Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Novel Stereocontrolled Amidoglycosylation of Alcohols with Acetylated Glycals and Sulfamate Ester

Teiichi Murakami,* Yukari Sato, Kyoko Yoshioka and Mutsuo Tanaka
Biomedical Research Institute
National Institute of Advanced Industrial Science and Technology (AIST)
Tsukuba Central 6, Tsukuba, Ibaraki 305-8566, Japan

Experimental

General

Melting points were determined with a Yanaco melting point apparatus MP-500D. Optical rotations were measured with a JASCO DIP-1000 polarimeter and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer or on a Bruker Avance III-500 (500 MHz for ^{1}H and 125.8 MHz for ^{13}C) spectrometer. ^{1}H chemical shifts (δ) are given in ppm relative to internal $(CH_3)_4Si$ (δ 0.00) in $CDCl_3$ and ^{13}C chemical shifts (δ) are given in ppm relative to $CDCl_3$ (δ 77.0). Elemental analyses were performed in the analytical section in this Institute (AIST). Mass spectra (MS) were recorded on a Waters micromass ZQ spectrometer with electrospray ionisation (ESI) in the positive ion mode. Thin layer chromatography (TLC) and column chromatography were performed on Merck pre-coated silica gel $60F_{254}$ plates and silica gel (Kanto Chemicals, neutral, 100-210 μm, or Wakogel C-300, 45-75 μm), respectively. $Rh_2(NHCOCF_3)_4$ was prepared from $Rh_2(OAc)_4$ and CF_3CONH_2 in chlorobenzene according to the following: K. Guthikonda and J. Du Bois, *J. Am. Chem. Soc.*, 2002, **124**, 13672; Supporting information, p. 2.

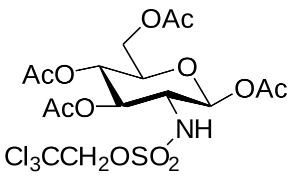
General procedure for amidoacetoxylation

To a mixture of glycal (0.2 mmol), $Cl_3CCH_2OSO_2NH_2$ (80 mg, 0.35 mmol), $Rh_2(NHCOCF_3)_4$ (12 mg, 0.02 mmol), and MgO (32 mg, 0.8 mmol) under nitrogen was added PhCl (3 mL), and the

* Corresponding author. fax: +81-29-861-6122; e-mail: t-murakami@aist.go.jp

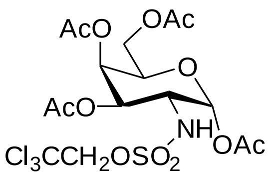
resulting light-purple suspension was cooled with an ice-water bath. $PhI(OAc)_2$ (80 mg, 0.36 mmol) was added in several portions for 1 h, and the resulting light-brown suspension was stirred at 5 °C for 1 h and then at rt for 10 h. The reaction mixture was filtered, washed with CH_2Cl_2, and the combined filtrates were concentrated under reduced pressure. The residue was purified by silica gel chromatography eluting with hexane-EtOAc mixture.

1,3,4,6-tetra-*O*-Acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranose (2a-β)



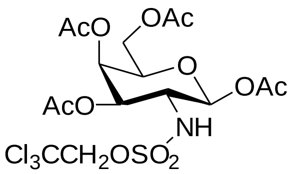
R_f 0.33 (3:2 hexane/EtOAc); $[\alpha]_D^{25}$ +8.3 (c 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 3H), 2.11 (s, 3H), 2.17 (s, 3H), 2.23 (s, 3H), 3.95 (dt, 1H, *J* = 8.9, 11.1 Hz), 4.06 (dt, 1H, *J* = 0.9, 6.5 Hz), 4.12 (dd, 1H, *J* = 6.3, 11.2 Hz), 4.16 (dd, 1H, *J* =6.7, 11.2 Hz), 4.64 (s, 2H), 5.08 (dd, 1H, *J* = 3.3, 11.1 Hz), 5.40 (d, 1H, *J* = 3.3 Hz), 5.67 (d, 1H, *J* = 9.0 Hz), 5.72 (d, 1H, *J* = 8.8 Hz).

1,3,4,6-tetra-*O*-Acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-α-D-galactopyranose (2b-α)



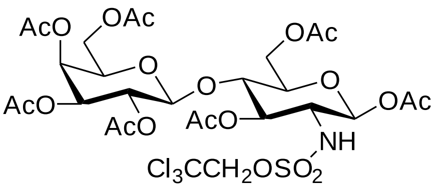
R_f 0.24 (3:2 hexane/EtOAc); $[\alpha]_D^{25}$ +105.4 (c 1.92, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 3H), 2.10 (s, 3H), 2.17 (s, 3H), 2.21 (s, 3H), 4.07 (dd, 1H, *J* = 6.7, 11.2 Hz), 4.10 (dd, 1H, *J* = 6.7, 11.2 Hz), 4.15 (ddd, 1H, *J* = 3.6, 9.6, 11.2 Hz), 4.25 (dt, 1H, *J* = 0.9, 6.7 Hz), 4.61 (d, 1H, *J* = 10.8 Hz), 4.66 (d, 1H, *J* = 10.8 Hz), 5.14 (d, 1H, *J* = 9.6 Hz), 5.24 (dd, 1H, *J* = 3.2, 11.3 Hz), 5.45 (dd, 1H, *J* = 1.0, 3.1 Hz), 6.40 (d, 1H, *J* = 3.6 Hz); ^{13}C NMR ($CDCl_3$): δ 20.57, 20.60, 20.78, 20.84, 52.0, 61.1, 66.9, 67.4, 68.5, 78.3, 90.9, 93.1, 169.0, 170.0, 170.4, 171.0; MS (ESI) *m/z* calcd for $C_{16}H_{22}{}^{35}Cl_3NO_{12}S$ 556.99; found (%) 579.85 ($[M(^{35}Cl_3)+Na]^+$, 94), 581.96 ($[M(^{35}Cl_2+^{37}Cl)+Na]^+$, 100), 583.95 ($[M(^{35}Cl+^{37}Cl_2)+Na]^+$, 39).

1,3,4,6-tetra-*O*-Acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranose (2b-β)



R_f 0.33 (3:2 hexane/EtOAc); $[\alpha]_D^{25}$ +8.3 (c 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 3H), 2.11 (s, 3H), 2.17 (s, 3H), 2.23 (s, 3H), 3.95 (dt, 1H, *J* = 8.9, 11.1 Hz), 4.06 (dt, 1H, *J* = 0.9, 6.5 Hz), 4.12 (dd, 1H, *J* = 6.3, 11.2 Hz), 4.16 (dd, 1H, *J* =6.7, 11.2 Hz), 4.64 (s, 2H), 5.08 (dd, 1H, *J* = 3.3, 11.1 Hz), 5.40 (d, 1H, *J* = 3.3 Hz), 5.67 (d, 1H, *J* = 9.0 Hz), 5.72 (d, 1H, *J* = 8.8 Hz).

1,3,6-tri-*O*-Acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-(2,2,2-trichloro ethoxysulfonyl)amido-β-D-glucopyranose (2c-β)



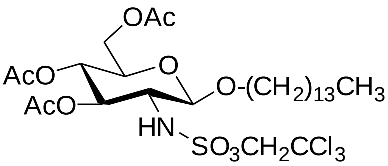
R_f 0.27 (1:1 hexane/EtOAc); ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 2.13 (s, 3H), 2.17 (s, 6H), 2.18 (s, 3H), 2.23 (s, 3H), 3.73 (q, 1H, *J* = 8.7 Hz), 3.86 (m, 2H), 3.91 (t, 1H, *J* = 7.2 Hz), 4.10 (dd, 1H, *J* = 7.1, 11.2 Hz), 4.14 (m, 1H), 4.18 (dd, 1H, *J* = 6.3, 11.0 Hz), 4.45 (dd, 1H, *J* = 1.9, 12 Hz), 4.49 (d, 1H, *J* = 7.8 Hz), 4.65 (s, 2H), 5.00 (dd, 1H, *J* = 2.5, 10.5 Hz), 5.10 (dd, 1H, *J* = 7.8, 10.5 Hz), 5.17 (t, 1H), 5.38 (dd, 1H, *J* = 0.8, 3.3 Hz), 5.74 (d, 1H, *J* = 7.8 Hz), 6.02 (d, 1H, *J* = 9.4 Hz); ^{13}C NMR ($CDCl_3$): δ 20.49, 20.63 (3C), 20.81, 20.91, 21.01, 57.2, 60.9, 61.9, 66.6, 69.0, 70.7, 70.9, 71.7, 73.5, 74.5, 78.6, 91.9, 93.3, 100.7, 169.2, 169.6, 170.07, 170.13, 170.32, 170.38, 170.9; MS (ESI) *m/z* calcd for $C_{28}H_{38}{}^{35}Cl_3NO_{20}S$ 845.08; found (%) 868.08 ($[M(^{35}Cl_3)+Na]^+$, 91), 870.07 ($[M(^{35}Cl_2+^{37}Cl)+Na]^+$, 100), 872.00 ($[M(^{35}Cl+^{37}Cl_2)+Na]^+$, 38).

General procedure for amidoglycosylation

To a mixture of glycal (0.2 mmol), alcohol (0.4 mmol), $Cl_3CCH_2OSO_2NH_2$ (80 mg, 0.35 mmol), $Rh_2(NHCOCF_3)_4$ (12 mg, 0.02 mmol), and activated powdered molecular sieves 4Å (160 mg) under nitrogen was added PhCl (3 mL), and the resulting light-purple suspension was cooled with an ice-water bath. PhIO (80 mg, 0.36 mmol) was added in several portions for 1 h, and the resulting light-brown suspension was stirred at 5 °C for 1 h and then at rt for 5-15 h with monitoring the reaction by TLC. The reaction mixture was filtered, washed with CH_2Cl_2, and the combined filtrates were concentrated under reduced pressure to remove CH_2Cl_2. The residue was purified by silica gel chromatography, usually eluting with hexane-EtOAc mixture.

Tetradecyl

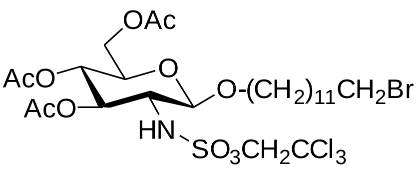
3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (3a)



R_f 0.35 (2:1 hexane/EtOAc); $[\alpha]_D^{25}$ -18.0 (c 2.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, *J* = 6.9 Hz), 1.25 (s-like, 20H), 1.32 (m, 2H), 1.66 (quint, 2H, *J* = 7.3 Hz), 2.04 (s, 3H), 2.10 (s, 3H), 2.13 (s, 3H), 3.56 (dt, 1H, *J* = 9.3, 7.1 Hz), 3.58 (q, 1H, *J* = 9.0 Hz), 3.69 (ddd, 1H, *J* = 2.3, 4.9, 8.8 Hz), 3.88 (dt, 1H, *J* = 9.4, 7.3 Hz), 4.14 (dd, 1H, *J* = 2.3, 12.3 Hz), 4.27 (dd, 1H, *J* = 4.9, 12.3 Hz), 4.43 (d, 1H, *J* = 8.2 Hz), 4.68 (d, 1H, *J* = 10.9 Hz), 4.72 (d, 1H, *J* = 10.9 Hz), 5.08 (t, 1H, *J* = 9.5 Hz), 5.12 (t, 1H, *J* = 9.5 Hz), 5.36 (d, 1H, *J* = 8.9 Hz); ^{13}C NMR ($CDCl_3$): δ 14.1, 20.6, 20.7, 20.8, 22.7, 25.8, 29.34, 29.36, 29.49, 29.58, 29.64, 31.9, 59.0, 62.0, 68.4, 70.6, 71.8, 72.8, 78.7, 93.4, 100.8, 169.3, 170.7, 171.6; MS (ESI) *m/z* calcd for $C_{28}H_{48}{}^{35}Cl_3NO_{11}S$ 711.20; found (%) 734.21 ($[M(^{35}Cl_3)+Na]^+$, 97), 736.21 ($[M(^{35}Cl_2+^{37}Cl)+Na]^+$, 100), 738.16 ($[M(^{35}Cl+^{37}Cl_2)+Na]^+$, 43).

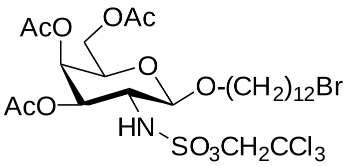
12-Bromododecyl

3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (4a)



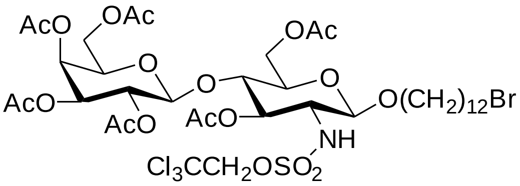
mp 71-73 °C; R_f 0.33 (2:1 hexane/EtOAc); $[\alpha]_D^{25}$ -17.8 (c 2.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.26 (s-like, 14H), 1.42 (m, 2H), 1.66 (m, 2H), 1.85 (quint, 2H, *J* = 7.3 Hz), 2.05 (s, 3H), 2.10 (s, 3H), 2.13 (s, 3H), 3.41 (t, 2H, *J* = 6.9 Hz), 3.57 (dt, 1H, *J* = 9.4, 7.0 Hz), 3.58 (q, 1H, *J* = 9.0 Hz), 3.71 (ddd, 1H, *J* = 2.3, 4.8, 9.4 Hz), 3.88 (dt, 1H, *J* = 9.4, 7.3 Hz), 4.14 (dd, 1H, *J* = 2.3, 12.3 Hz), 4.28 (dd, 1H, *J* = 4.8, 12.3 Hz), 4.44 (d, 1H, *J* = 8.2 Hz), 4.68 (d, 1H, *J* = 10.9 Hz), 4.72 (d, 1H, *J* = 10.9 Hz), 5.08 (t, 1H, *J* = 9.5 Hz), 5.13 (t, 1H, *J* = 9.5 Hz), 5.52 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$): δ 20.58, 20.73, 20.85, 25.8, 28.1, 28.7, 29.34, 29.39, 29.47, 29.49, 32.8, 34.1, 59.0, 62.0, 68.4, 70.6, 71.8, 72.9, 78.6, 93.4, 100.7, 169.3, 170.7, 171.6; Anal. Calcd for $C_{26}H_{43}BrCl_3NO_{11}S$: C, 40.88; H, 5.67; N, 1.83; S, 4.20. Found: C, 41.16; H, 5.63; N, 1.84; S, 4.39.

12-Bromododecyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (4b)



R_f 0.33 (2:1 hexane/EtOAc); $[\alpha]_D^{25}$ -35.5 (c 1.92, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.27 (s-like, 14H), 1.42 (m, 2H), 1.68 (m, 2H), 1.85 (quint, 2H, *J* = 7.2 Hz), 2.06 (s, 3H), 2.10 (s, 3H), 2.18 (s, 3H), 3.41 (t, 2H, *J* = 6.9 Hz), 3.58 (dt, 1H, *J* = 9.3, 7.2 Hz), 3.73 (q, 1H, *J* = 9.0 Hz), 3.90 (dt, 1H, *J* = 9.4, 7.3 Hz), 3.93 (t, 1H, *J* = 6.6 Hz), 4.12 (dd, 1H, *J* = 6.7, 11.2 Hz), 4.20 (dd, 1H, *J* = 6.5, 11.2 Hz), 4.46 (d, 1H, *J* = 8.4 Hz), 4.71 (s, 2H), 5.07 (dd, 1H, *J* = 3.5, 10.9 Hz), 5.37 (d, 1H, *J* = 3.5 Hz), 5.44 (br, 1H); ^{13}C NMR ($CDCl_3$): δ 20.68 (2C), 20.82, 25.8, 28.1, 28.7, 29.39, 29.47, 29.50, 32.8, 34.0, 56.1, 61.3, 66.9, 70.66, 70.71, 78.6, 93.4, 101.0, 170.2, 170.5, 171.2.

Bromododecyl 3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (4c)

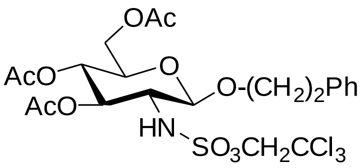


R_f 0.24 (3:2 hexane/EtOAc); $[\alpha]_D^{25}$ -13.0 (c 2.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.24-1.35 (m, 14H), 1.42 (m, 2H), 1.64 (m, 2H), 1.85 (quint, 2H, *J* = 7.2 Hz), 1.98 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.13 (s, 3H), 2.157 (s, 3H), 2.164 (s, 3H), 3.41 (t, 2H, *J* = 6.9 Hz), 3.52 (dt, 1H, *J* = 9.5, 6.9 Hz), 3.55 (dt, 1H, *J* = 7.5, 9.0 Hz), 3.67 (ddd, 1H, *J* = 2.5, 5.2, 8.4 Hz), 3.80 (t, 1H, *J* = 8.5 Hz), 3.83 (dt, 1H, *J* = 9.5, 7.2 Hz), 3.91 (t, 1H, *J* = 6.7 Hz), 4.10 (dd, 1H, *J* = 7.1, 11.1 Hz), 4.14 (dd, 1H, *J* = 5.2, 12.2 Hz), 4.17 (dd, 1H, *J* = 6.5, 11.1 Hz), 4.44 (d, 1H, *J* = 7.6 Hz), 4.49 (dd, 1H, *J* = 2.5, 12.0 Hz), 4.50 (d, 1H, *J* = 7.8 Hz), 4.69 (d, 1H, *J* = 10.9 Hz), 4.72 (d, 1H, *J* = 10.9 Hz), 4.99 (dd, 1H, *J* = 3.4, 10.5 Hz), 5.08 (dd, 1H, *J* = 8.4, 9.4 Hz), 5.10 (dd, 1H, *J* = 7.8, 10.5 Hz), 5.37 (dd, 1H, *J* = 0.9, 3.4 Hz), 5.71 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$): δ 20.51, 20.65 (3C), 20.85, 20.97, 25.8, 28.1, 28.7, 29.35, 29.39, 29.47, 32.8, 34.1, 58.3, 60.9, 62.2, 66.6, 69.1, 70.4, 70.7, 70.8, 72.4, 72.6, 75.6, 78.6, 93.4, 100.5, 100.9, 169.5, 170.06, 170.12, 170.36, 170.42, 171.2; MS (ESI) *m/z* calcd for

$C_{38}H_{59}{}^{79}Br^{35}Cl_3NO_{19}S$ 1049.17; found (%) 1072.16 ([M(^{79}Br+^{35}Cl$_3$)+Na]$^+$, 54), 1074.21 ([M(^{35}Cl$_2$+^{37}Cl)+Na]$^+$, 100), 1076.13 ([M(^{35}Cl+^{37}Cl$_2$)+Na]$^+$, 78).

2-Phenylethyl

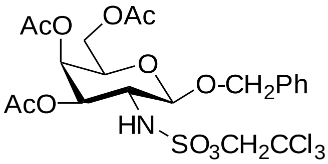
3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (6a)



R$_f$ 0.34 (3:2 hexane/EtOAc); $[\alpha]_D^{25}$ -14.4 (c 0.90, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 2.04 (s, 3H), 2.09 (s, 3H), 2.12 (s, 3H), 2.99 (t, 2H, *J* = 7.6 Hz), 3.60 (q, 1H, *J* = 9.0 Hz), 3.69 (ddd, 1H, *J* = 2.5, 4.9, 9.6 Hz), 3.80 (dt, 1H, *J* = 10.2, 7.7 Hz), 4.11 (dt, 1H, *J* = 10.1, 7.6 Hz), 4.13 (dd, 1H, *J* = 2.5, 12.3 Hz), 4.26 (dd, 1H, *J* = 4.9, 12.3 Hz), 4.46 (d, 1H, *J* = 8.2 Hz), 4.64 (d, 1H, *J* = 10.9 Hz), 4.68 (d, 1H, *J* = 10.9 Hz), 5.07 (t, 1H, *J* = 9.4 Hz), 5.12 (t, 1H, *J* = 9.6 Hz), 5.52 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR (CDCl$_3$): δ 20.6, 20.7, 20.9, 36.0, 58.9, 61.9, 68.4, 70.9, 71.9, 72.8, 78.6, 93.4, 100.7, 126.7, 128.6 (2C), 128.9 (2C), 137.6, 169.4, 170.7, 171.6.

