 (C-6), 66.2 (C-5), 59.1 (C-2), 25.5 ($C(\underline{C}H_3)_3$), 17.8 ($\underline{C}(CH_3)_3$), -4.2 (CH_3), -5.5 (CH_3); ESI HRMS for $C_{28}H_{36}F_3NNaO_6Si$ $[M+Na]^+$: calcd 590.2156, found 590.2153.

***tert*-Butyldiphenylsilyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside 12b:** From **12a** (0.183 g, 0.250 mmol); room temperature; reaction time: 40 min. **12b** (0.125 g, 72%) as a white foam after flash chromatography (cyclohexane/EtOAc 95:5 to 90:10); $[\alpha]^{22}_D$ +0.1 (*c* 1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.67-7.56 (m, 4H, 4H-Ar), 7.48 – 7.22 (m, 16H, 16H-Ar), 6.12 (d, J = 8.9 Hz, 1H, NH), 5.55 (s, 1H, CH-Ph), 4.86 (d, J = 11.9 Hz, 1H, CHPh), 4.70 (d, $J_{1,2}$ = 7.9 Hz, 1H, H-1), 4.64 (d, J = 11.9 Hz, 1H, CHPh), 4.07 (dd, $J_{6a,6b}$ = 10.5 Hz, $J_{6a,5}$ = 5.1 Hz, 1H, H-6a), 3.99-3.88 (m, 1H, H-2), 3.76-3.65

(m, 3H, H-3, H-4 and H-6b), 3.16-3.06 (m, 1H, H-5), 1.06 (s, 9H, C($C\underline{H}_3$)$_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 157.2 (q, *J* = 36.8 Hz, $CF_3\underline{C}$=O), 137.8, 137.3, 136.0, 135.8, 132.9, 132.5, 130.2, 130.0, 129.2, 128.6, 128.4, 128.1, 127.8, 127.6, 126.1 (24C, 24C-Ar), 115.7 (q, *J* = 288.7 Hz, $\underline{C}F_3C$=O), 101.3 (CH-Ph), 95.7 (C-1), 82.6 (C-4), 76.0 (C-3), 74.1 (CH_2Ph), 68.4 (C-6), 65.9 (C-5), 58.5 (C-2), 26.8 (C($\underline{C}H_3$)$_3$), 19.1 ($\underline{C}$(CH_3)$_3$); ESI HRMS for $C_{38}H_{40}F_3NNaO_6Si$ $[M+Na]^+$: calcd 714.2469, found 714.2473.

General procedure for one-pot acetalation/benzylation/benzylidene opening

To a solution of persilylated substrate in dry CH_2Cl_2 (c = 0.2 M) were added benzaldehyde (3 equiv) and AW300 molecular sieves (1 g per g of substrate). The mixture was stirred at room temperature for 15 min. then trifluoromethanesulfonic acid (5 mol%) and triethylsilane (1.2 equiv) were added. After stirring for 10-20 min., additional triethylsilane (5 equiv), dry acetonitrile (final CH_2Cl_2/MeCN solvent ratio of 4:1, c = 0.15 M) and extra trifluoromethanesulfonic acid (5-15 mol%) were added. The solution was stirred for another 1-5h, diluted with CH_2Cl_2, filtered through a celite pad and washed with satd. aq. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 then the combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude material was purified by flash chromatography to afford the desired compound.

(2-Methyl-5-*tert*-butylphenyl) 3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-1-thio-β-D-glucopyranoside 5d: From **5a** (0.176 g, 0.269 mmol); added TfOH: 10 mol%; 0°C; reaction time: 2h. **5d** (0.119 g, 72%) as a white foam after flash chromatography (cyclohexane/EtOAc 9:1 to 3:1); $[\alpha]^{22}_D$ +2.5 (*c* 1, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.58-7.11 (m, 13H, 13H-Ar), 6.34 (d, *J* = 7.7 Hz, 1H, NH), 5.00 (d, $J_{1,2}$ = 10.4 Hz, 1H, H-1), 4.82 (d, *J* = 11.7 Hz, 1H, CHPh), 4.71 (d, *J* = 11.7 Hz, 1H, CHPh), 4.63 (d, *J* = 11.8 Hz, 1H, CHPh), 4.57 (d, *J* = 11.8 Hz, 1H, CHPh), 3.89-3.73 (m, 4H, H-3, H-4, H-6a and H-6b), 3.67 (m, 1H, H-2), 3.58-3.53 (m, 1H, H-5), 2.94 (br s, 1H, OH), 2.34 (s, 3H, CH_3), 1.27 (s, 9H, C($C\underline{H}_3$)$_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 149.7, 137.8, 137.5, 137.0, 131.8, 130.1, 128.7, 128.6, 128.4, 128.2, 128.0, 125.4 (18C, 18C-Ar), 86.7 (C-1), 80.9 (C-3 or C-4), 77.7 (C-5), 74.5 (CH_2Ph), 73.9 (CH_2Ph), 73.5 (C-3 or C-4), 70.5 (C-6), 55.2 (C-2), 31.3 (C($\underline{C}H_3$)$_3$), 20.2 (CH_3); ESI HRMS for $C_{33}H_{38}F_3NNaO_5S$ $[M+Na]^+$: calcd 640.2315, found 640.2285.

(2-Methyl-5-*tert*-butylphenyl) 3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside 6d: From **6a** (0.187 g, 0.266 mmol); added TfOH: 10 mol%; 0°C; reaction time: 2h30. **6d** (0.128 g, 72%) as a white foam after flash chromatography (cyclohexane/EtOAc 9:1 to 3:1); $[\alpha]^{22}_{D}$ -0.1 (*c* 1, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.66 (s, 1H, H-Ar), 7.37-7.32 (m, 10H, 10H-Ar), 7.24 (d, *J* = 8.2 Hz, 1H, H-Ar), 7.13 (d, *J* = 8.2 Hz, 1H, H-Ar), 6.98 (d, *J* = 8.2 Hz, 1H, NH), 5.14 (d, $J_{1,2}$ = 10.0 Hz, 1H, H-1), 4.84 (d, *J* = 11.4 Hz, 1H, CHPh), 4.79 (d, *J* = 11.4 Hz, 1H, CHPh), 4.64 (d, *J* = 12.3 Hz, 1H, CHPh), 4.58 (d, *J* = 12.3 Hz, 1H, CHPh), 3.98 (dd, $J_{3,2}$ = $J_{3,4}$ = 9.4 Hz, 1H, H-3), 3.84-3.69 (m, 4H, H-2, H-4, H-6a and H-6b), 3.61-3.55 (m, 1H, H-5), 2.90 (br s, 1H, OH), 2.39 (s, 3H, CH_3), 1.29 (s, 9H, $C(C\underline{H}_3)_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 161.7 ($NH\underline{C}$=O), 149.7, 138.0, 137.6, 137.1, 137.0, 132.0, 131.9, 130.2, 130.1, 128.7, 128.6, 128.3, 128.2, 128.0, 127.9, 125.3 (18C, 18C-Ar), 85.8 (C-1), 81.2 (C-3), 77.7 (C-5), 74.9 (CH_2Ph), 73.8 (CH_2Ph), 73.4 (C-4), 70.5 (C-6), 56.7 (C-2), 31.3 ($C(\underline{C}H_3)_3$), 20.5 (CH_3); ESI HRMS for $C_{33}H_{38}Cl_3NNaO_5S$ $[M+Na]^+$: calcd 688.1428, found 688.1426.

(2-Methyl-5-*tert*-butylphenyl) 3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl amino)-1-thio-β-D-glucopyranoside 7d: From **7a** (0.120 g, 0.163 mmol); added TfOH: 10 mol%; room temperature; reaction time: 4h30. **7d** (0.076 g, 67%) as a white foam after flash chromatography (cyclohexane/EtOAc 4:1 to 3:1); $[\alpha]^{22}_{D}$ +16.7 (*c* 1, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 1.9 Hz, 1H, H-Ar), 7.37-7.33 (m, 10H, 10H-Ar), 7.22 (d, *J* = 7.9 Hz, 1H, H-Ar), 7.12 (d, *J* = 7.9 Hz, 1H, H-Ar), 5.12 (d, *J* = 8.3 Hz, 1H, NH), 4.95 (d, $J_{1,2}$ = 10.5 Hz, 1H, H-1), 4.82-4.76 (m, 4H, CH_2Ph, CH_2CCl_3), 4.63 (d, *J* = 12.1 Hz, 1H, CHPh), 4.57 (d, *J* = 12.1 Hz, 1H, CHPh), 3.84-3.73 (m, 4H, H-3, H-4, H-6a and H-6b), 3.57-3.44 (m, 2H, H-2 and H-5), 2.89 (br s, 1H, OH), 2.37 (s, 3H, CH_3), 1.28 (s, 9H, $C(C\underline{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8 ($NH\underline{C}$=O), 149.7, 138.2, 137.6, 136.7, 132.3, 130.0, 129.7, 128.7, 128.6, 128.3, 128.1, 128.0, 127.9, 125.0 (18C, 18C-Ar), 95.4 ($CH_2\underline{C}Cl_3$), 86.5 (C-1), 81.8 (C-3), 77.7 (C-5), 74.7 ($\underline{C}H_2CCl_3$), 74.6 (CH_2Ph), 73.3 (CH_2Ph), 73.3 (C-4), 70.6 (C-6), 56.2 (C-2), 34.5 ($\underline{C}(CH_3)_3$), 31.3 ($C(\underline{C}H_3)_3$), 20.3 (CH_3); ESI HRMS for $C_{34}H_{40}Cl_3NNaO_6S$ $[M+Na]^+$: calcd 718.1534, found 718.1527.

(2-Methyl-5-*tert*-butylphenyl) 2-allyloxycarbonylamino-3,6-di-*O*-benzyl-2-deoxy-1-thio-β-D-glucopyranoside 8d: From **8a** (0.176 g, 0.274 mmol); added TfOH: 15 mol%; room temperature; reaction time: 3h30. **8d** (0.100 g, 60%) as a white foam after flash chromatography (cyclohexane/EtOAc 4:1 to 3:1); $[\alpha]^{22}_{D}$ +2.0 (*c* 1, $CHCl_3$); ^{1}H NMR (250

MHz, $(CD_3)_2CO$) δ 7.69 (d, *J* = 1.9 Hz, 1H, H-Ar), 7.39-7.26 (m, 10H, 10H-Ar), 7.21 (d, *J* = 7.9 Hz, 1H, H-Ar), 7.13 (d, *J* = 7.9 Hz, 1H, H-Ar), 6.73 (d, *J* = 8.5 Hz, 1H, NH), 6.03-5.88 (m, 1H, $CH_2C\underline{H}=CH_2$), 5.32 (dd, J_{trans} = 17.4 Hz, *J* = 1.5 Hz, 1H, $CH_2CH=C\underline{H}_2$), 5.15 (dd, J_{cis} = 10.5 Hz, *J* = 1.5 Hz, 1H, $CH_2CH=C\underline{H}_2$), 4.97-4.74 (m, 3H, H-1, 2CHPh), 4.57 (s, 4H, 2CHPh, $C\underline{H}_2CH=CH_2$), 3.88 (dd, $J_{6a,6b}$ = 10.7 Hz, $J_{6a,5}$ = 1.8 Hz, 1H, H-6a), 3.79-3.55 (m, 5H, H-2, H-3, H-4, H-5 and H-6b), 2.33 (s, 3H, CH_3), 1.28 (s, 9H, $C(C\underline{H}_3)_3$); ^{13}C NMR (90 MHz, $(CD_3)_2CO$) δ 155.9 ($NH\underline{C}=O$), 150.2, 140.2, 139.7, 136.2, 134.8, 134.7, 130.4, 129.0, 128.8, 128.4, 128.1, 128.0, 124.7, (19C, 18C-Ar, $CH_2\underline{C}H=CH_2$), 116.2 ($CH_2CH=\underline{C}H_2$), 87.4 (C-1), 84.3 (C-3), 80.0 (C-5), 74.4 (CH_2Ph), 72.9 (CH_2Ph), 71.0 (C-4), 69.9 (C-6), 64.7 ($\underline{C}H_2CH=CH_2$), 56.1 (C-2), 34.1 ($\underline{C}(CH_3)_3$), 30.8 ($C(\underline{C}H_3)_3$), 19.4 (CH_3); ESI HRMS for $C_{35}H_{43}NNaO_6S$ $[M+Na]^+$: calcd 628.2703, found 628.2695.

(2-Methyl-5-*tert*-butylphenyl) 3,6-di-*O*-benzyl-2-deoxy-2-methoxycarbonylamino-1-thio-β-D-glucopyranoside 9d: From **9a** (0.198 g, 0.321 mmol); added TfOH: 15 mol%; room temperature; reaction time: 5h. **9d** (0.092 g, 49%) as a white foam after flash chromatography (cyclohexane/EtOAc 9:1 to 3:1); $[\alpha]^{22}_D$ +18.9 (*c* 1, MeOH); ^{1}H NMR (250 MHz, $(CD_3)_2CO$) δ 7.68 (s, 1H, H-Ar), 7.38-7.11 (m, 12H, 12H-Ar), 6.63 (d, *J* = 12.2 Hz, 1H, NH), 4.96-4.88 (m, 2H, H-1 and CHPh), 4.76 (d, *J* = 11.7 Hz, 1H, CHPh), 4.57 (s, 2H, CH_2Ph), 3.88 (dd, $J_{6a,6b}$ = 9.8 Hz, $J_{6a,5}$ = 1.6 Hz, 1H, H-6a), 3.76-3.53 (m, 8H, H-2, H-3, H-4, H-5, H-6b and CH_3), 2.33 (s, 3H, CH_3), 1.28 (s, 9H, $C(C\underline{H}_3)_3$); ^{13}C NMR (63 MHz, $(CD_3)_2CO$) δ 156.6 ($NH\underline{C}=O$), 150.3, 140.3, 139.7, 136.3, 134.8, 130.4, 129.0, 128.9, 128.4, 128.1, 128.0, 124.8 (18C, 18C-Ar), 87.3 (C-1), 84.3 (C-3), 80.0 (C-5), 74.4 (CH_2Ph), 72.9 (CH_2Ph), 71.0 (C-4), 69.9 (C-6), 56.1 (C-2), 34.1 ($\underline{C}(CH_3)_3$), 30.8 ($C(\underline{C}H_3)_3$), 19.4 (CH_3); ESI HRMS for $C_{33}H_{41}NNaO_6S$ $[M+Na]^+$: calcd 602.2547, found 602.2542.

Methyl 3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranoside 10d: From **10a** (0.112 g, 0.221 mmol); added TfOH: 5 mol%; 0°C; reaction time: 2h. **10d** (0.070 g, 67%) as a white foam after flash chromatography (cyclohexane/EtOAc 7:3 to 3:2); $[\alpha]^{22}_D$ +58.4 (*c* 1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.38-7.28 (m, 10H, 10H-Ar), 6.30 (d, *J* = 9.8 Hz, 1H, NH), 4.79-4.54 (m, 5H, H-1 and $2CH_2Ph$), 4.22 (ddd, $J_{2,3} = J_{2,NH}$ = 9.8 Hz, $J_{2,1}$ = 3.8 Hz, 1H, H-2), 3.85-3.58 (m, 5H, H-3, H-4, H-5, H-6a and H-6b), 3.38 (s, 3H, CH_3), 2.73 (br s, 1H, OH); ^{13}C NMR (90 MHz, $CDCl_3$) δ 138.0, 137.7, 128.8, 128.6, 128.2, 128.0, 127.9 (12C, 12C-Ar), 97.8 (C-1), 79.1 (C-3), 74.5 (CH_2Ph), 73.8 (CH_2Ph), 72.6 (C-4 or C-5), 70.1

(C-6), 70.0 (C-4 or C-5), 55.3 (CH_3), 52.7 (C-2); ESI HRMS for $C_{23}H_{26}F_3NNaO_6$ $[M+Na]^+$: calcd 492.1604, found 492.1580.

***tert*-Butyldiphenylsilyl 3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside 12d:** To a solution of **12a** (85 mg, 0.116 mmol) in dry CH_2Cl_2 (650 µL) was added AW300 molecular sieves (85 mg). The mixture was stirred at room temperature for 15 min., cooled to 0°C then benzaldehyde (35 µL, 0.349 mmol), trifluoromethane sulfonic acid (5 mol%) and triethylsilane (22 µL, 0.139 mmol) were successively added. The mixture was stirred at 0°C for 15 min. then triethylsilane (94 µL, 0.582 mmol) and trifluoroacetic acid (17 µL, 0.232 mmol) were added. After stirring for 35 min. at 0°C, the solution was diluted with CH_2Cl_2, filtered through a celite pad and washed with satd. aq. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, then the combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (cyclohexane/EtOAc 3:1) to afford **12d** (0.055 g, 68%) as a white foam. $[\alpha]^{22}_D$ -10.1 (*c* 1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.72-7.62 (m, 4H, 4H-Ar), 7.45- 7.26 (m, 6H, 6H-Ar), 6.16 (d, J = 8.8 Hz, 1H, NH), 4.81-4.64 (m, 3H, H-1 and 2CHPh), 4.53 (d, J = 11.9 Hz, 1H, CHPh), 4.43 (d, J = 11.9 Hz, 1H, CHPh), 3.98-3.87 (m, 1H, H-2), 3.80 dd, $J_{4,3} = J_{4,5}$ = 9.0 Hz, 1H, H-4), 3.64-3.49 (m, 3H, H-3, H-6a and H-6b), 3.17-3.09 (m, 1H, H-5), 2.88 (br s, 1H, OH), 1.09 (s, 9H, $C(C\underline{H}_3)_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 138.0, 137.7, 136.0, 135.9, 133.1, 132.6, 130.1, 129.9, 128.7, 128.6, 128.2, 128.1, 128.0, 127.8, 127.5 (24C, 24C-Ar), 95.3 (C-1), 79.9 (C-3), 73.9 (CH_2Ph), 73.9 (CH_2Ph), 73.5 (2C, C-4 and C-5), 70.4 (C-6), 57.8 (C-2), 26.7 ($C(\underline{C}H_3)_3$), 19.1 ($\underline{C}(CH_3)_3$); ESI HRMS for $C_{38}H_{42}F_3KNO_6Si$ $[M+K]^+$: calcd 732.2365, found 732.2363.

General procedure for one-pot acetalation/benzylation/glycosylation

To a solution of persilylated substrate in dry CH_2Cl_2 (c = 0.2 M) were added benzaldehyde (2.2 equiv) and 3Å molecular sieves (1 g per g of substrate). The mixture was stirred at room temperature for 15 min. Trifluoromethanesulfonic acid (10 mol%) and triethylsilane (1.1 equiv) were then added. After stirring for 15 min. at room temperature, the mixture was cooled then **12d** (0.8 equiv) in dry CH_2Cl_2 (c = 0.1 M) was added followed by *N*-iodosuccinimide (1.5 equiv). The solution was stirred until total consumption of the starting acceptor, then diluted with CH_2Cl_2, filtered through a celite pad and washed with satd. aq. $NaHCO_3$ and $Na_2S_2O_3$. The aqueous phase was extracted with CH_2Cl_2. The organic layers

were combined, dried over Na_2SO_4, filtered and concentrated. The mixture was purified by a LH20 size exclusion chromatography (CH_2Cl_2/MeOH 1:1) to furnish the desired disaccharide.

***tert*-Butyldiphenylsilyl (3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside 13:** From **6a** (53 mg, 0.075 mmol); -30 to -5°C; reaction time: 1h30. **13** (50 mg, 70%) as a white foam; $[\alpha]^{22}_D$ -33.0 (*c* 1, CH_2Cl_2/MeOH 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.59 (m, 4H, 4H-Ar), 7.54-7.26 (m, 21H, 21H-Ar), 6.45 (d, J = 8.2 Hz, 1H, NH), 6.28 (d, J = 8.7 Hz, 1H, NH), 5.52 (s, 1H, CH-Ph), 4.88 (d, J = 11.7 Hz, 1H, CHPh), 4.82 (d, J = 11.7 Hz, 1H, CHPh), 4.71-4.55 (m, 5H, H-1, H-1' and 3CHPh), 4.30 (d, J = 12.1 Hz, 1H, CHPh), 4.23 (dd, $J_{6a',6b'}$ = 10.5 Hz, $J_{6a',5'}$ = 4.9 Hz, 1H, H-6a'), 4.11 (dd, $J_{4,3} = J_{4,5}$ = 8.7 Hz, 1H, H-4), 3.98-3.89 (m, 1H, H-2), 3.80-3.47 (m, 6H, H-2', H-3, H-3', H-4', H-6a and H-6b'), 3.35-3.24 (m, 2H, H-5' and H-6b), 3.35 (m, 1H, H-5), 1.05 (s, 9H, C(C<u>H</u>$_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8 (NH<u>C</u>=O), 138.3, 138.0, 137.9, 137.3, 136.1, 135.9, 133.2, 132.7, 130.1, 129.9, 129.3, 128.7, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.5, 126.2 (36C, 36C-Ar), 101.3 (CH-Ph), 99.4 (C-1'), 95.1 (C-1), 82.6 (C-4'), 77.7 (C-3), 76.0 (C-3'), 75.7 (C-4), 74.4 (C-5), 74.3 (CH_2Ph), 74.0 (CH_2Ph), 73.6 (CH_2Ph), 68.5 (C-6'), 67.7 (C-6), 65.9 (C-5'), 58.1 (C-2'), 57.3 (C-2), 26.7 (C(<u>C</u>H$_3$)$_3$), 19.0 (<u>C</u>(CH$_3$)$_3$); ESI HRMS for $C_{60}H_{62}Cl_3F_3N_2NaO_{11}Si$ $[M+Na]^+$: calcd 1199.3033, found 1199.3009.

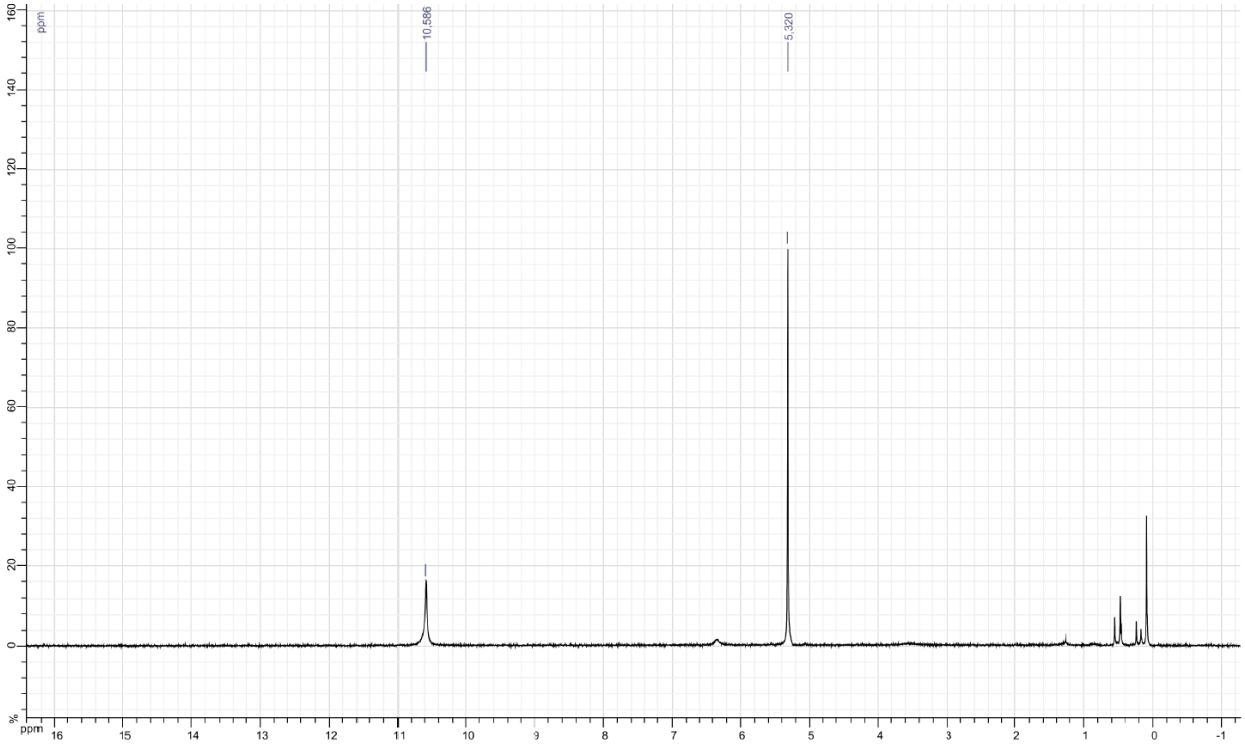
***tert*-Butyldiphenylsilyl (3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside 14:** From **7a** (60 mg, 0.082 mmol); -30 to -5°C; reaction time: 2h. **14** (58 mg, 73%) as a white foam; $[\alpha]^{22}_D$ -31.5 (*c* 1, CH_2Cl_2/MeOH 4:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.73-7.62 (m, 4H, 4H-Ar), 7.54-7.21 (m, 26H, 26H-Ar), 6.28 (d, J = 8.6 Hz, 1H, NH), 5.52 (s, 1H, CH-Ph), 4.90 (d, J = 11.8 Hz, 1H, CHPh), 4.84 (d, J = 11.4 Hz, 1H, CHPh), 4.70-4.63 (m, 5H, H-1', 2CHPh and CH_2CCl_3), 4.57 (d, J = 11.8 Hz, 1H, CHPh), 4.41 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1), 4.26 (d, J = 11.4 Hz, 1H, CHPh), 4.19 (dd, $J_{6a',6b'}$ = 10.4 Hz, $J_{6a',5'}$ = 5.0 Hz, 1H, H-6a'), 4.04 (dd, $J_{4,3} = J_{4,5}$ = 8.4 Hz, 1H, H-4), 3.98-3.91 (m, 1H, H-2), 3.66-3.58 (m, 3H, H-3, H-4' and H-6a), 3.52-3.41 (m, 3H, H-2', H-3' and H-6b'), 3.31 (dd, $J_{6b,6a}$ = 10.9 Hz, $J_{6b,5}$ = 2.7 Hz, 1H, H-6b), 3.26-3.19 (m, 1H, H-5'), 3.03 (m, 1H, H-5), 1.08 (s, 9H, C(C<u>H</u>$_3$)$_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 154.1 (NH<u>C</u>=O), 138.3, 138.2, 137.9, 137.4, 133.2, 132.7, 130.2, 129.9, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 126.1 (36C, 36C-Ar), 101.2 (CH-Ph),

100.9 (C-1'), 95.6 ($CH_2\underline{C}Cl_3$), 95.1 (C-1), 82.3 (C-4'), 77.9 (C-3), 77.3 (C-3'), 76.4 (C-4), 74.5 (CH_2Ph or $CHCCl_3$), 74.4 (C-5), 74.1 (CH_2Ph), 74.0 (CH_2Ph or $CHCCl_3$), 73.7 (CH_2Ph), 68.5 (C-6'), 67.6 (C-6), 65.8 (C-5'), 57.7 (C-2'), 57.4 (C-2), 26.7 ($C(\underline{C}H_3)_3$), 19.1 ($\underline{C}(CH_3)_3$); ESI HRMS for $C_{61}H_{64}Cl_3F_3N_2NaO_{12}Si$ $[M+Na]^+$: calcd 1229.3138, found 1229.3176.

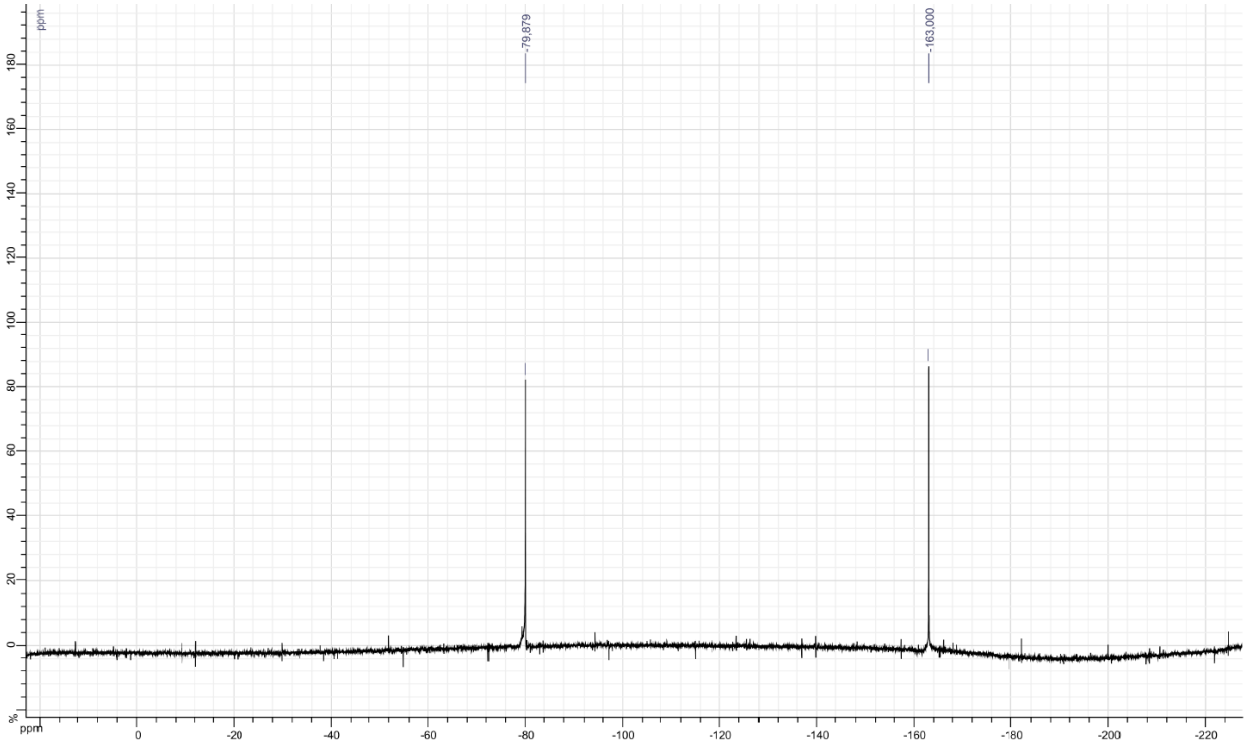
Procedure for the ^{1}H and ^{19}F experiments

A solution of trifluoromethanesulfonic acid (2 µL, 22 µmol) in dry CD_2Cl_2 (2 mL) was prepared under argon. C_6F_6 (one drop) was added as a standard for ^{19}F NMR (δ -163 ppm). After stirring at room temperature for 5 min., 1 mL of the solution was put into a NMR tube then ^{1}H and ^{19}F NMR spectra were recorded. 3Å or 4Å AW 300 molecular sieves (150 mg) were added to the NMR tube and the suspension was stirred at room temperature for 15 min. After settling, ^{1}H and ^{19}F NMR spectra were recorded.