Benzyl

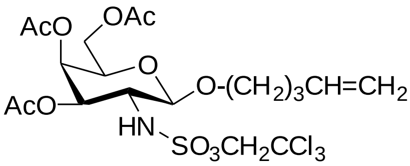
3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (7b)



R$_f$ 0.28 (3:2 hexane/EtOAc); $[\alpha]_D^{25}$ -44.4 (c 1.45, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 2.05 (s, 3H), 2.08 (s, 3H), 2.18 (s, 3H), 3.80 (dt, 1H, *J* = 10.9, 8.6 Hz), 3.90 (dt, 1H, *J* = 0.9, 6.6 Hz), 4.15 (dd, 1H, *J* = 6.5, 11.3 Hz), 4.22 (dd, 1H, *J* = 6.7, 11.3 Hz), 4.49 (d, 1H, *J* = 8.3 Hz), 4.56 (s, 2H), 4.68 (d, 1H, *J* = 11.6 Hz), 4.94 (d, 1H, *J* = 11.0 Hz), 5.01 (dd, 1H, *J* = 3.4, 10.9 Hz), 5.21 (d, 1H, *J* = 8.7 Hz), 5.36 (d, 1H, *J* = 3.4 Hz), 7.30-7.40 (m, 5H); ^{13}C NMR (CDCl$_3$): δ 20.7 (2C), 20.8, 56.0, 61.4, 66.9, 70.7, 70.9, 71.0, 78.6, 93.3, 99.2, 128.5, 128.6, 128.7, 135.8, 170.2, 170.5, 171.2; MS (ESI) *m/z* calcd for $C_{21}H_{26}{}^{35}Cl_3NO_{11}S$ 605.03; found (%) 627.96 ([M(^{35}Cl$_3$)+Na]$^+$, 92), 629.94 ([M(^{35}Cl$_2$+^{37}Cl)+Na]$^+$, 100), 631.93 ([M(^{35}Cl+^{37}Cl$_2$)+Na]$^+$, 41).

4-Pentenyl

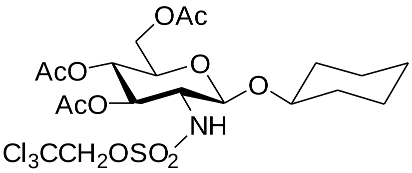
3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (8b)



mp 84-86 °C; R_f 0.36 (3:2 hexane/EtOAc); $[\alpha]_D^{25}$ -23.1 (c 1.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.79 (quint, 2H, *J* = 7.2 Hz), 2.06 (s, 3H), 2.10 (s, 3H), 2.15 (m, 2H), 2.18 (s, 3H), 3.61 (dt, 2H, *J* = 9.6, 7.0 Hz), 3.74 (dt, 1H, *J* = 11.1, 8.4 Hz), 3.91 (t, 1H, *J* = 7.0 Hz), 3.92 (dt, 1H, *J* = 9.5, 7.0 Hz), 4.12 (dd, 1H, *J* = 6.7, 11.3 Hz), 4.19 (dd, 1H, *J* = 6.7, 11.3 Hz), 4.46 (d, 1H, *J* = 8.2 Hz), 4.68 (d, 1H, *J* = 11.0 Hz), 4.71 (d, 1H, *J* = 11.0 Hz), 4.99 (m, 1H),, 5.04 (m, 1H), 5.05 (dd, 1H, *J* = 3.4, 11.0 Hz), 5.20 (d, 1H, *J* = 8.4 Hz), 5.37 (d, 1H, *J* = 3.3 Hz), 5.80 (ddt, 1H, *J* = 17.0, 10.2, 6.7 Hz); ^{13}C NMR ($CDCl_3$): δ 20.7 (2C), 20.8, 28.6, 29.9, 56.1, 61.4, 66.9, 69.9, 70.7, 78.6, 93.4, 101.0, 115.2, 137.6, 170.2, 170.5, 171.3; Anal. Calcd for $C_{19}H_{28}Cl_3NO_{11}S$: C, 39.02; H, 4.83; N, 2.39; S, 5.48. Found: C, 38.83; H, 4.86; N, 2.34; S, 5.39.

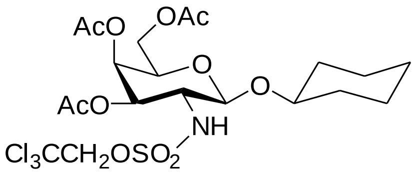
Cyclohexyl

3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (9a)



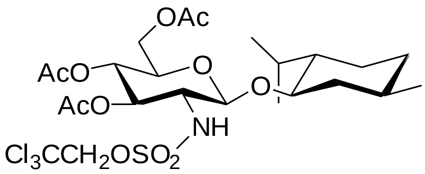
R_f 0.35 (3:2 hexane/EtOAc); $[\alpha]_D^{25}$ -21.8 (c 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.10-1.50 (m, 5H), 1.57 (m, 1H), 1.78 (m, 2H), 1.98 (m, 2H), 2.05 (s, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 3.57 (q, 1H, *J* = 9.1 Hz), 3.70 (m, 2H), 4.12 (dd, 1H, *J* = 2.5, 12.3 Hz), 4.28 (dd, 1H, *J* = 5.1, 12.3 Hz), 4.58 (d, 1H, *J* = 8.2 Hz), 4.72 (s, 2H), 5.07 (t, 1H, *J* = 9.5 Hz), 5.14 (t, 1H, *J* = 9.7 Hz), 5.55 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$): δ 20.58, 20.73, 20.88, 24.2, 24.3, 25.4, 31.7, 33.5, 59.0, 62.1, 68.6, 71.7, 73.0, 78.4, 78.7, 93.4, 98.7, 169.4, 170.8, 171.7; MS (ESI) *m/z* calcd for $C_{20}H_{30}{}^{35}Cl_3NO_{11}S$ 597.06; found (%) 619.95 ($[M(^{35}Cl_3)+Na]^+$, 100), 622.00 ($[M(^{35}Cl_2+^{37}Cl)+Na]^+$, 97), 623.92 ($[M(^{35}Cl+^{37}Cl_2)+Na]^+$, 39).

Cyclohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (9b)



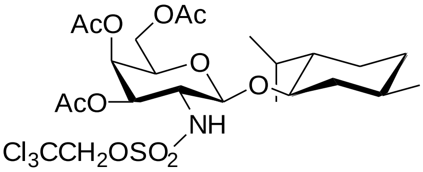
R_f 0.31 (2:1 hexane/EtOAc); $[\alpha]_D^{25}$ -30.2 (c 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.10-1.50 (m, 5H), 1.57 (m, 1H), 1.79 (m, 2H), 2.01 (m, 2H) 2.06 (s, 3H), 2.10 (s, 3H), 2.18 (s, 3H), 3.69 (dt, 1H, *J* = 3.3, 10.0 Hz), 3.72 (dt, 1H, *J* = 10.9, 8.6 Hz), 3.93 (t, 1H, *J* = 6.7 Hz), 4.10 (dd, 1H, *J* = 6.7, 11.2 Hz), 4.21 (dd, 1H, *J* = 6.6, 11.3 Hz), 4.60 (d, 1H, *J* = 8.3 Hz), 4.73 (s, 2H), 5.07 (dd, 1H, *J* = 3.5, 10.7 Hz), 5.36 (d, 1H, *J* = 3.5 Hz), 5.53 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$): δ 20.65, 20.71, 20.85, 24.2, 24.4, 25.4, 31.7, 33.6, 56.2, 61.3, 66.9, 70.6, 70.9.1, 78.5, 78.6, 93.4, 99.1, 170.3, 170.5, 171.3; MS (ESI) *m/z* calcd for $C_{20}H_{30}{}^{35}Cl_3NO_{11}S$ 597.06; found (%) 620.02 ([M($^{35}Cl_3$)+Na]$^+$, 94), 622.00 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 623.99 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 39).

L-Menthyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (10a)



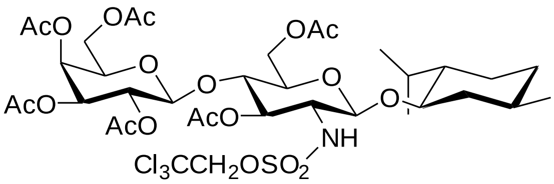
R_f 0.40 (2:1 hexane/EtOAc); $[\alpha]_D^{25}$ -53.4 (c 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.74 (d, 3H, *J* = 6.8 Hz), 0.82 (m, 1H), 0.87 (d, 3H, *J* = 7.0 Hz), 0.93 (d, 3H, *J* = 6.5 Hz), 0.98 (m, 1H), 1.00 (q, 1H, *J* = 11.7 Hz), 1.30 (m, 2H), 1.67 (m, 2H), 2.02 (m, 1H), 2.05 (s, 3H), 2.07 (s, 3H), 2.14 (s, 3H), 2.22 (m, 1H), 3.55 (q, 1H, *J* = 9.1 Hz), 3.56 (dt, 1H, *J* = 3.3, 11.0 Hz), 3.70 (ddd, 1H, *J* = 2.7, 5.3, 9.5 Hz), 4.14 (dd, 1H, *J* = 2.7, 12.1 Hz), 4.20 (dd, 1H, *J* = 5.3, 12.1 Hz), 4.54 (d, 1H, *J* = 8.3 Hz), 4.75 (2H), 5.07 (t, 1H, *J* = 9.5 Hz), 5.13 (t, 1H, *J* = 9.5 Hz), 5.38 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$): δ 15.3, 20.58, 20.66, 20.80, 20.88, 22.2, 23.1, 25.1, 31.5, 34.2, 40.0, 47.6, 58.9, 62.4, 68.7, 71.5, 73.2, 77.6, 78.8, 93.4, 97.3, 169.4, 170.7, 171.7.

L-Menthyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (10b)



R_f 0.40 (2:1 hexane/EtOAc); $[\alpha]_D^{25}$ -54.3 (c 0.84, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.74 (d, 3H, *J* = 6.8 Hz), 0.82 (m, 1H), 0.88 (d, 3H, *J* = 7.0 Hz), 0.93 (d, 3H, *J* = 6.5 Hz), 0.98 (m, 1H), 1.00 (q, 1H, *J* = 11.7 Hz), 1.30 (m, 2H), 1.67 (m, 2H), 2.04 (s, 3H), 2.07 (m, 1H), 2.11 (s, 3H), 2.20 (s, 3H), 2.27 (m, 1H), 3.53 (dt, 1H, *J* = 4.1, 10.7 Hz), 3.66 (q, 1H, *J* = 9.4 Hz), 3.92 (t, 1H, *J* = 6.7 Hz), 4.08 (dd, 1H, *J* = 6.6, 11.2 Hz), 4.20 (dd, 1H, *J* = 6.8, 11.2 Hz), 4.54 (d, 1H, *J* = 8.2 Hz), 4.75 (2H), 5.08 (dd, 1H, *J* = 3.5, 10.7 Hz), 5.35 (d, 1H, *J* = 3.5 Hz), 5.50 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$): δ 15.3, 20.64, 20.75, 20.88, 22.2, 23.0, 25.0, 31.5, 34.2, 40.2, 47.6, 56.0, 61.5, 67.1, 70.5, 71.1, 77.9, 78.7, 93.4, 97.9, 170.4, 170.6, 171.4; MS (ESI) *m/z* calcd for $C_{24}H_{38}{}^{35}Cl_3NO_{11}S$ 653.12; found (%) 676.09 ($[M(^{35}Cl_3)+Na]^+$, 95), 678.05 ($[M(^{35}Cl_2+^{37}Cl)+Na]^+$, 100), 680.07 ($[M(^{35}Cl+^{37}Cl_2)+Na]^+$, 40).

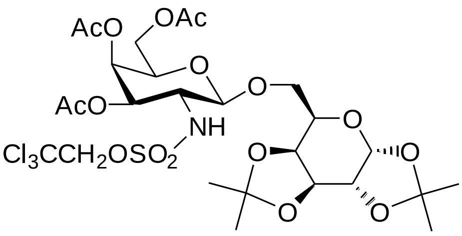
L-Menthyl 3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (10c)



R_f 0.30 (3:2 hexane/EtOAc); $[\alpha]_D^{25}$ -32.7 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.72 (d, 3H, *J* = 6.8 Hz), 0.80 (m, 1H), 0.86 (d, 3H, *J* = 7.0 Hz), 0.93 (d, 3H, *J* = 6.4 Hz), 0.96 (m, 1H), 0.99 (q, 1H, *J* = 11.6 Hz), 1.30 (m, 2H), 1.66 (m, 2H), 1.98 (s, 3H), 2.05 (m, 1H), 2.05 (s, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 2.15 (m, 1H), 2.16 (s, 6H), 3.47 (q, 1H, *J* = 9.2 Hz), 3.53 (dt, 1H, *J* = 3.9, 10.7 Hz), 3.69 (m, 1H), 3.79 (t, 1H, *J* = 9.7 Hz), 3.91 (t, 1H, *J* = 6.7 Hz), 4.10 (dd, 1H, *J* = 7.0, 10.5 Hz), 4.10 (m, 1H), 4.16 (dd, 1H, *J* = 6.4, 11.1 Hz), 4.52 (d, 1H, *J* = 7.8 Hz), 4.55 (d, 1H, *J* = 8.2 Hz), 4.74 (s, 2H), 5.00 (dd, 1H, *J* = 3.4, 10.4 Hz), 5.09 (1H), 5.10 (1H), 5.37 (d, 1H, *J* = 3.4 Hz), 5.76 (d, 1H, *J* = 9.1 Hz); ^{13}C NMR ($CDCl_3$): δ 15.3, 20.52, 20.59, 20.63, 20.73, 20.77, 20.98, 22.3, 23.1, 25.1, 31.5, 34.2, 40.0, 47.6, 59.0, 60.9, 62.1, 66.7, 69.1, 70.76, 70.84, 72.3, 73.2, 76.4, 77.3, 78.7, 93.5, 97.0, 101.1, 169.4, 170.1 (2C), 170.35, 170.43, 171.4; MS (ESI) *m/z* calcd for $C_{36}H_{54}{}^{35}Cl_3NO_{19}S$ 941.21; found (%) 964.26 ($[M(^{35}Cl_3)+Na]^+$, 81), 966.27 ($[M(^{35}Cl_2+^{37}Cl)+Na]^+$, 100), 968.27

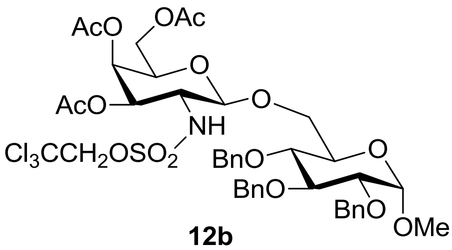
([M(^{35}Cl+^{37}Cl$_2$)+Na]$^+$, 41).

6-*O*-[3,4,6-tri-*O*-Acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranosyl] -1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (11b)



R_f 0.27 (3:2 hexane/EtOAc); $[\alpha]_D^{25}$ -46.4 (c 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 3H), 1.34 (s, 3H), 1.46 (s, 3H), 1.60 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 2.15 (s, 3H), 3.72 (ddd, 1H, *J* = 7.2, 8.2, 10.9 Hz), 3.92 (dd, 1H, *J* = 8.8, 12.7 Hz), 3.95 (dt, 1H, *J* = 0.8, 6.7 Hz), 4.00 (dd, 1H, *J* = 2.5, 12.6 Hz), 4.12 (dd, 1H, *J* = 6.7, 11.2 Hz), 4.17 (dd, 1H, *J* = 2.0, 8.0 Hz), 4.19 (dd, 1H, *J* = 6.6, 11.2 Hz), 4.34 (dd, 1H, *J* = 2.3, 5.2 Hz), 4.59 (dd, 1H, *J* = 2.3, 7.9 Hz), 4.71 (d, 1H, *J* = 11 Hz), 4.74 (d, 1H, *J* = 11 Hz), 4.83 (d, 1H, *J* = 8.4 Hz), 5.04 (dd, 1H, *J* = 3.3, 10.9 Hz), 5.37 (dd, 1H, *J* = 0.8, 3.3 Hz), 5.59 (d, 1H, J = 5.2 Hz), 5.82 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$): δ 20.6, 20.7, 24.2, 24.7, 25.87, 25.92, 55.8, 61.2, 66.8, 68.5, 68.8, 70.0, 70.6, 70.84, 70.88, 70.95, 78.7, 93.7, 96.2, 101.2, 109.2, 109.5, 170.1, 170.4, 170.6; MS (ESI) *m/z* calcd for $C_{26}H_{38}{}^{35}Cl_3NO_{16}S$ 757.10; found (%) 780.05 ([M(^{35}Cl$_3$)+Na]$^+$, 92), 782.04 ([M(^{35}Cl$_2$+^{37}Cl)+Na]$^+$, 100), 784.02 ([M(^{35}Cl+^{37}Cl$_2$)+Na]$^+$, 39).

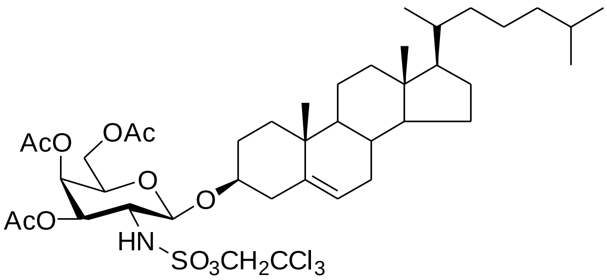
Methyl 6-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranosyl] -2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (12b)



12b

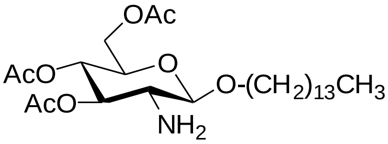
R_f 0.25 (3:2 hexane/EtOAc); ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 3H), 2.06 (s, 3H), 2.12 (s, 3H), 3.40 (s, 3H), 3.45 (dd, 1H, *J* = 8.8, 10.0 Hz), 3.65 (dd, 1H, *J* = 6.0, 11.0 Hz), 3.70 (dt, 1H, *J* = 10.7, 7.7 Hz), 3.81 (dt, 1H, *J* = 1.0, 7.0 Hz), 3.86 (m, 1H), 4.00 (t, 1H, *J* = 9.3 Hz), 4.10 (m, 3H), 4.28 (d, 1H, *J* = 8.4 Hz), 4.60 (d, 1H, *J* = 3.3 Hz), 4.64 (s, 2H), 4.64 (d, 2H, *J* = 11.9 Hz), 4.79 (d, 1H, *J* = 12.1 Hz), 4.81 (d, 1H, *J* = 11.1 Hz), 4.89 (d, 1H, *J* = 11.5 Hz), 4.96 (dd, 1H, *J* = 3.4, 11.0 Hz), 4.99 (d, 1H, *J* = 11.2 Hz), 5.07 (d, 1H, *J* = 7.4 Hz), 5.34 (dd, 1H, *J* = 0.9, 3.4 Hz), 7.27-7.40 (m, 15H); MS (ESI) *m/z* calcd for $C_{42}H_{50}{}^{35}Cl_3NO_{16}S$ 961.19; found (%) 984.18 ($[M(^{35}Cl_3)+Na]^+$, 100), 986.17 ($[M(^{35}Cl_2+^{37}Cl)+Na]^+$, 95), 988.17 ($[M(^{35}Cl+^{37}Cl_2)+Na]^+$, 32)..