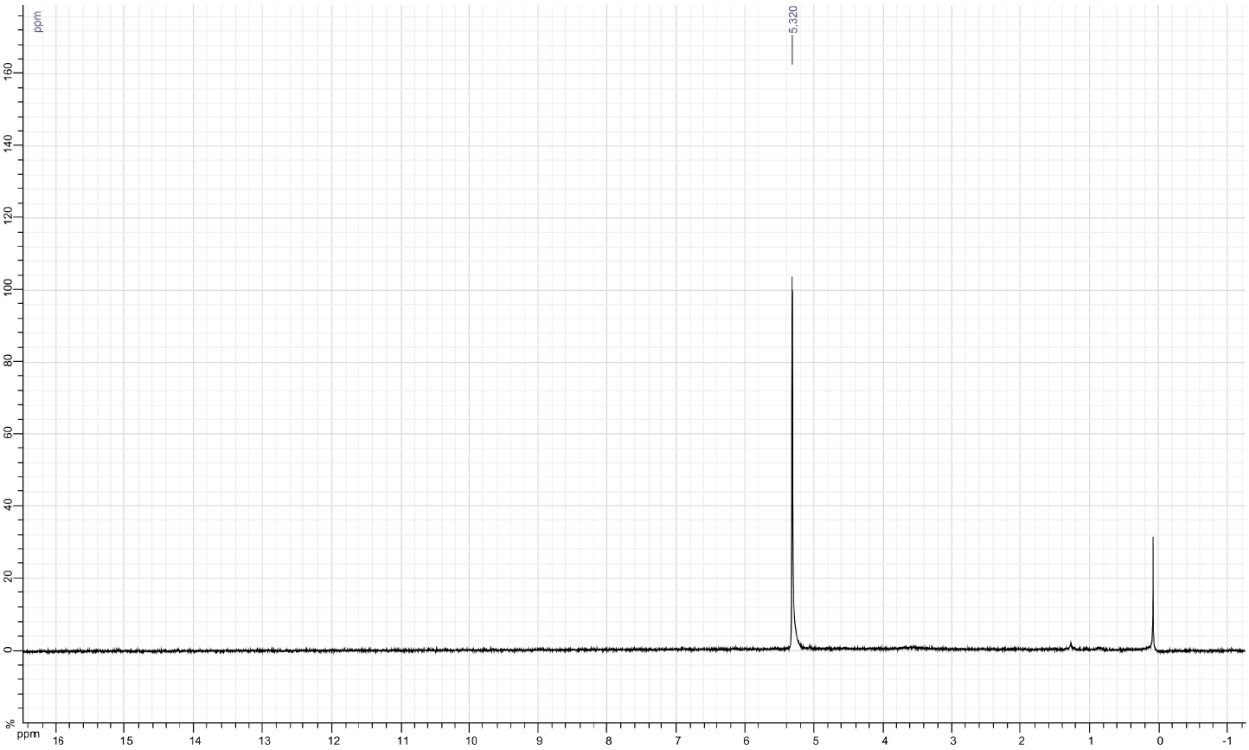
Copy of ^{1}H NMR spectrum of a 10mM solution of TfOH (360 MHz, CD_2Cl_2)



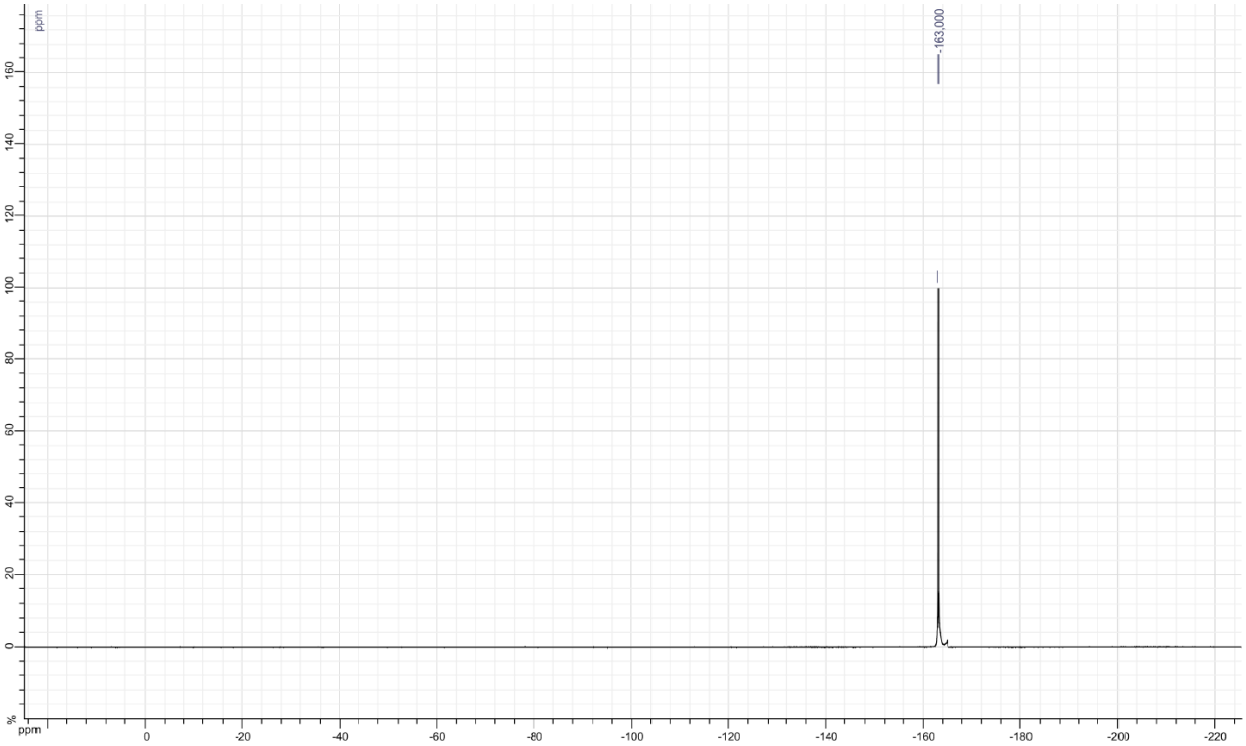
Copy of ^{19}F NMR spectrum of a 10mM solution of TfOH (235 MHz, CD_2Cl_2)



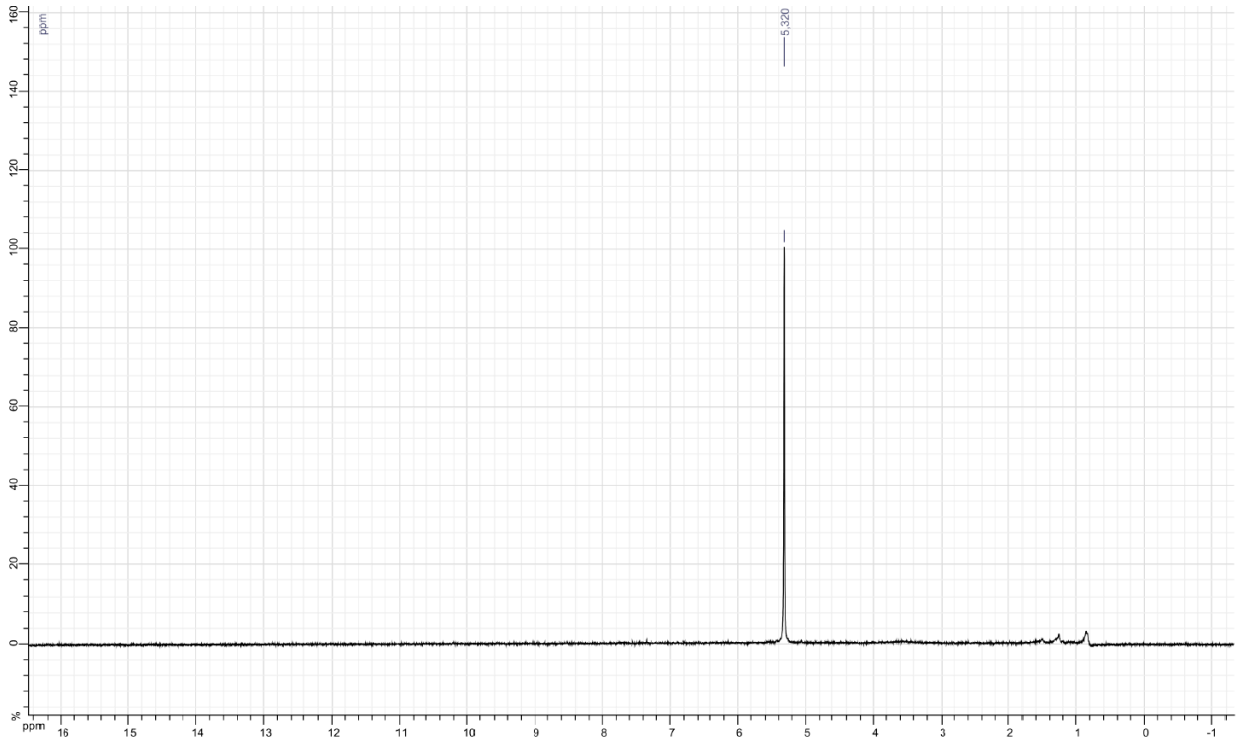
Copy of ^{1}H NMR spectrum of a 10mM solution of TfOH with 3Å molecular sieves (360 MHz, CD_2Cl_2)



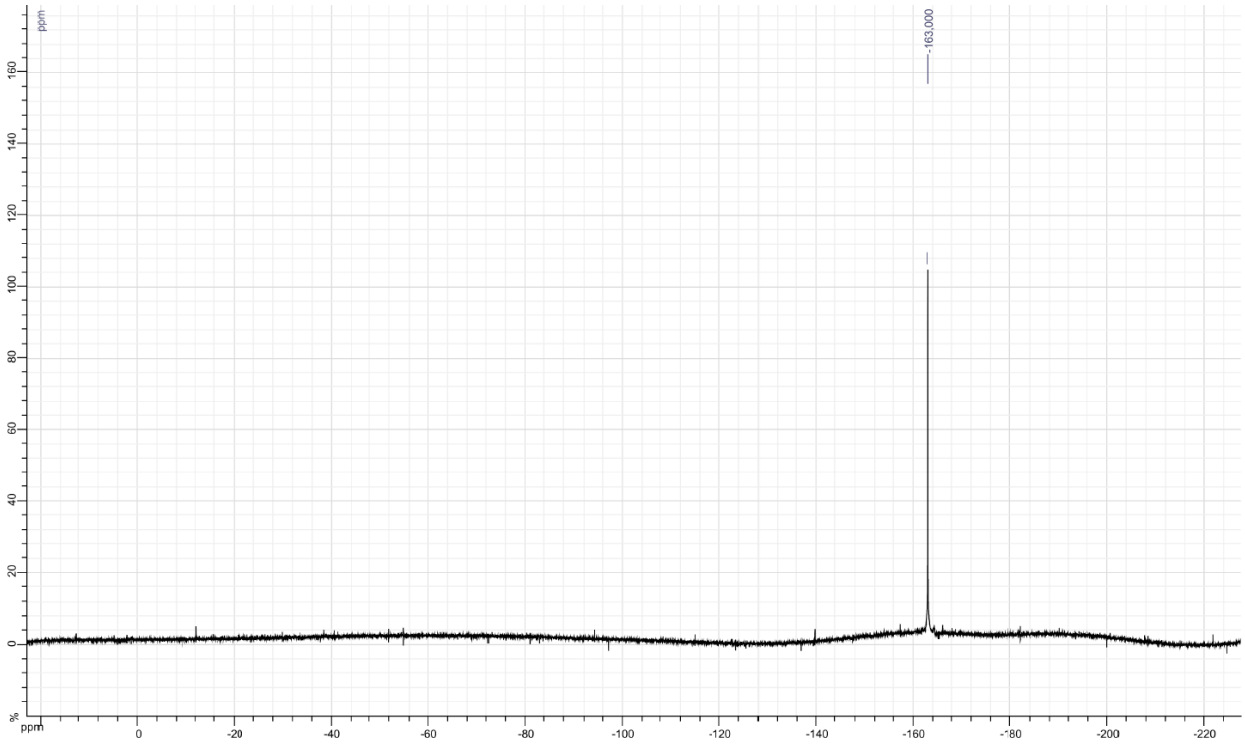
Copy of ^{19}F NMR spectrum of a 10mM solution of TfOH with 3Å molecular sieves (235 MHz, CD_2Cl_2)



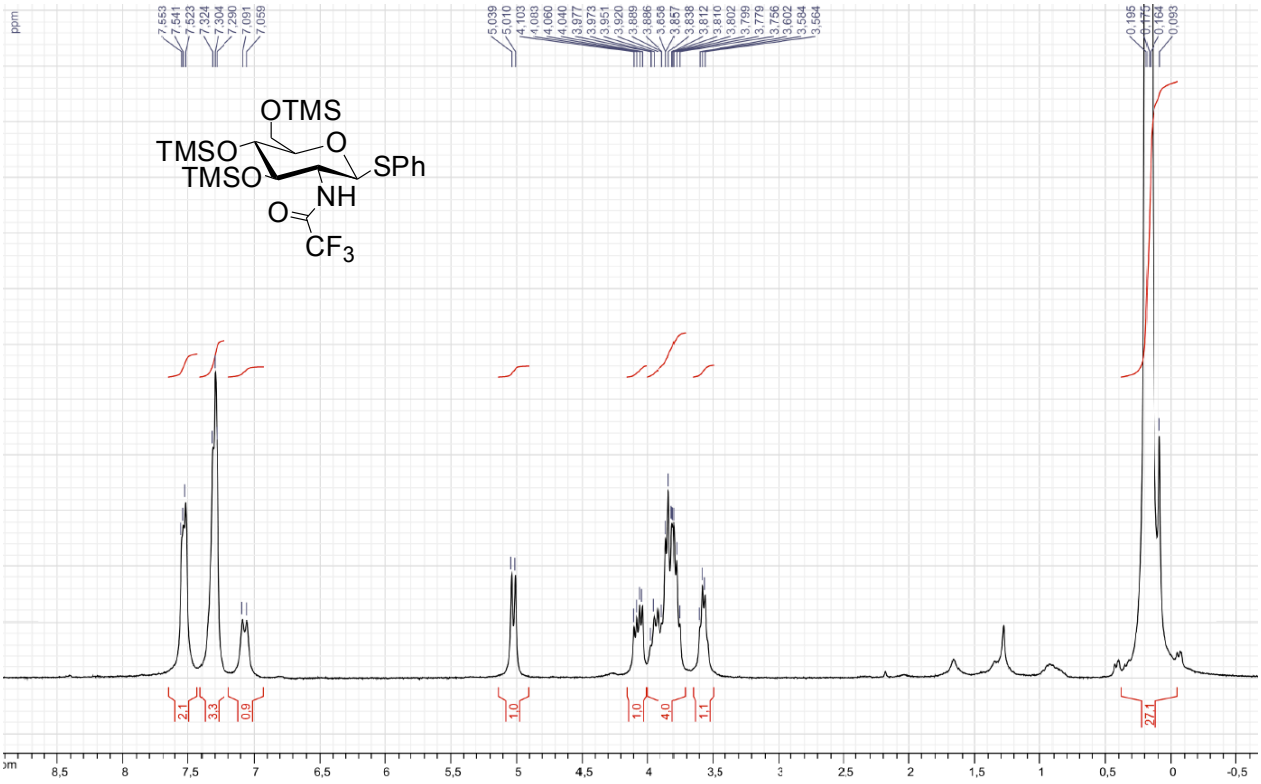
Copy of ^{1}H NMR spectrum of a 10mM solution of TfOH with 4Å AW300 molecular sieves (360 MHz, CD_2Cl_2)



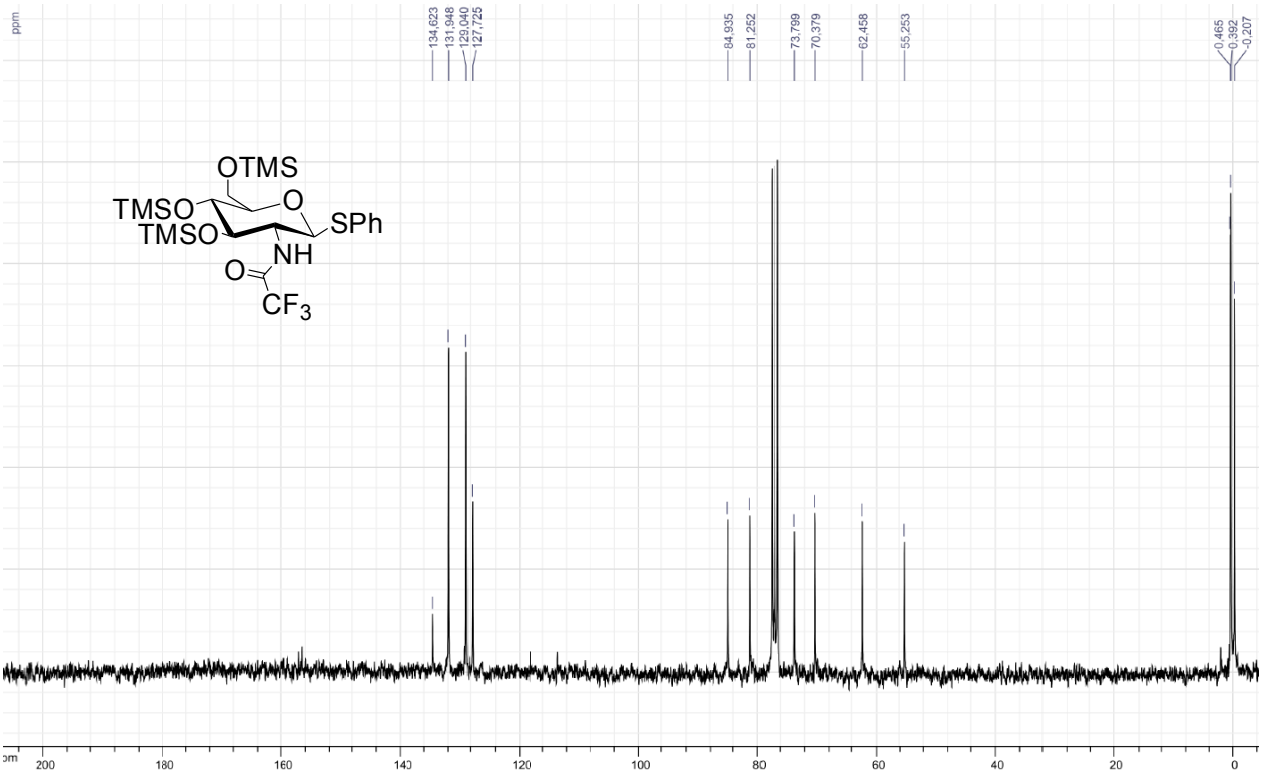
Copy of ^{19}F NMR spectrum of a 10mM solution of TfOH with 4Å AW300 molecular sieves (235 MHz, CD_2Cl_2)



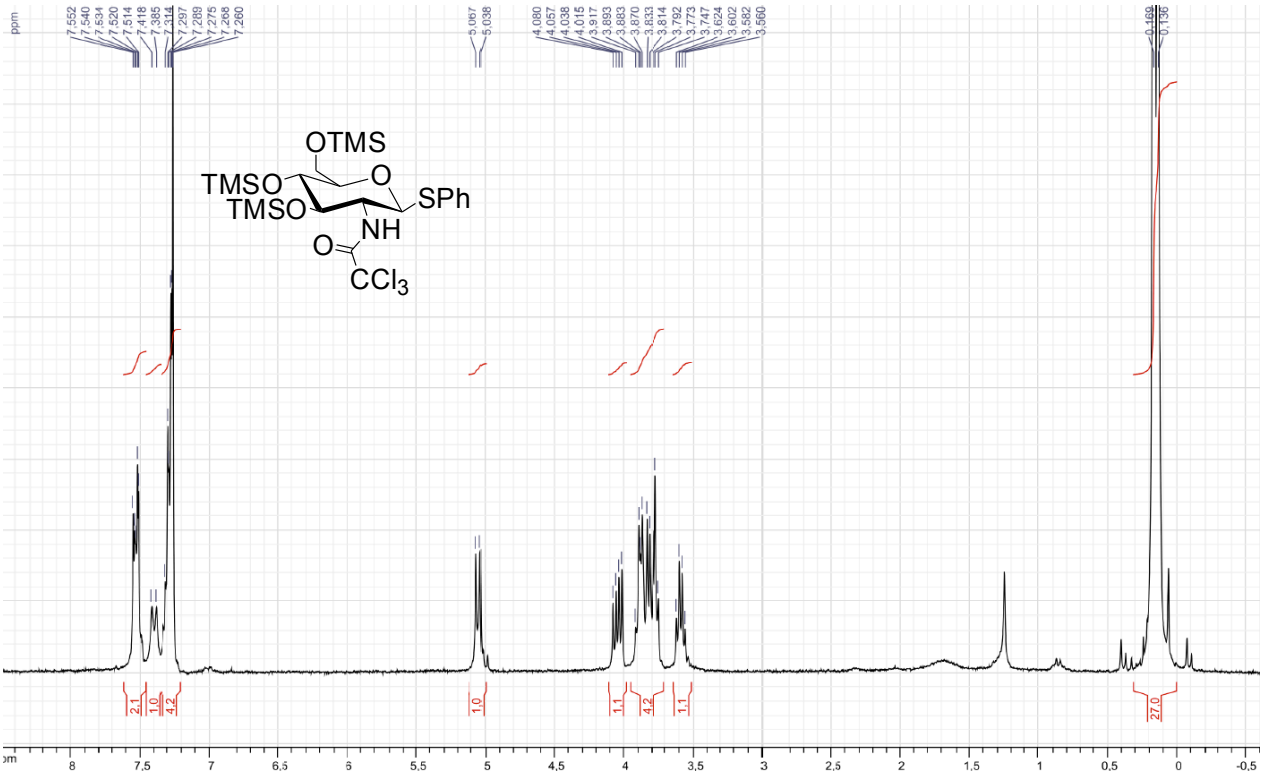
Copy of ^{1}H NMR spectrum of compound 1a (250 MHz, $CDCl_3$)



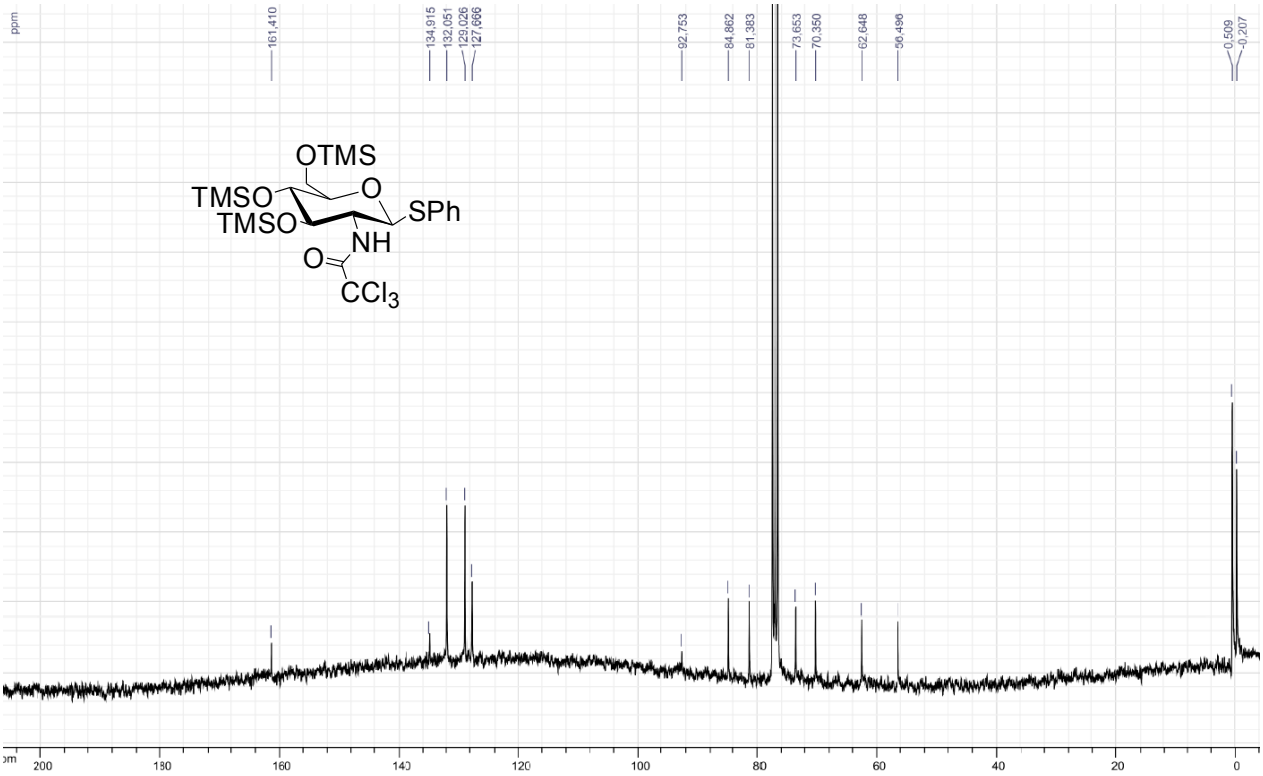
Copy of ^{13}C NMR spectrum of compound 1a (63 MHz, $CDCl_3$)



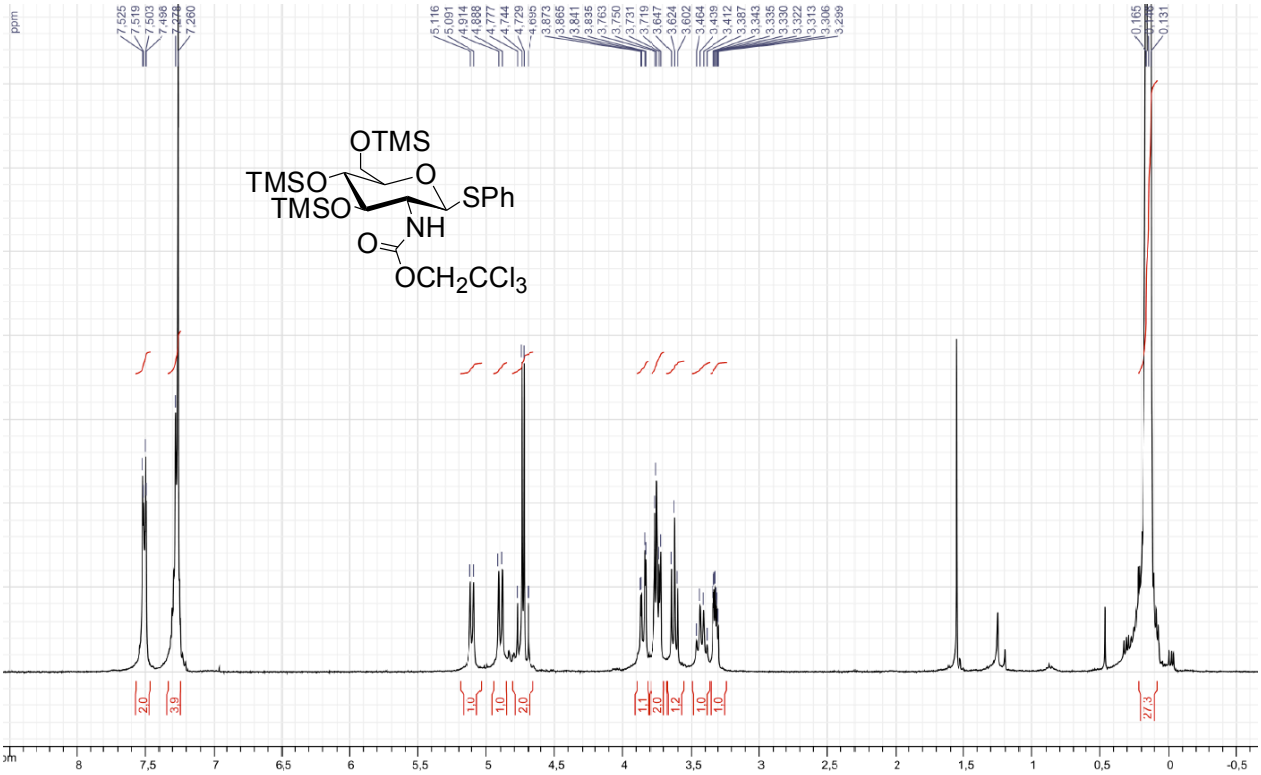
Copy of ^{1}H NMR spectrum of compound 2a (250 MHz, $CDCl_3$)



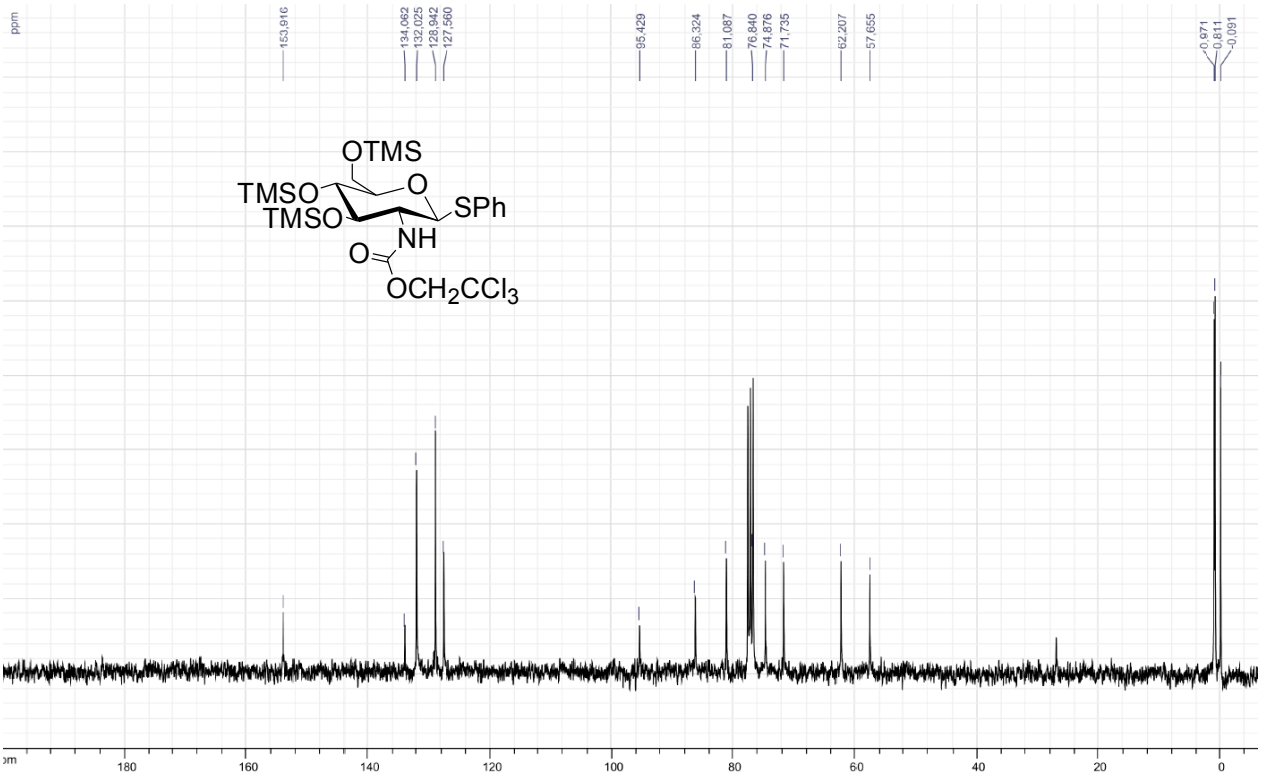
Copy of ^{13}C NMR spectrum of compound 2a (63 MHz, $CDCl_3$)



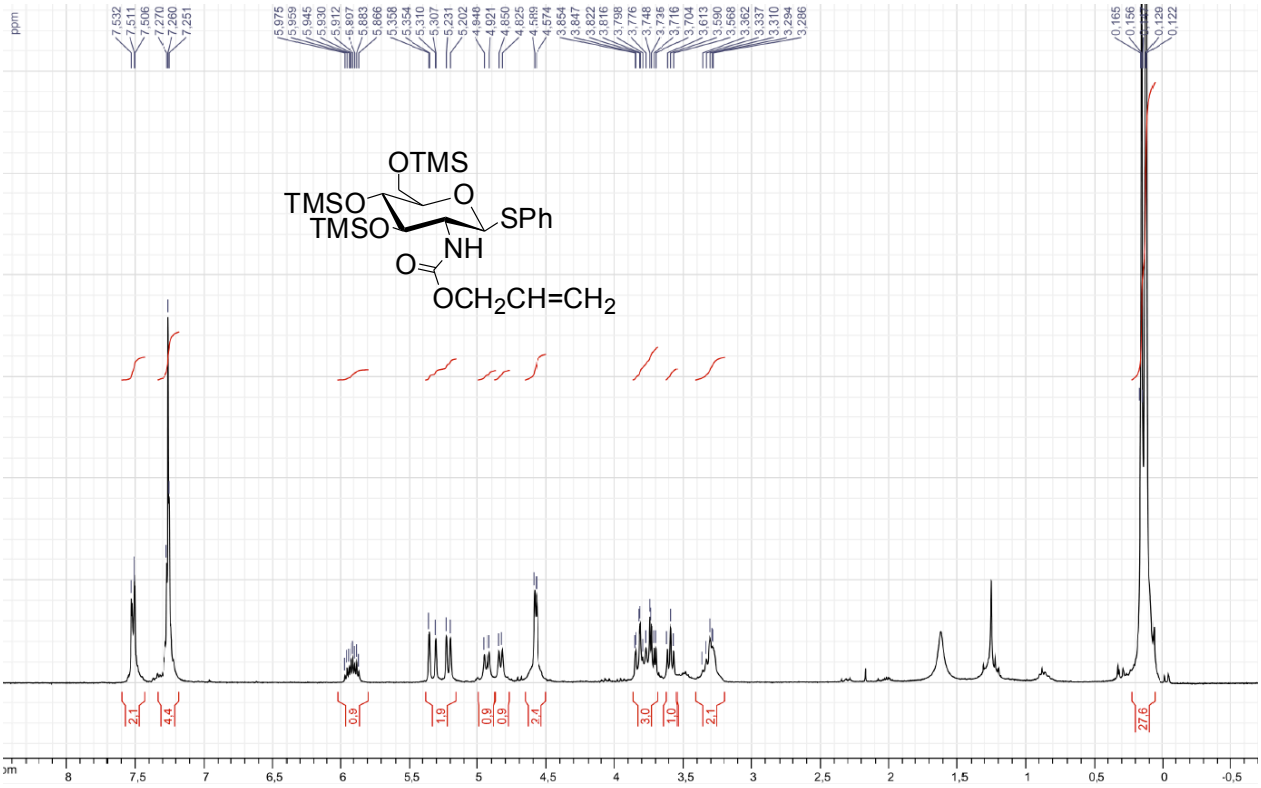
Copy of ^{1}H NMR spectrum of compound 3a (360 MHz, $CDCl_3$)



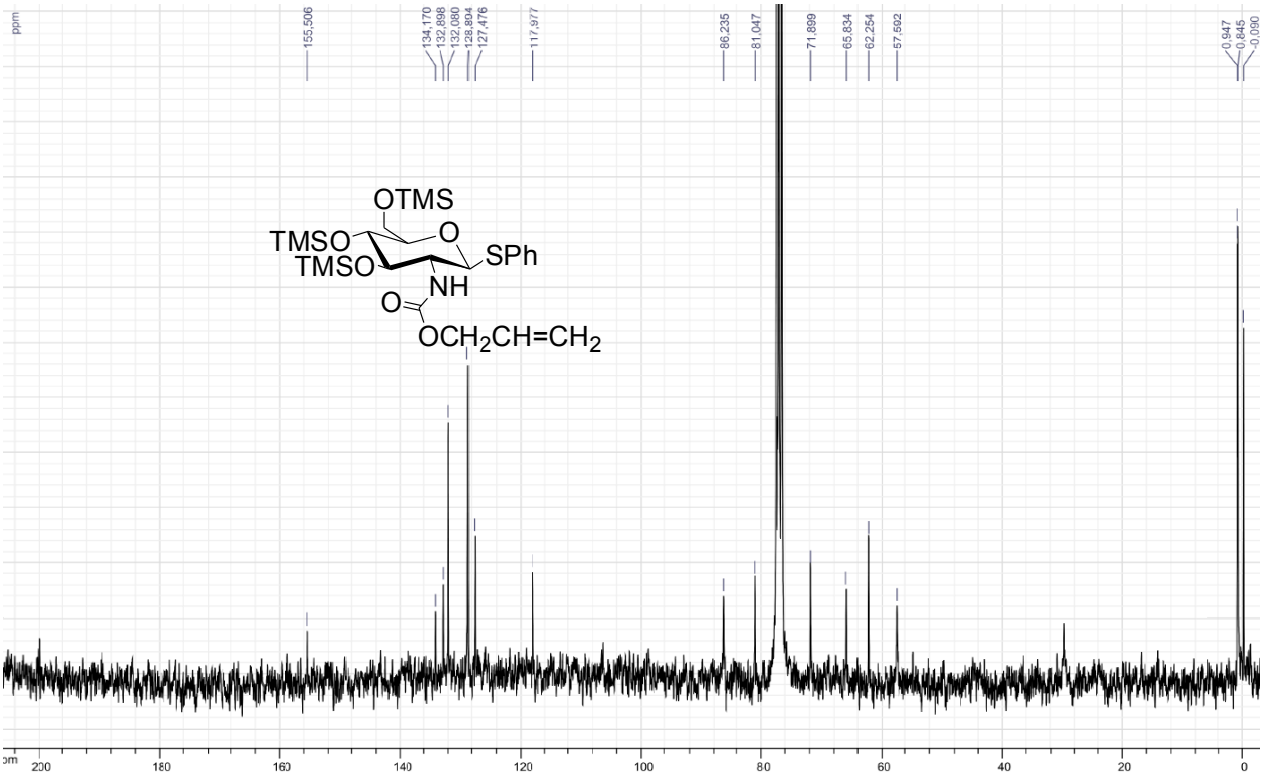
Copy of ^{13}C NMR spectrum of compound 3a (75 MHz, $CDCl_3$)



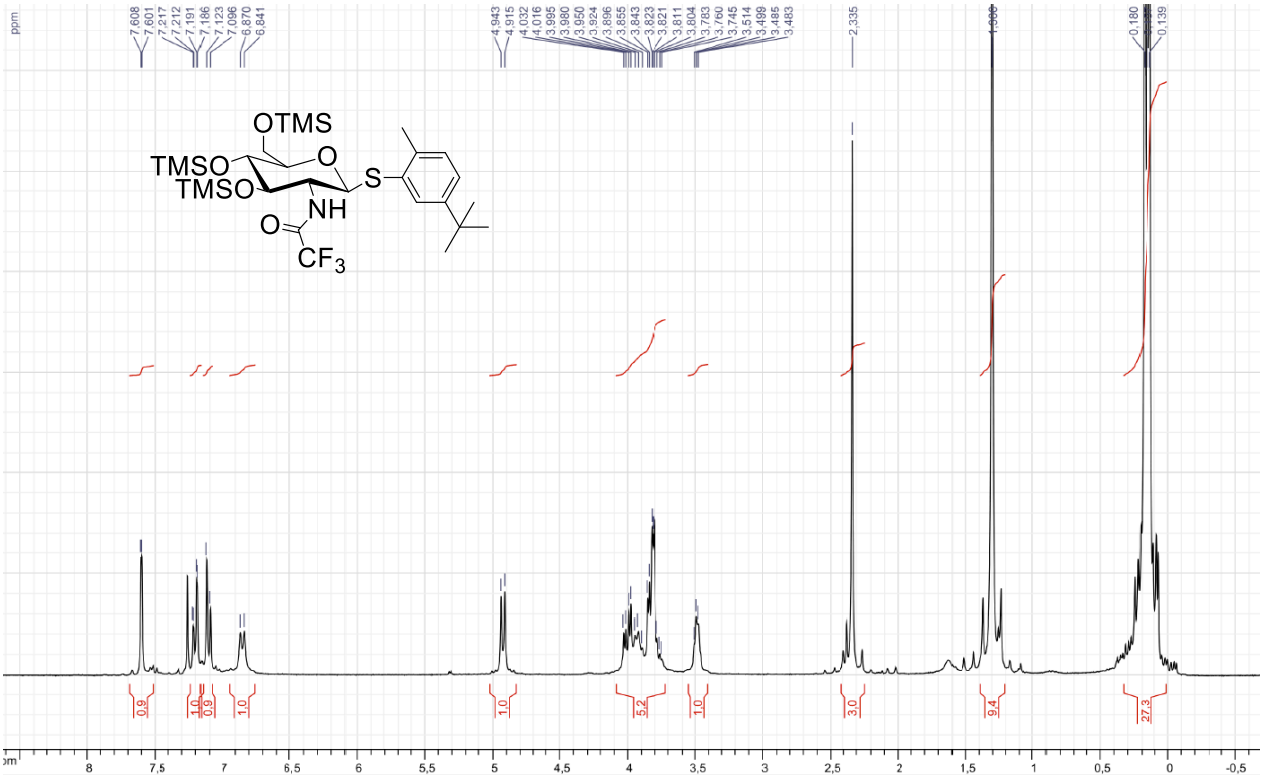
Copy of ^{1}H NMR spectrum of compound 4a (360 MHz, $CDCl_3$)



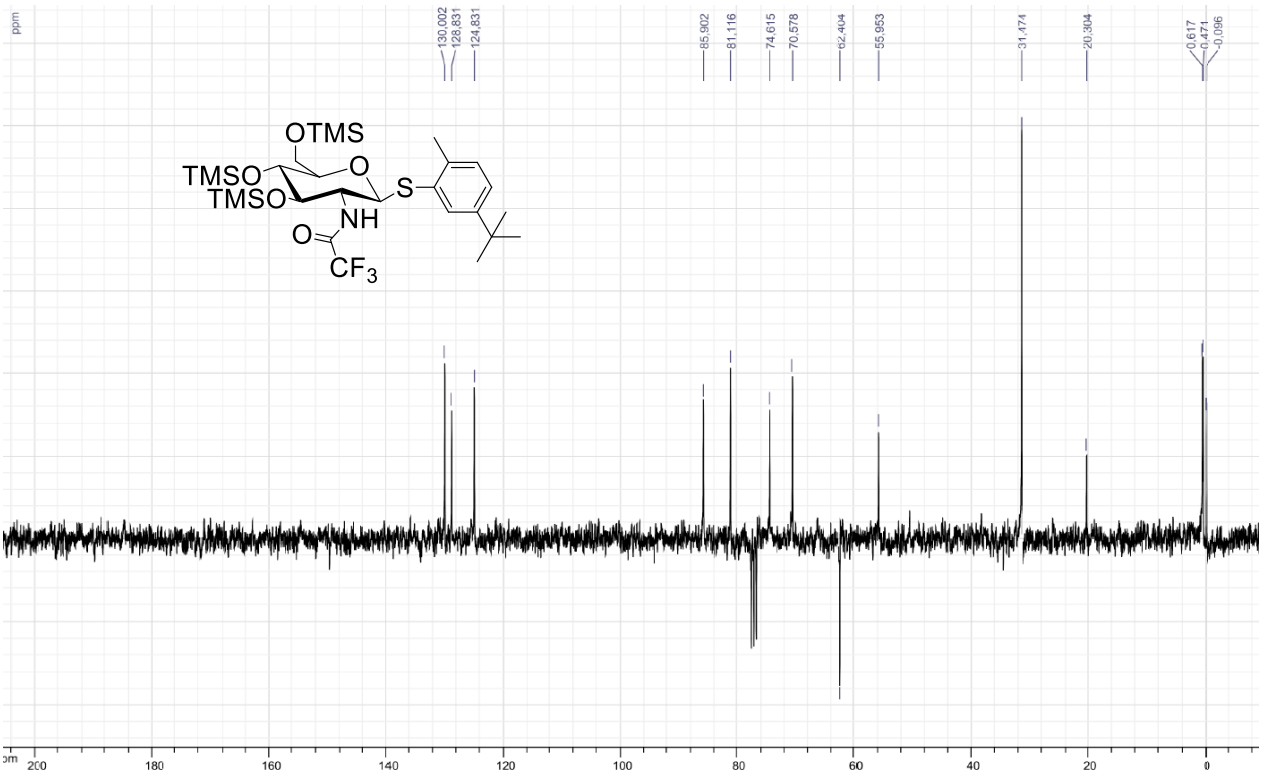
Copy of ^{13}C NMR spectrum of compound 4a (63 MHz, $CDCl_3$)



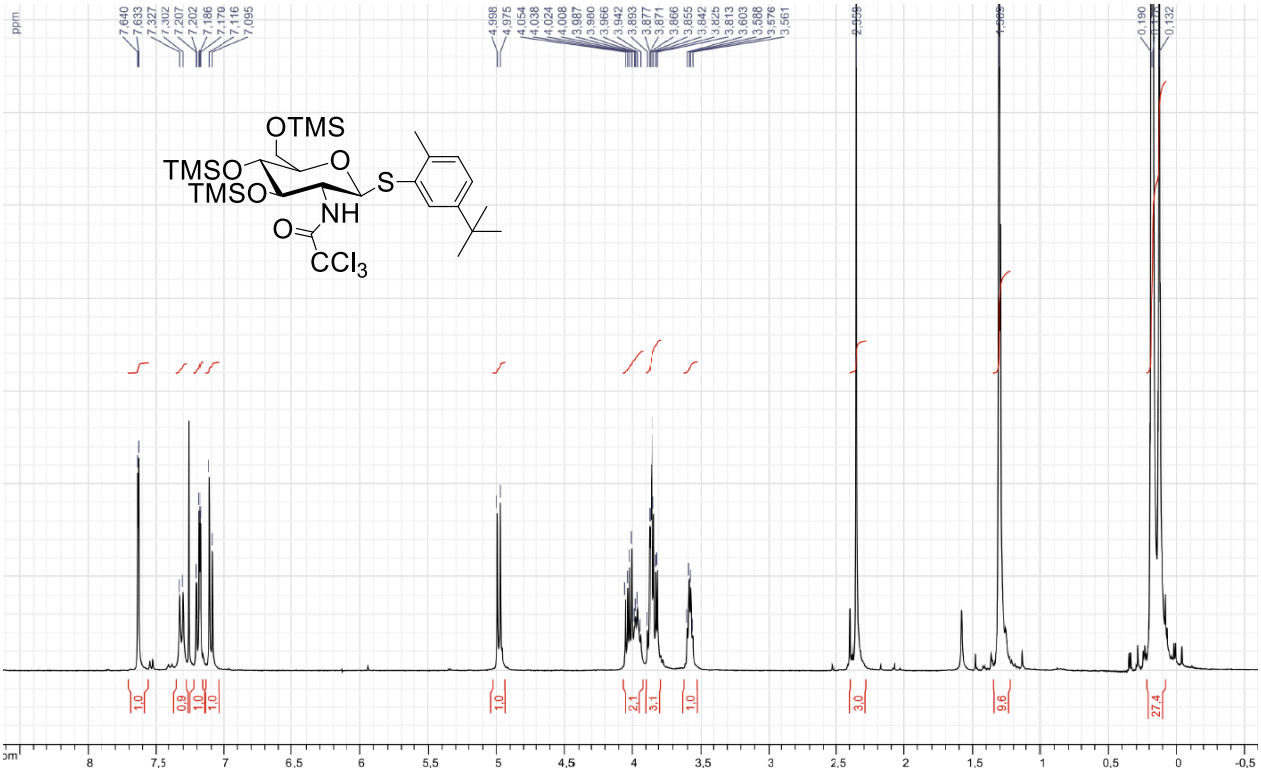
Copy of ^{1}H NMR spectrum of compound 5a (300 MHz, $CDCl_3$)



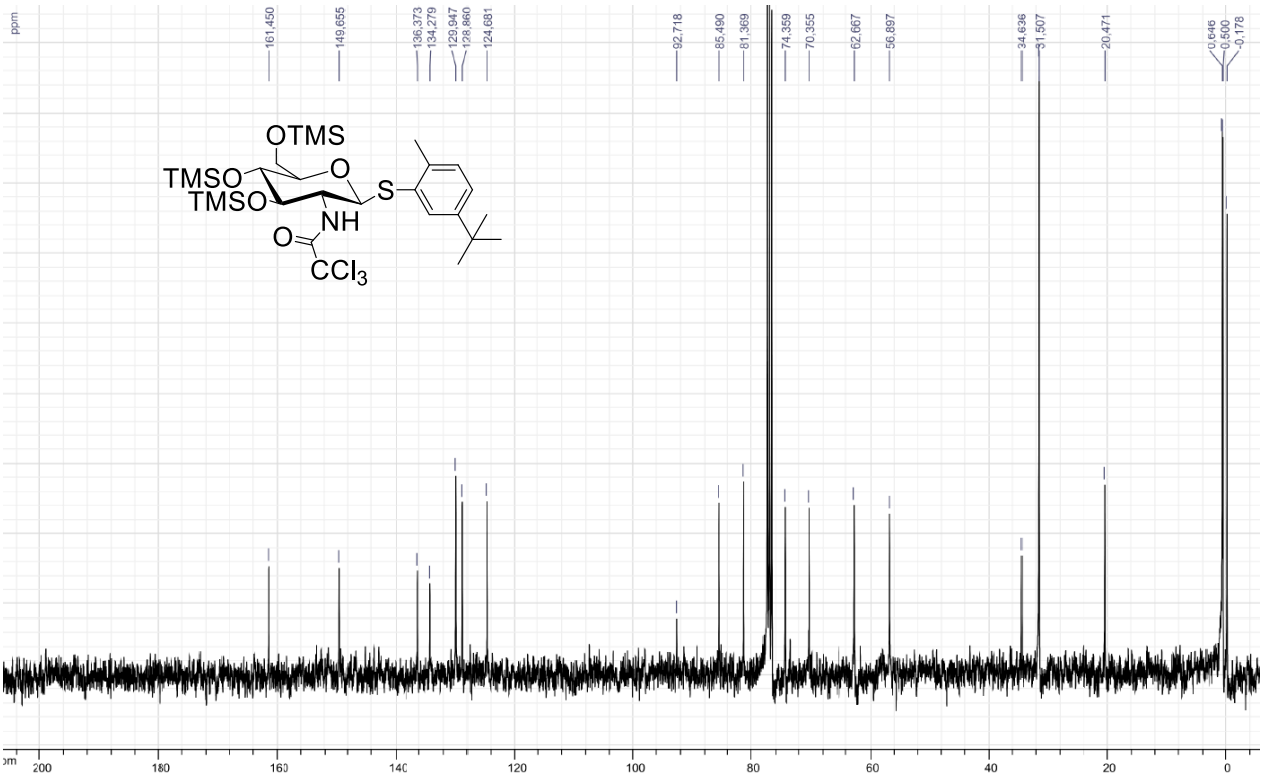
Copy of ^{13}C NMR spectrum (DEPT 135) of compound 5a (75 MHz, $CDCl_3$)



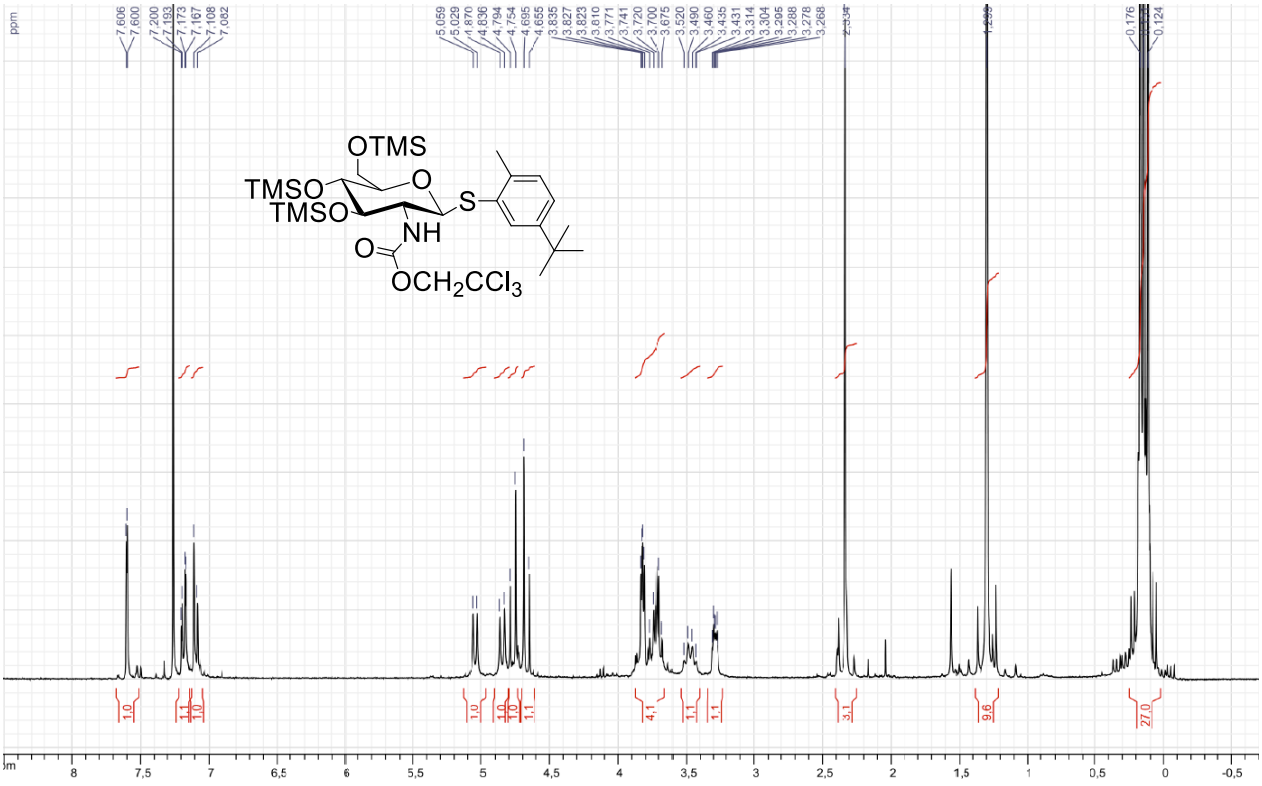
Copy of ^{1}H NMR spectrum of compound 6a (360 MHz, $CDCl_3$)



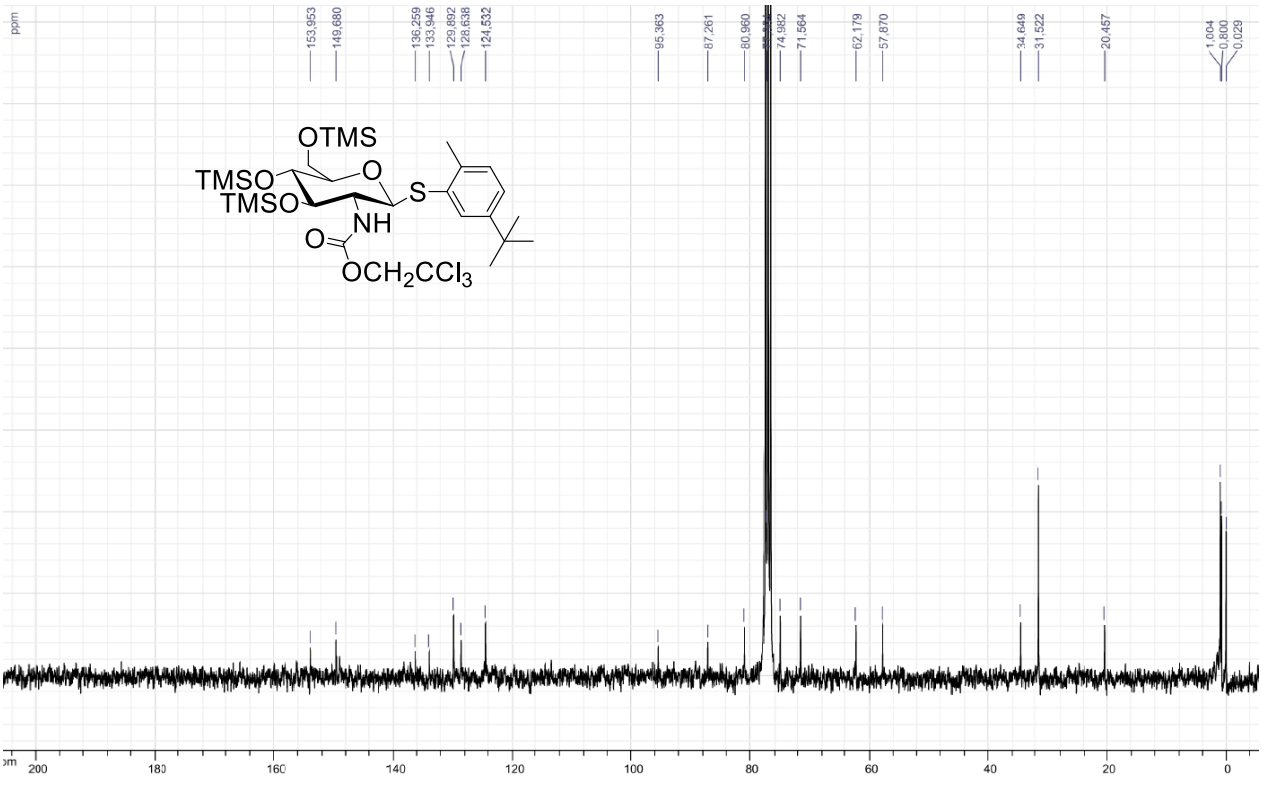
Copy of ^{13}C NMR spectrum of compound 6a (90 MHz, $CDCl_3$)



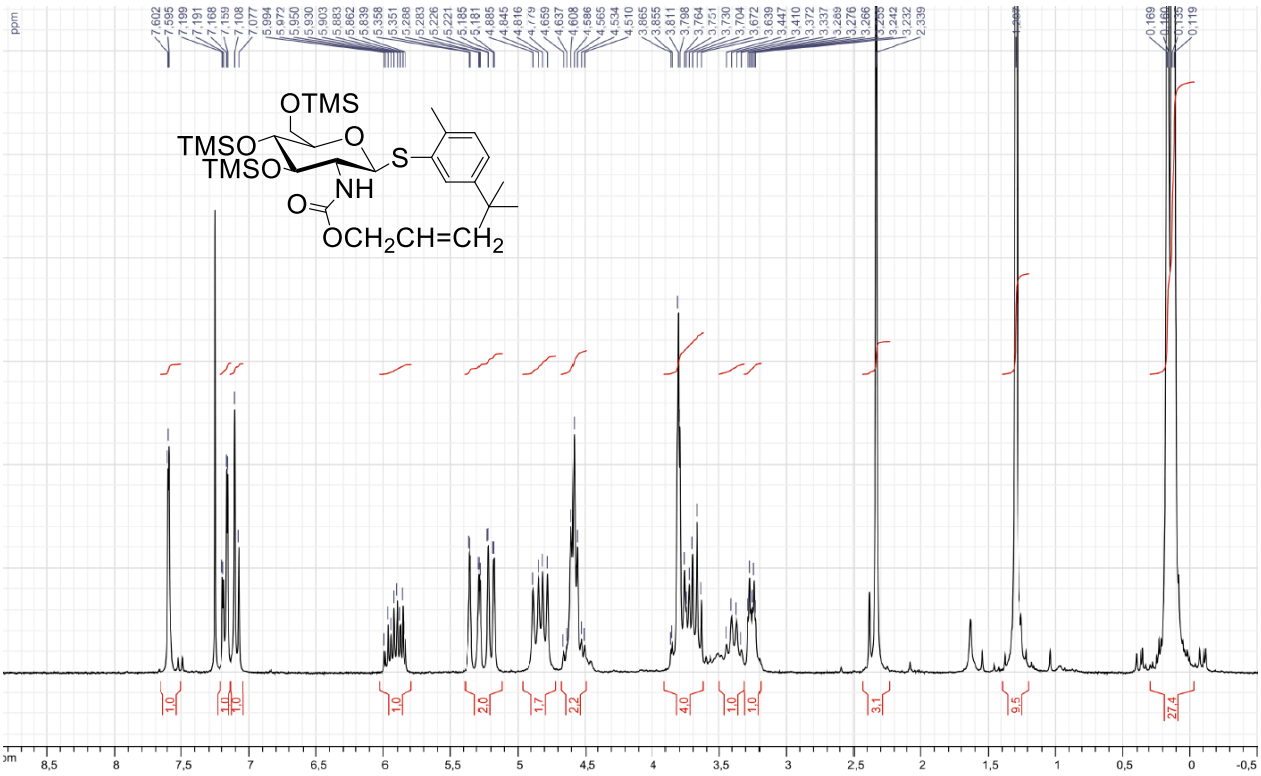
Copy of ^{1}H NMR spectrum of compound 7a (300 MHz, $CDCl_3$)



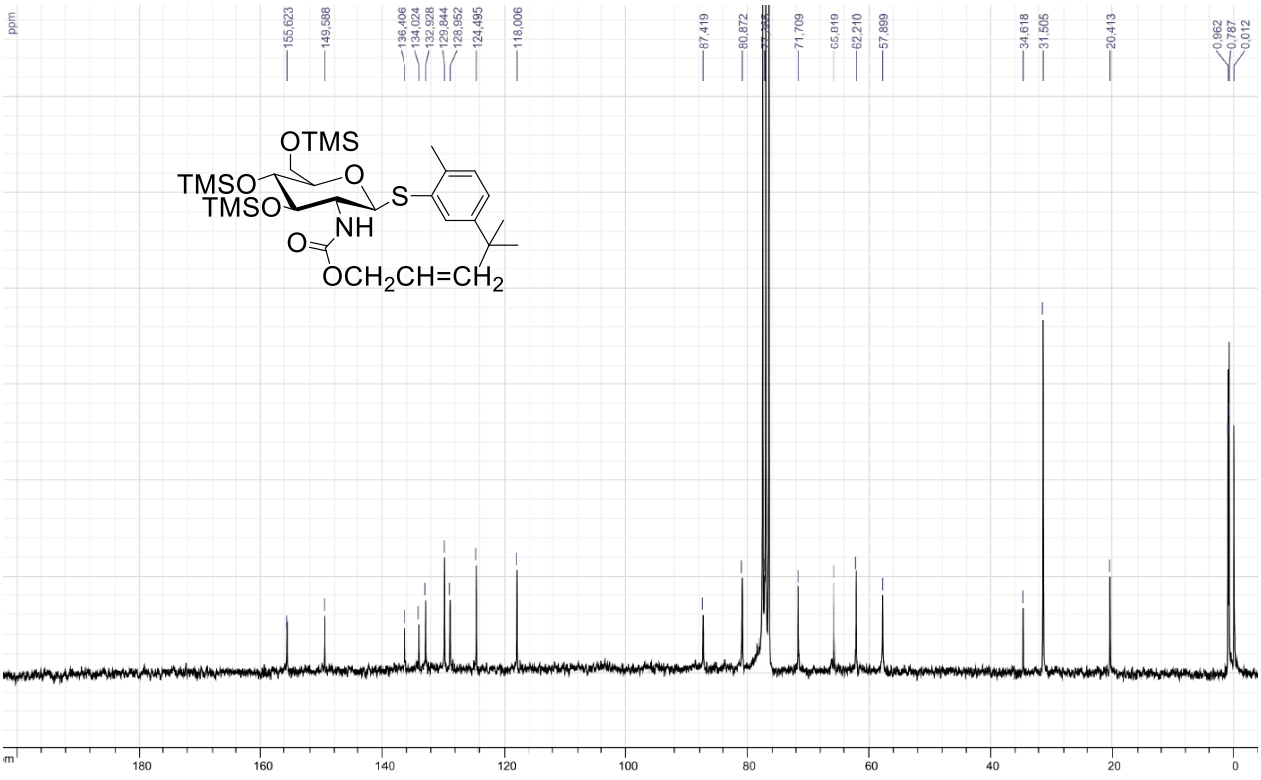
Copy of ^{13}C NMR spectrum of compound 7a (75 MHz, $CDCl_3$)