Cholest-5-en-3β-yl
3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (13b)



*R*f 0.30 (3:1 hexane/EtOAc); $[\alpha]_D^{25}$ -32.0 (c 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.67 (s, 3H), 0.86 (d, 3H, *J* = 6.6 Hz), 0.87 (d, 3H, *J* = 6.6 Hz), 0.91 (d, 3H, *J* = 6.4 Hz), 1.00 (s, 3H), 0.90-2.05 (m, 26H), 2.05 (s, 3H), 2.10 (s, 3H), 2.17 (s, 3H), 2.33 (m, 1H), 2.39 (ddd, 1H, *J* = 2.1, 4.8, 13.1 Hz), 3.62 (tt, 1H, *J* = 4.7, 11.4 Hz), 3.74 (dt, 1H, *J* = 11.1, 8.5 Hz), 3.90 (t, 1H, *J* = 7.0 Hz), 4.10 (dd, 1H, *J* = 7.0, 11.2 Hz), 4.19 (dd, 1H, *J* = 6.6, 11.2 Hz), 4.57 (d, 1H, *J* = 8.2 Hz), 4.73 (s, 2H), 5.01 (dd, 1H, *J* = 2.4, 8.8 Hz), 5.05 (dd, 1H, *J* = 3.5, 11.0 Hz), 5.37 (d, 1H, *J* = 3.5 Hz); ^{13}C NMR ($CDCl_3$): δ 11.8, 18.7, 19.3, 20.68, 20.71, 20.9, 21.0, 22.5, 22.8, 23.8, 24.3, 28.0, 28.2, 29.6, 31.8, 31.9, 35.8, 36.2, 36.7, 37.2, 38.5, 39.5, 39.7, 42.3, 50.1, 56.1, 56.7, 61.3, 66.9, 70.7, 70.9, 78.7, 79.7, 93.4, 99.2, 122.5, 139.9, 170.2, 170.4, 171.2; MS (ESI) *m/z* calcd for $C_{41}H_{64}{}^{35}Cl_3NO_{11}S$ 883.33; found (%) 906.33 ($[M(^{35}Cl_3)+Na]^+$, 94), 908.25 ($[M(^{35}Cl_2+^{37}Cl)+Na]^+$, 100), 910.30 ($[M(^{35}Cl+^{37}Cl_2)+Na]^+$, 34).

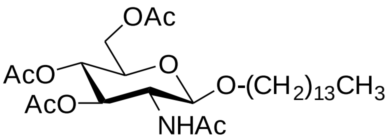
Tetradecyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside (15)



*R*f 0.50 (EtOAc); ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, *J* = 6.9 Hz), 1.25 (s-like, 22H), 1.62 (m, 2H), 2.02 (s, 3H), 2.074 (s, 3H), 2.077 (s, 3H), 2.93 (dd, 1H, *J* = 8.2, 9.7 Hz), 3.51 (dt, 1H, *J* = 9.5, 7.0 Hz), 3.68 (ddd, 1H, *J* = 2.4, 4.9, 9.6 Hz), 3.90 (dt, 1H, *J* = 9.5, 6.7 Hz), 4.11 (dd, 1H, *J* = 2.4, 12.2

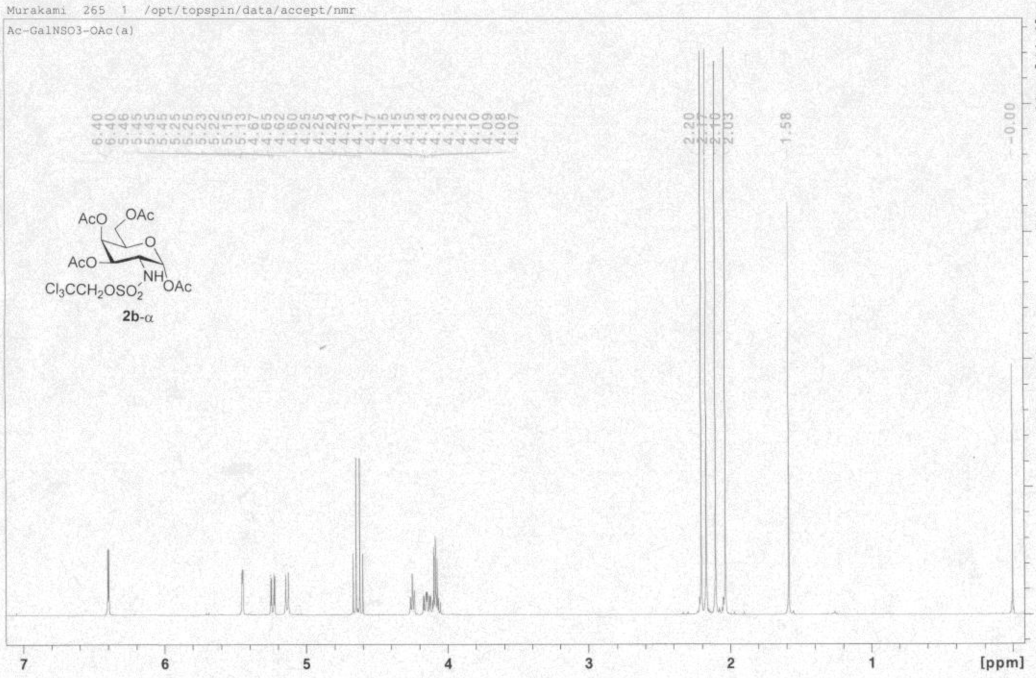
Hz), 4.24 (d, 1H, *J* = 8.0 Hz), 4.29 (dd, 1H, *J* = 4.9, 12.2 Hz), 4.98 (t, 1H, *J* = 9.3 Hz), 5.01 (t, 1H, *J* = 9.3 Hz).

Tetradecyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (16)



To a mixture of **3a** (43 mg, 0.06 mmol) and powdered anhydrous $CuSO_4$ (5 mg, 0.03 mmol) in tetrahydrofuran (1 mL) was added acetic acid (0.1 mL) and acetic anhydride (0.1 mL). Zinc (42 mg, 0.6 mmol) was added in 2 portions for 10 min, and the resulting dark-grey suspension was stirred for 3 h. The reaction mixture was filtered and washed with EtOAc, and the combined filtrates were mixed with H_2O, and the layers were separated. The organic layer was washed with aq. NaCl, and the combined aqueous layers were extracted with EtOAc. The combined organic extracts were dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel chromatography eluting with hexane-EtOAc (1:2) to give **16** (26 mg, 80%) as a colorless solid.

mp 126-129 °C; R_f 0.30 (1:2 hexane/EtOAc); $[\alpha]_D^{25}$ -6.3 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, *J* = 6.9 Hz), 1.25 (s-like, 22H), 1.57 (m, 2H), 1.95 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.09 (s, 3H), 3.47 (dt, 1H, *J* = 9.6, 6.9 Hz), 3.71 (ddd, 1H, *J* = 2.5, 4.7, 10.0 Hz), 3.82 (dt, 1H, *J* = 10.4, 8.5 Hz), 3.86 (dt, 1H, *J* = 9.6, 6.8 Hz), 4.13 (dd, 1H, *J* = 2.3, 12.3 Hz), 4.27 (dd, 1H, *J* = 4.7, 12.3 Hz), 4.69 (d, 1H, *J* = 8.2 Hz), 5.07 (t, 1H, *J* = 9.6 Hz), 5.32 (dd, 1H, *J* = 9.4, 10.5 Hz), 5.64 (d, 1H, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$): δ 14.1, 20.6, 20.7, 20.8, 22.7, 25.8, 29.34, 29.36, 29.49, 29.58, 29.64, 31.9, 59.0, 62.0, 68.4, 70.6, 71.8, 72.8, 78.7, 93.4, 100.8, 169.3, 170.7, 171.6; Anal. Calcd for $C_{28}H_{49}NO_9$: C, 61.86; H, 9.08; N, 2.58. Found: C, 61.50; H, 8.95; N, 2.53.



Murakami 265 1 /opt/topspin/data/accept/nmr
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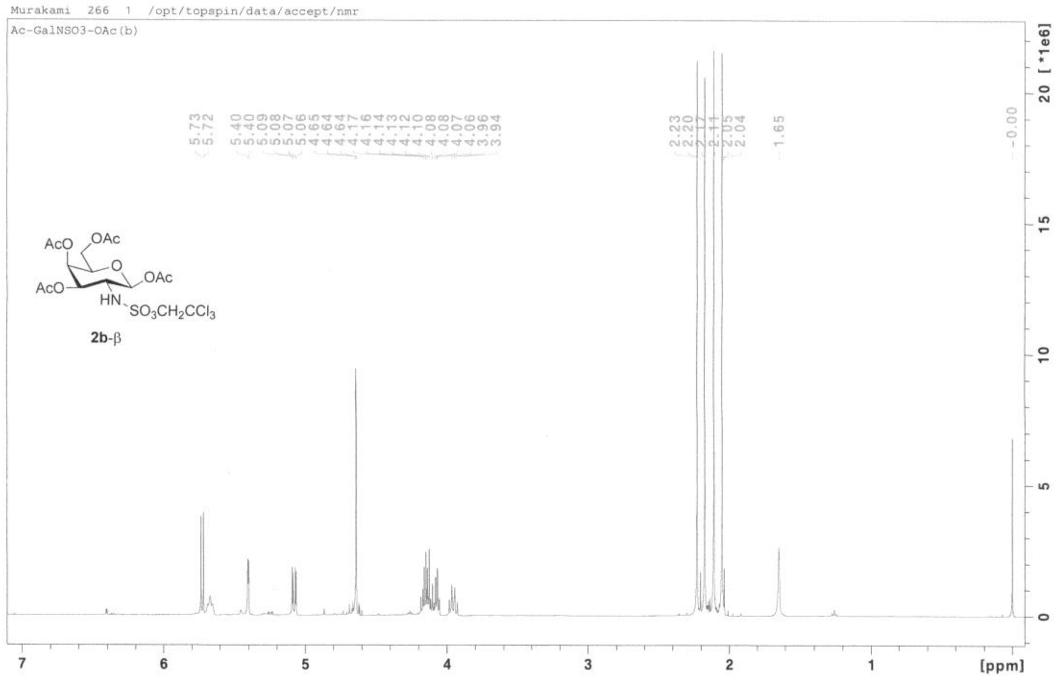
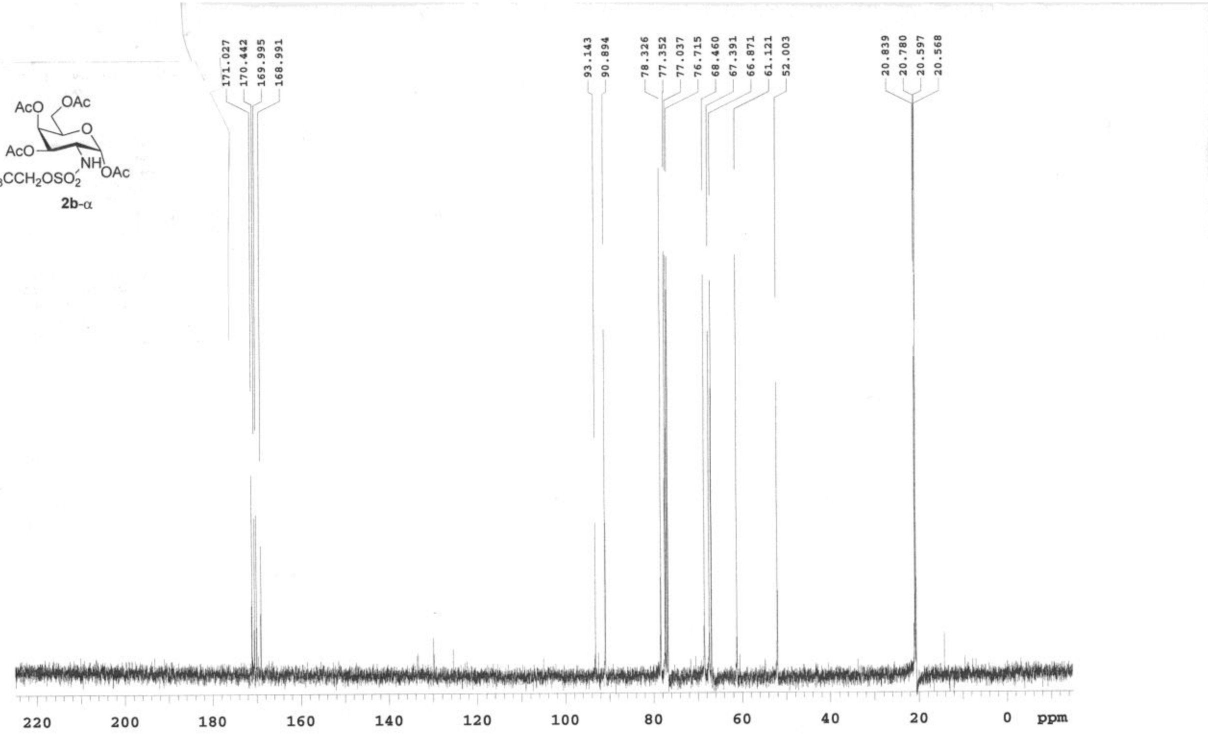
6.40
6.40
5.46
5.45
5.45
5.45
5.25
5.23
5.22
5.15
5.13
4.67
4.65
4.62
4.60
4.25
4.25
4.24
4.23
4.17
4.15
4.15
4.15
4.14
4.13
4.12
4.10
4.09
4.08
4.07
2.20
2.17
2.10
2.03
1.58
-0.00
AcO
OAc
AcO
NH
OAc
Cl3CCH2OSO2
2b-α
[*1e6]
[ppm]

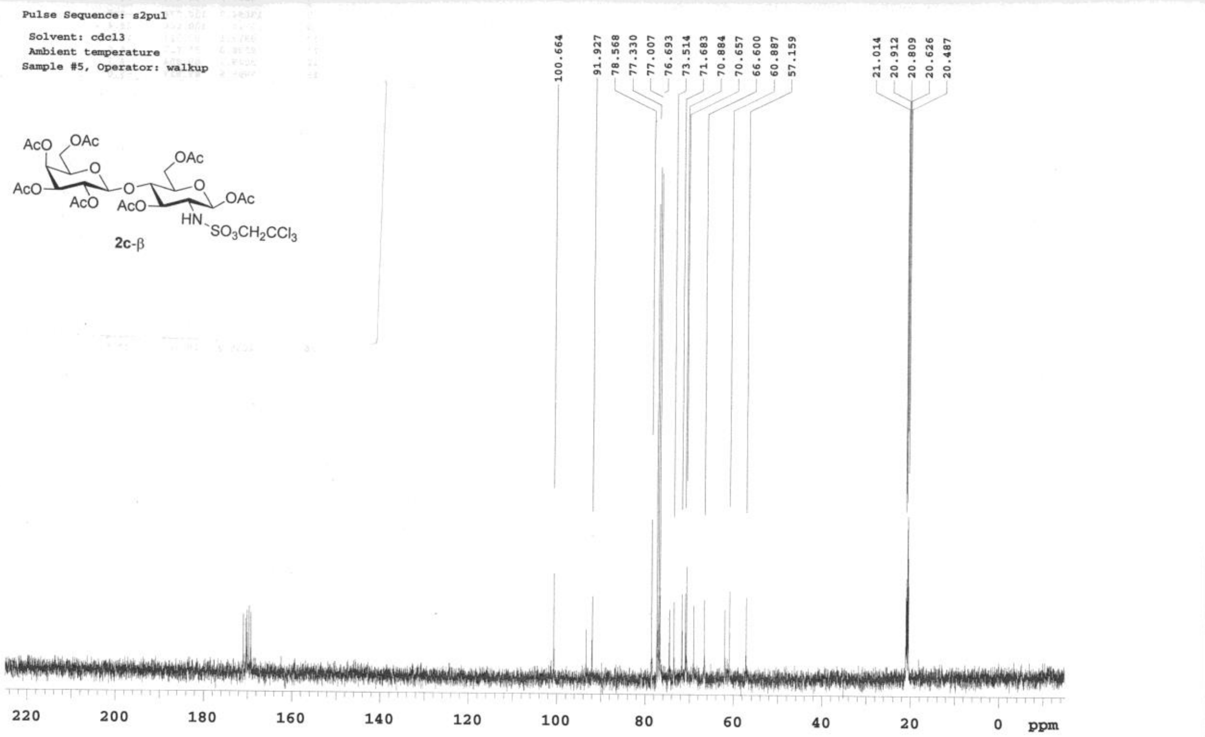


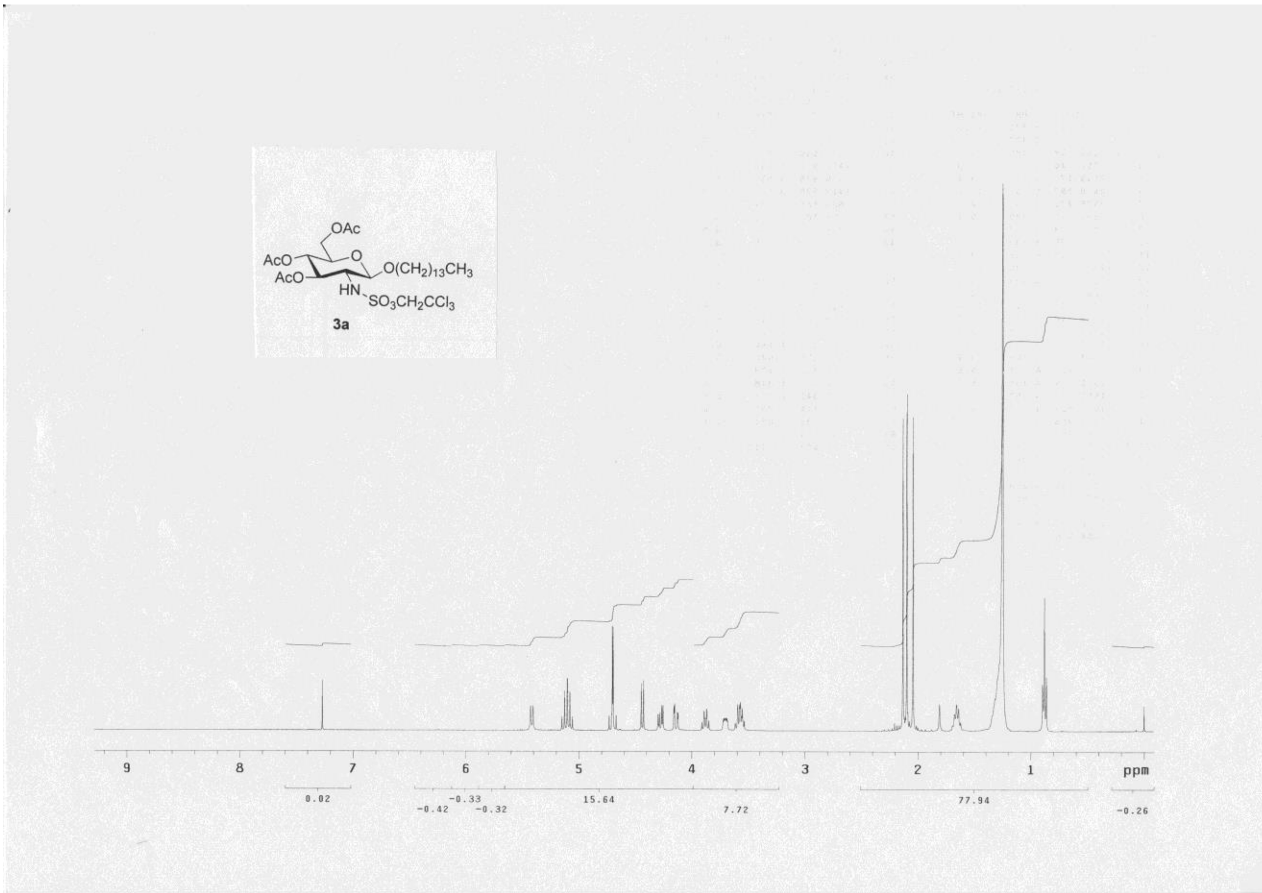
Murakami 266 1 /opt/topspin/data/accept/nmr
Ac-GalNSO3-OAc(b)
5.73
5.72
5.40
5.40
5.09
5.08
5.07
5.06
4.65
4.64
4.64
4.17
4.16
4.14
4.13
4.12
4.10
4.08
4.07
4.06
3.96
3.94
2.23
2.20
2.17
2.11
2.05
2.04
1.65
-0.00
AcO
OAc
OAc
AcO
HN
SO3CH2CCl3
2b-β
[*1e6]
[ppm]