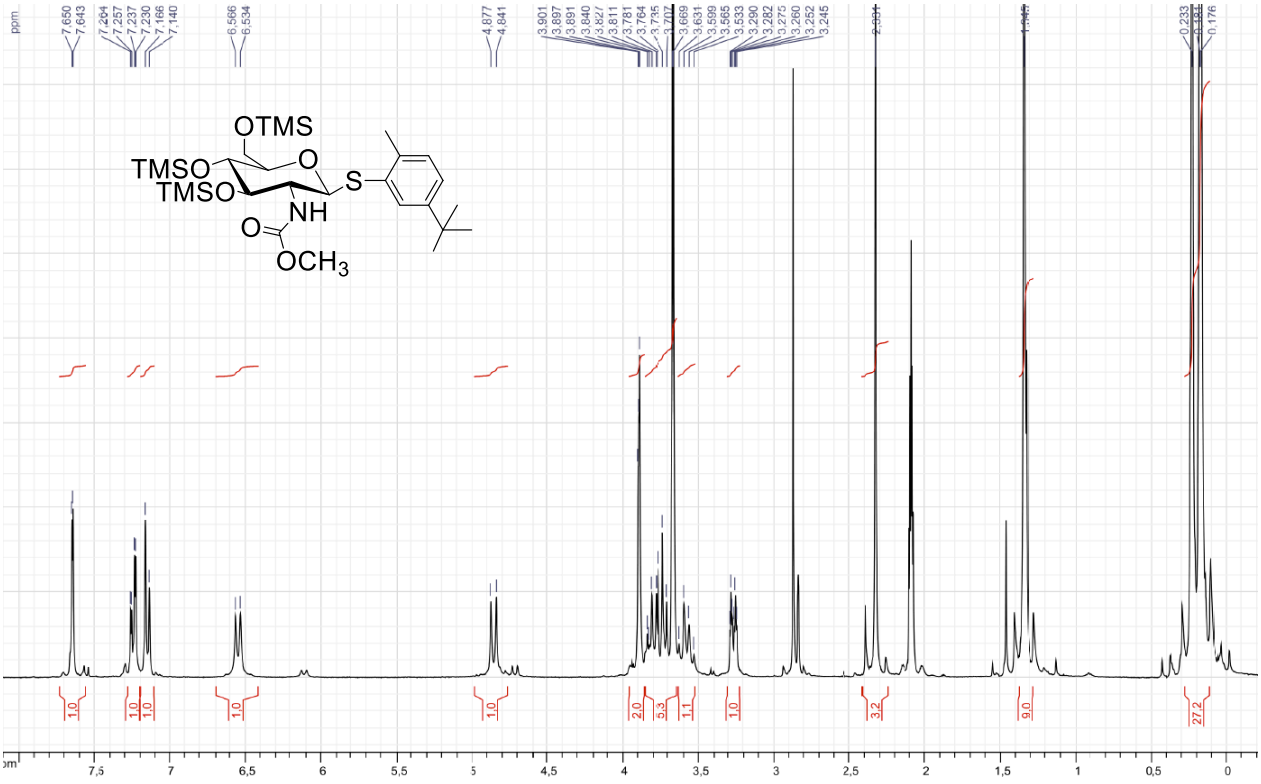
Copy of ^{1}H NMR spectrum of compound 8a (250 MHz, $CDCl_3$)



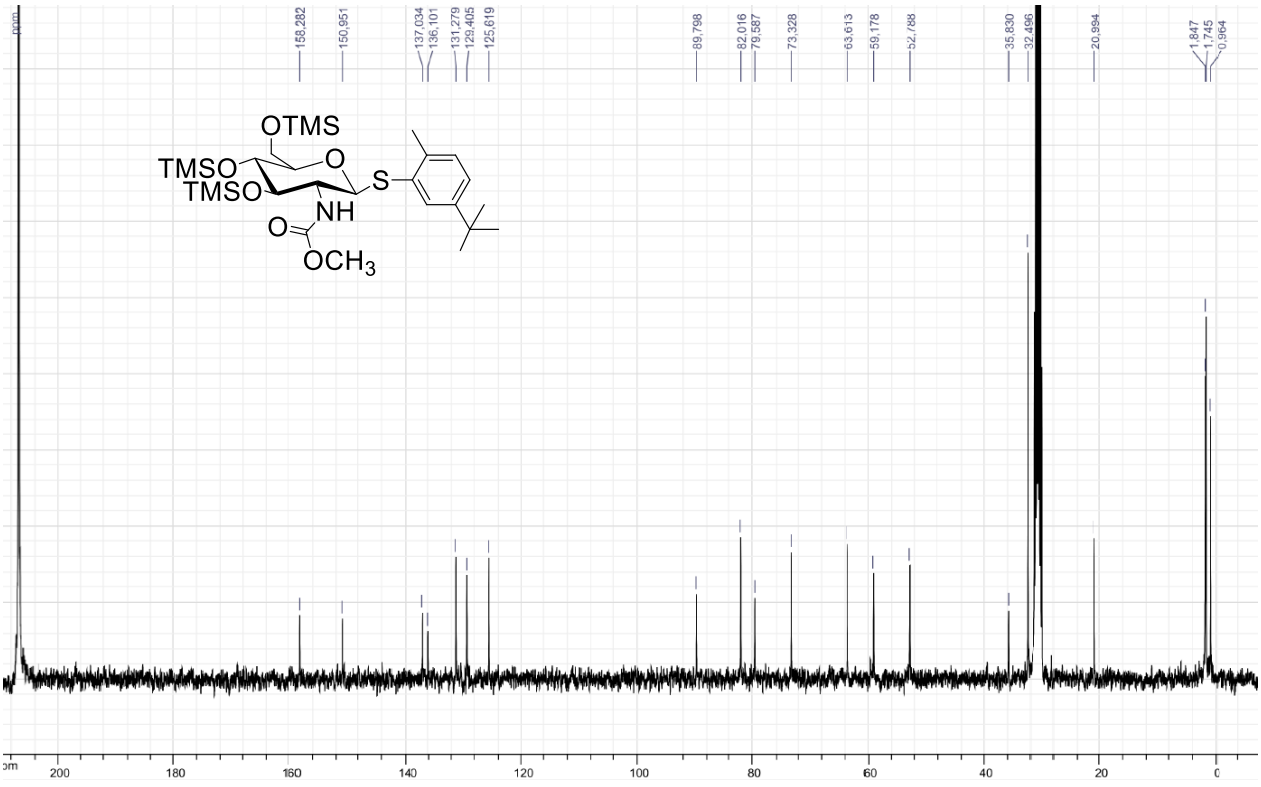
Copy of ^{13}C NMR spectrum of compound 8a (63 MHz, $CDCl_3$)



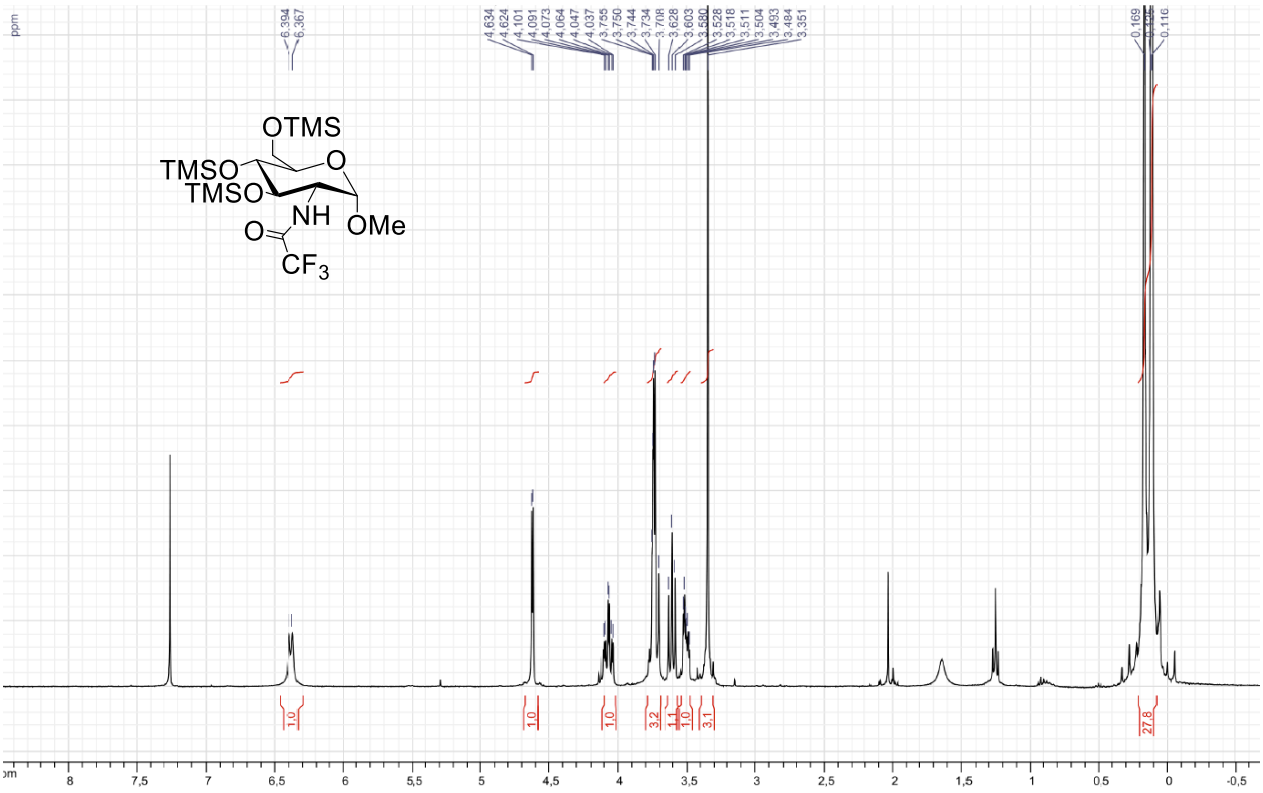
Copy of ^{1}H NMR spectrum of compound 9a (300 MHz, $(CD_3)_2CO$)



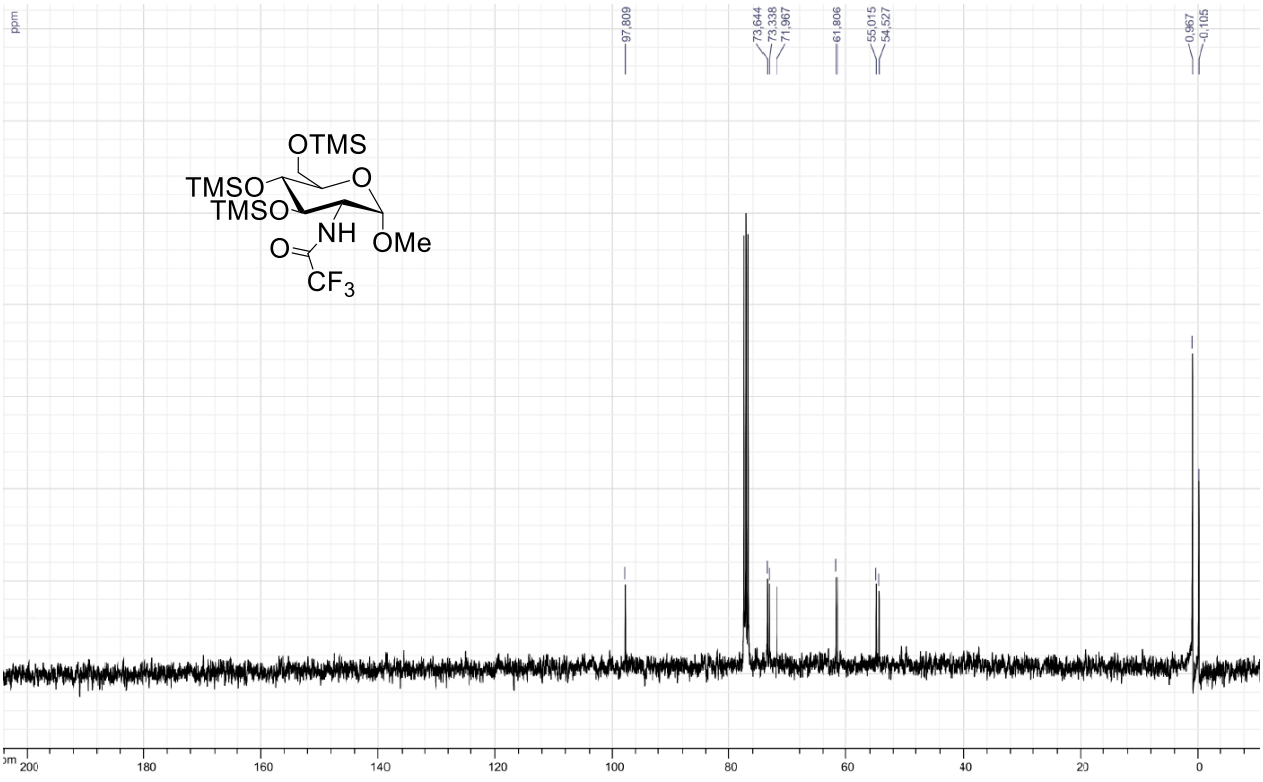
Copy of ^{13}C NMR spectrum of compound 9a (90 MHz, $(CD_3)_2CO$)



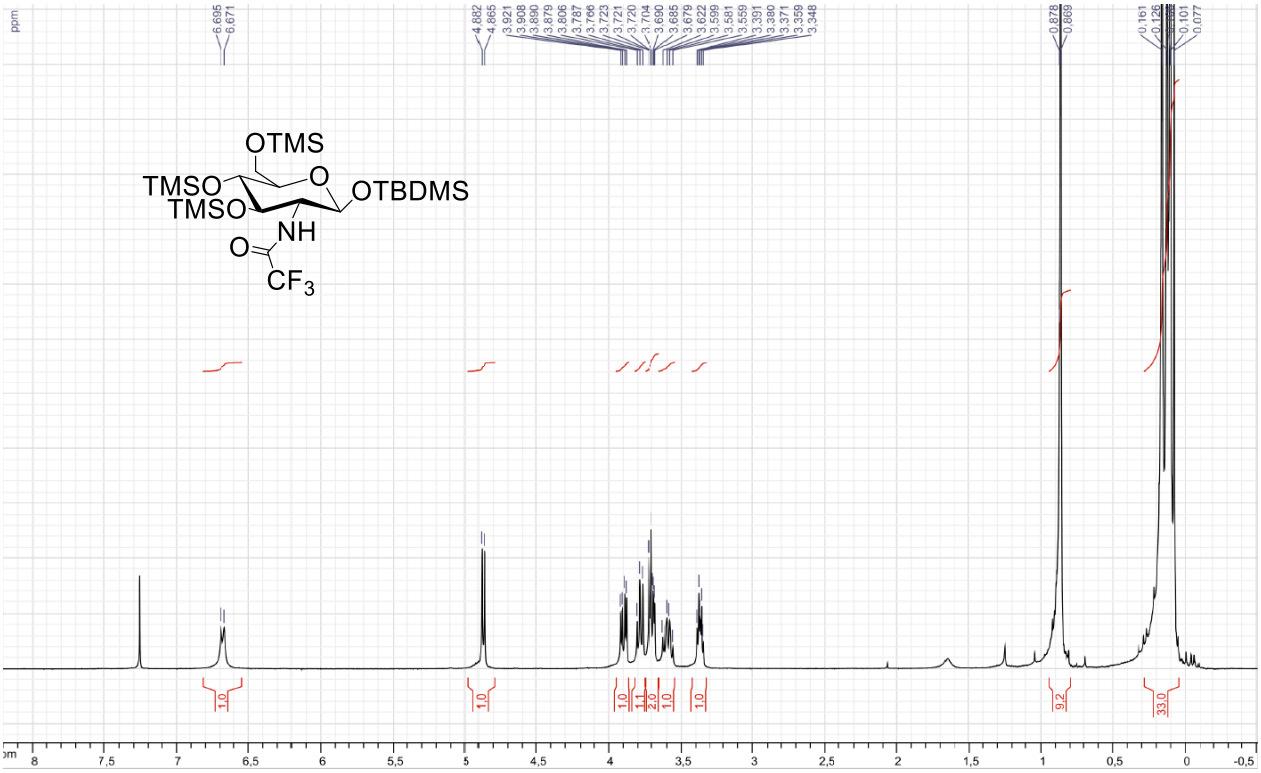
Copy of ^{1}H NMR spectrum of compound 10a (360 MHz, $CDCl_3$)



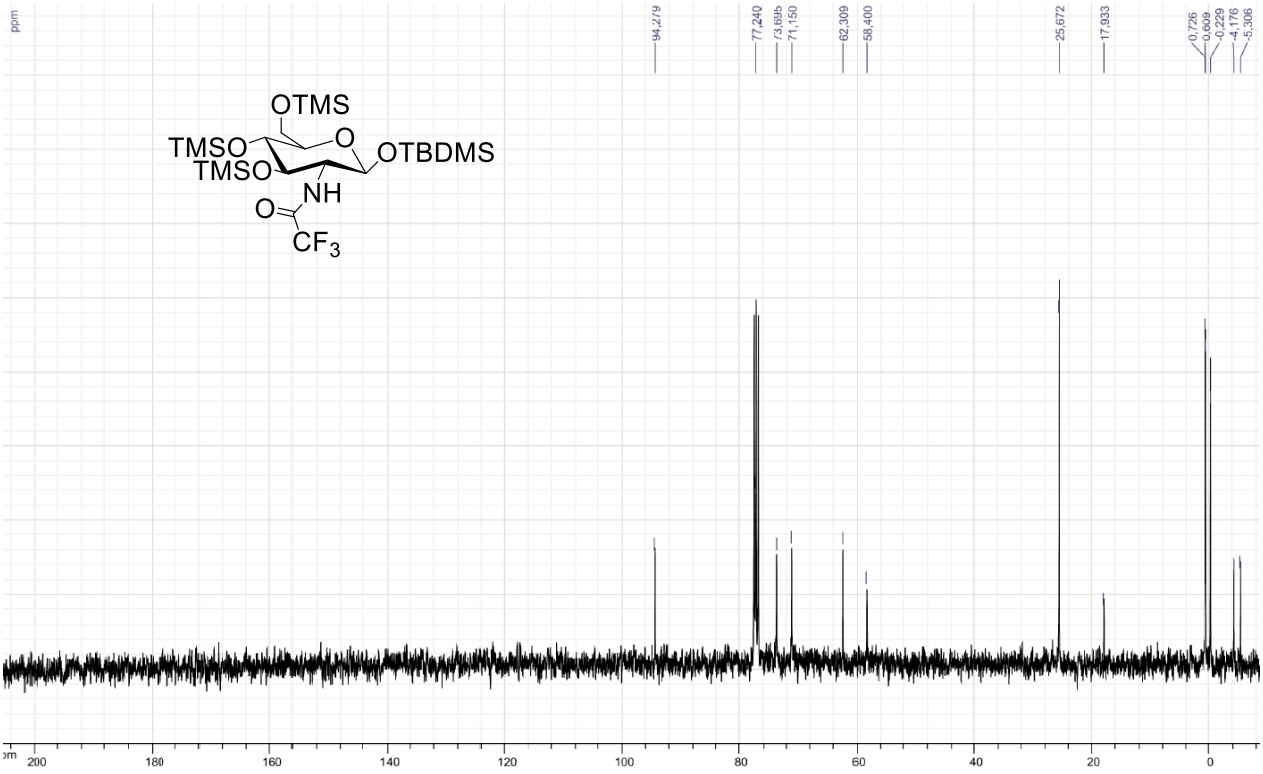
Copy of ^{13}C NMR spectrum of compound 10a (90 MHz, $CDCl_3$)



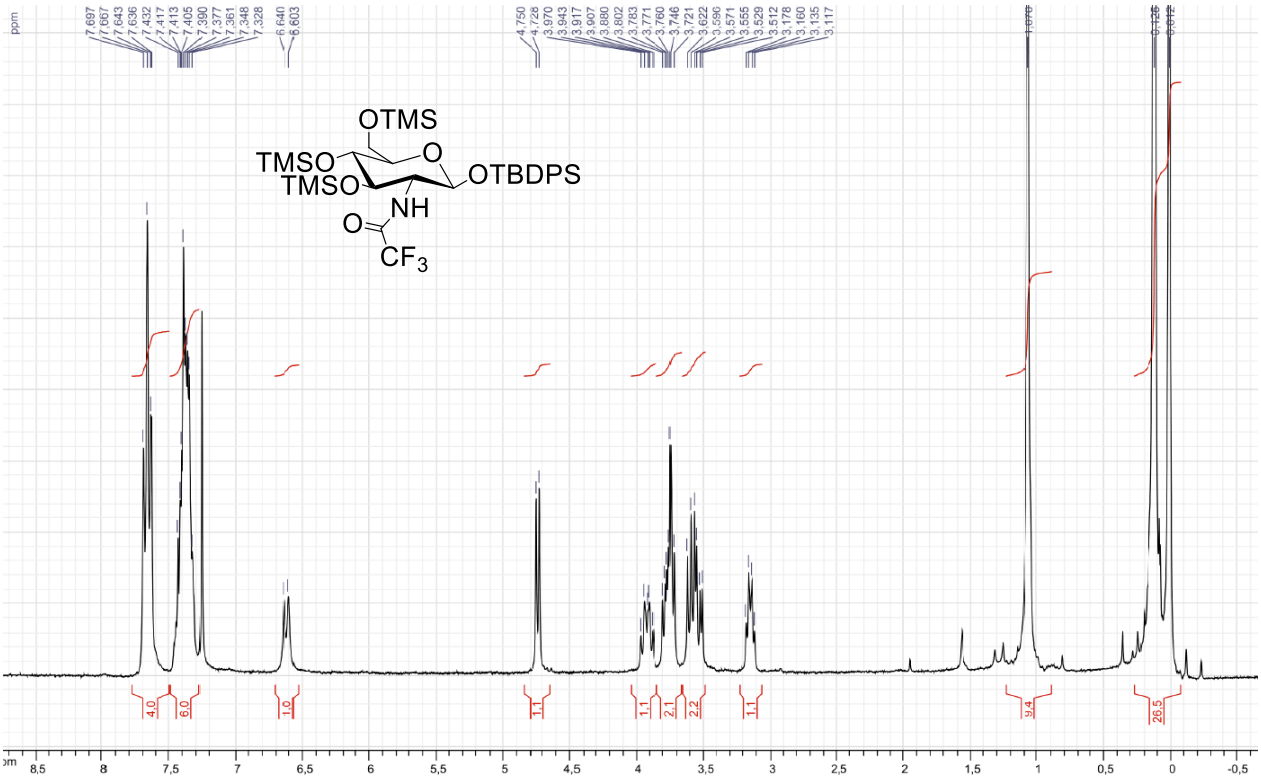
Copy of ^{1}H NMR spectrum of compound 11a (360 MHz, $CDCl_3$)



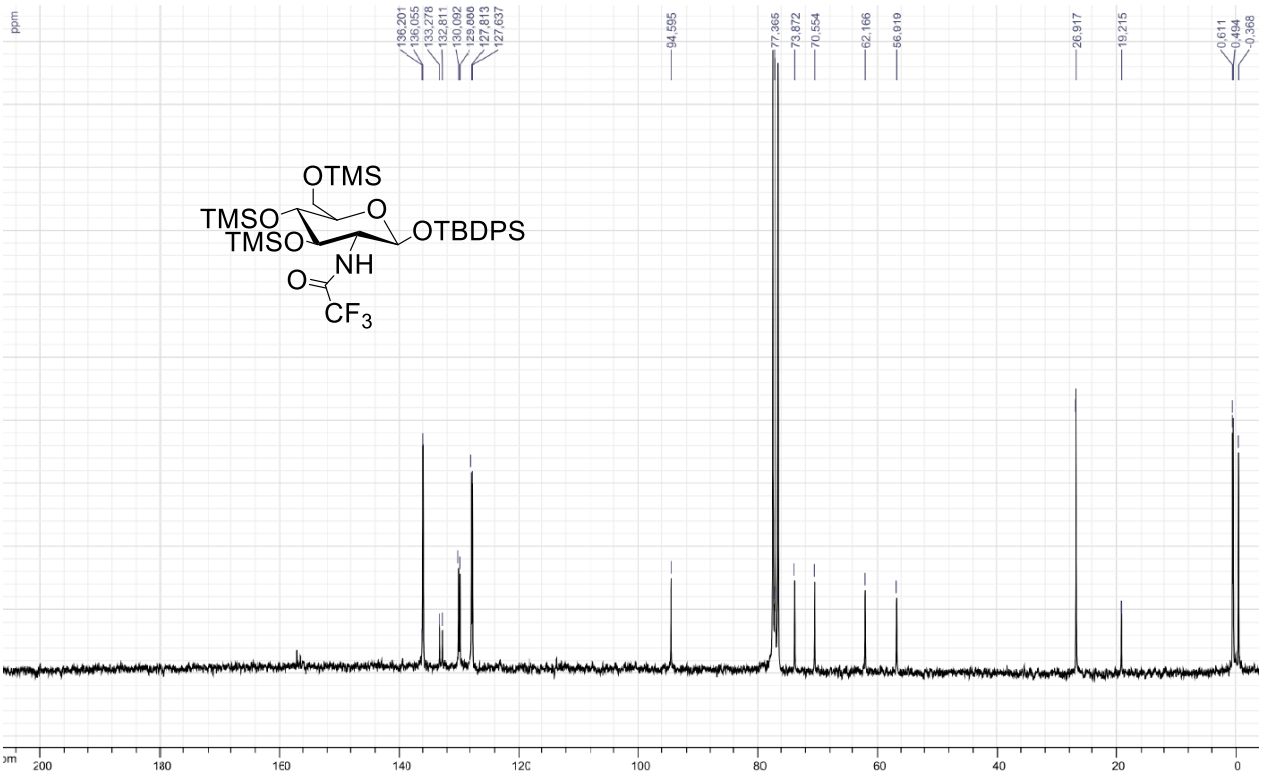
Copy of ^{13}C NMR spectrum of compound 11a (90 MHz, $CDCl_3$)



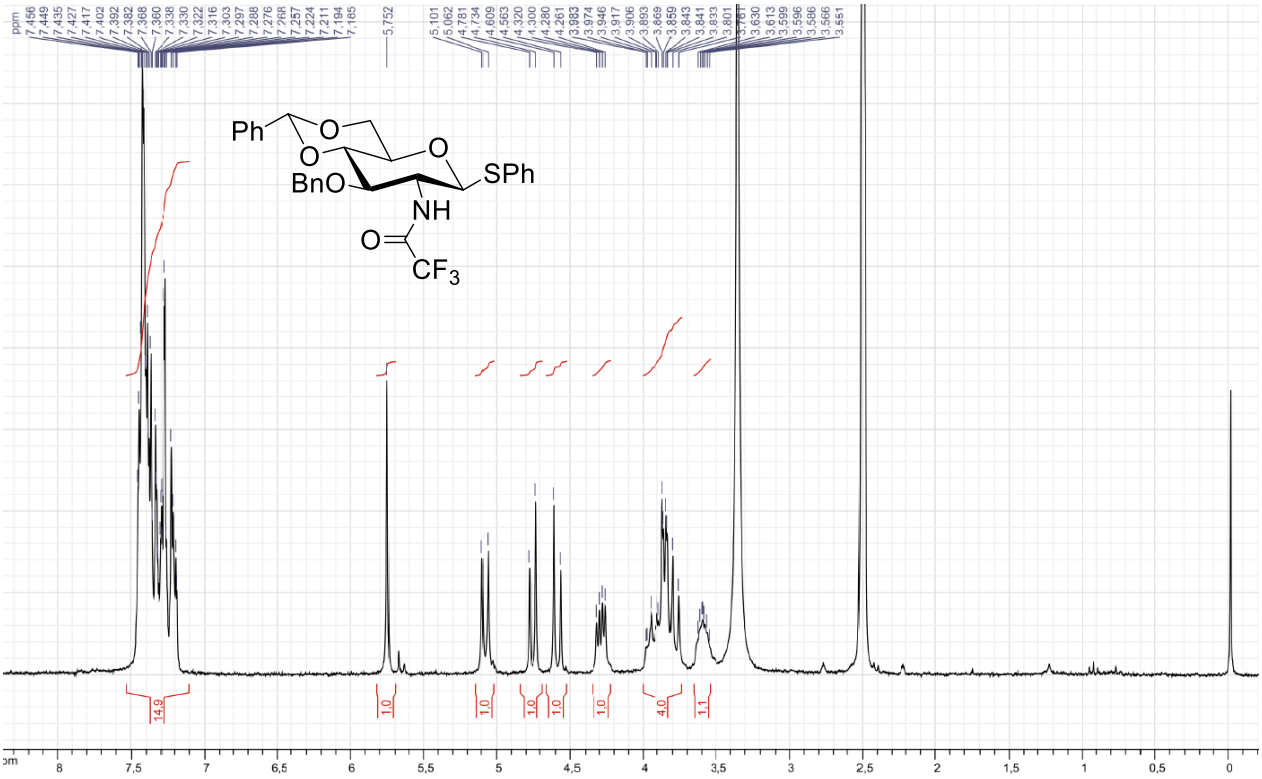
Copy of ^{1}H NMR spectrum of compound 12a (250 MHz, $CDCl_3$)



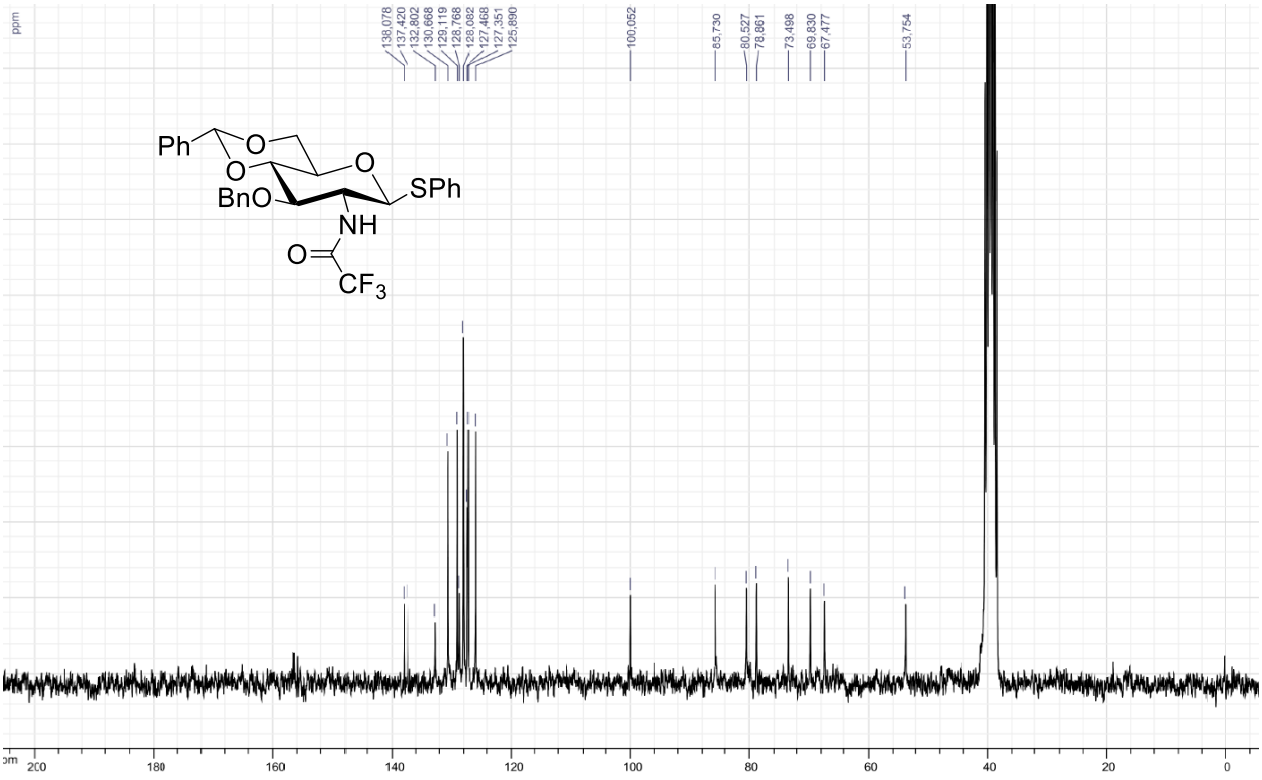
Copy of ^{13}C NMR spectrum of compound 12a (63 MHz, $CDCl_3$)