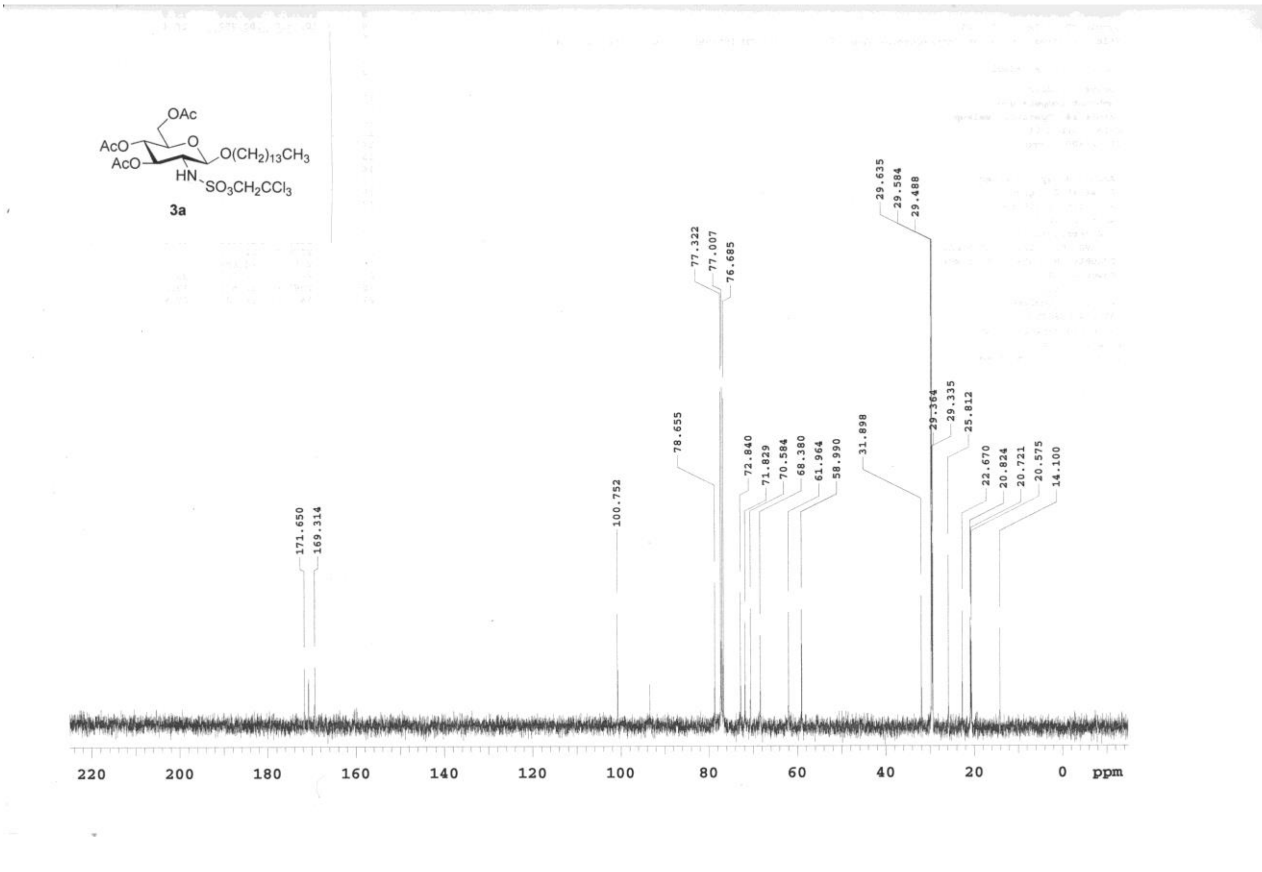
2b-α


171.027
170.442
169.995
168.991
93.143
90.894
78.326
77.352
77.037
76.715
68.460
67.391
66.871
61.121
52.003
20.839
20.780
20.597
20.568
220 200 180 160 140 120 100 80 60 40 20 0 ppm

2c-β


Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #5, Operator: walkup
100.664
91.927
78.568
77.330
77.007
76.693
73.514
71.683
70.884
70.657
66.600
60.887
57.159
21.014
20.912
20.809
20.626
20.487
220 200 180 160 140 120 100 80 60 40 20 0 ppm


OAc
AcO
AcO
O
O(CH2)13CH3
HN
SO3CH2CCl3
3a
9
8
7
6
5
4
3
2
1
ppm
0.02
-0.33
-0.42
-0.32
15.64
7.72
77.94
-0.26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AcO
AcO
O
O(CH2)13CH3
HN
SO3CH2CCl3
3a
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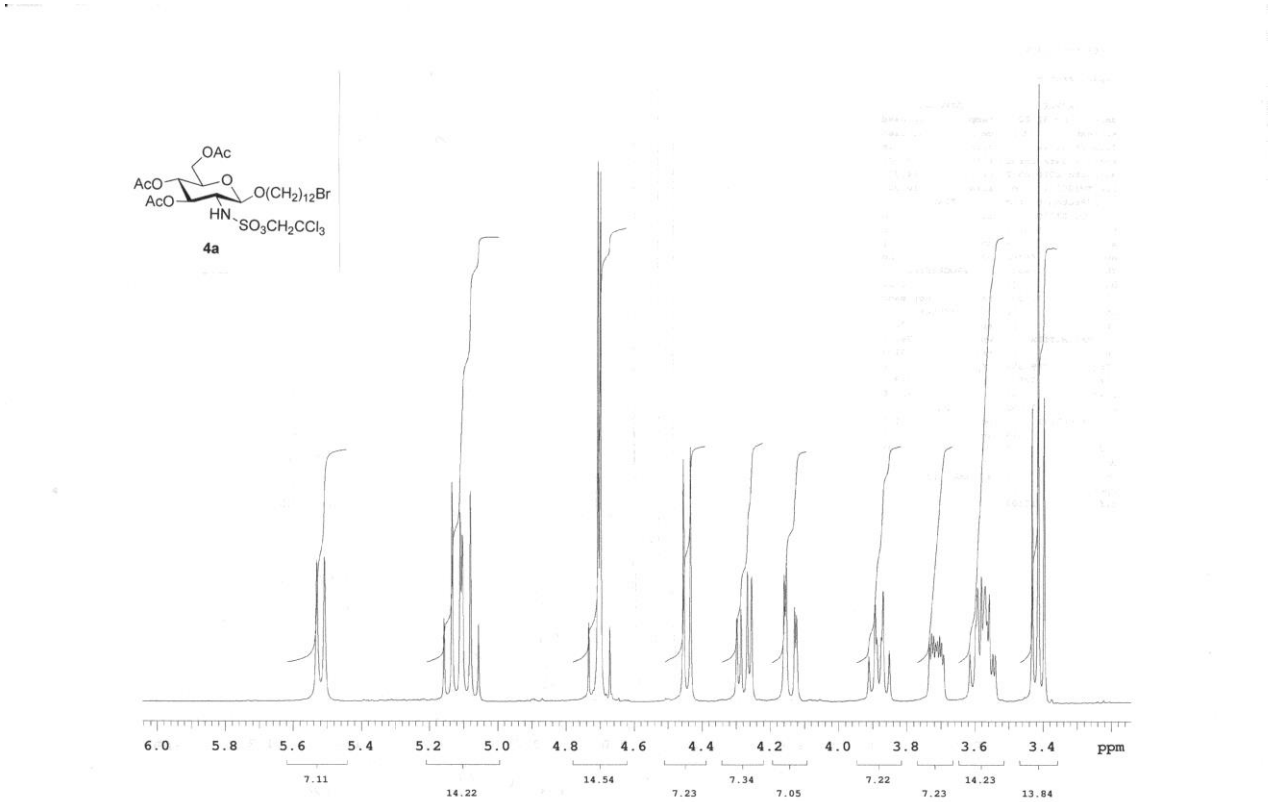
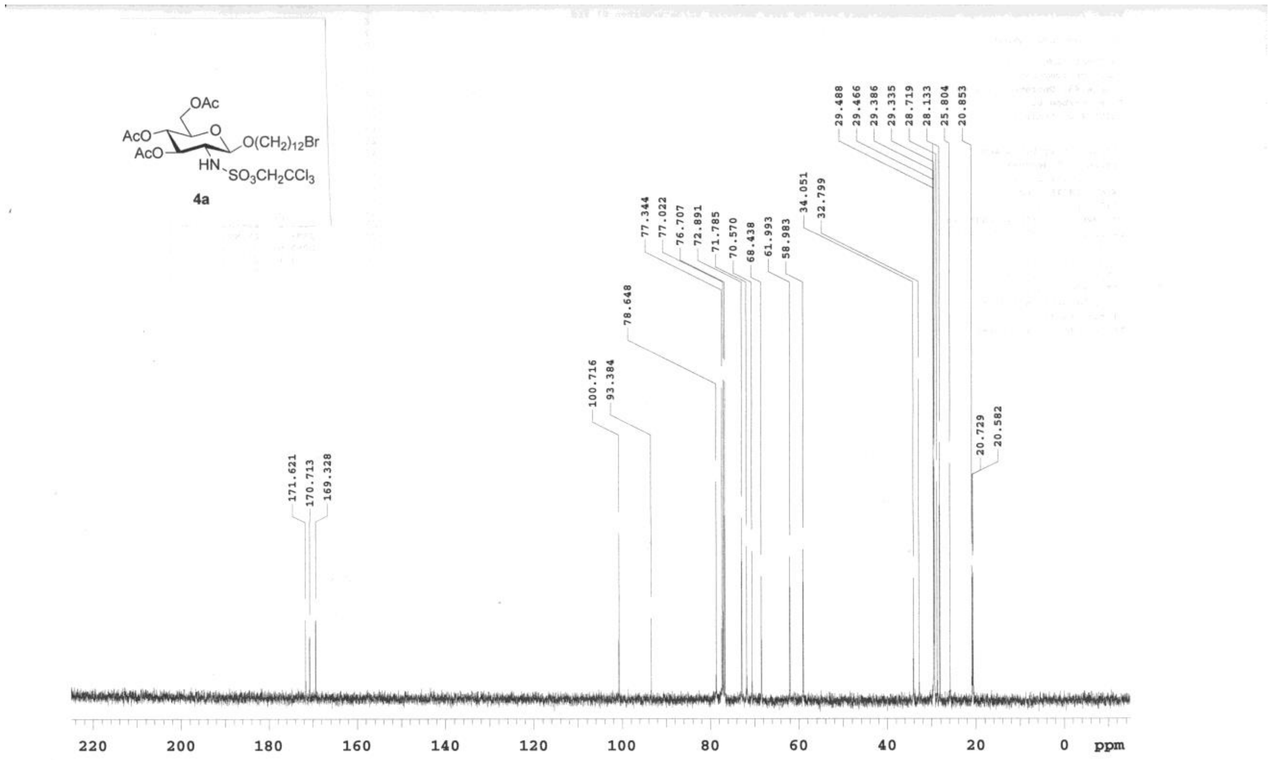
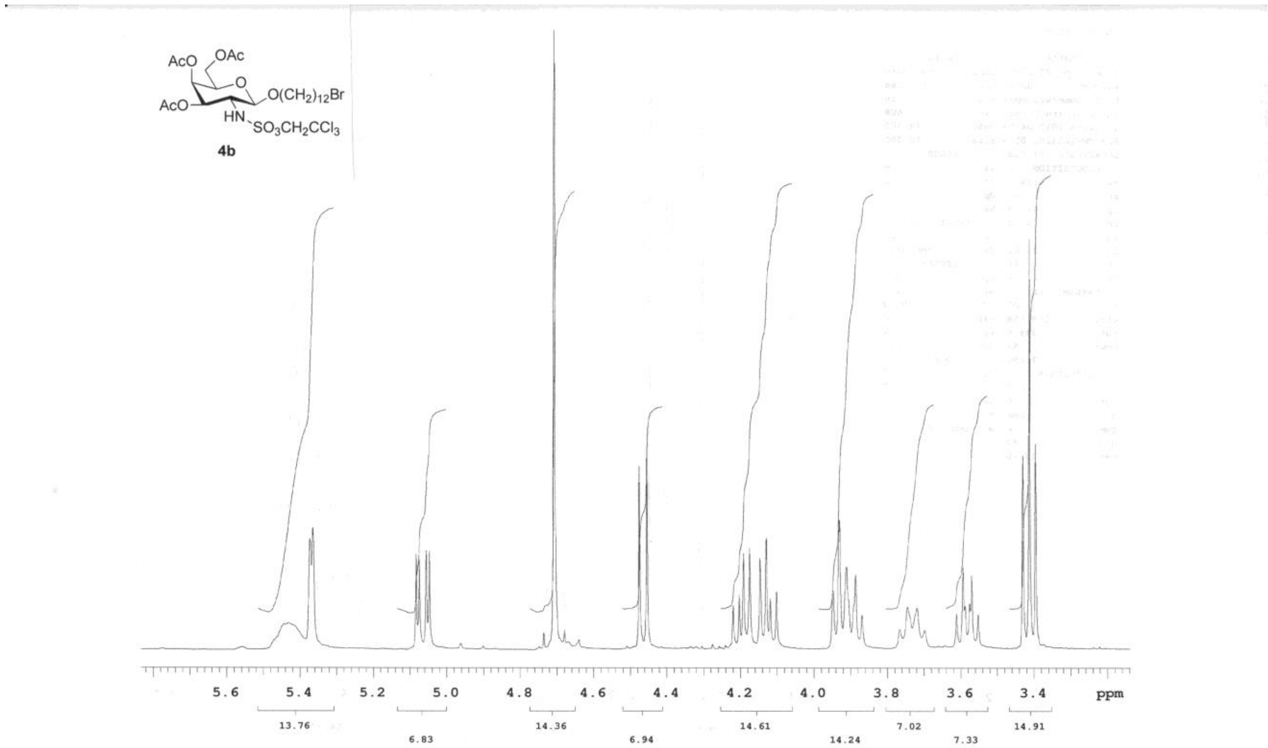
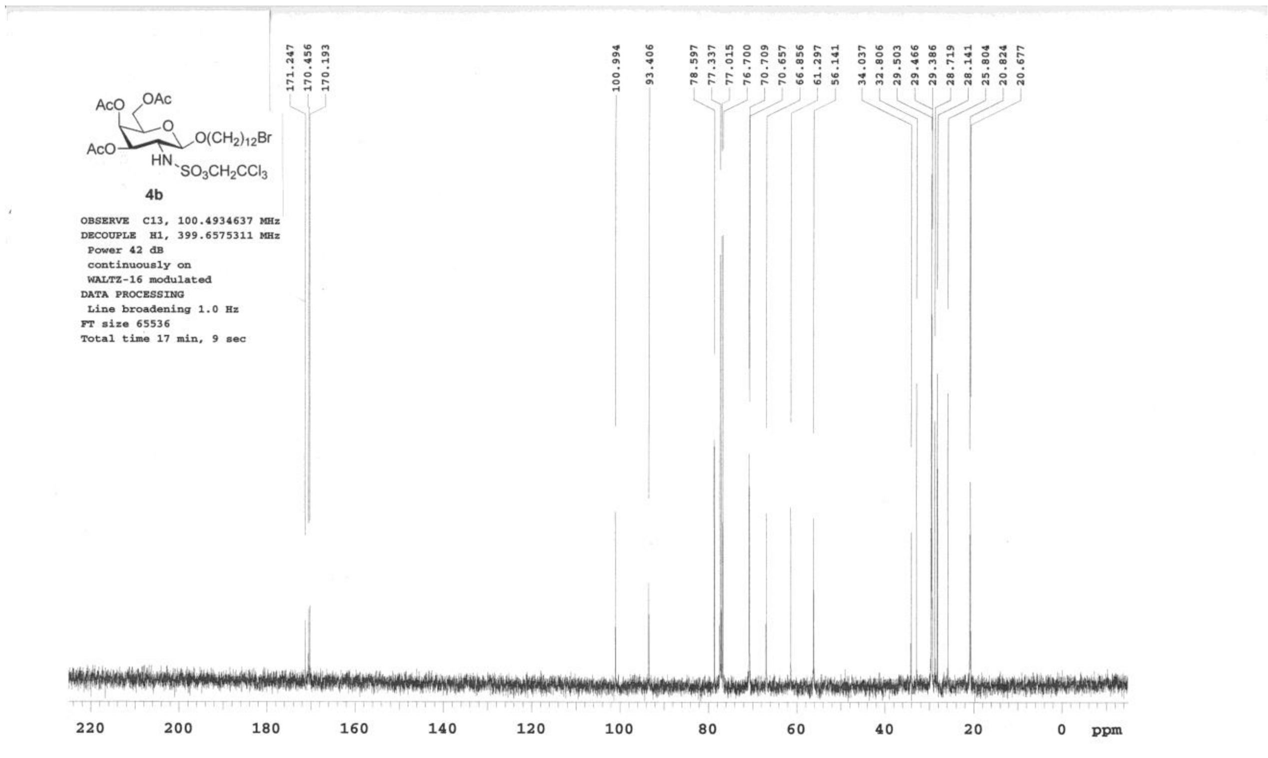
169.314
100.752
78.655
77.322
77.007
76.685
72.840
71.829
70.584
68.380
61.964
58.990
31.898
29.635
29.584
29.488
29.364
29.335
25.812
22.670
20.824
20.721
20.575
14.100
220
200
180
160
140
120
100
80
60
40
20
0
ppm


AcO
AcO
OAc
O
O(CH2)12Br
HN
SO3CH2CCl3
4a
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 ppm
7.11
14.22
14.54
7.23
7.34
7.05
7.22
7.23
14.23
13.84

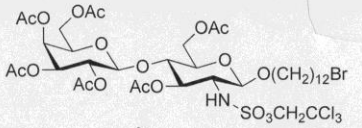

AcO
AcO
OAc
O
O(CH2)12Br
HN
SO3CH2CCl3
4a
171.621
170.713
169.328
100.716
93.384
78.648
77.344
77.022
76.707
72.891
71.785
70.570
68.438
61.993
58.983
34.051
32.799
29.488
29.466
29.386
29.335
28.719
28.133
25.804
20.853
20.729
20.582
220 200 180 160 140 120 100 80 60 40 20 0 ppm