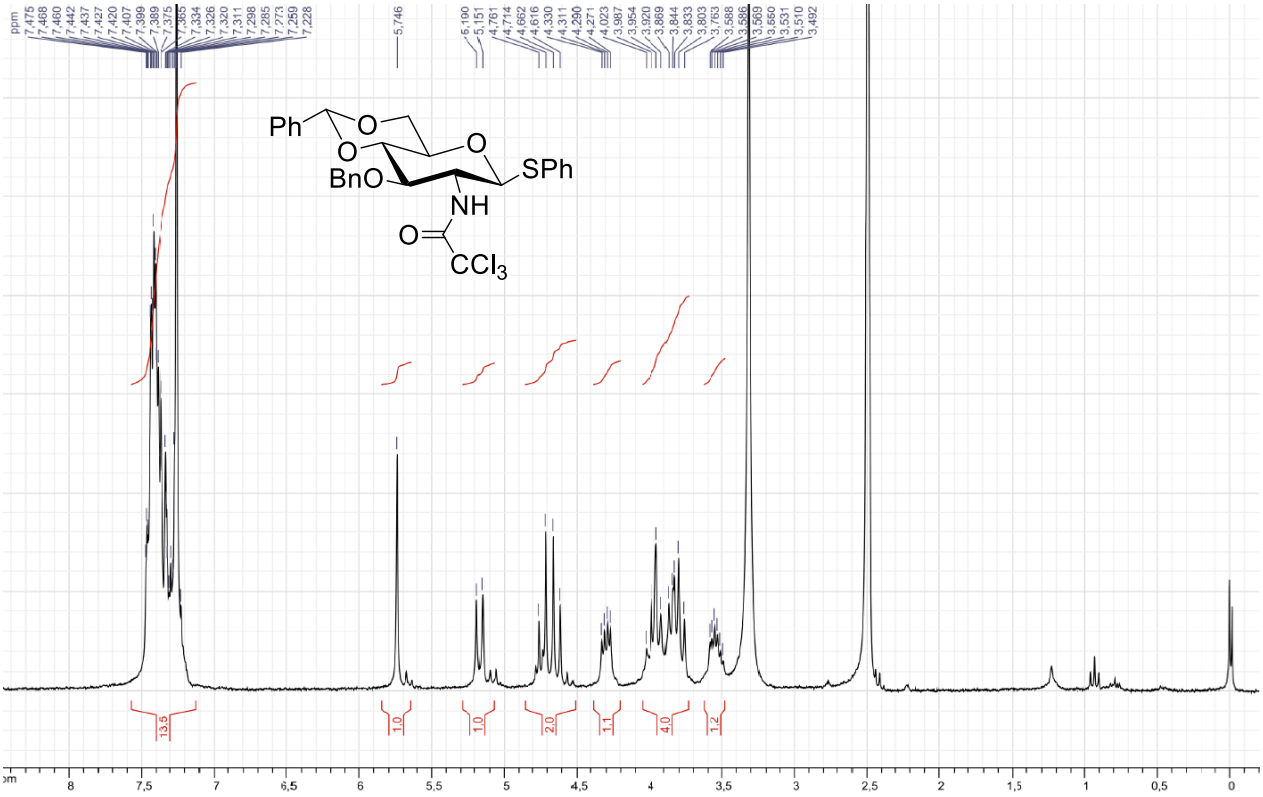
Copy of ^{1}H NMR spectrum of compound 1b (250 MHz, DMSO)



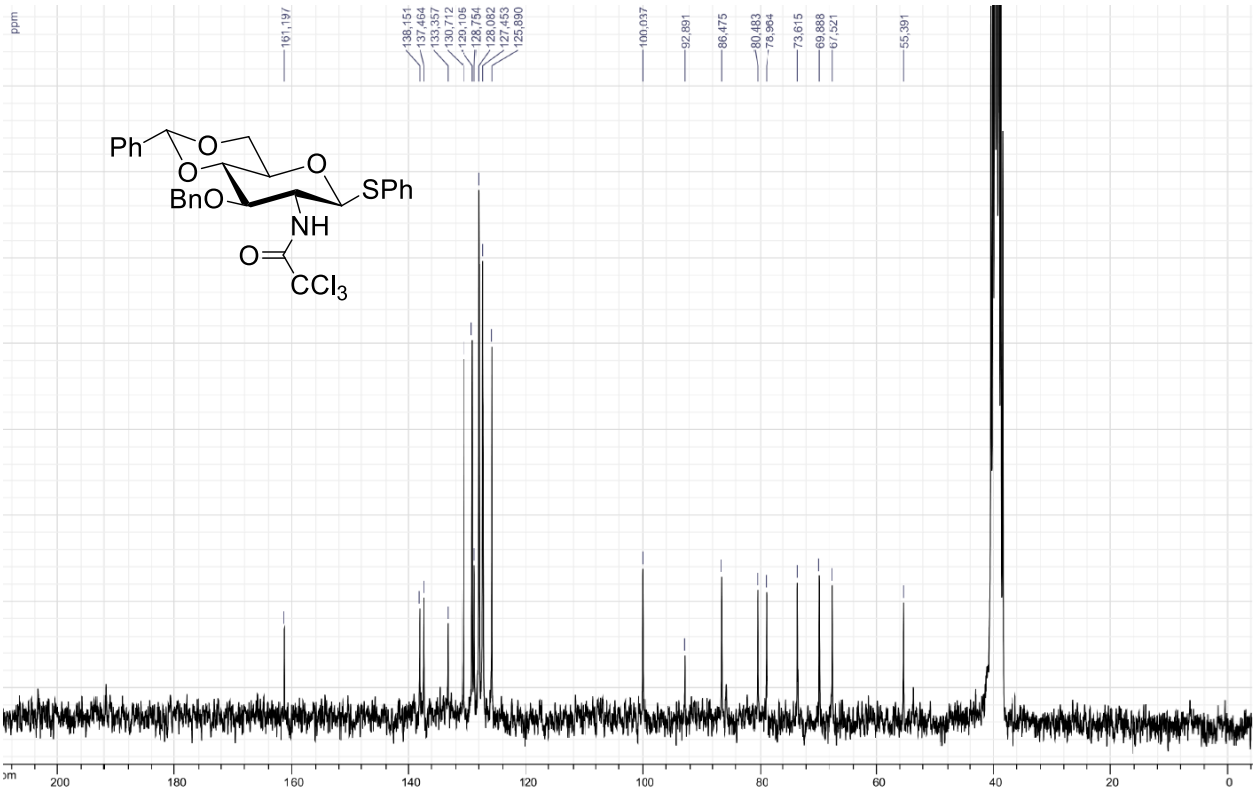
Copy of ^{13}C NMR spectrum of compound 1b (63 MHz, DMSO)



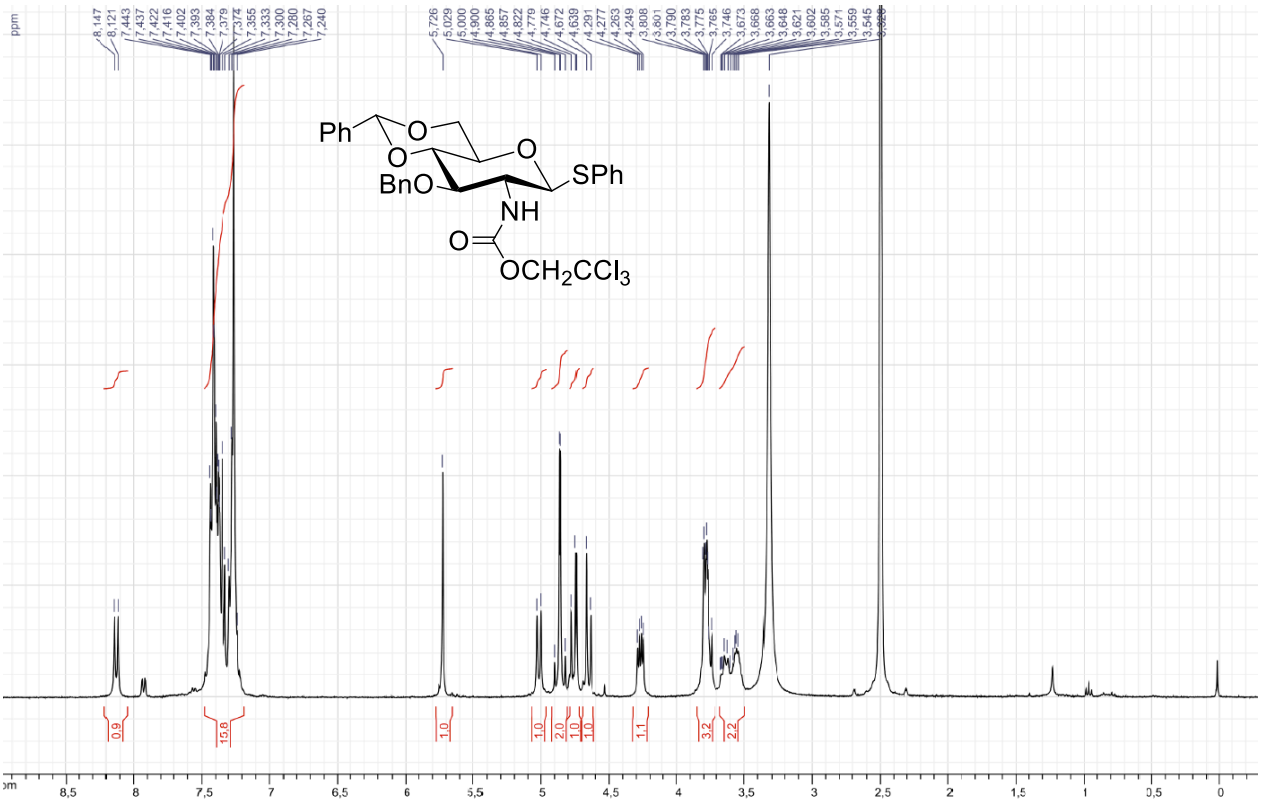
Copy of ^{1}H NMR spectrum of compound 2b (250 MHz, DMSO)



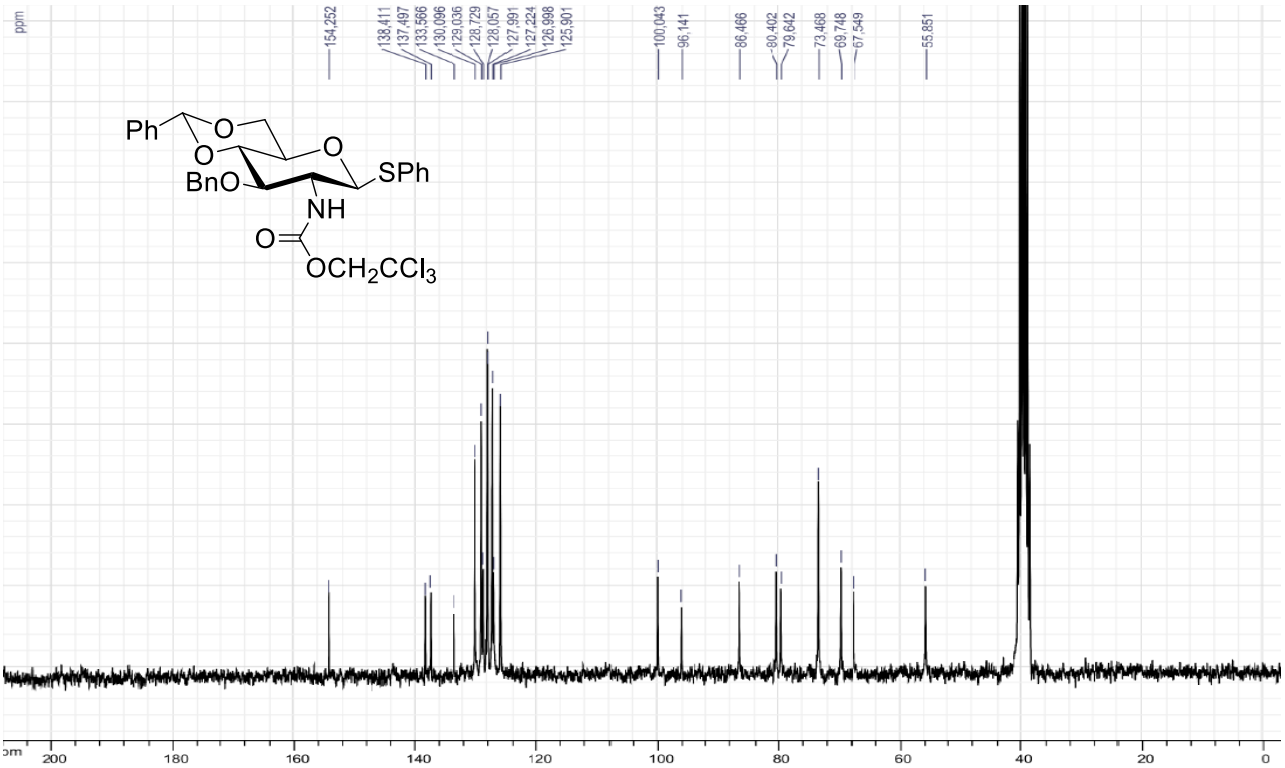
Copy of ^{13}C NMR spectrum of compound 2b (63 MHz, DMSO)



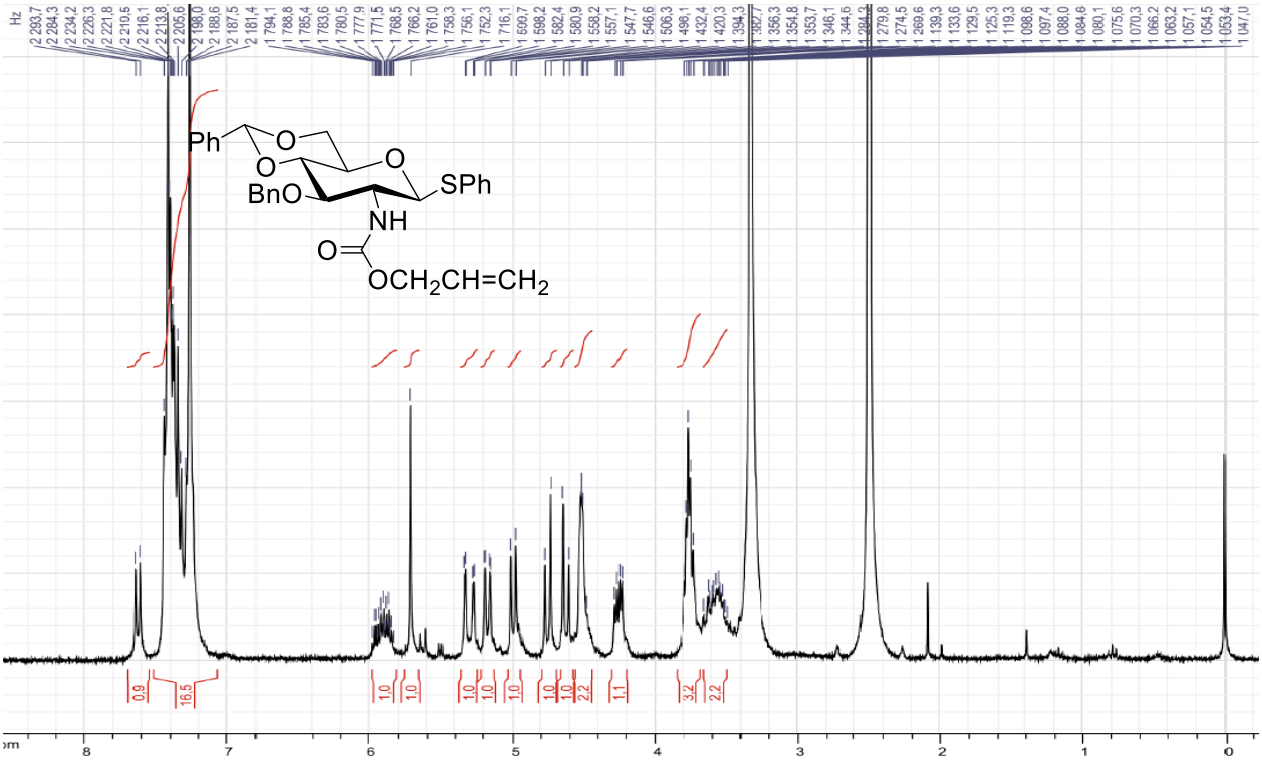
Copy of ^{1}H NMR spectrum of compound 3b (360 MHz, DMSO)



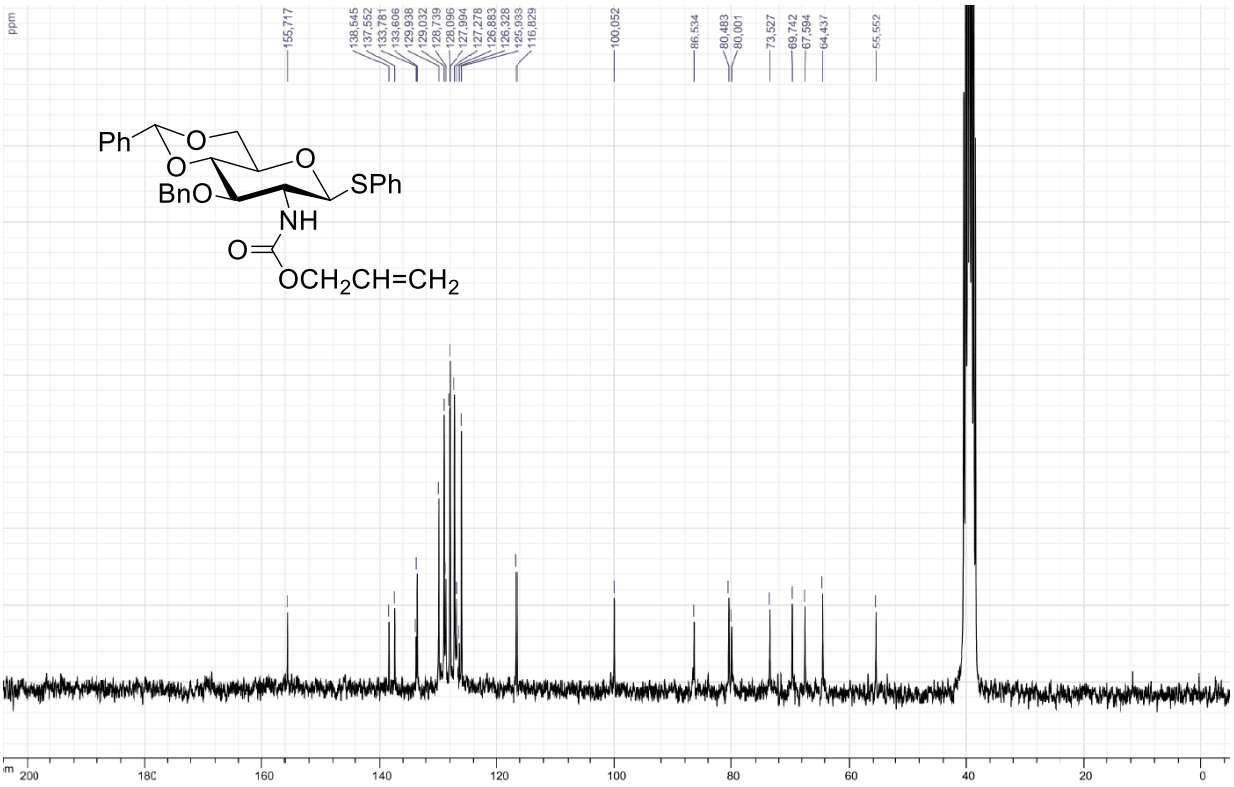
Copy of ^{13}C NMR spectrum of compound 3b (90 MHz, DMSO)



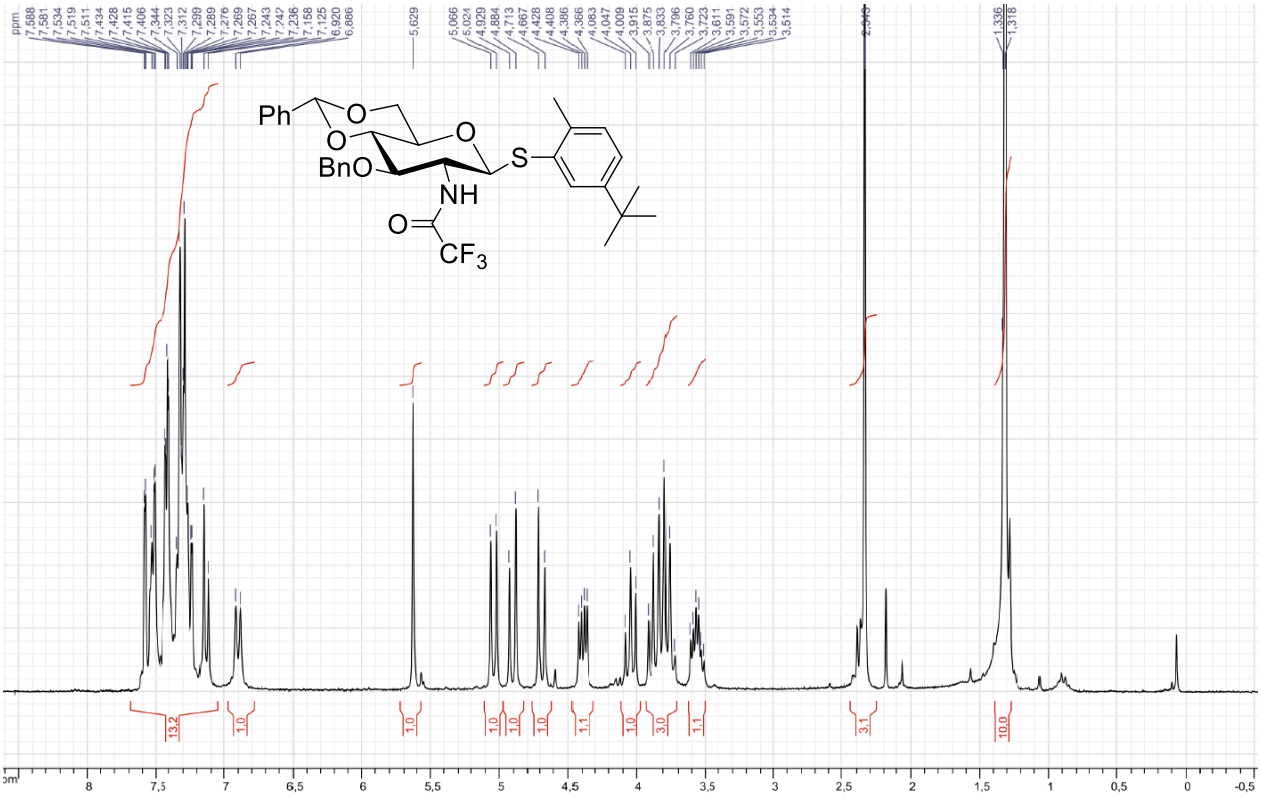
Copy of ^{1}H NMR spectrum of compound 4b (360 MHz, DMSO)



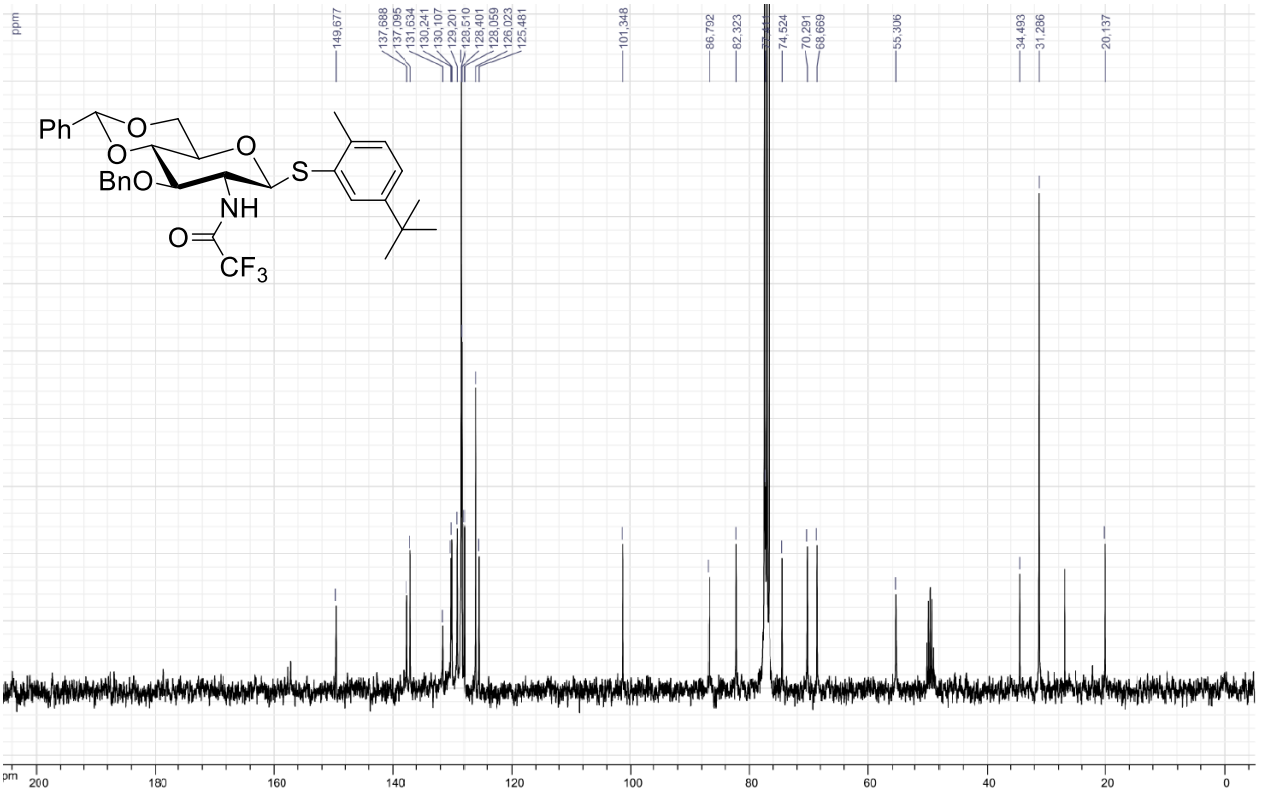
Copy of ^{13}C NMR spectrum of compound 3b (90 MHz, DMSO)



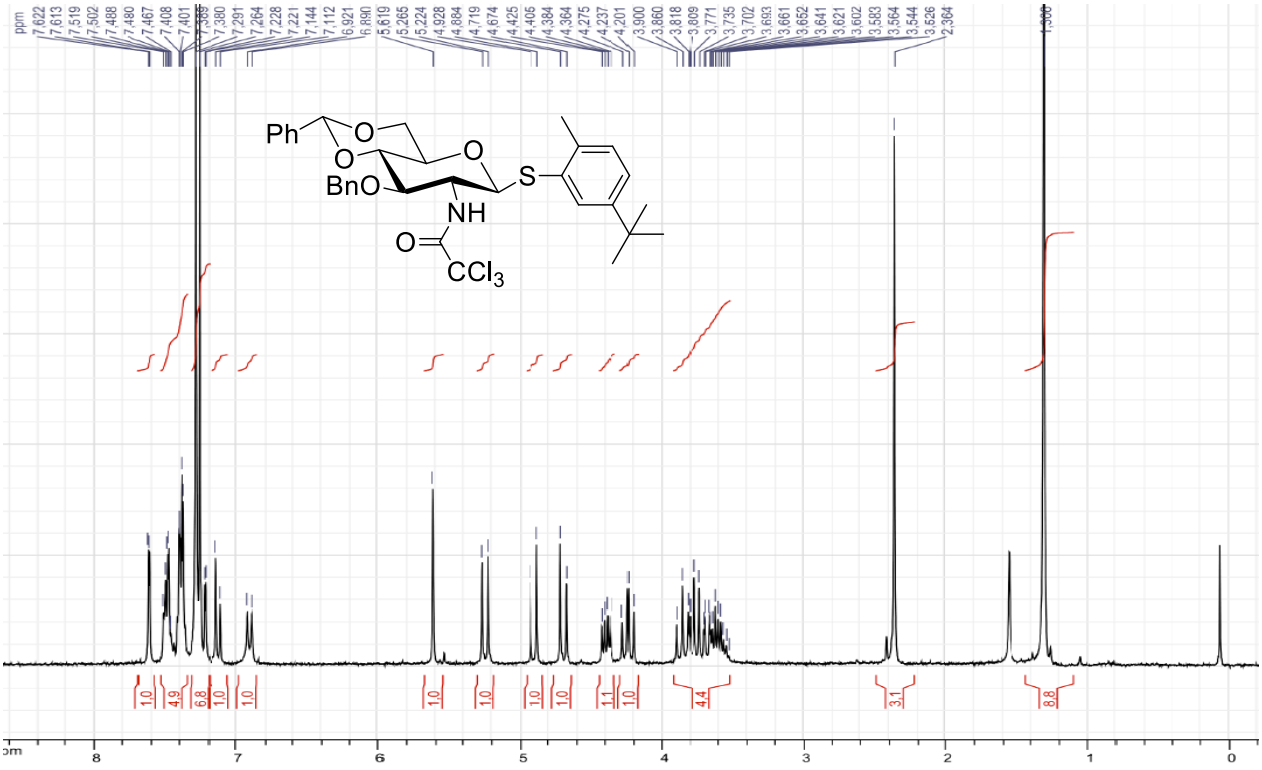
Copy of ^{1}H NMR spectrum of compound 5b (360 MHz, DMSO)



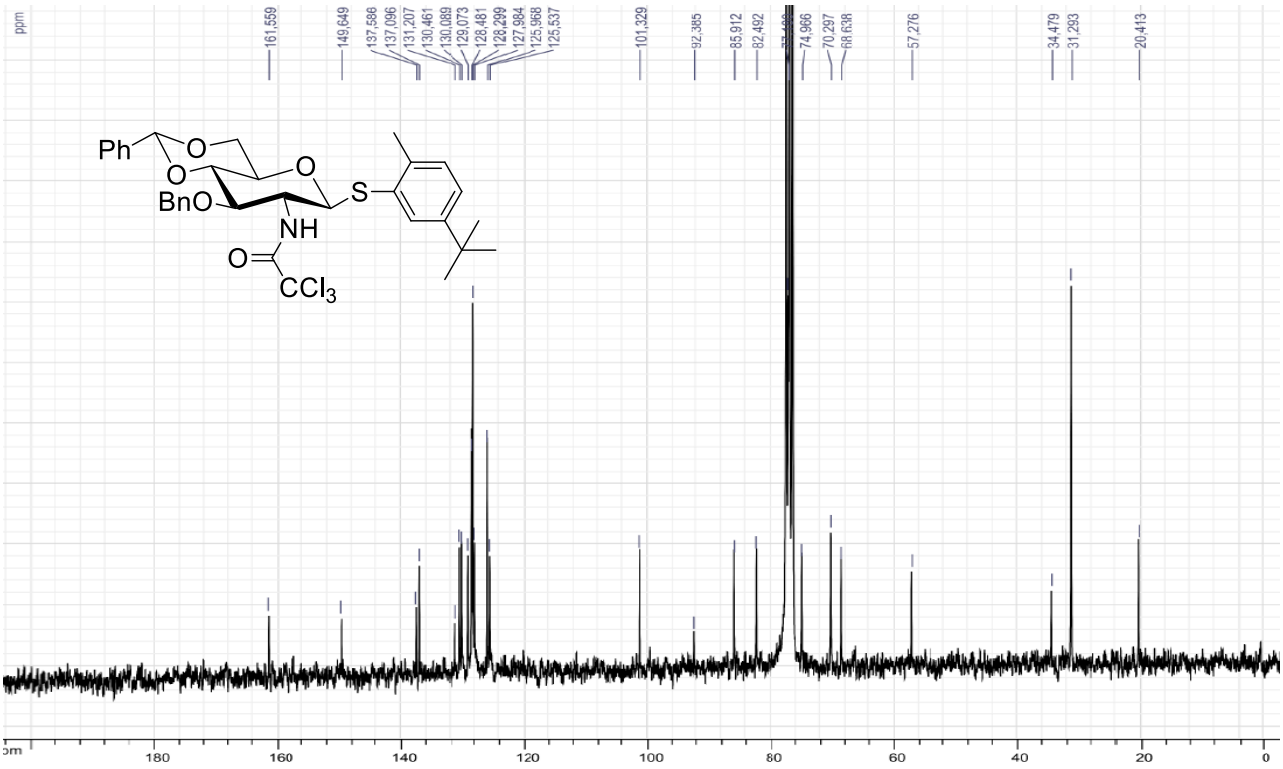
Copy of ^{13}C NMR spectrum of compound 5b (90 MHz, DMSO)