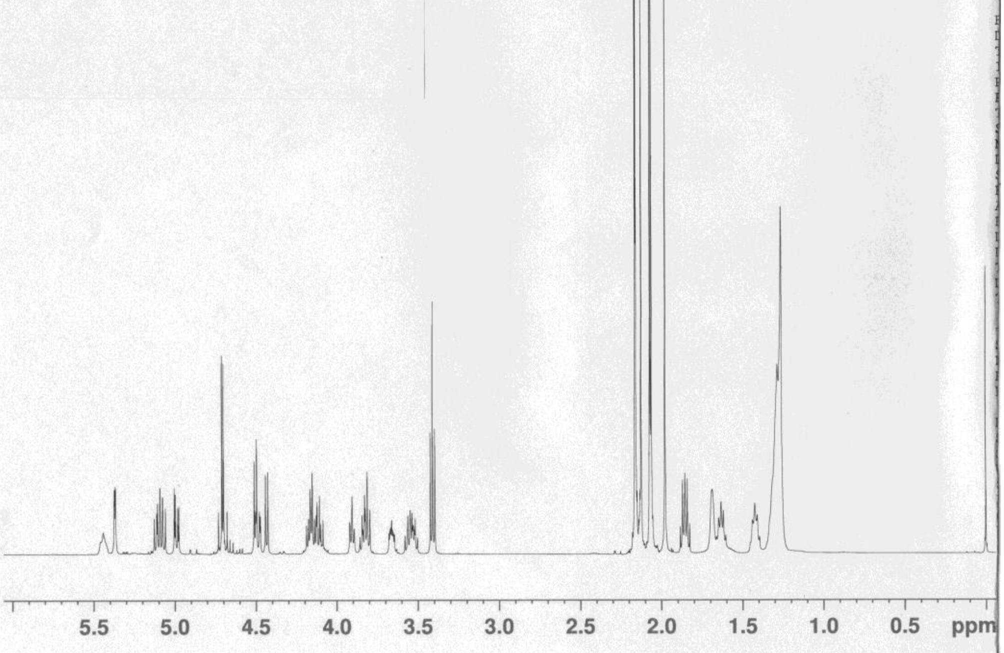
AcO OAc
O
O(CH2)12Br
AcO
HN
SO3CH2CCl3
4b
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 ppm
13.76 6.83 14.36 6.94 14.61 14.24 7.02 7.33 14.91



171.247 170.456 170.193 100.994 93.406 78.597 77.337 77.015 76.700 70.709 70.657 66.856 61.297 56.141 34.037 32.806 29.503 29.466 29.386 28.719 28.141 25.804 20.824 20.677
AcO OAc
O
O(CH2)12Br
AcO
HN
SO3CH2CCl3
4b
OBSERVE C13, 100.4934637 MHz
DECOUPLE H1, 399.6575311 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 9 sec
220 200 180 160 140 120 100 80 60 40 20 0 ppm



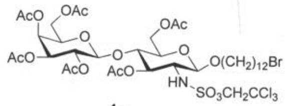
4c



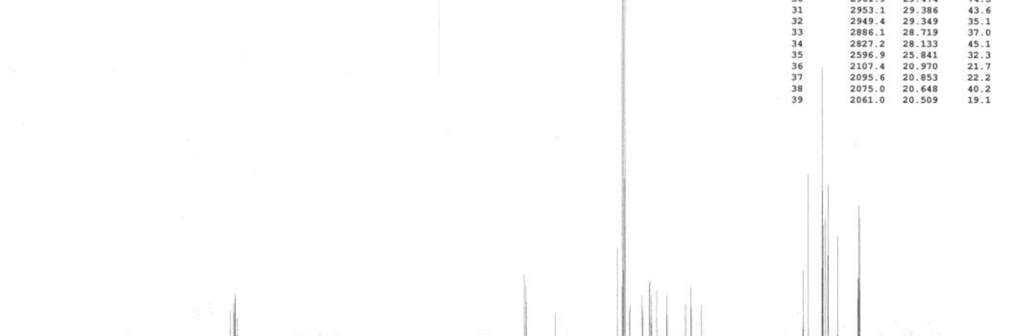
Pulse Sequence: s2pul

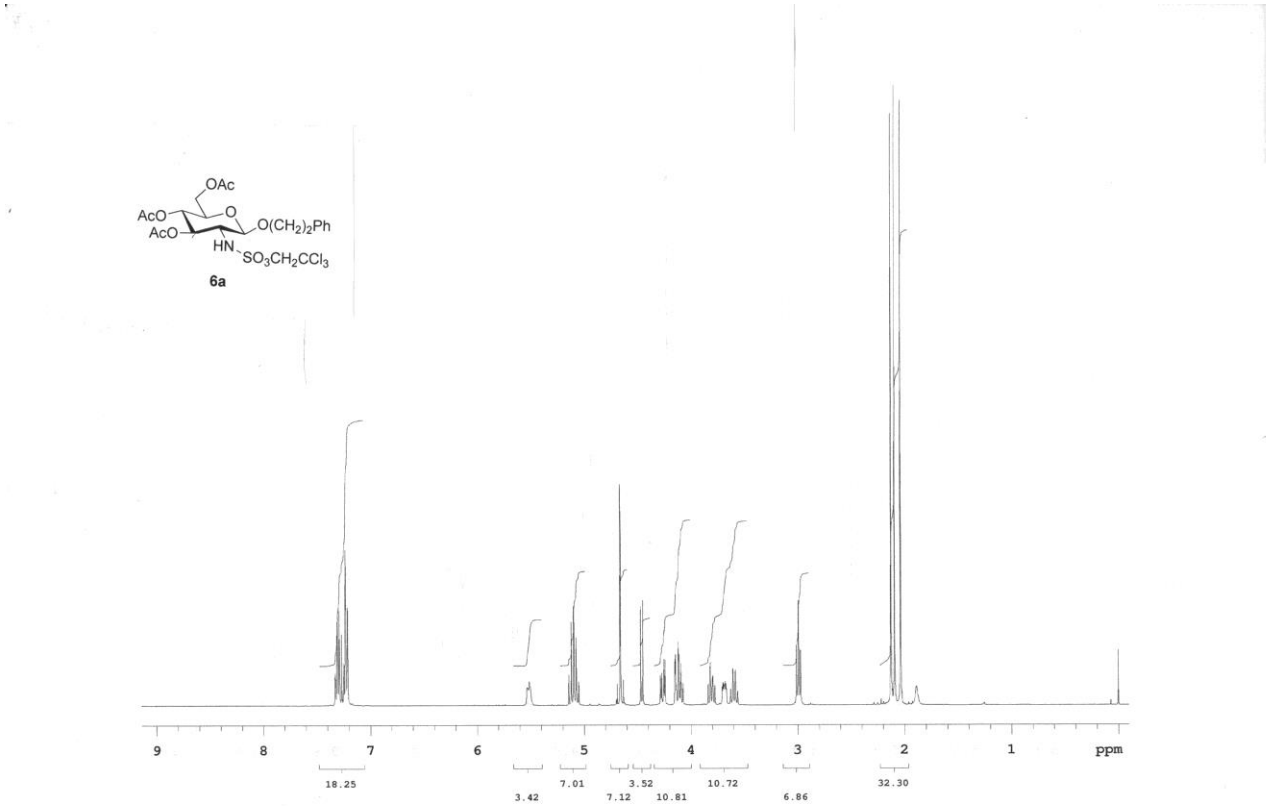
Solvent: cdcl3
Ambient temperature
Sample #4, Operator: walkup
File: Carbon_02
INOVA-400 "vnmr1"

INDEX	FREQUENCY	PPM	HEIGHT
1	17207.0	171.225	13.9
2	17126.1	170.420	15.7
3	17120.2	170.361	13.1
4	17095.9	170.119	17.9
5	17090.0	170.061	16.7
6	17038.5	169.548	11.8
7	14465.3	143.943	-5.4
8	14264.4	141.943	-7.9
9	14004.6	139.358	5.3
10	10141.9	100.921	22.8
11	10098.5	100.489	20.0
12	9392.6	93.465	13.1
13	7894.8	78.560	29.6
14	7772.6	77.344	94.7
15	7740.2	77.022	92.5
16	7708.6	76.707	91.6
17	7595.2	75.579	15.3
18	7297.1	72.613	17.6
19	7277.3	72.415	13.6
20	7114.6	70.797	20.6
21	7108.7	70.738	21.6
22	7070.4	70.357	17.6
23	6945.3	69.112	18.9
24	6695.8	66.629	17.7
25	6246.8	62.161	15.5
26	6115.1	60.850	19.7
27	5862.6	58.338	15.3
28	3421.9	34.051	24.0
29	3296.1	32.799	47.9
30	2961.9	29.474	74.5
31	2953.1	29.386	43.6
32	2949.4	29.349	35.1
33	2886.1	28.719	37.0
34	2827.2	28.133	45.1
35	2596.9	25.841	32.3
36	2107.4	20.970	21.7
37	2095.6	20.853	22.2
38	2075.0	20.648	40.2
39	2061.0	20.509	19.1

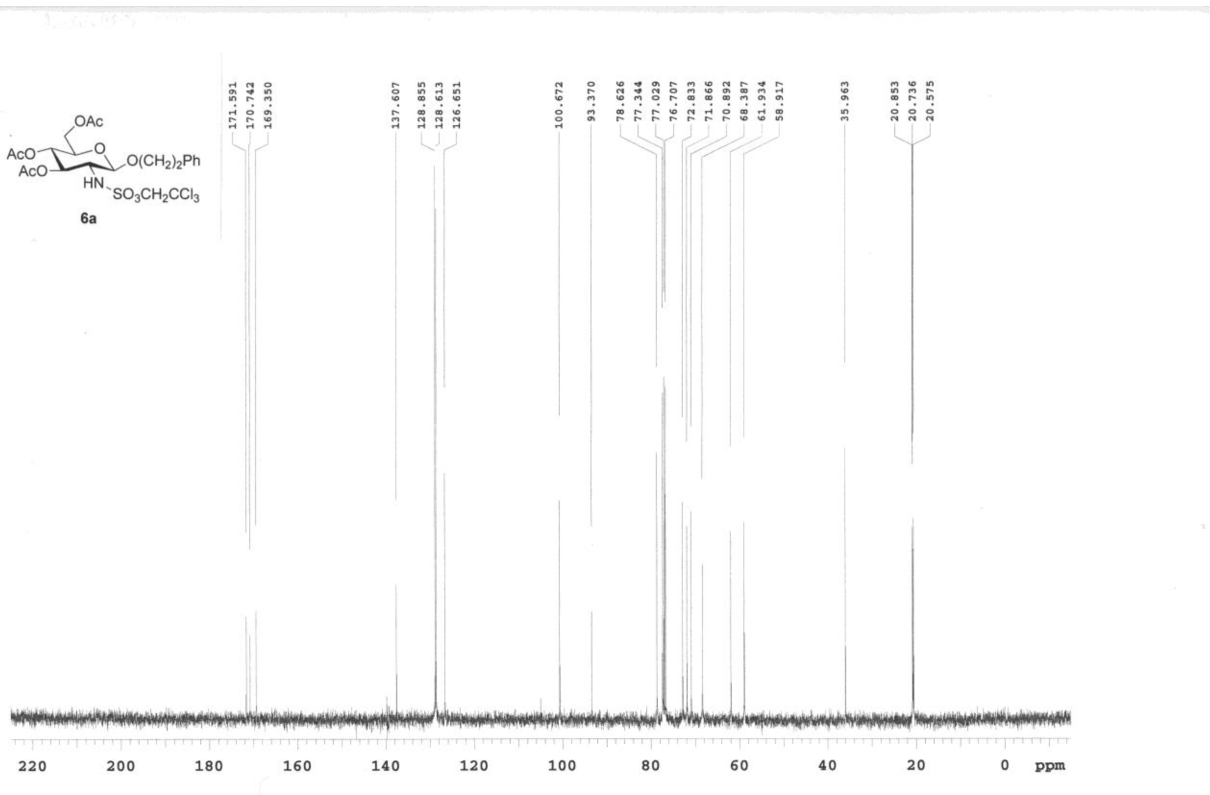


4c

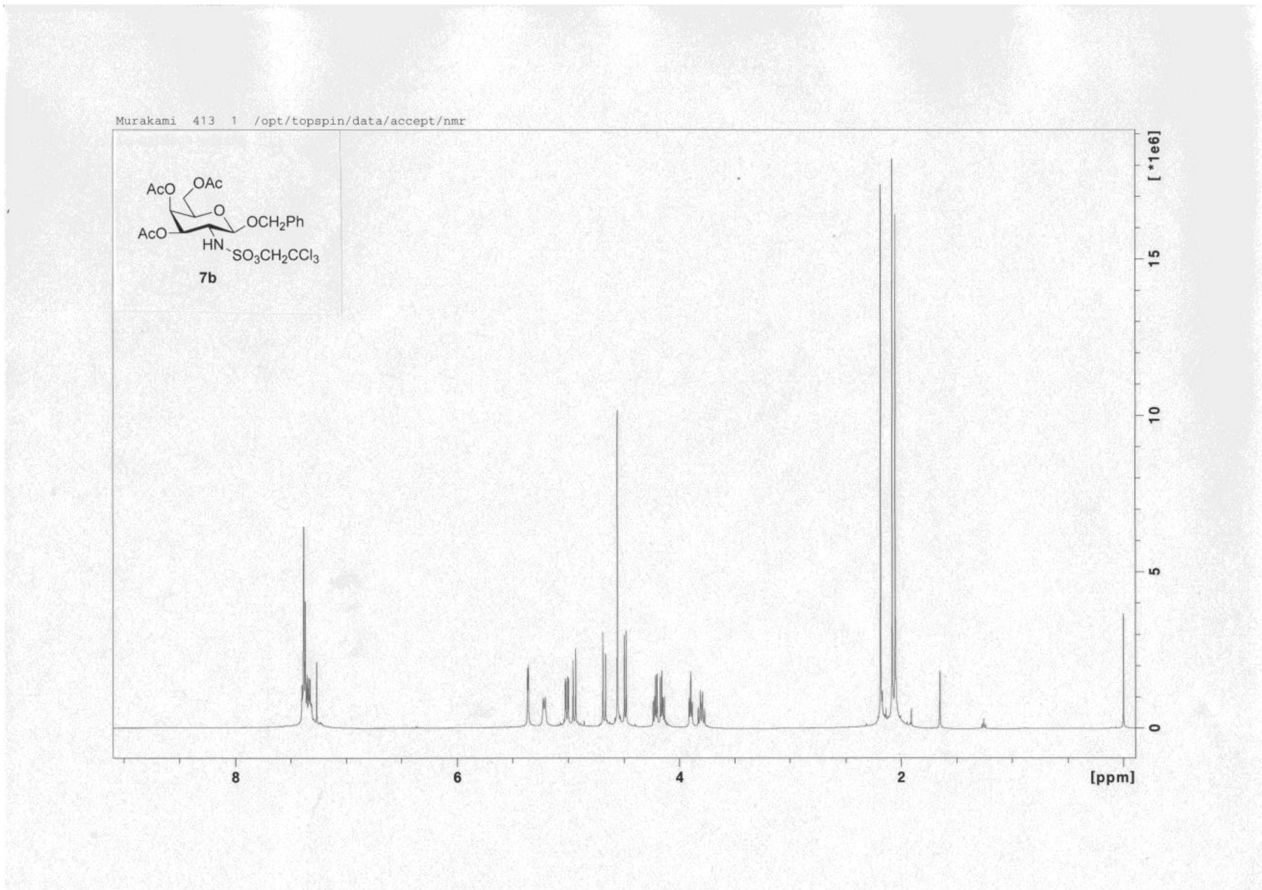




OAc
AcO
AcO
O
O(CH2)2Ph
HN
SO3CH2CCl3
6a
9
8
7
6
5
4
3
2
1
ppm
18.25
3.42
7.01
7.12
3.52
10.81
10.72
6.86
32.30

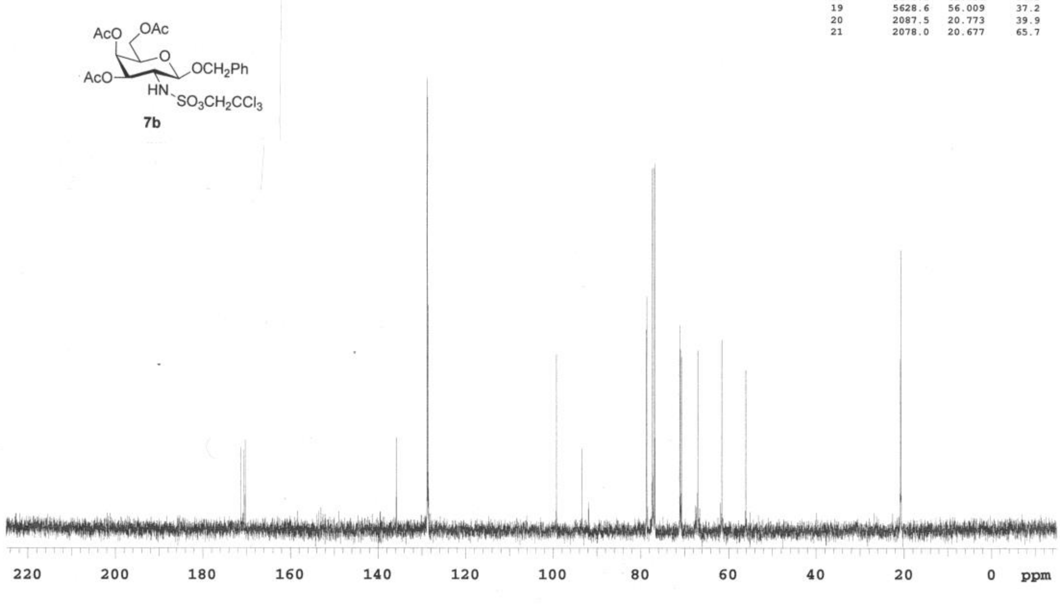


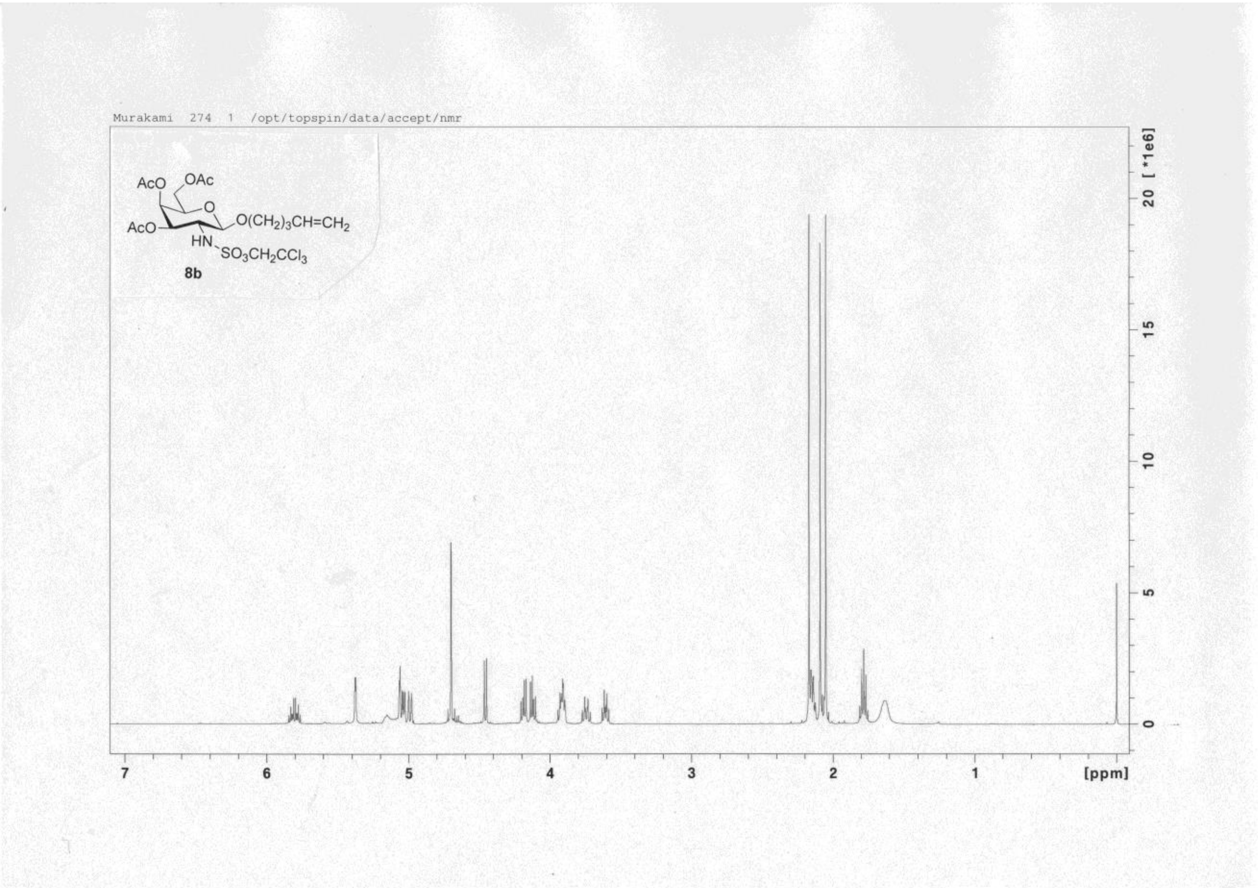
OAc
AcO
AcO
O
O(CH2)2Ph
HN
SO3CH2CCl3
6a
171.591
170.742
169.350
137.607
128.855
128.613
126.651
100.672
93.370
78.626
77.344
77.029
76.707
72.833
71.866
70.892
68.387
61.934
58.917
35.963
20.853
20.736
20.575
220
200
180
160
140
120
100
80
60
40
20
0
ppm



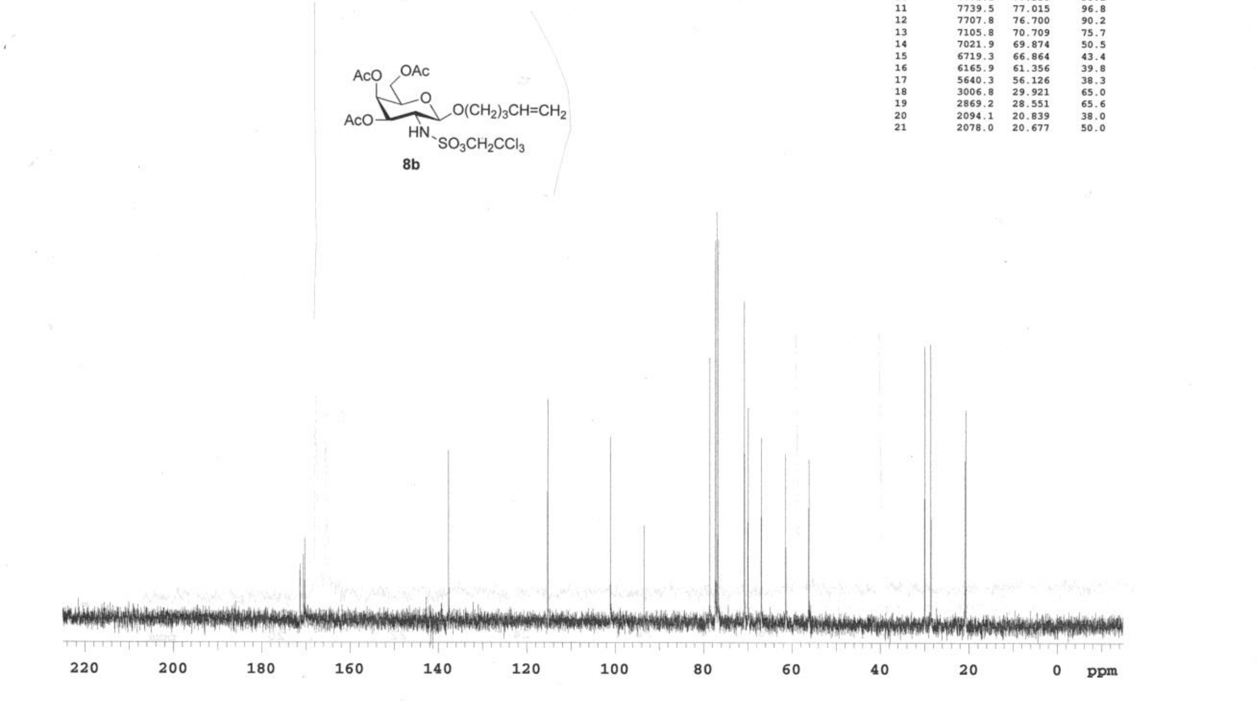
Solvent: cdcl3
Ambient temperature
Sample #4, Operator: walkup
File: Carbon_02
INOVA-400 "vnmr1"

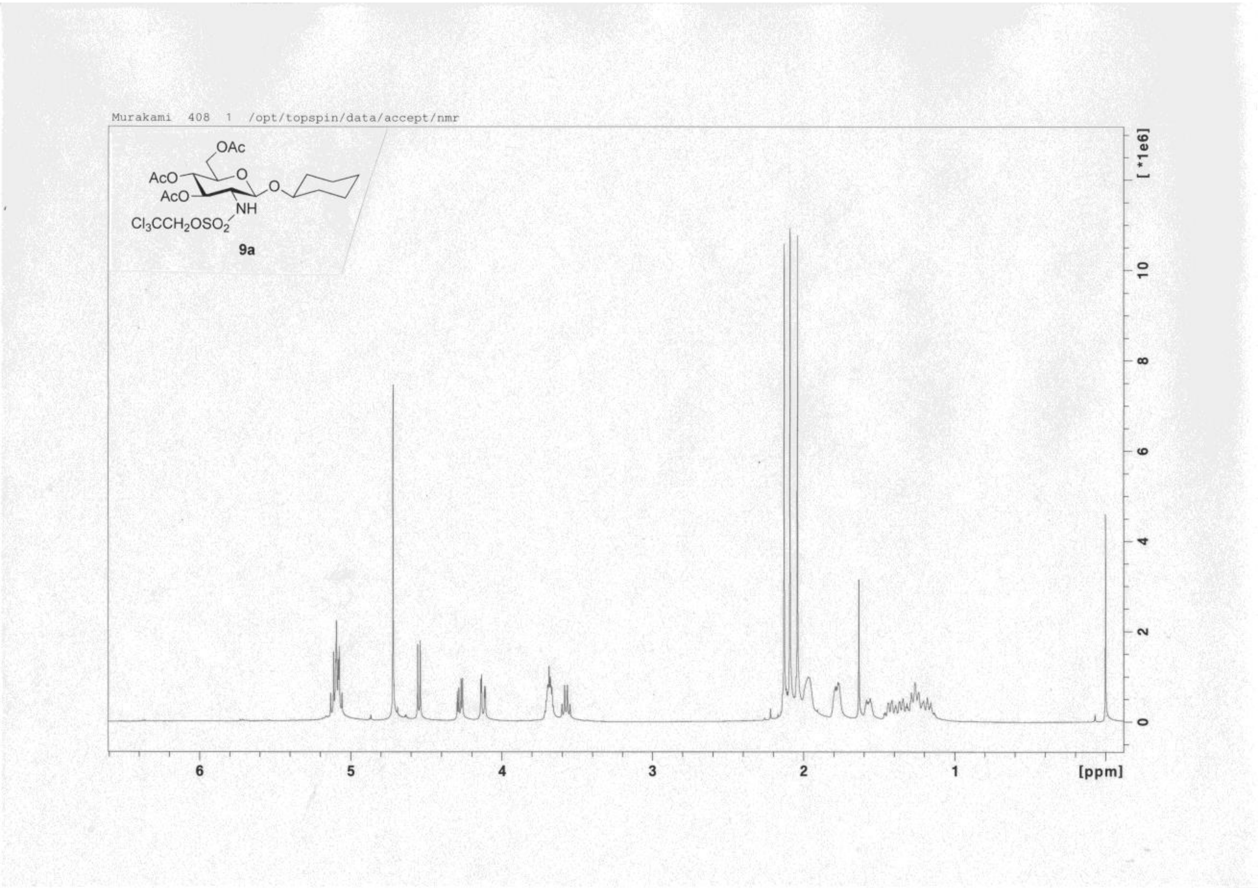
INDEX	FREQUENCY	PPM	HEIGHT
1	17207.8	171.233	19.1
2	17134.2	170.500	18.4
3	17104.7	170.207	20.9
4	13646.1	135.791	21.3
5	12939.5	128.760	106.7
6	12929.2	128.657	102.0
7	12912.3	128.489	52.7
8	9971.9	99.229	41.0
9	9380.1	93.340	18.7
10	7897.7	78.589	54.7
11	7771.9	77.337	85.0
12	7739.5	77.015	85.3
13	7707.8	76.700	86.3
14	7138.9	71.038	47.9
15	7123.4	70.884	42.2
16	7102.1	70.672	40.4
17	6726.7	66.937	42.0
18	6176.2	61.458	44.3
19	5628.6	56.009	37.2
20	2087.5	20.773	39.9
21	2078.0	20.677	65.7

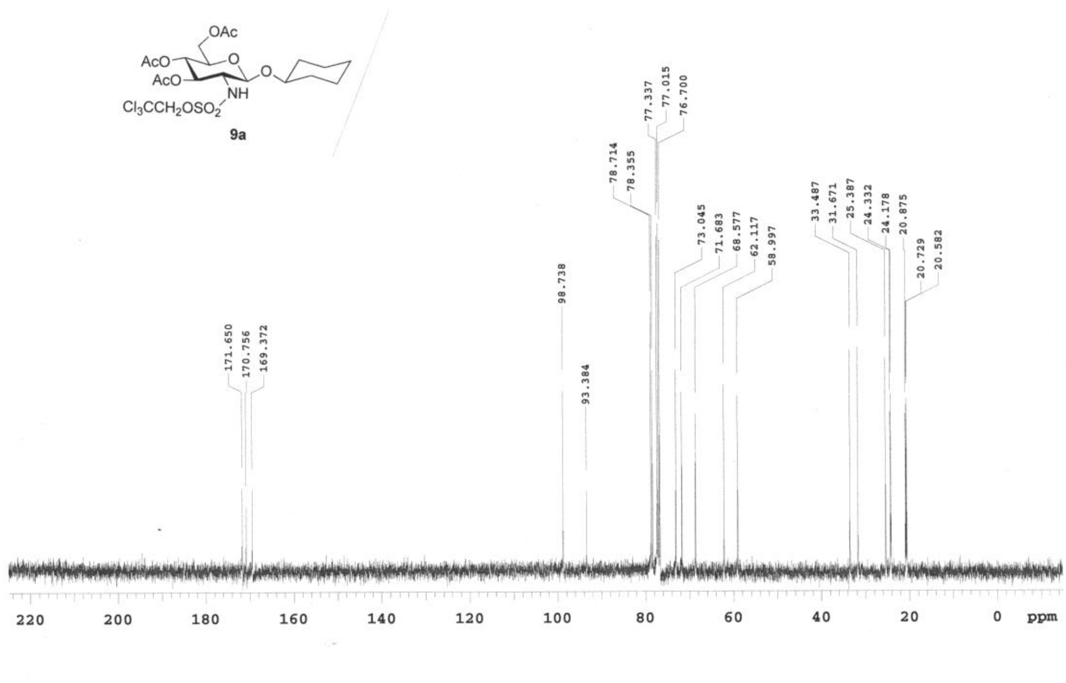


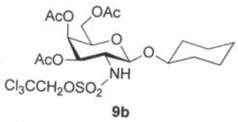


INDEX	FREQUENCY	PPM	HEIGHT
1	17212.2	171.277	13.7
2	17134.2	170.500	15.8
3	17105.4	170.215	19.6
4	14189.3	141.196	-6.5
5	13829.4	137.615	40.3
6	11577.9	115.210	52.5
7	10153.7	101.038	43.7
8	9383.0	93.370	22.7
9	7895.5	78.568	62.3
10	7771.1	77.330	90.1
11	7739.5	77.015	96.8
12	7707.8	76.700	90.2
13	7105.8	70.709	75.7
14	7021.9	69.874	50.5
15	6719.3	66.864	43.4
16	6165.9	61.356	39.8
17	5640.3	56.126	38.3
18	3006.8	29.921	65.0
19	2869.2	28.551	65.6
20	2094.1	20.839	38.0
21	2078.0	20.677	50.0

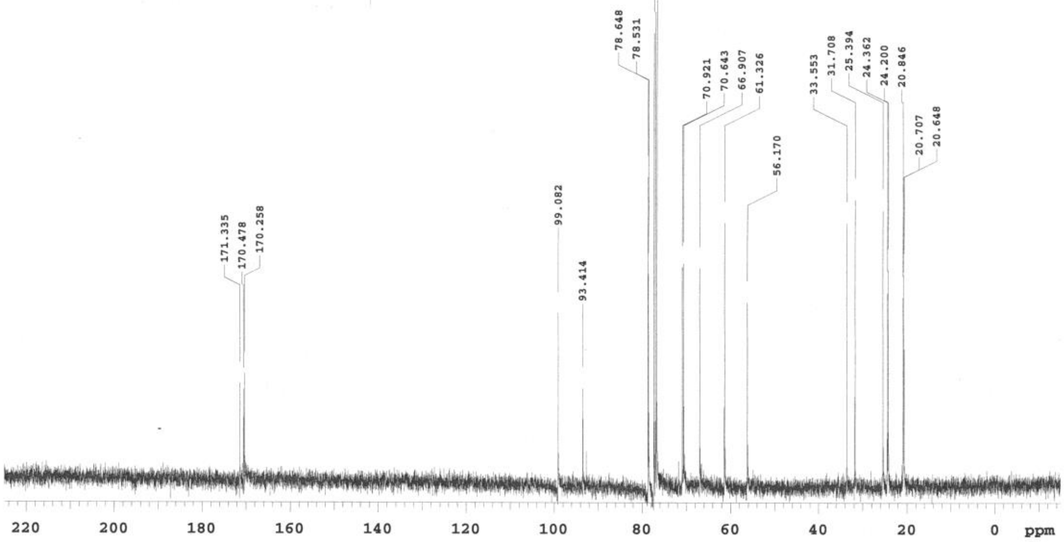



Murakami 408 1 /opt/topspin/data/accept/nmr
OAc
AcO
AcO
O
O
NH
Cl3CCH2OSO2
9a
[*1e6]
10
8
6
4
2
0
6
5
4
3
2
1
[ppm]

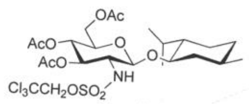

OAc
AcO
AcO
O
O
NH
Cl3CCH2OSO2
9a
171.650
170.756
169.372
98.738
93.384
78.714
78.355
77.337
77.015
76.700
73.045
71.683
68.577
62.117
58.997
33.487
31.671
25.387
24.332
24.178
20.875
20.729
20.582
220
200
180
160
140
120
100
80
60
40
20
0
ppm