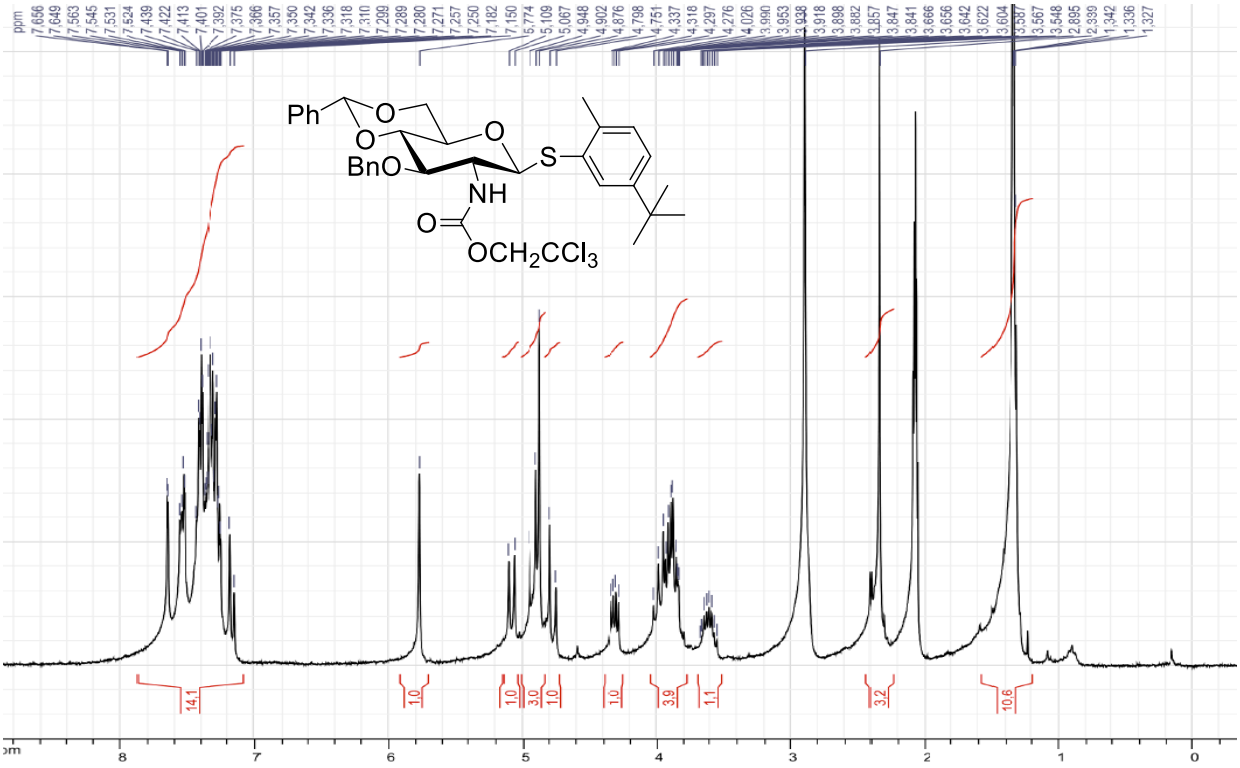
Copy of ^{1}H NMR spectrum of compound 6b (250 MHz, DMSO)



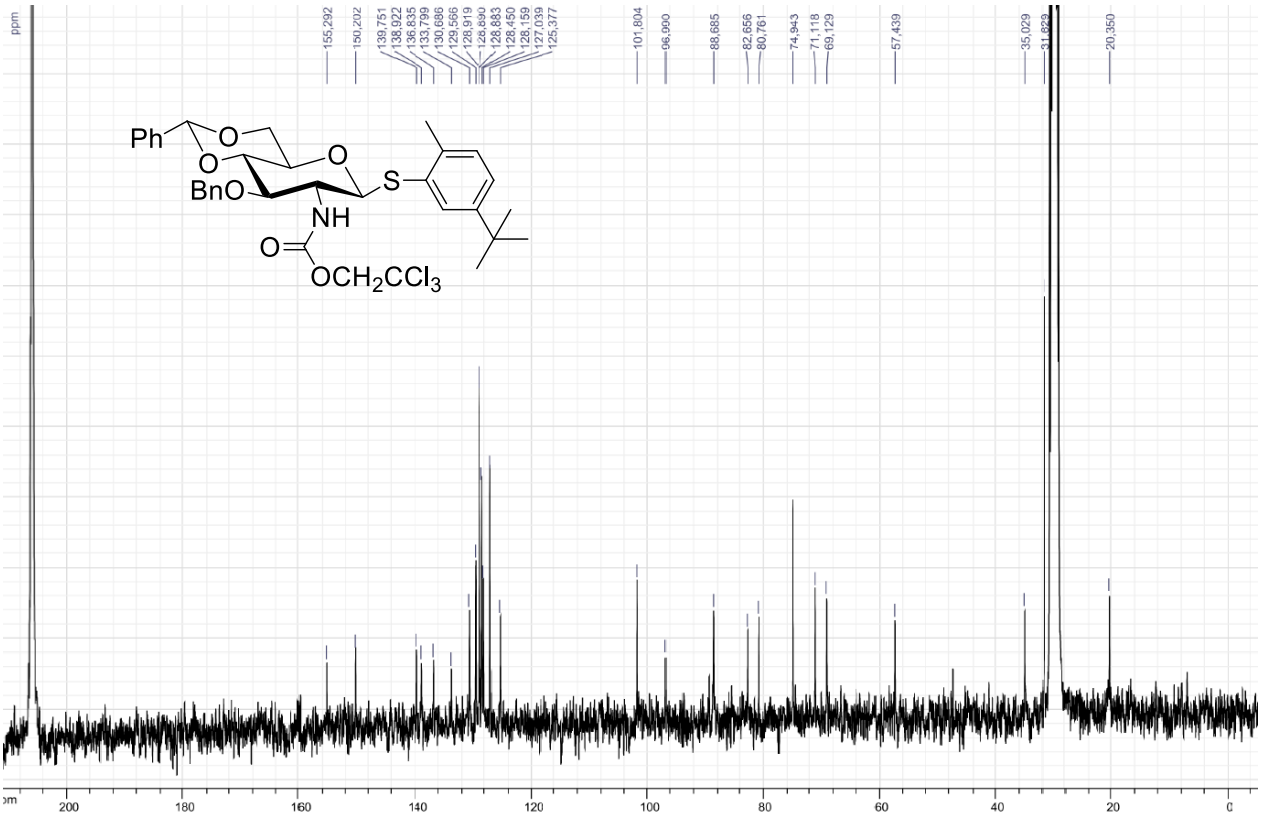
Copy of ^{13}C NMR spectrum of compound 6b (63 MHz, DMSO)



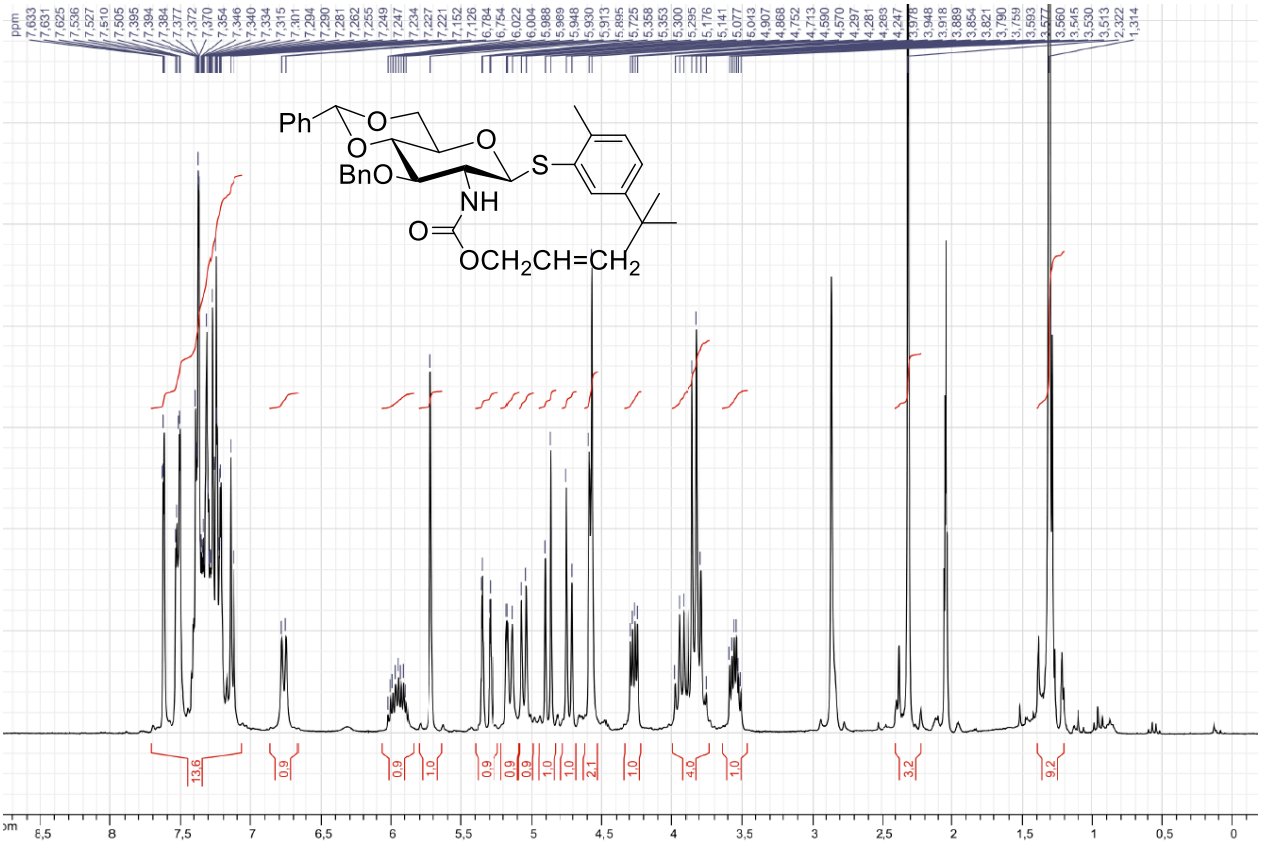
Copy of ^{1}H NMR spectrum of compound 7b (250 MHz, $(CD_3)_2CO$)



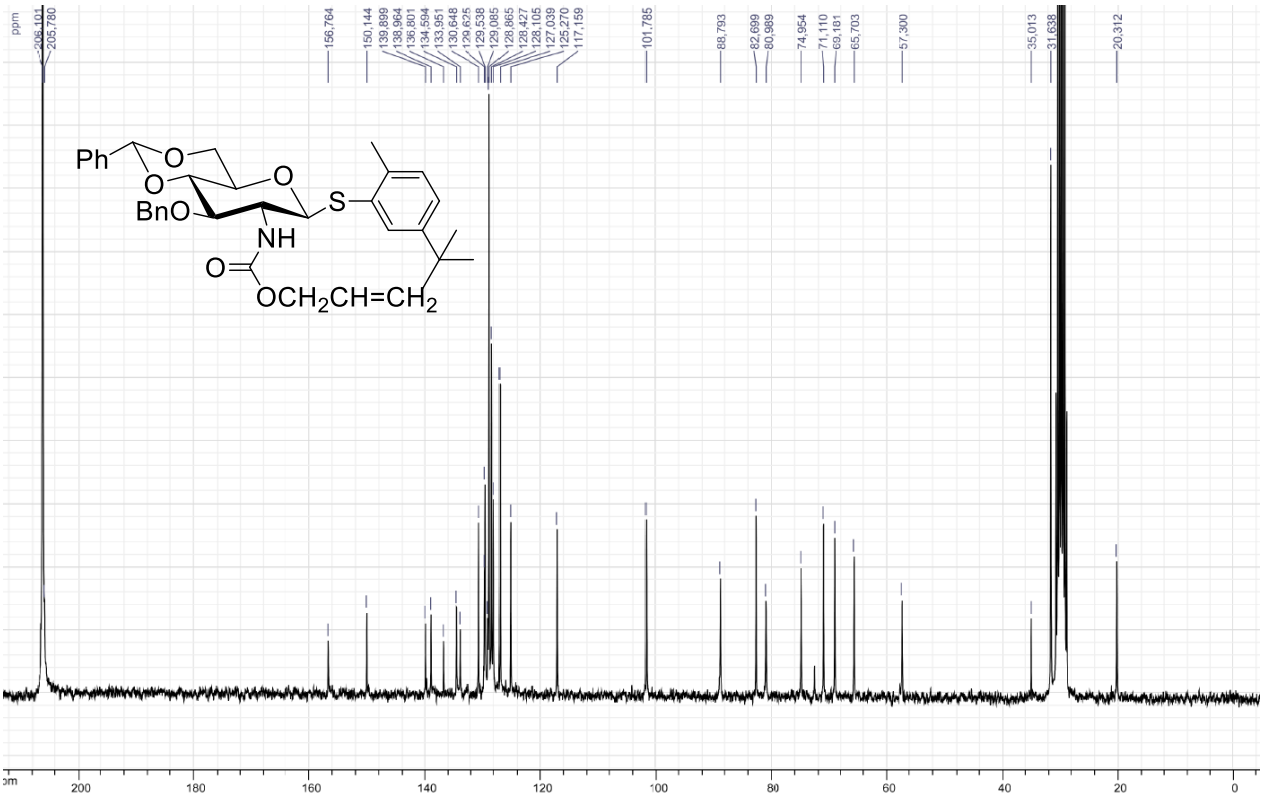
Copy of ^{13}C NMR spectrum of compound 7b (63 MHz, $(CD_3)_2CO$)



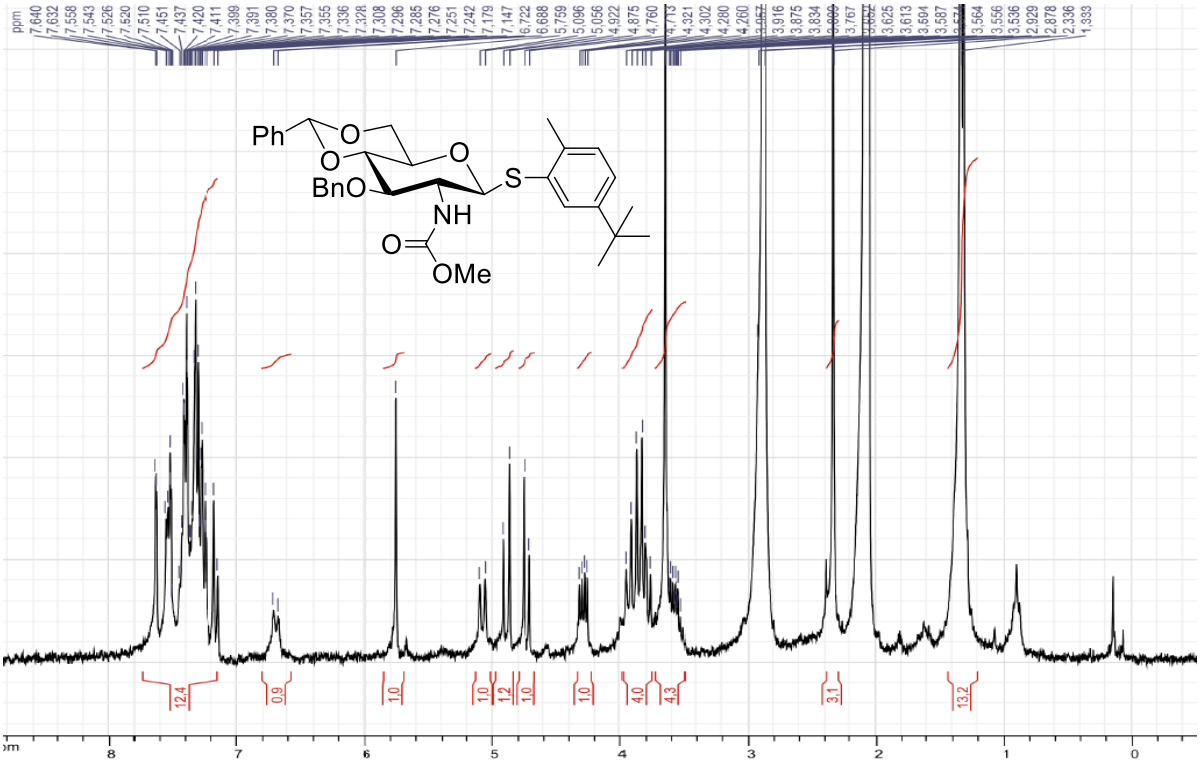
Copy of ^{1}H NMR spectrum of compound 8b (300 MHz, $(CD_3)_2CO$)



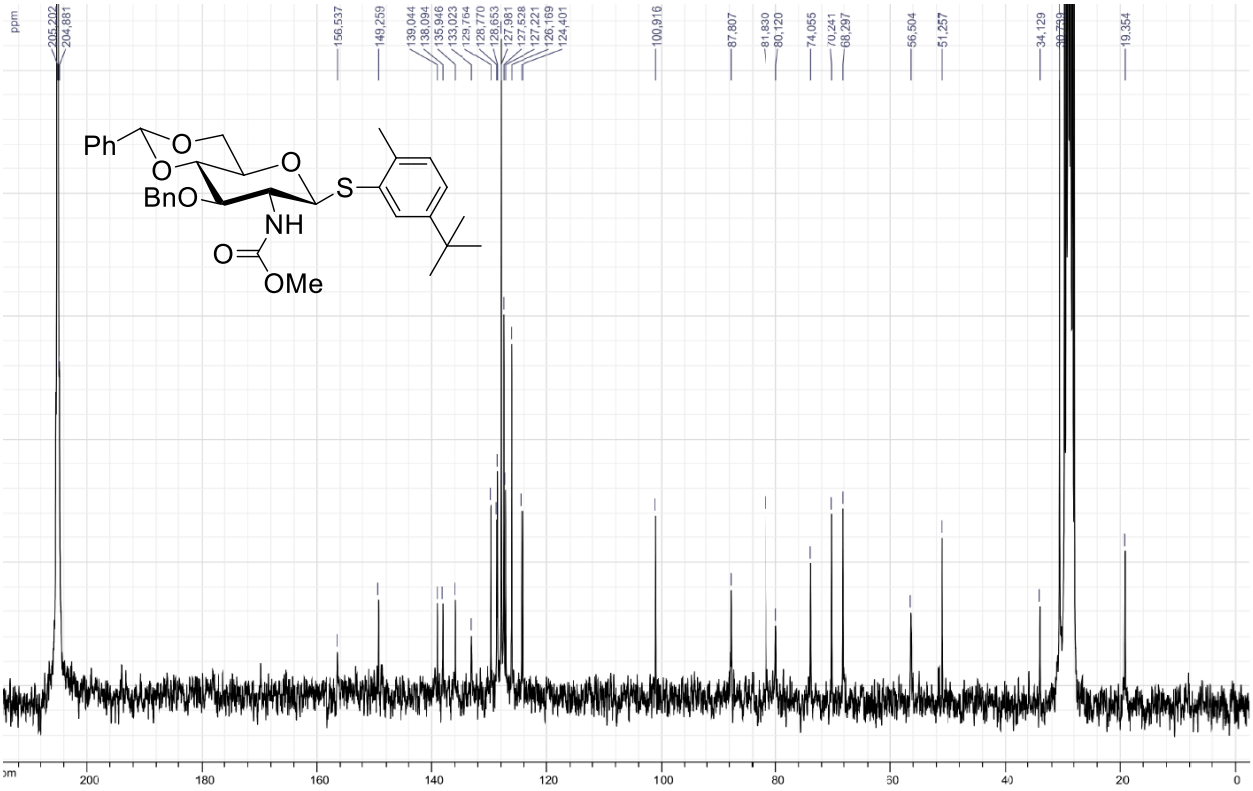
Copy of ^{13}C NMR spectrum of compound 8b (63 MHz, $(CD_3)_2CO$)



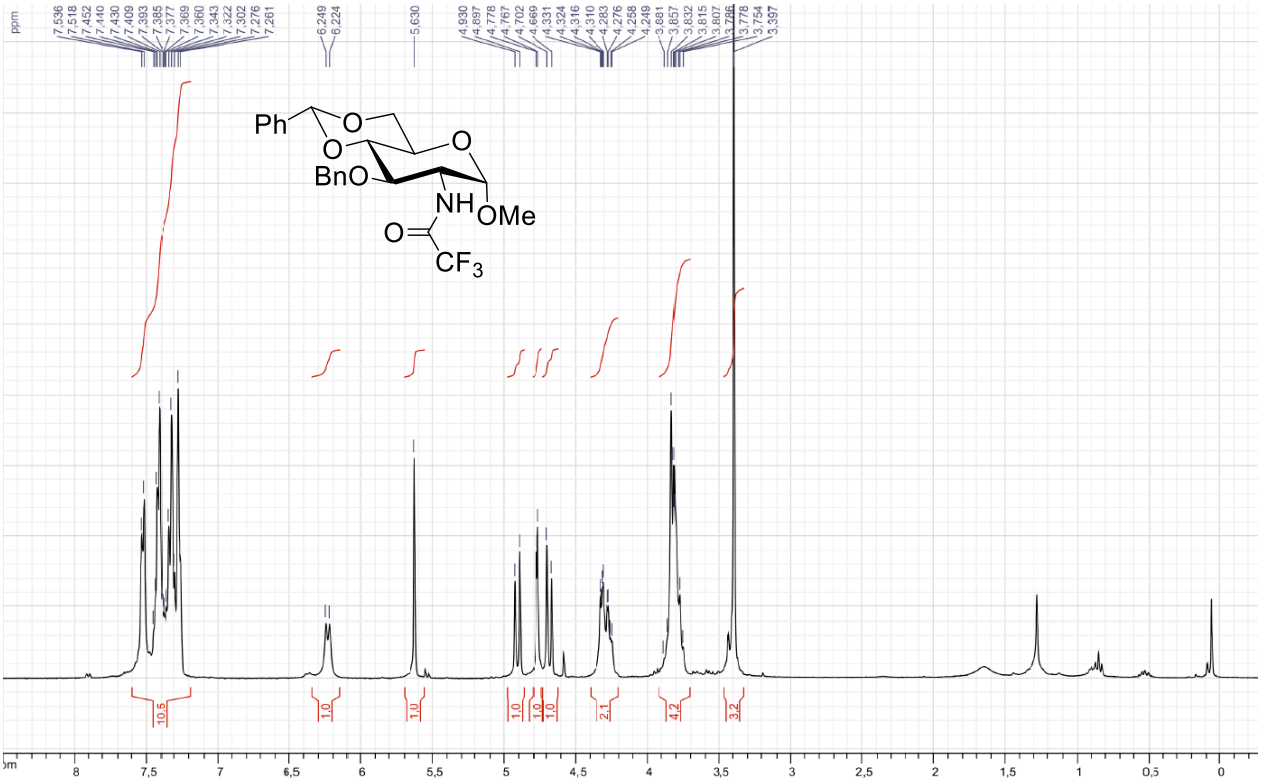
Copy of ^{1}H NMR spectrum of compound 9b (250 MHz, $(CD_3)_2CO$)



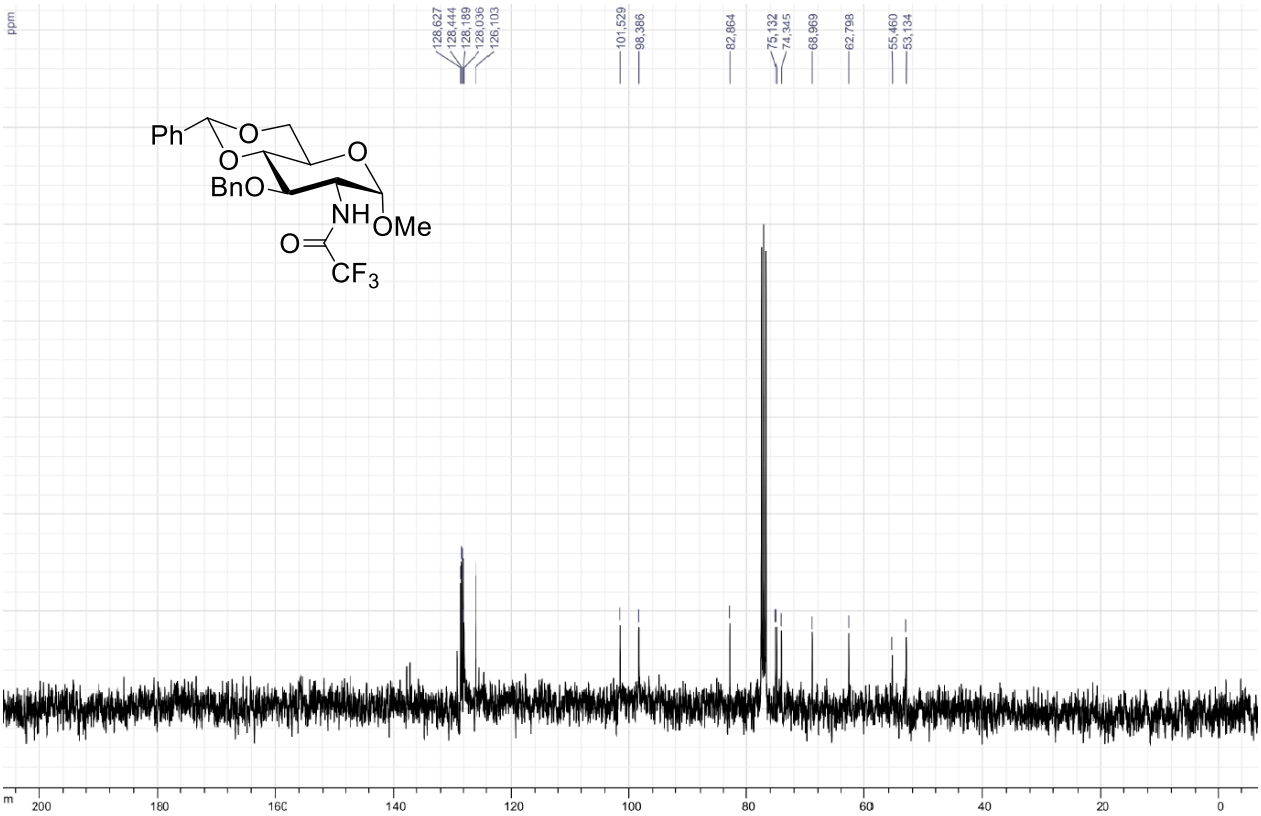
Copy of ^{13}C NMR spectrum of compound 9b (63 MHz, $(CD_3)_2CO$)



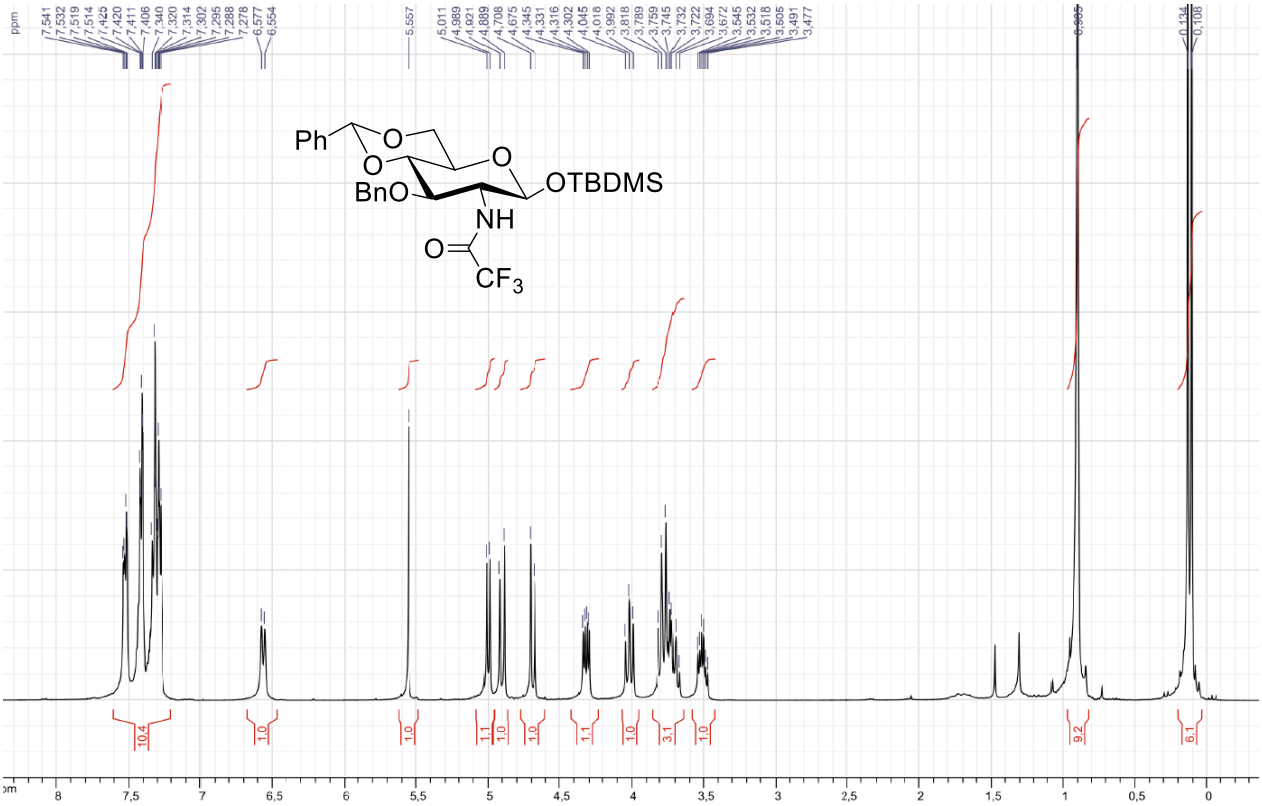
Copy of ^{1}H NMR spectrum of compound 10b (360 MHz, $CDCl_3$)



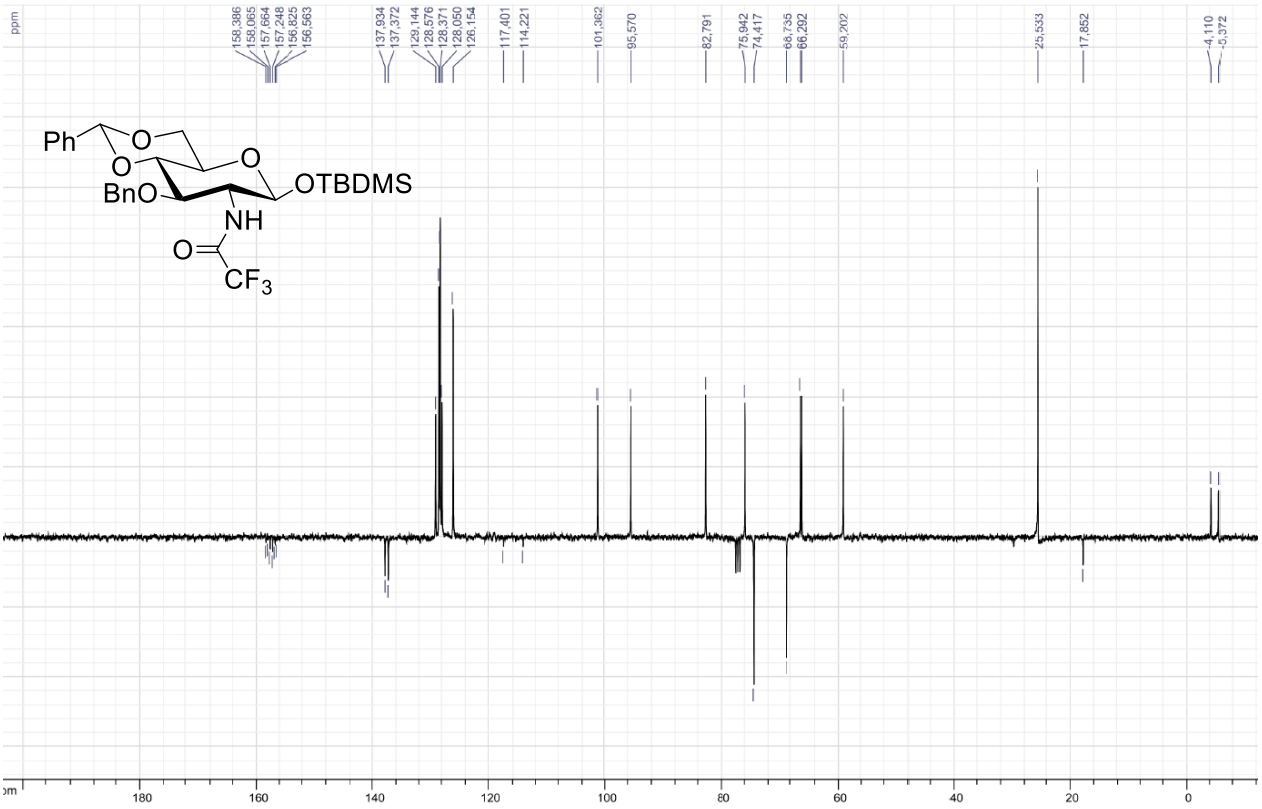
Copy of ^{13}C NMR spectrum of compound 10b (90 MHz, $CDCl_3$)



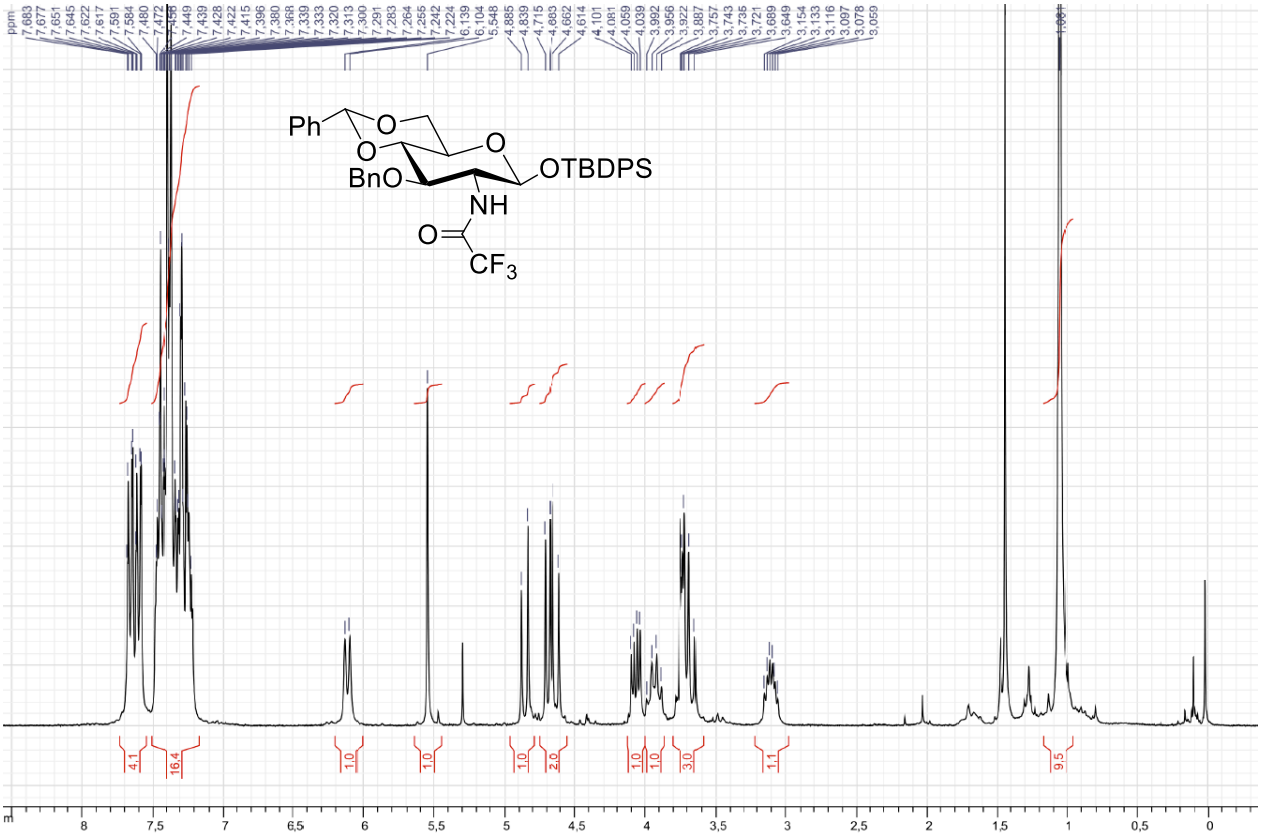
Copy of ^{1}H NMR spectrum of compound 11b (360 MHz, $CDCl_3$)



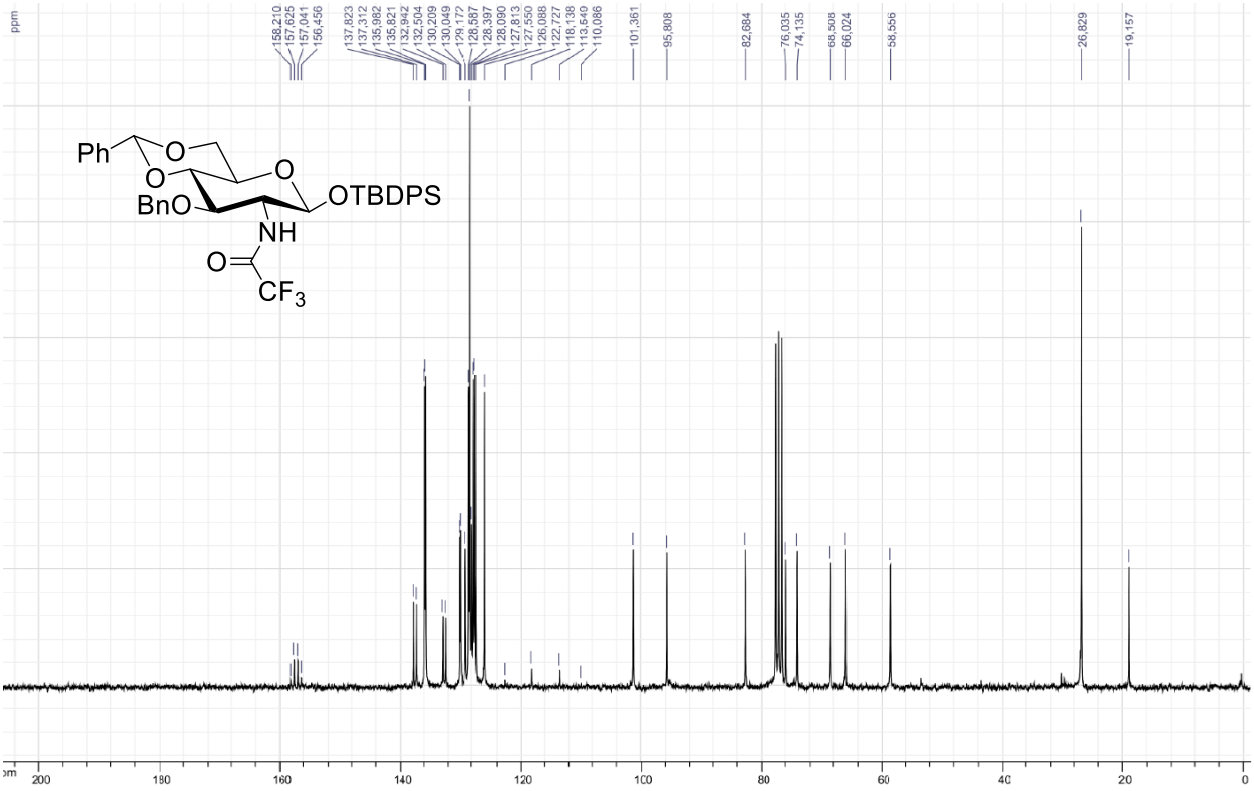
Copy of ^{13}C NMR spectrum (JMod) of compound 10b (90 MHz, $CDCl_3$)



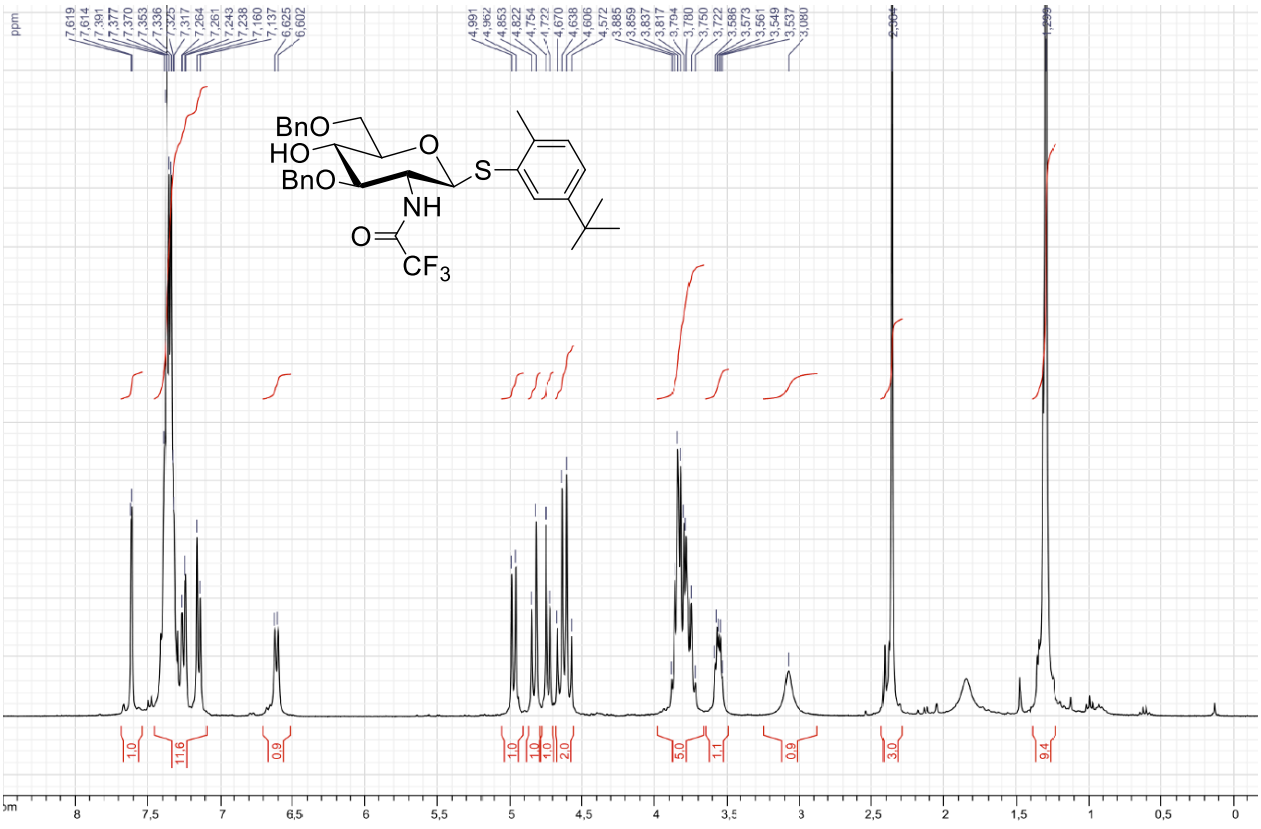
Copy of ^{1}H NMR spectrum of compound 12b (250 MHz, $CDCl_3$)



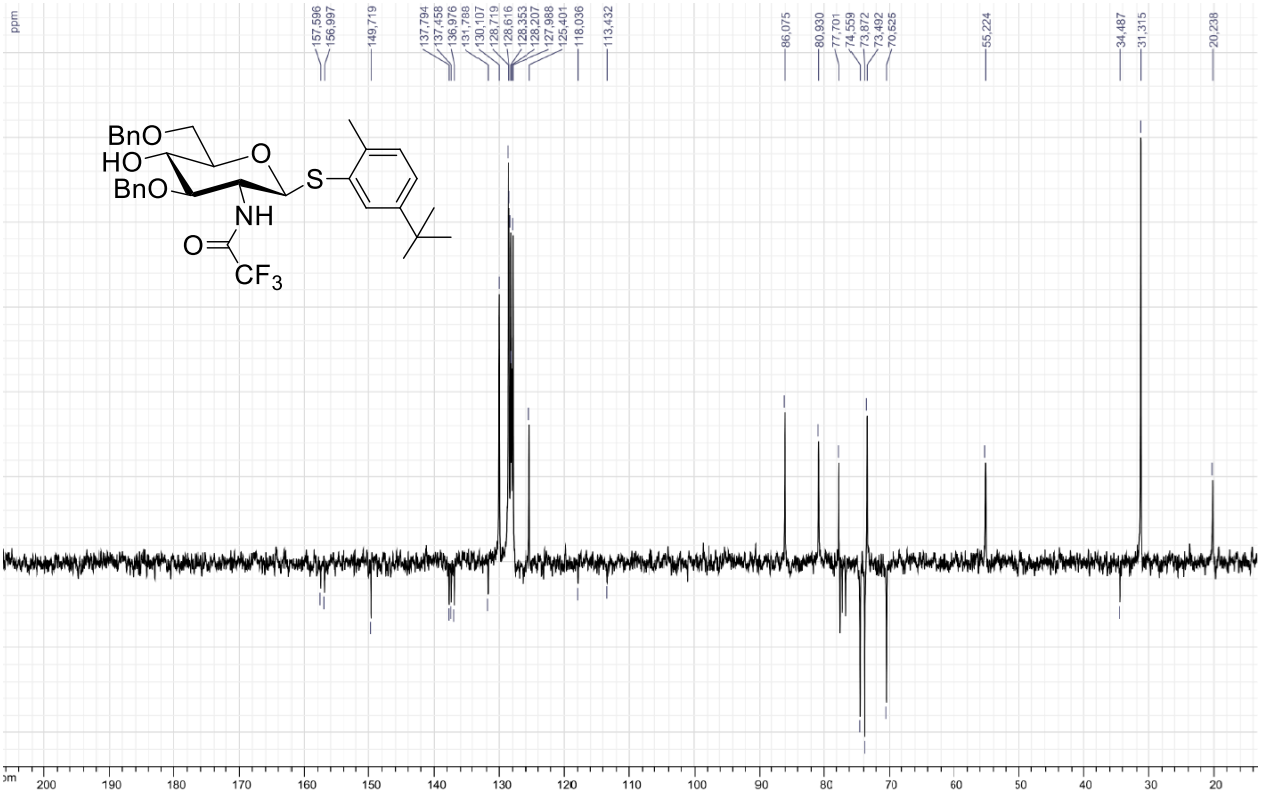
Copy of ^{13}C NMR spectrum of compound 12b (63 MHz, $CDCl_3$)



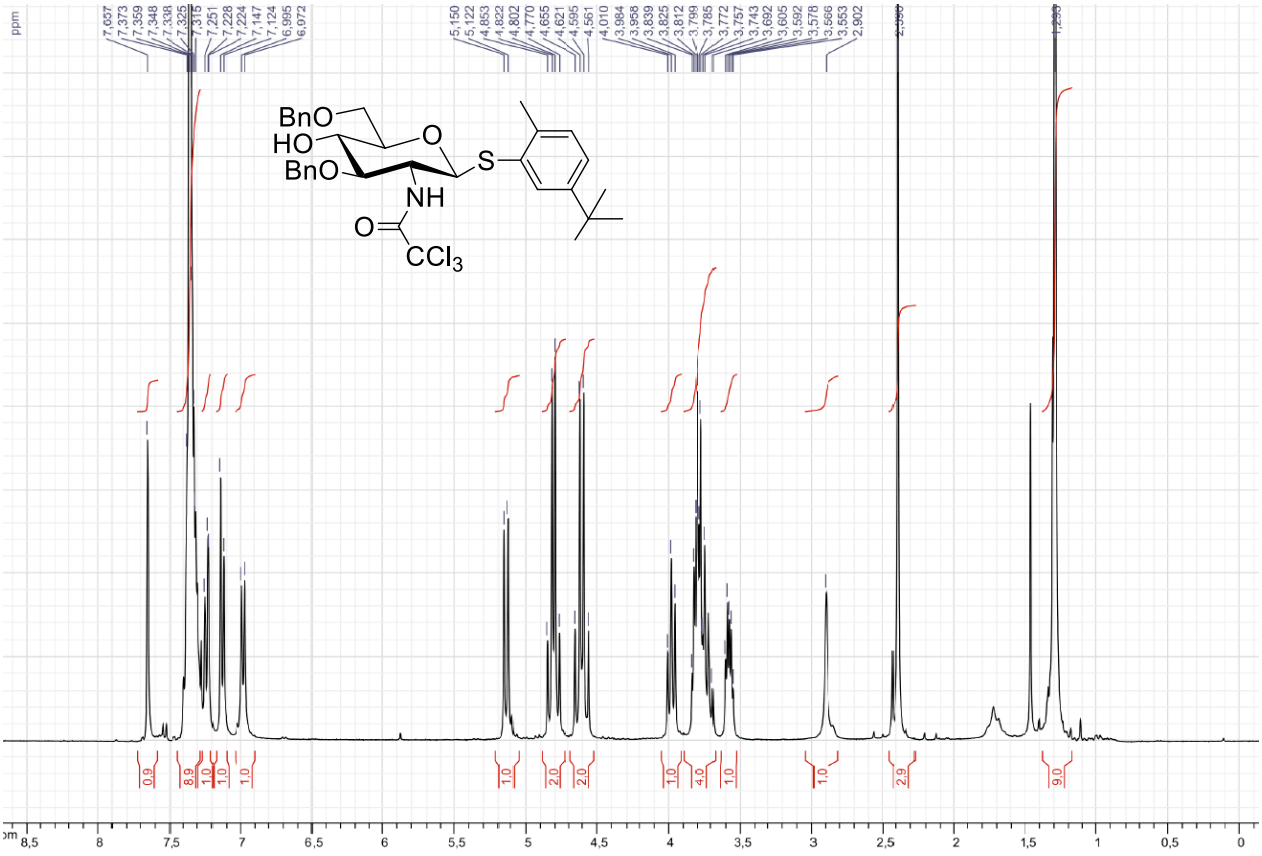
Copy of ^{1}H NMR spectrum of compound 5d (300 MHz, $CDCl_3$)



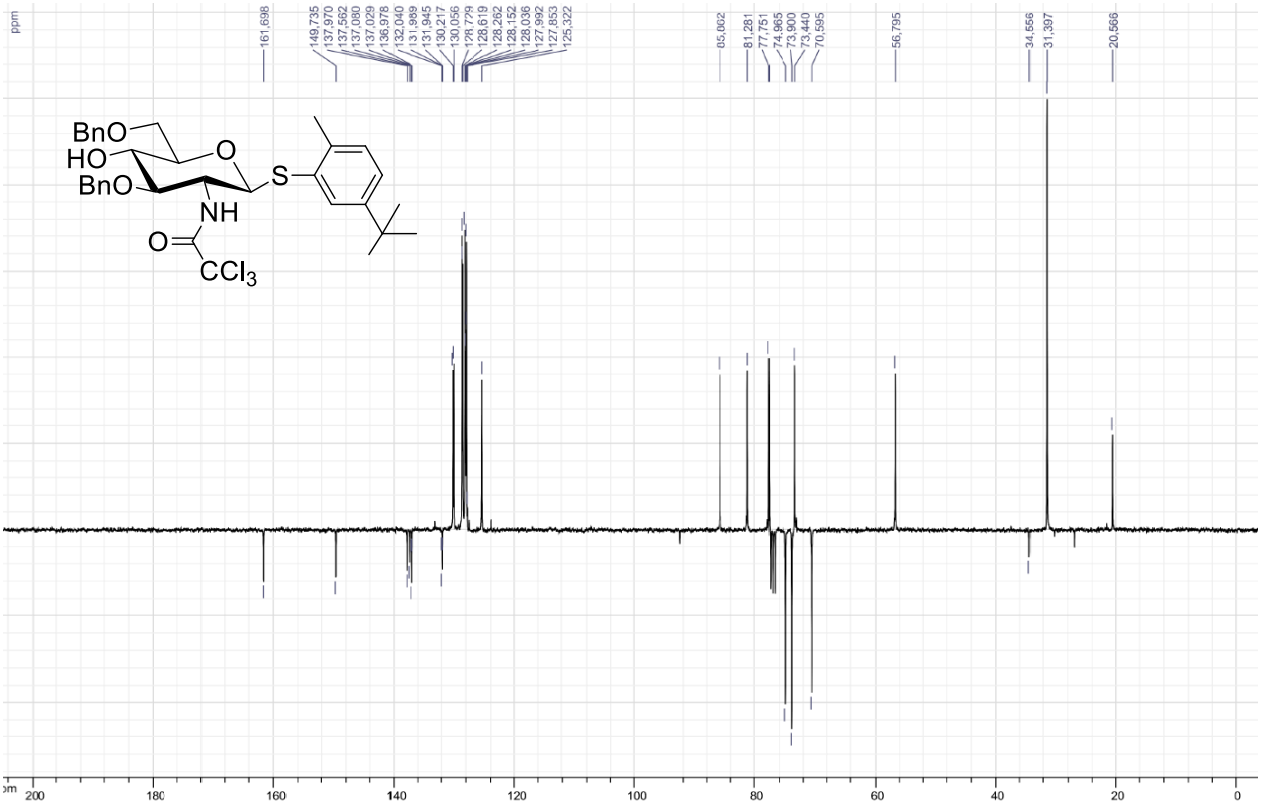
Copy of ^{13}C NMR spectrum (JMod) of compound 5d (75 MHz, $CDCl_3$)



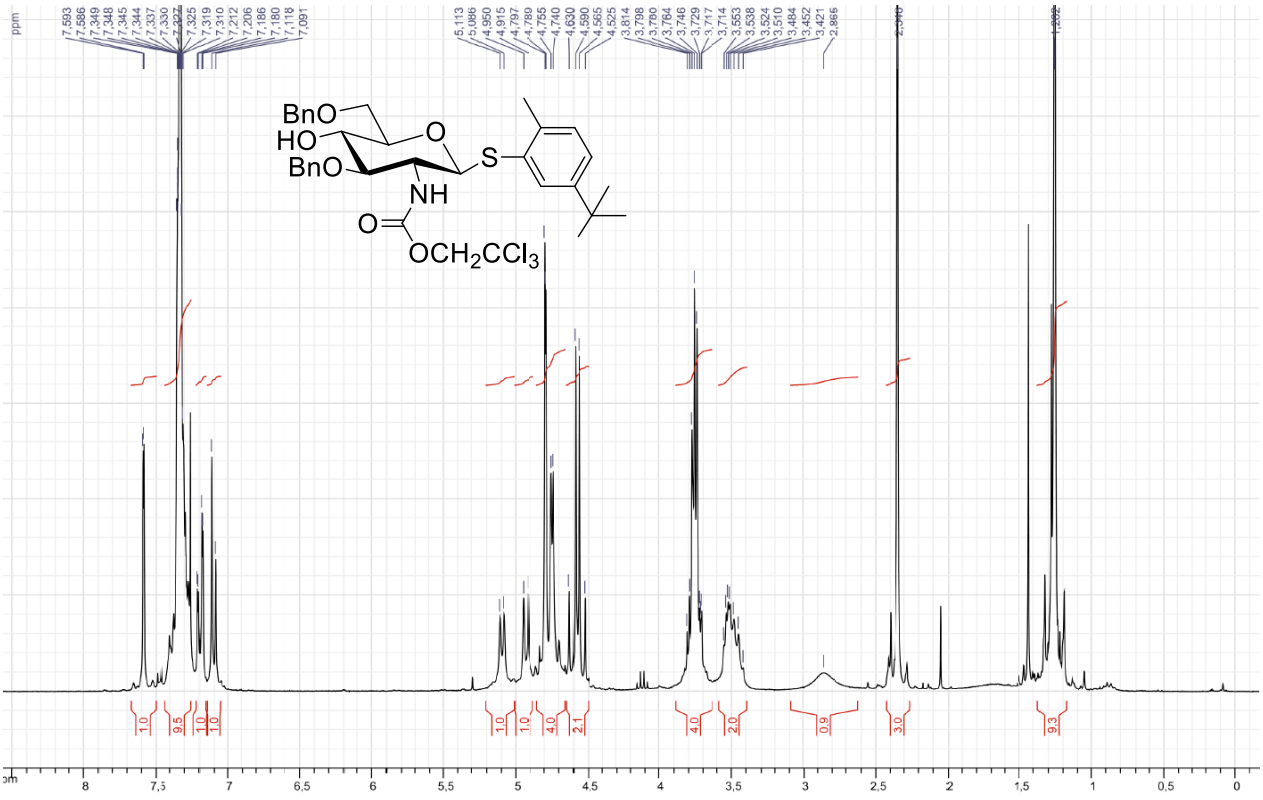
Copy of ^{1}H NMR spectrum of compound 6d (360 MHz, $CDCl_3$)



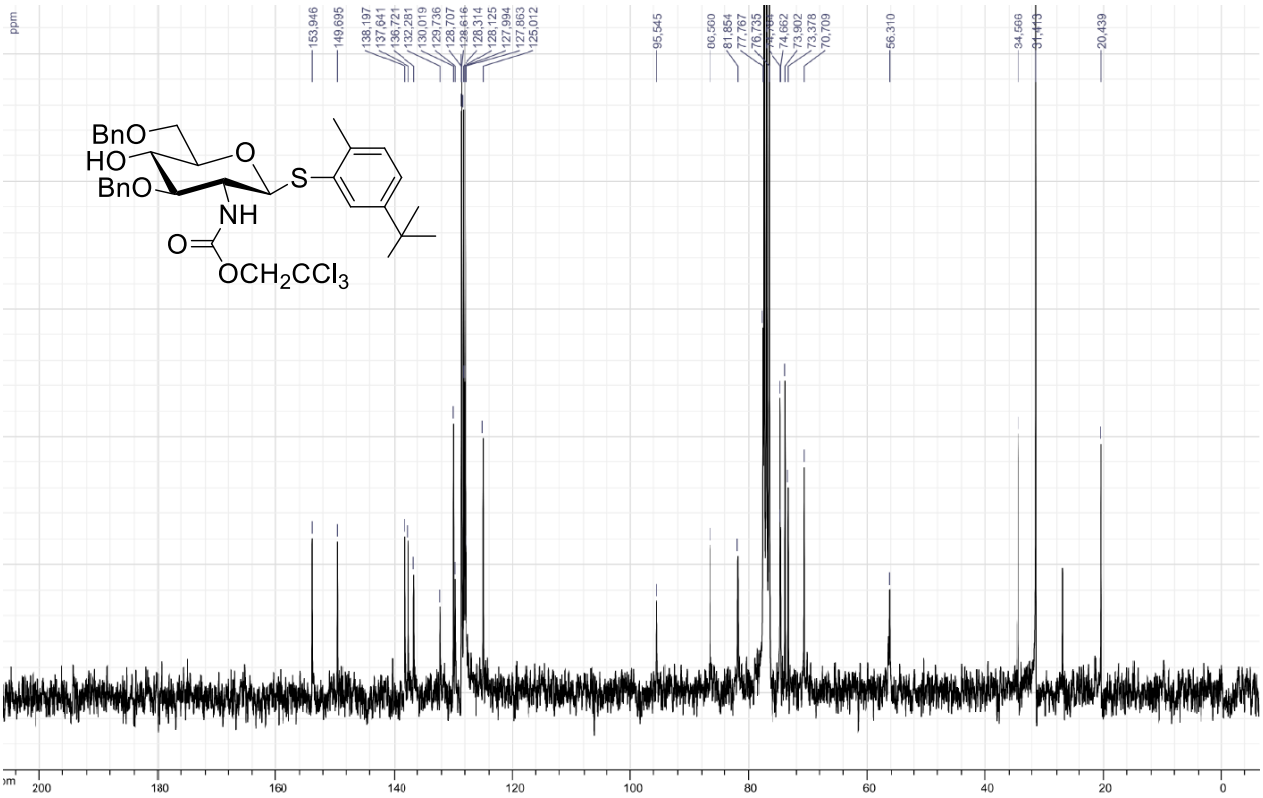
Copy of ^{13}C NMR spectrum (JMod) of compound 6d (90 MHz, $CDCl_3$)



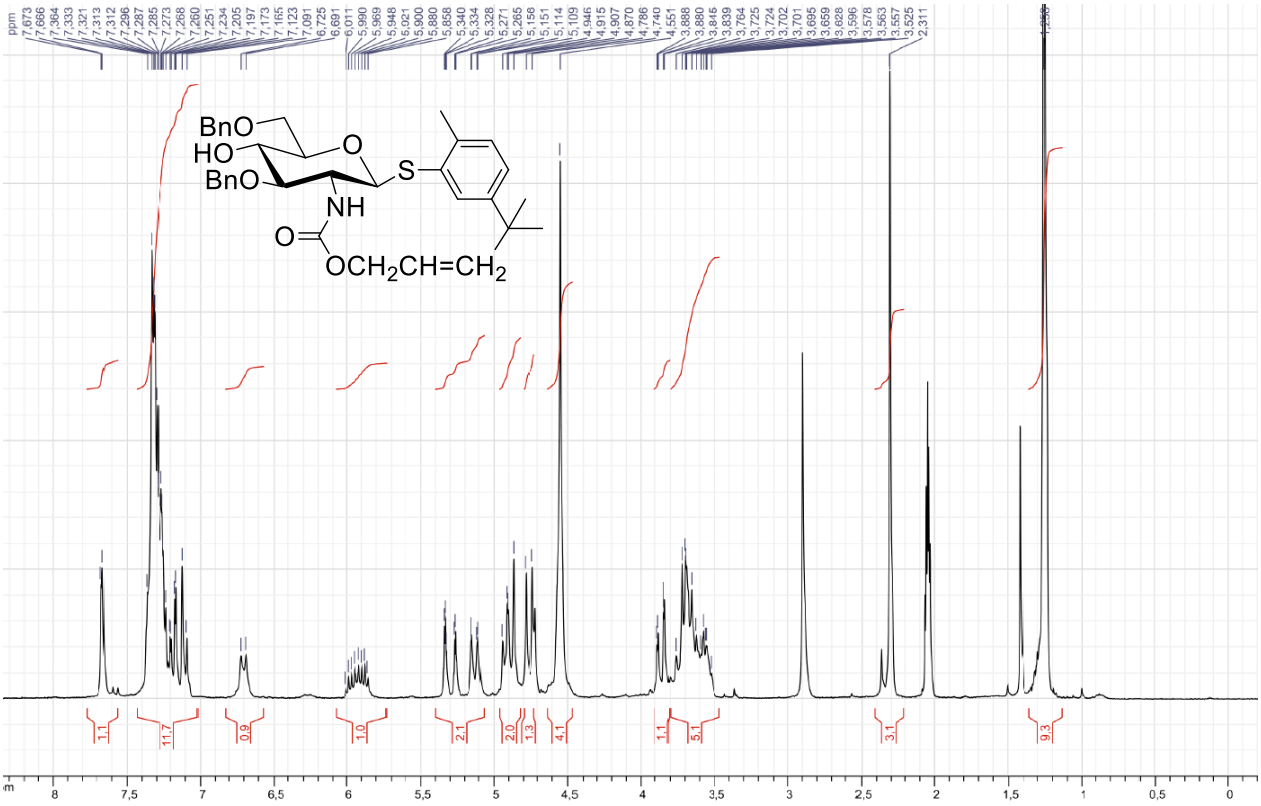
Copy of ^{1}H NMR spectrum of compound 7d (300 MHz, $CDCl_3$)