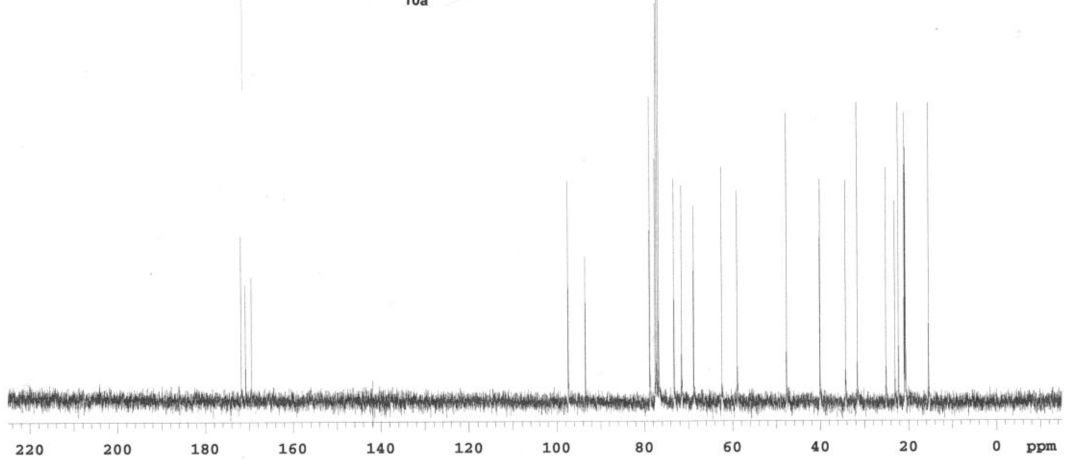
9b

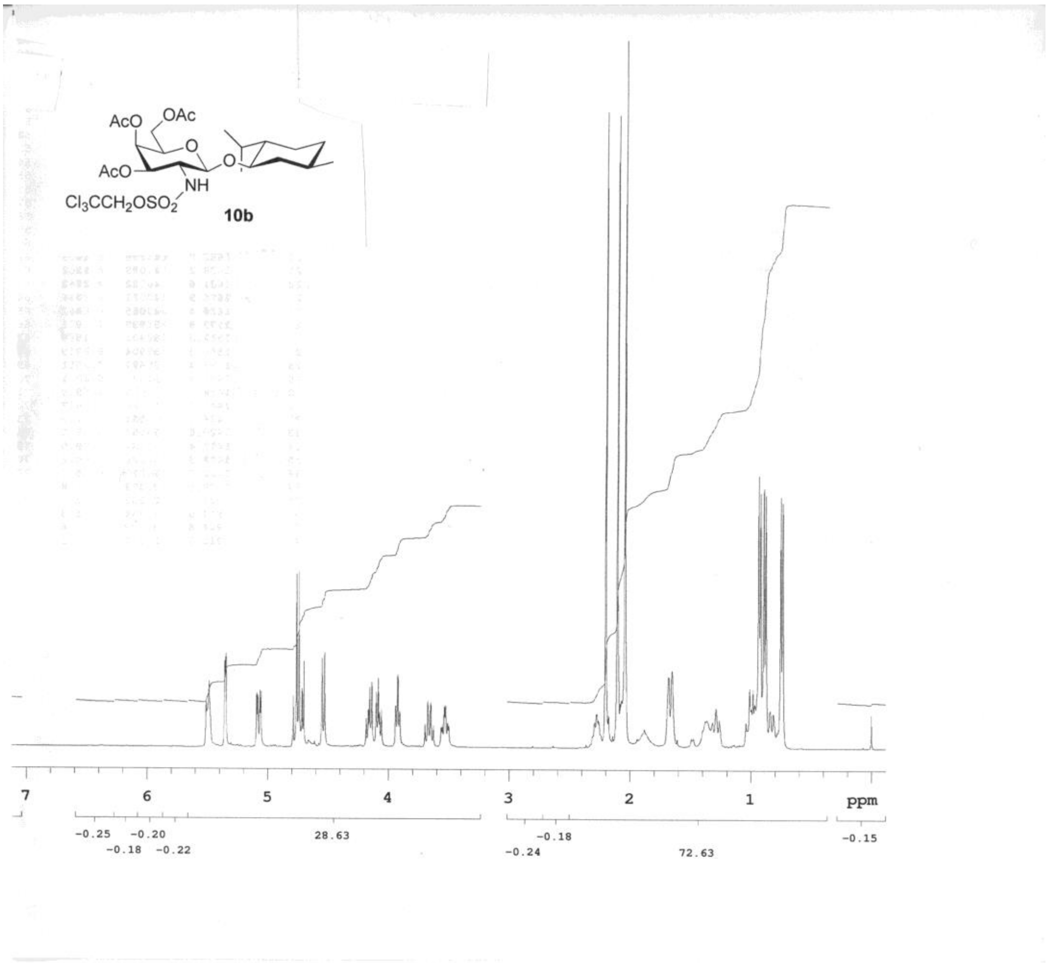


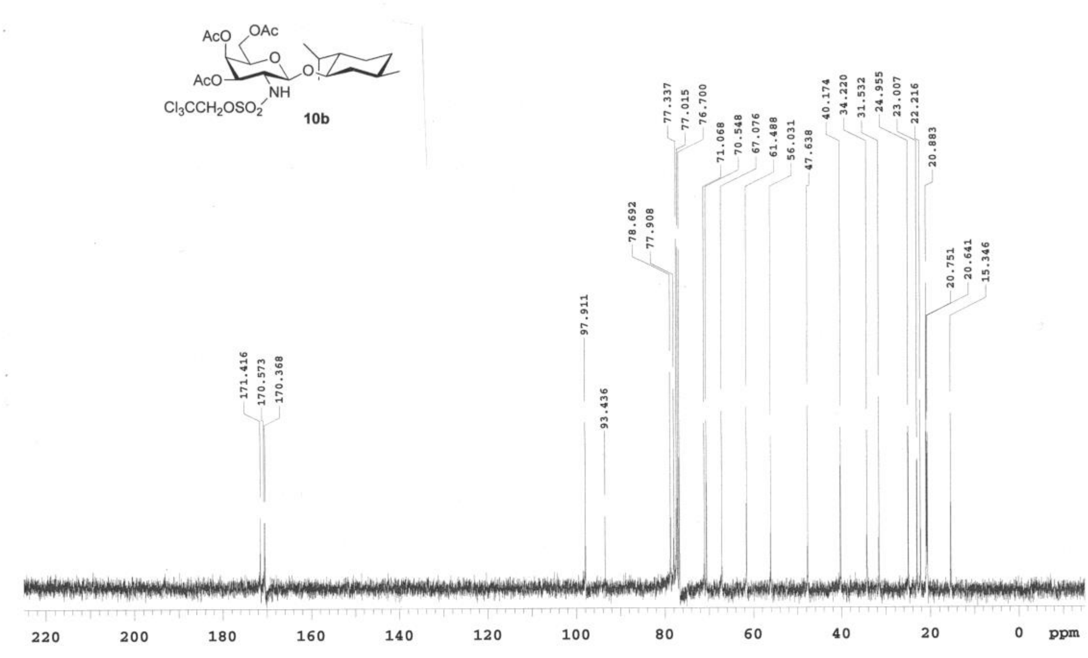
INDEX	FREQUENCY	PPM	HEIGHT
1	17259.3	171.745	39.2
2	17157.7	170.735	27.6
3	17023.0	169.394	29.5
4	9780.5	97.325	52.0
5	9386.7	93.406	34.0
6	7913.9	78.751	72.1
7	7795.4	77.571	57.4
8	7771.9	77.337	94.3
9	7739.5	77.015	101.7
10	7707.8	76.700	99.6
11	7359.0	73.228	52.7
12	7184.5	71.492	51.0
13	6907.8	68.739	46.1
14	6267.4	62.367	55.2
15	5914.9	58.858	49.6
16	4788.0	47.645	67.9
17	4021.1	40.013	52.3
18	3438.1	34.213	52.1
19	3168.7	31.532	70.5
20	2519.6	25.072	55.1
21	2317.2	23.058	47.2
22	2231.8	22.208	70.6
23	2098.6	20.883	55.7
24	2089.7	20.795	68.1
25	2076.5	20.663	53.7
26	2068.4	20.582	59.8
27	1542.1	15.346	70.4

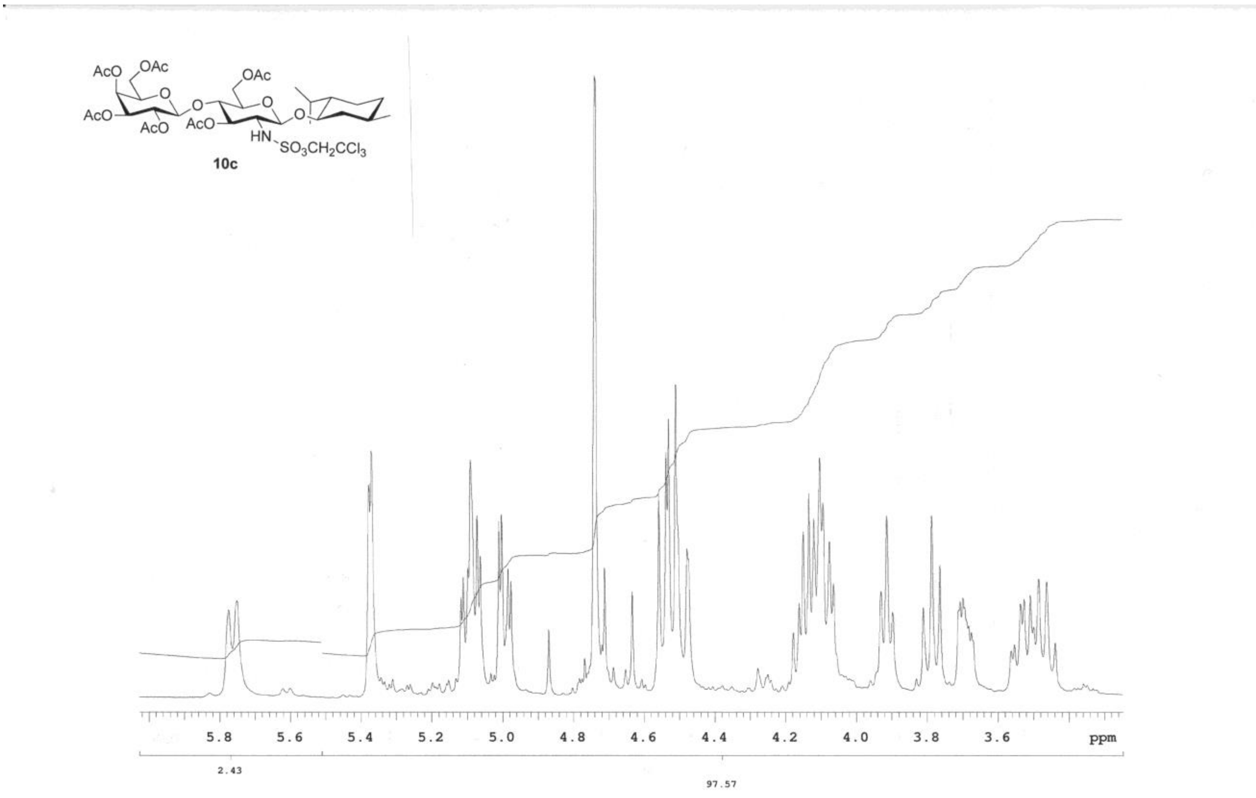


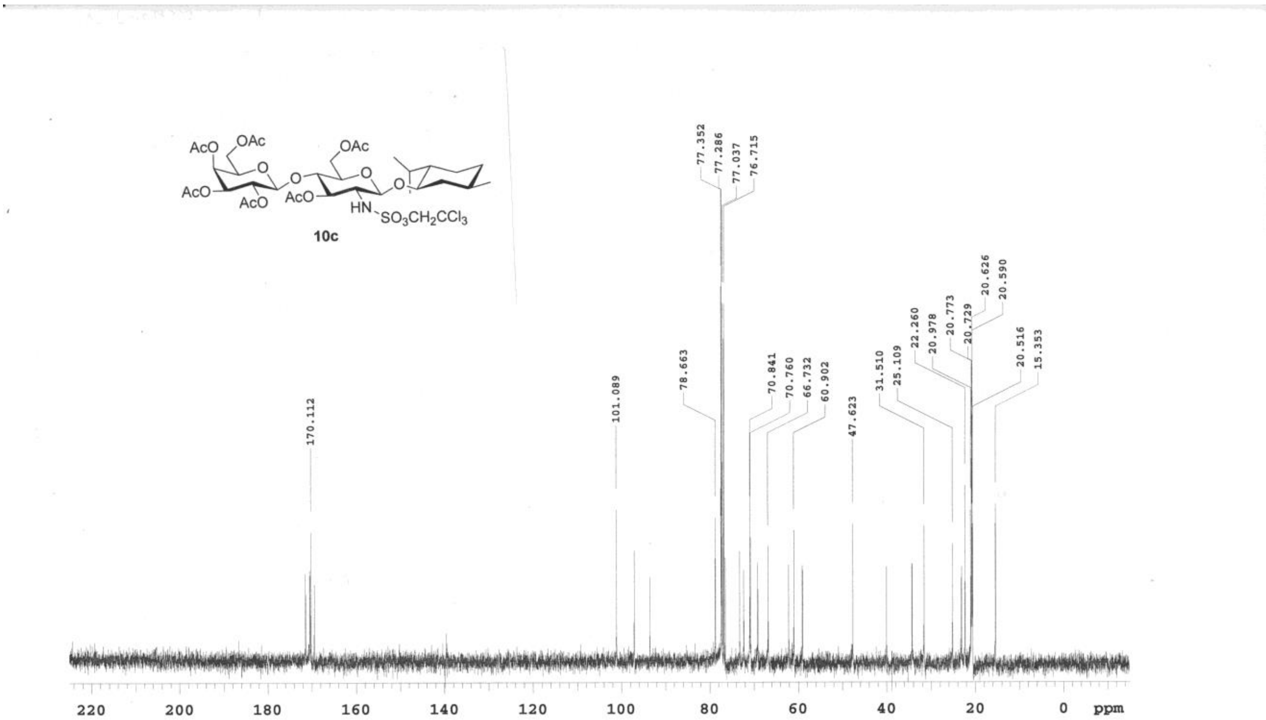
10a

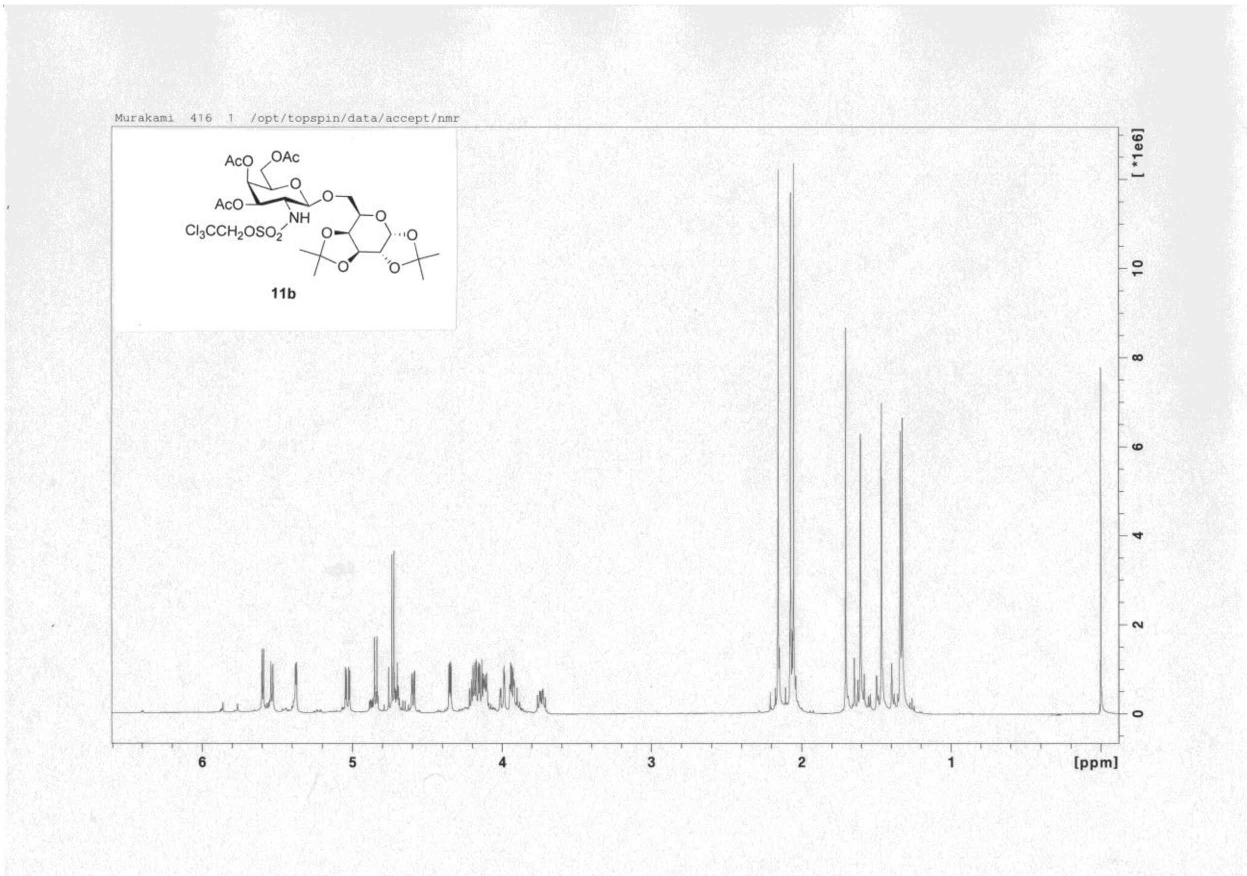


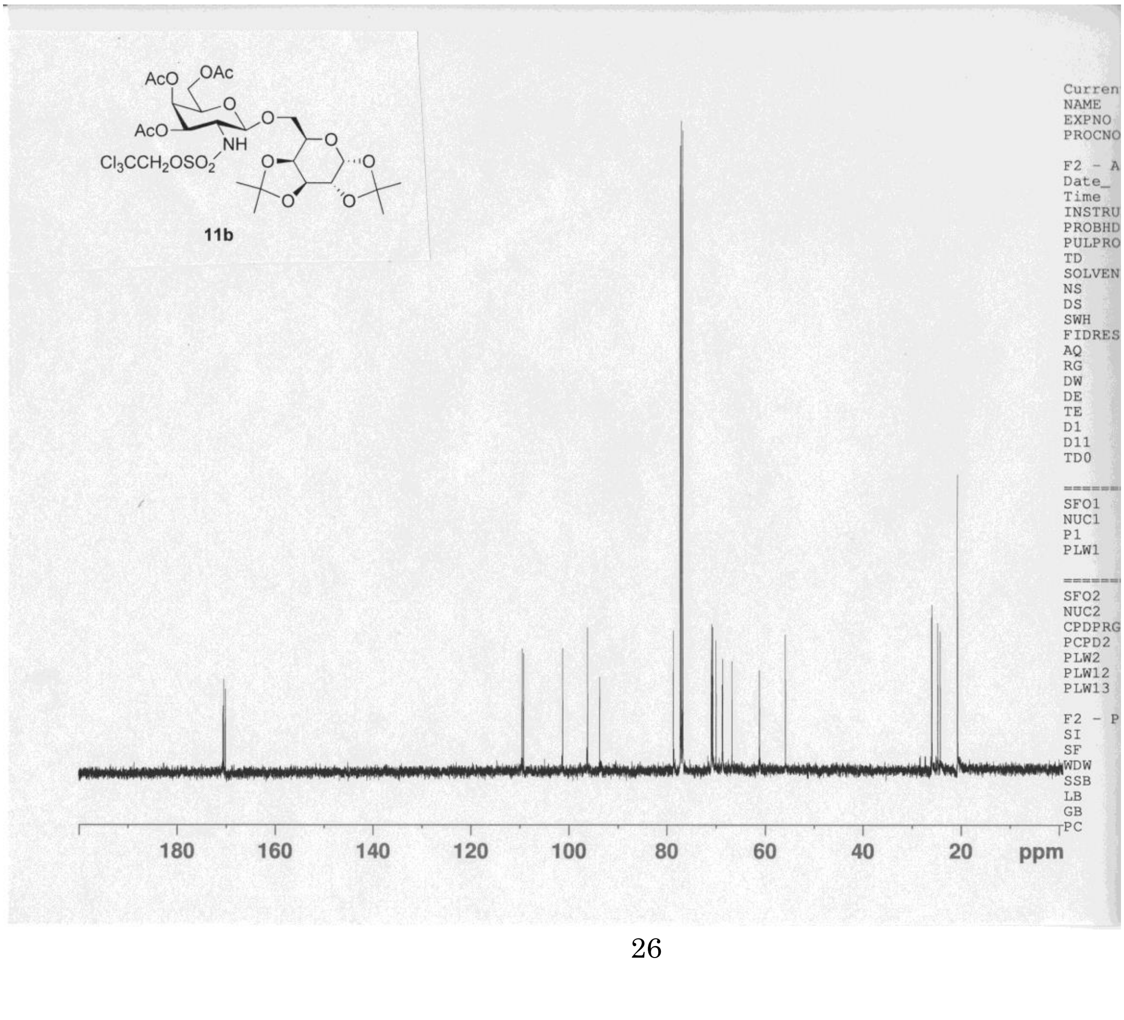

AcO
OAc
O
O
AcO
NH
Cl3CCH2OSO2
10b
7
6
5
4
3
2
1
ppm
-0.25 -0.20
-0.18 -0.22
28.63
-0.18
-0.24
72.63
-0.15

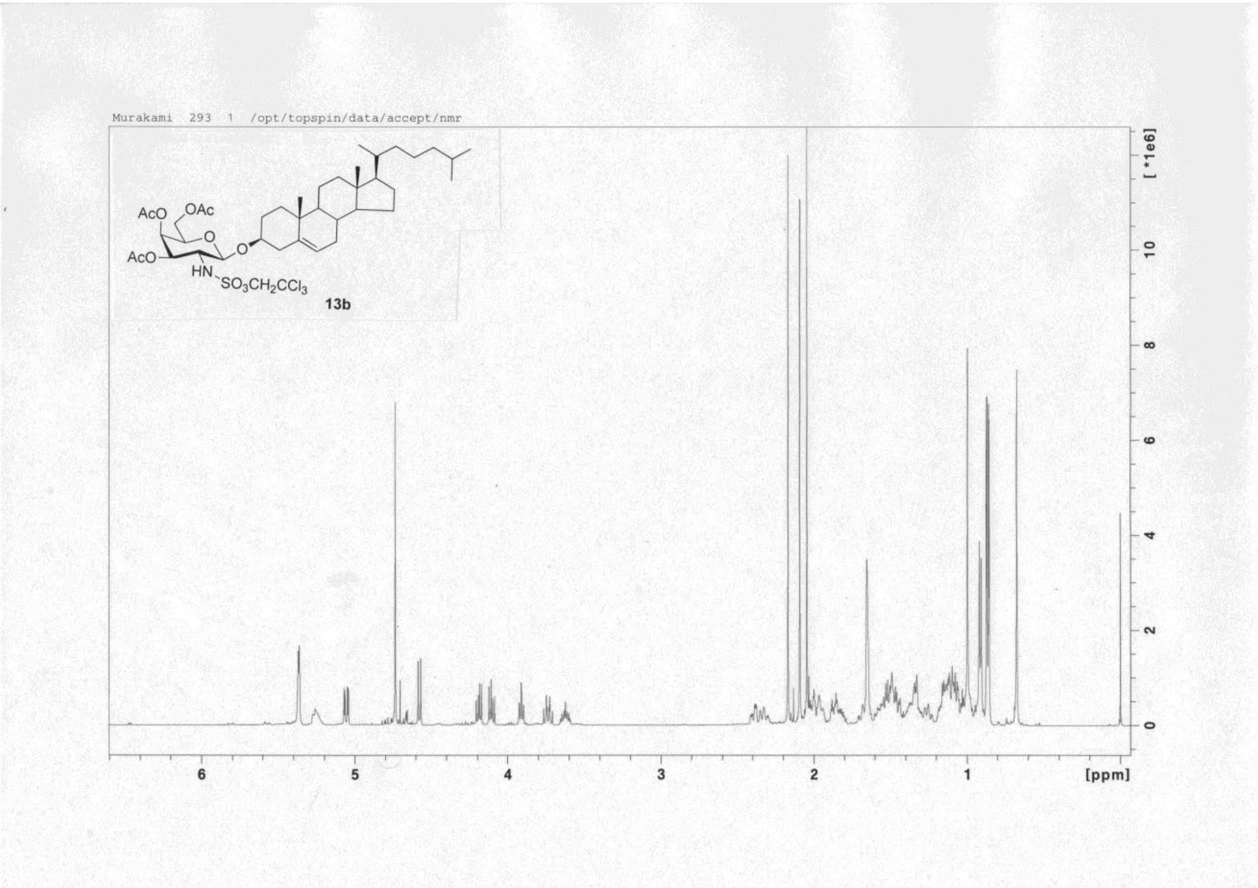

AcO
OAc
O
O
AcO
NH
Cl3CCH2OSO2
10b
171.416
170.573
170.368
97.911
93.436
78.692
77.908
77.337
77.015
76.700
71.068
70.548
67.076
61.488
56.031
47.638
40.174
34.220
31.532
24.955
23.007
22.216
20.883
20.751
20.641
15.346
220
200
180
160
140
120
100
80
60
40
20
0
ppm