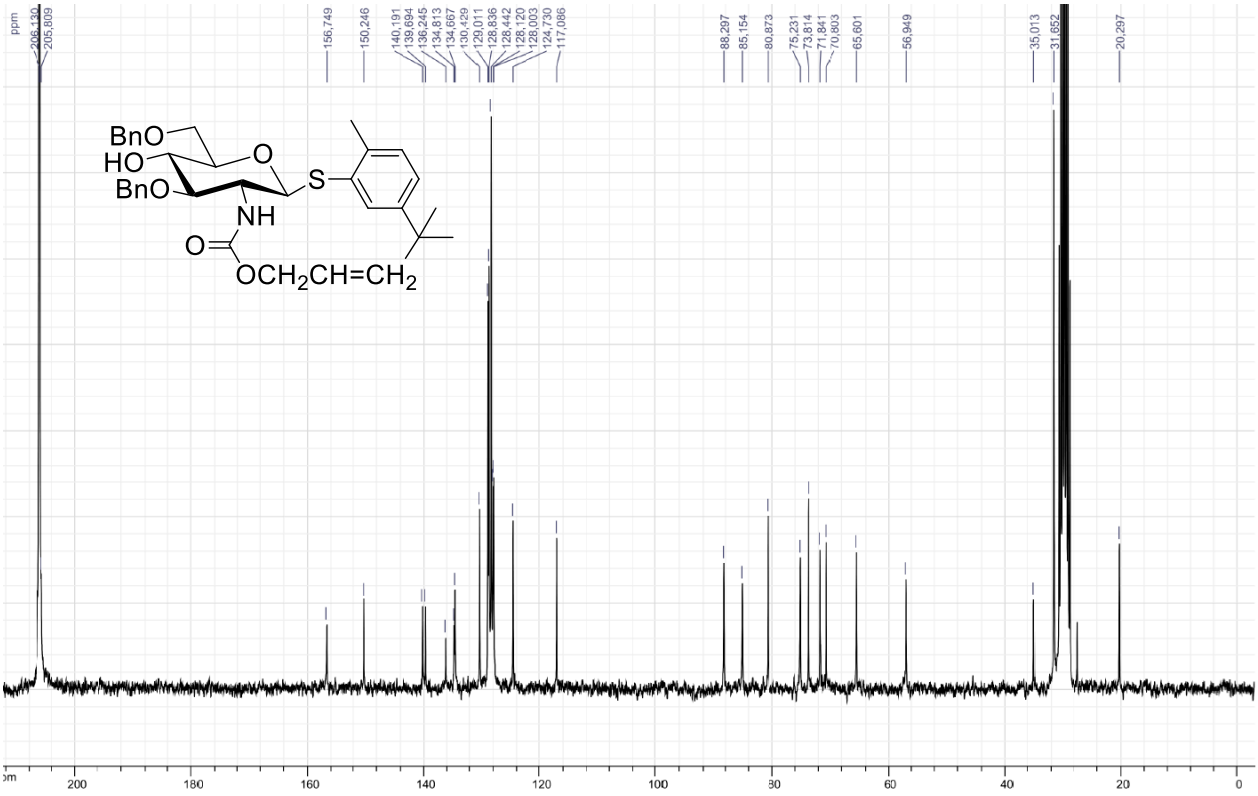
Copy of ^{13}C NMR spectrum of compound 7d (75 MHz, $CDCl_3$)



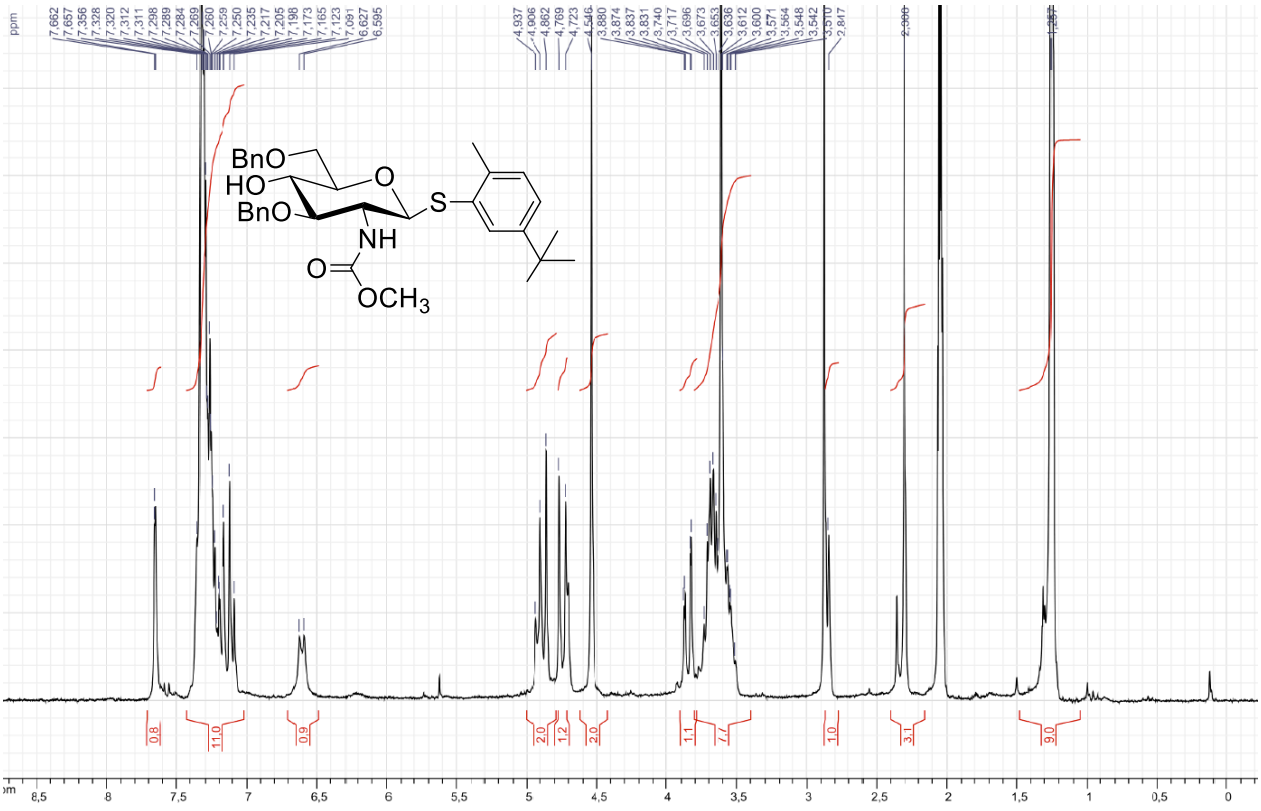
Copy of ^{1}H NMR spectrum of compound 8d (250 MHz, $(CD_3)_2CO$)



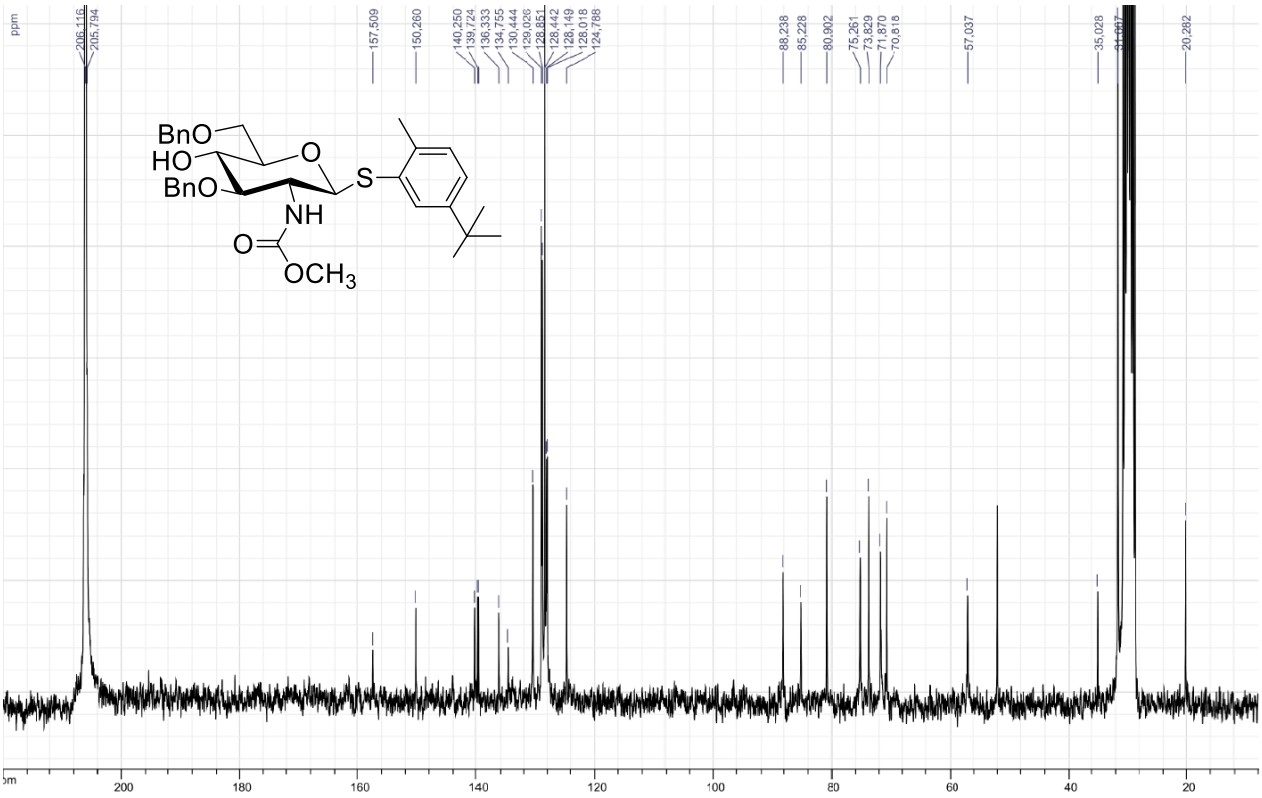
Copy of ^{13}C NMR spectrum of compound 8d (250 MHz, $(CD_3)_2CO$)



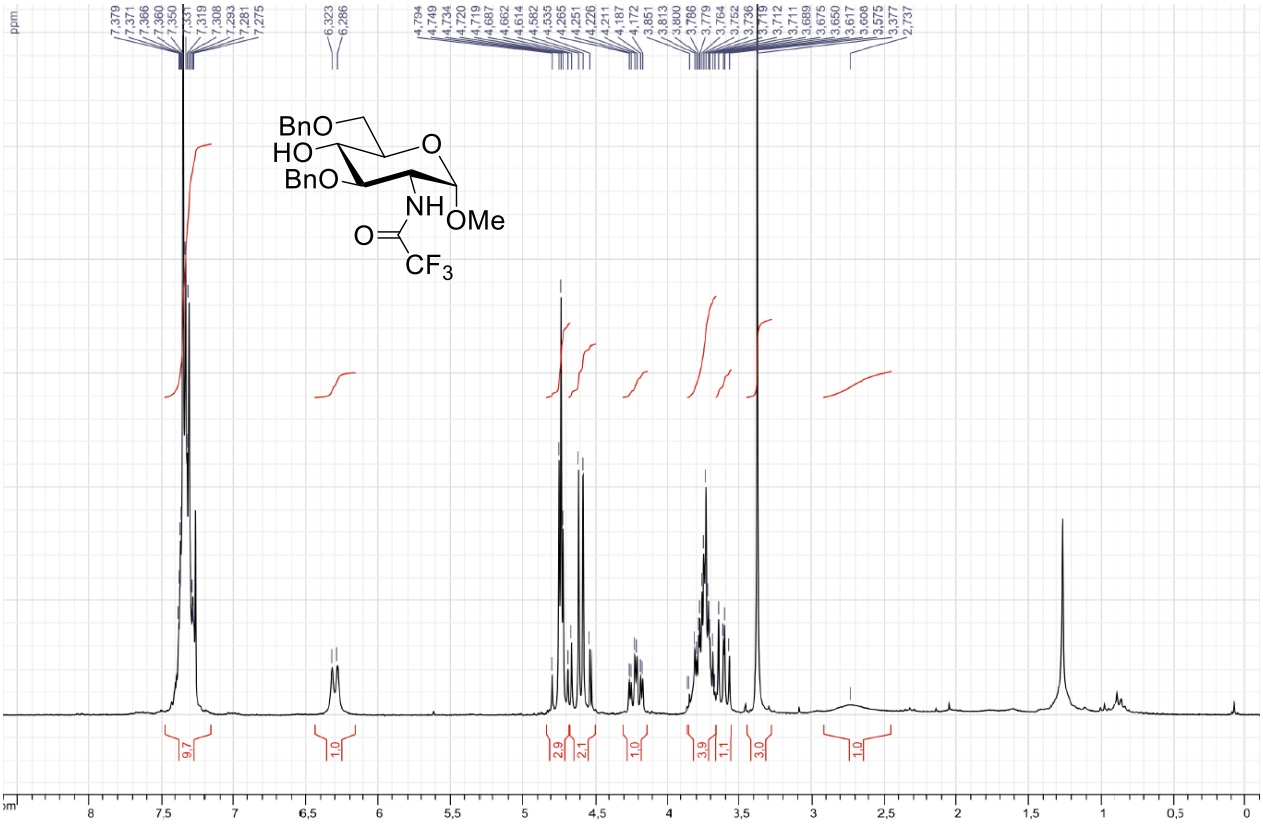
Copy of ^{1}H NMR spectrum of compound 9d (250 MHz, $(CD_3)_2CO$)



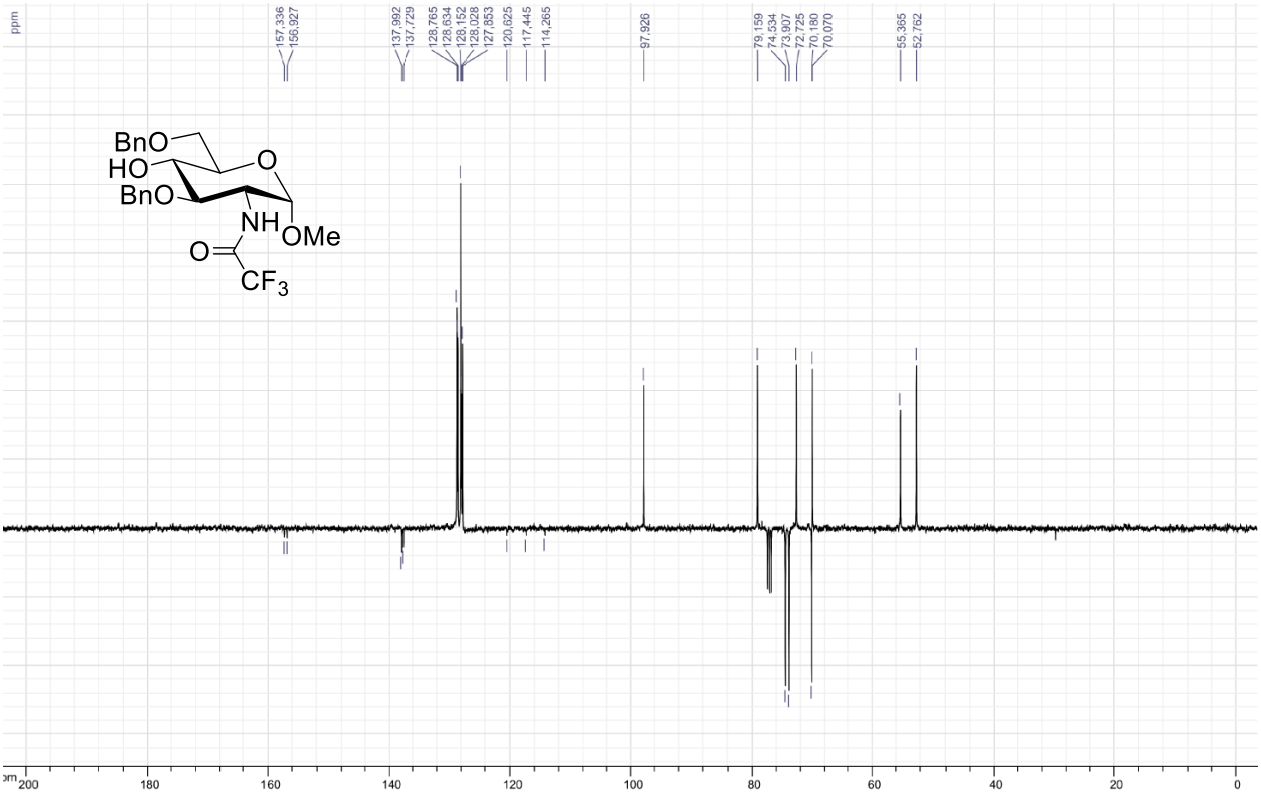
Copy of ^{13}C NMR spectrum of compound 9d (63 MHz, $(CD_3)_2CO$)



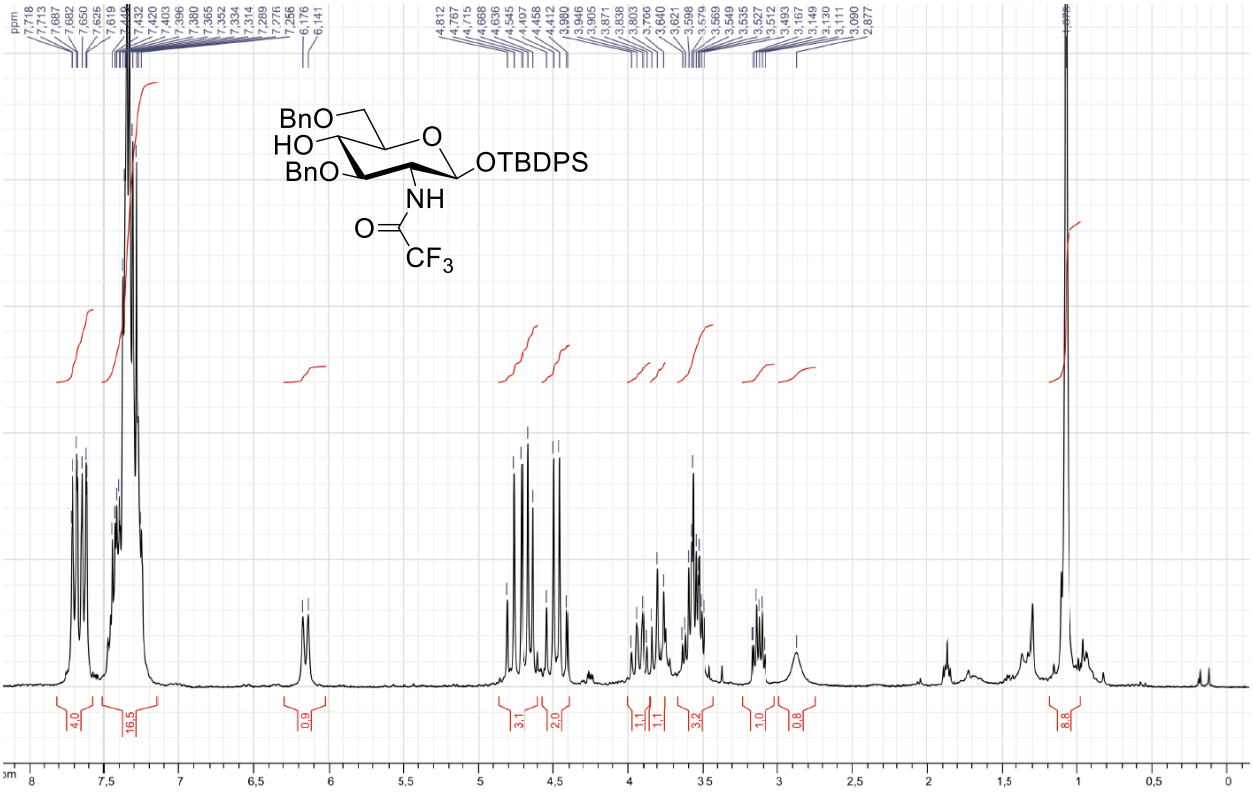
Copy of ^{1}H NMR spectrum of compound 10d (360 MHz, $CDCl_3$)



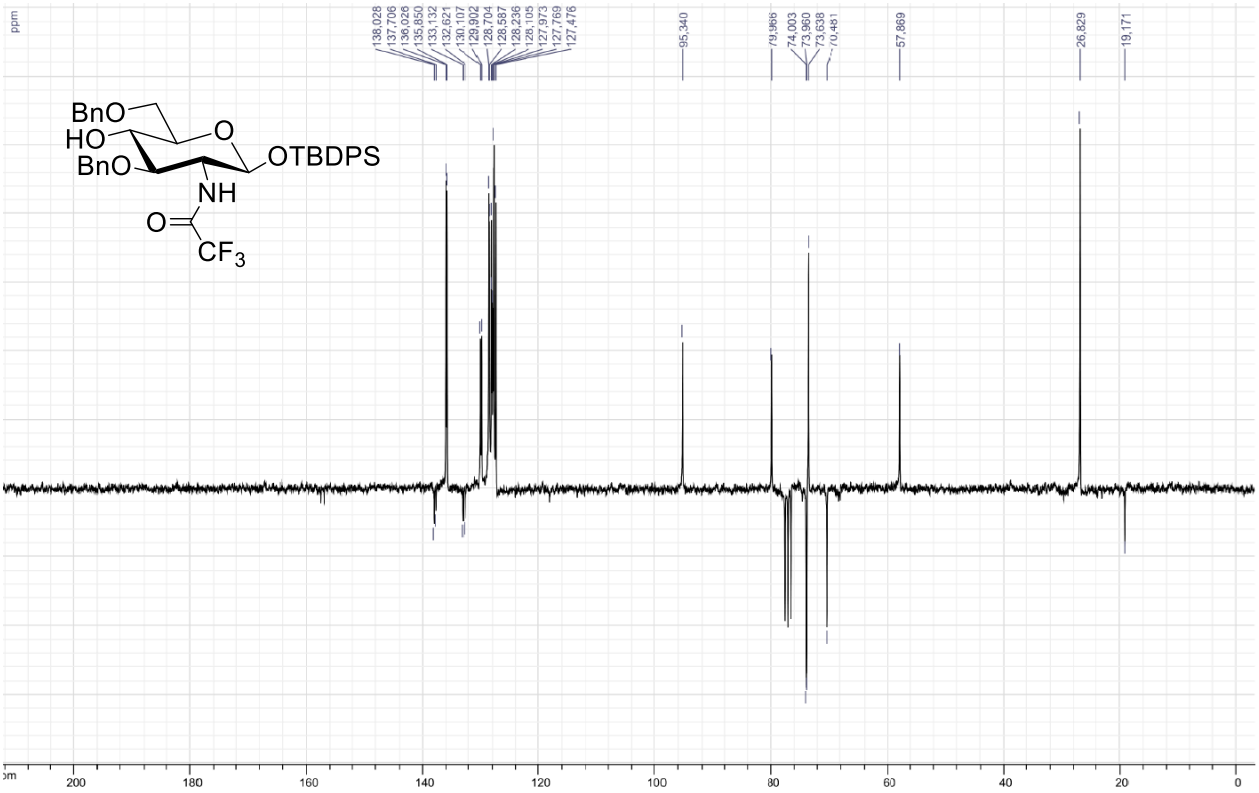
Copy of ^{13}C NMR spectrum (JMod) of compound 10d (90 MHz, $CDCl_3$)



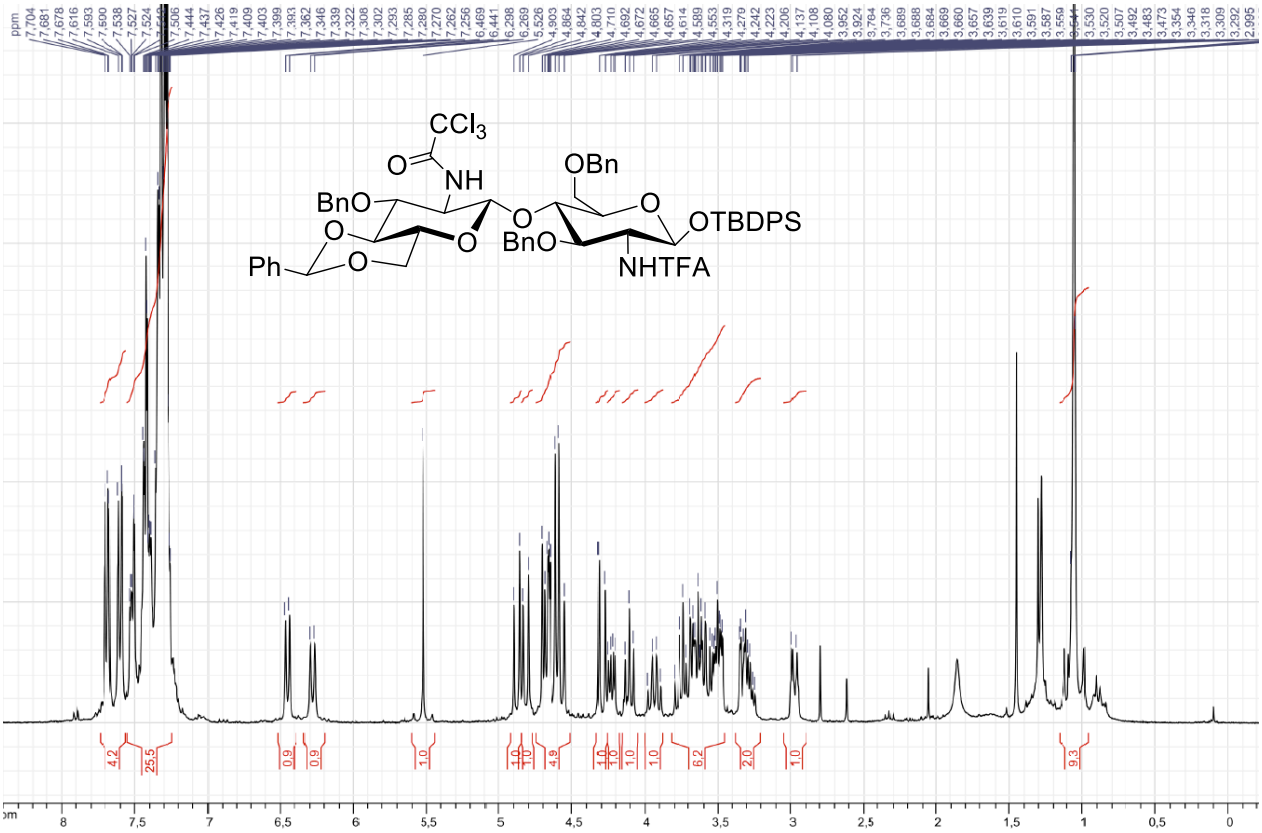
Copy of ^{1}H NMR spectrum of compound 12d (250 MHz, $CDCl_3$)



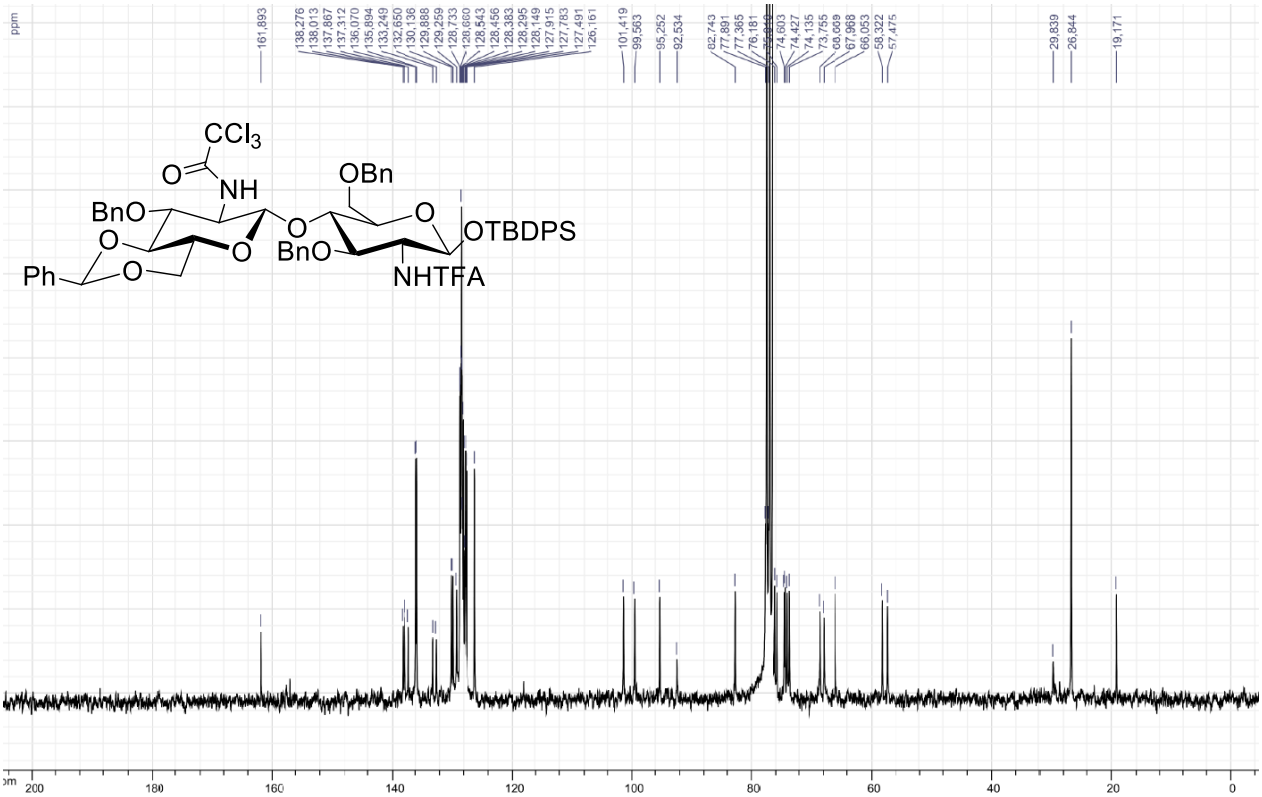
Copy of ^{13}C NMR spectrum (JMod) of compound 12d (63 MHz, $CDCl_3$)



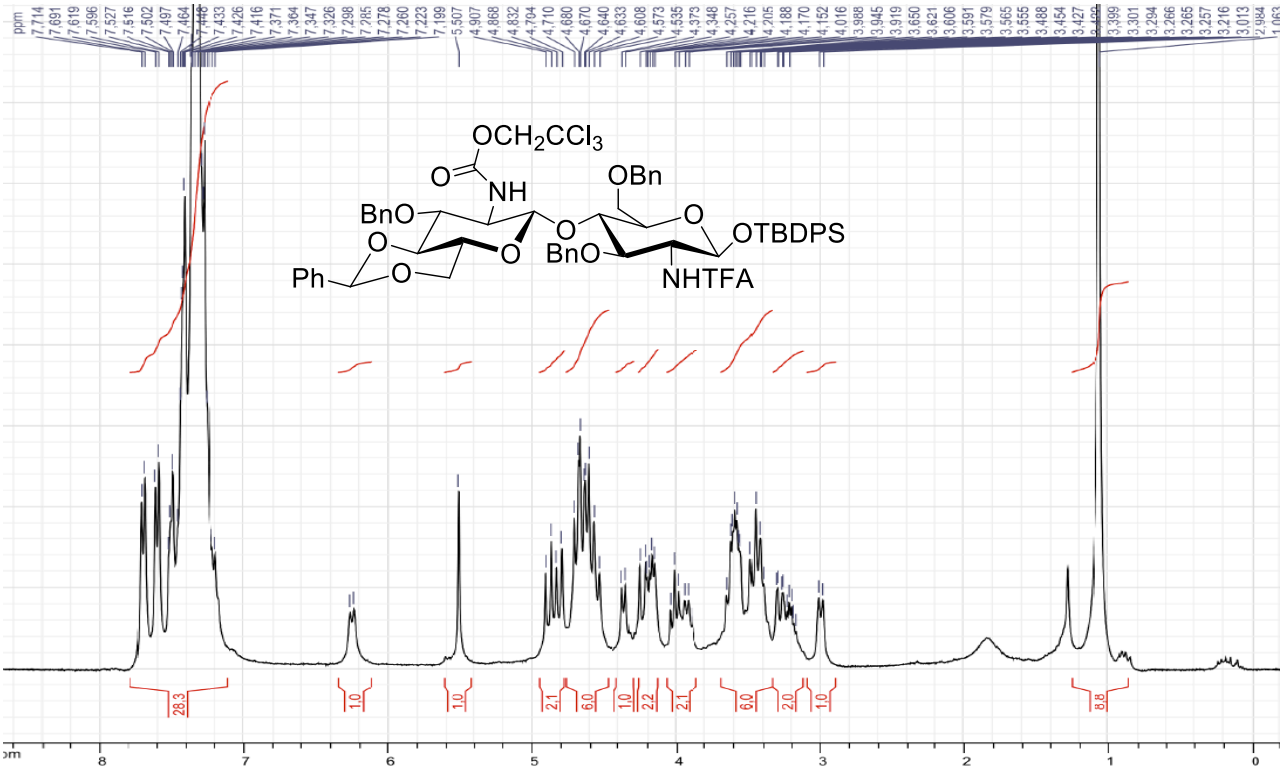
Copy of ^{1}H NMR spectrum of compound 13 (300 MHz, $CDCl_3$)



Copy of ^{13}C NMR spectrum of compound 13 (63 MHz, $CDCl_3$)



Copy of ^{1}H NMR spectrum of compound 14 (300 MHz, $CDCl_3$)



Copy of ^{13}C NMR spectrum of compound 14 (90 MHz, $CDCl_3$)