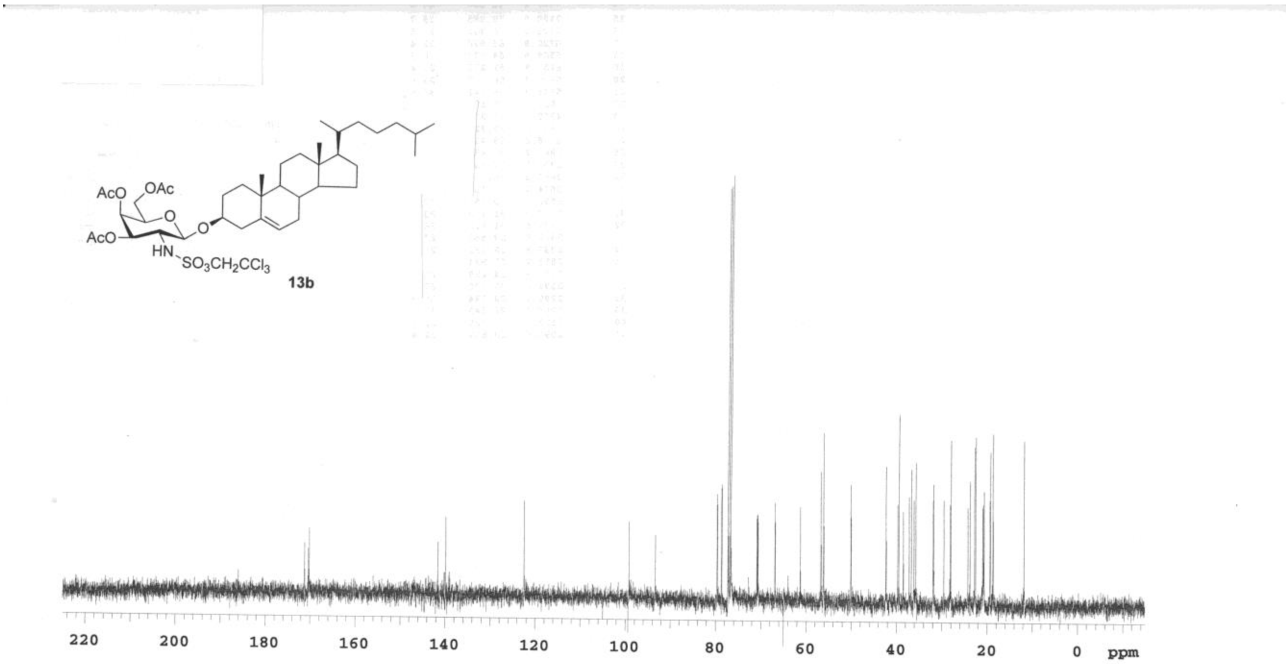

AcO
OAc
AcO
AcO
O
O
OAc
AcO
HN
O
SO3CH2CCl3
10c
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
ppm
2.43
97.57

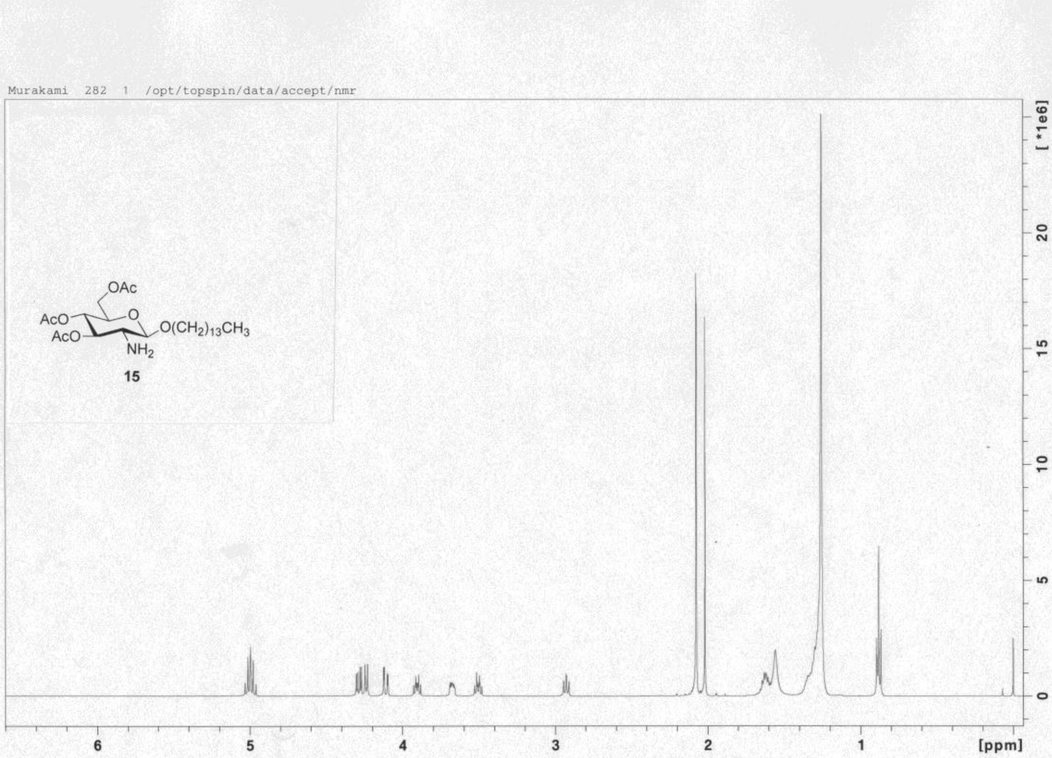

AcO
OAc
AcO
AcO
O
OAc
AcO
HN
SO3CH2CCl3
10c
170.112
101.089
78.663
77.352
77.286
77.037
76.715
70.841
70.760
66.732
60.902
47.623
31.510
25.109
22.260
20.978
20.773
20.729
20.626
20.590
20.516
15.353
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Murakami 416 1 /opt/topspin/data/accept/nmr
AcO
OAc
AcO
NH
Cl3CCH2OSO2
11b
[*1e6]
[ppm]

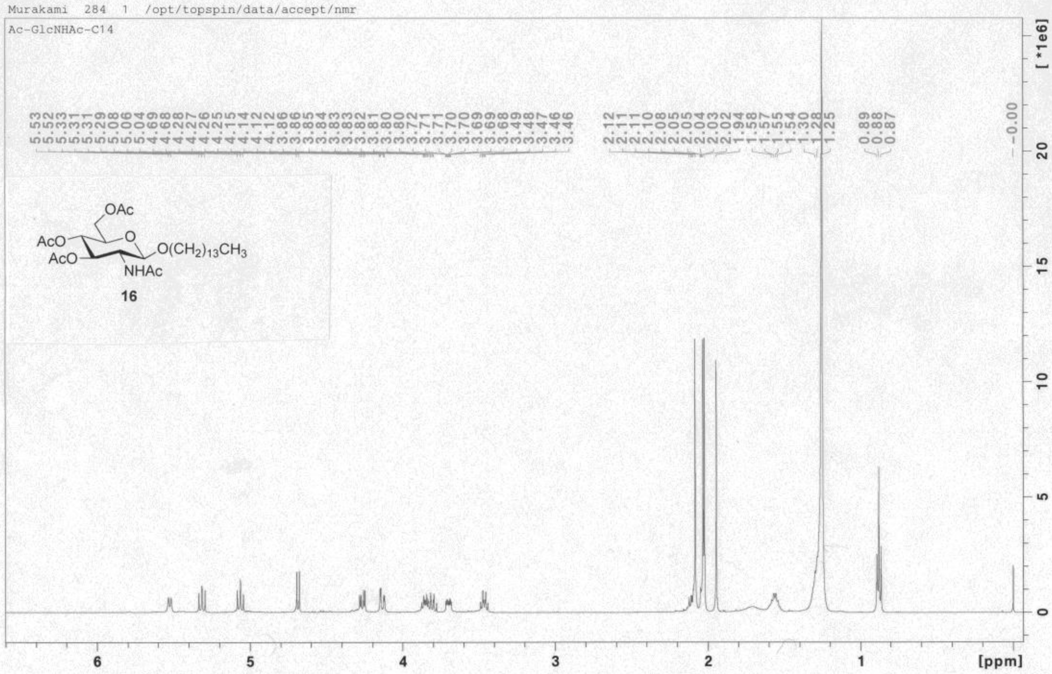

AcO
OAc
AcO
NH
Cl3CCH2OSO2
11b
Curren
NAME
EXPNO
PROCNO
F2 - A
Date_
Time
INSTRU
PROBHD
PULPRO
TD
SOLVEN
NS
DS
SWH
FIDRES
AQ
RG
DW
DE
TE
D1
D11
TD0
SFO1
NUC1
P1
PLW1
SFO2
NUC2
CPDPRG
PCPD2
PLW2
PLW12
PLW13
F2 - P
SI
SF
WDW
SSB
LB
GB
PC
ppm


Murakami 293 1 /opt/topspin/data/accept/nmr
AcO
OAc
AcO
HN
$SO_3CH_2CCl_3$
13b
[*1e6]
[ppm]

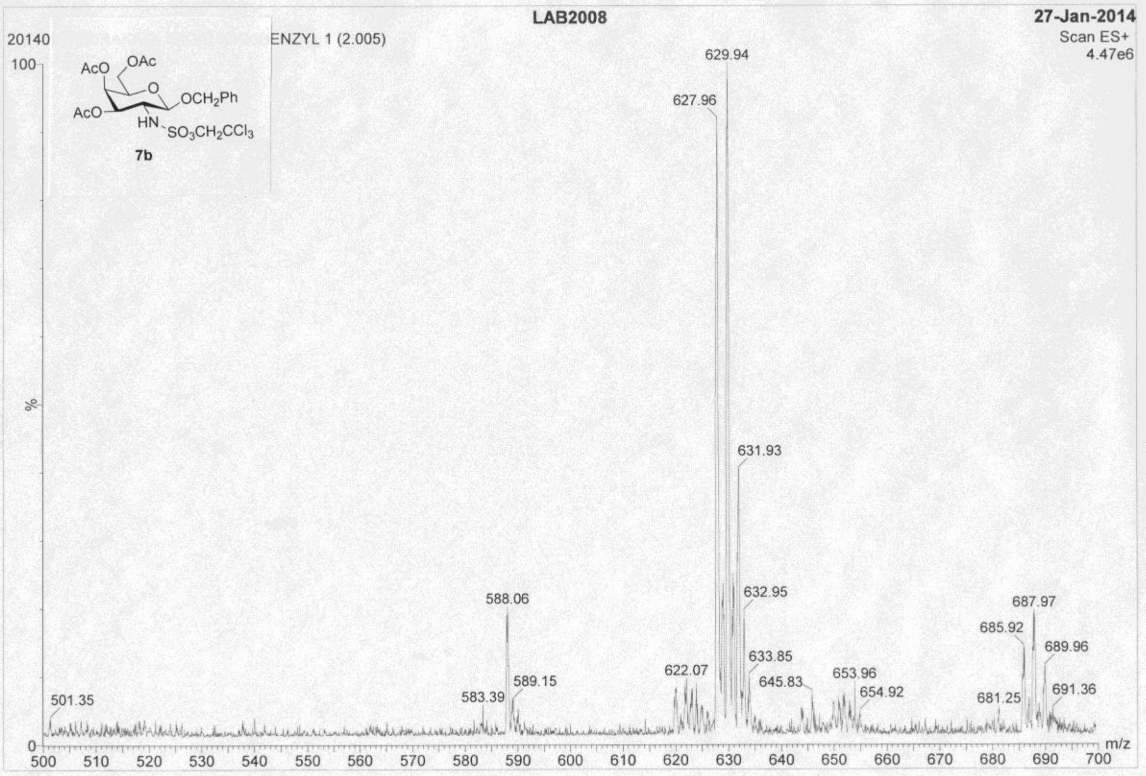

AcO
OAc
AcO
HN
$SO_3CH_2CCl_3$
13b
ppm



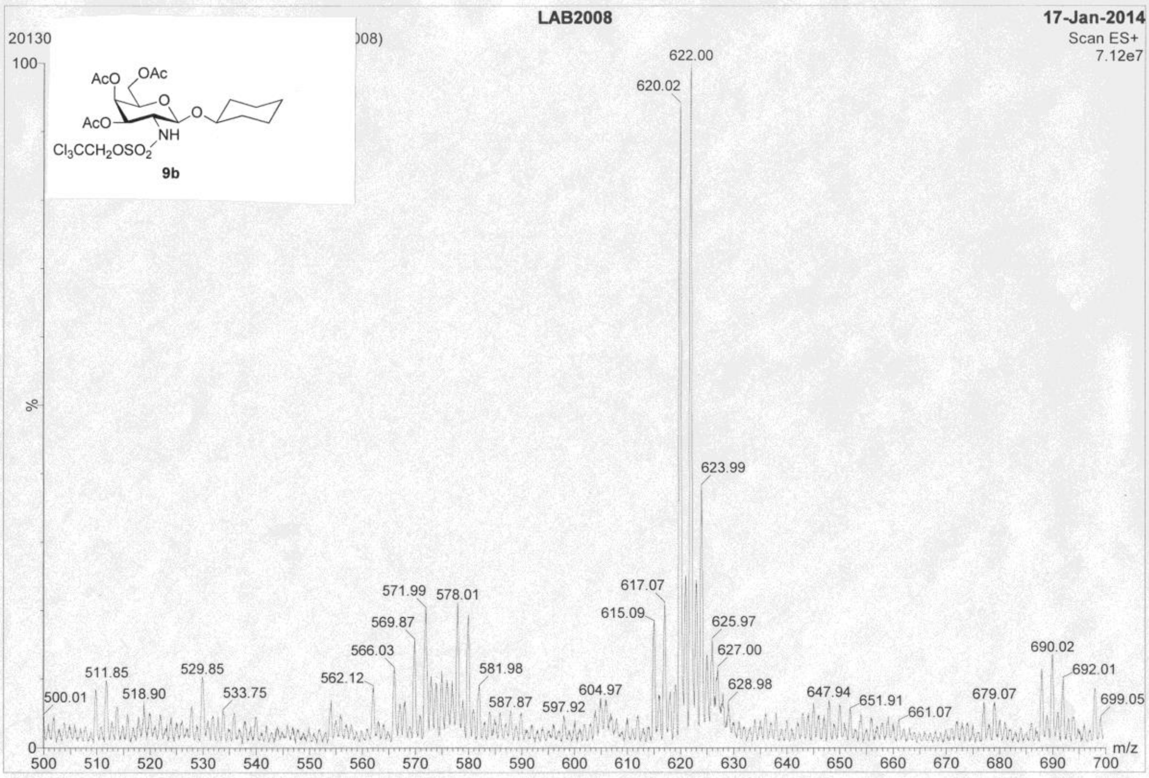
Murakami 282 1 /opt/topspin/data/accept/nmr
OAc
AcO
AcO
O
O(CH2)13CH3
NH2
15
[*1e6]
20
15
10
5
0
6
5
4
3
2
1
[ppm]



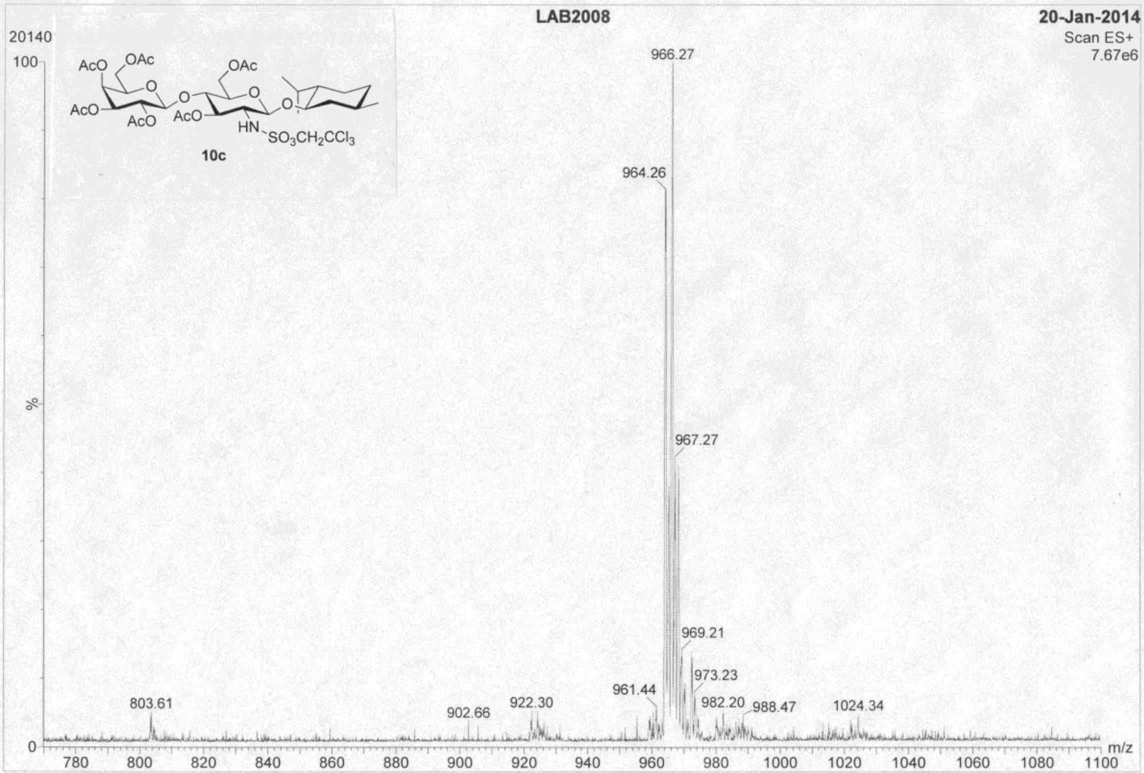
Murakami 284 1 /opt/topspin/data/accept/nmr
Ac-GlcNHAc-C14
5.53 5.52 5.33 5.31 5.31 5.29 5.08 5.06 5.04 4.69 4.68 4.28 4.27 4.26 4.25 4.15 4.14 4.12 4.12 3.86 3.86 3.85 3.84 3.83 3.83 3.82 3.81 3.80 3.80 3.72 3.71 3.71 3.70 3.70 3.69 3.69 3.68 3.68 3.49 3.48 3.47 3.46 3.46
2.12 2.11 2.11 2.10 2.08 2.05 2.05 2.04 2.04 2.03 2.02 1.94 1.58 1.57 1.55 1.55 1.54 1.30 1.28 1.25
0.89 0.88 0.87
-0.00
OAc
AcO
AcO
O
O(CH2)13CH3
NHAc
16
[*1e6]
20
15
10
5
0
6
5
4
3
2
1
[ppm]

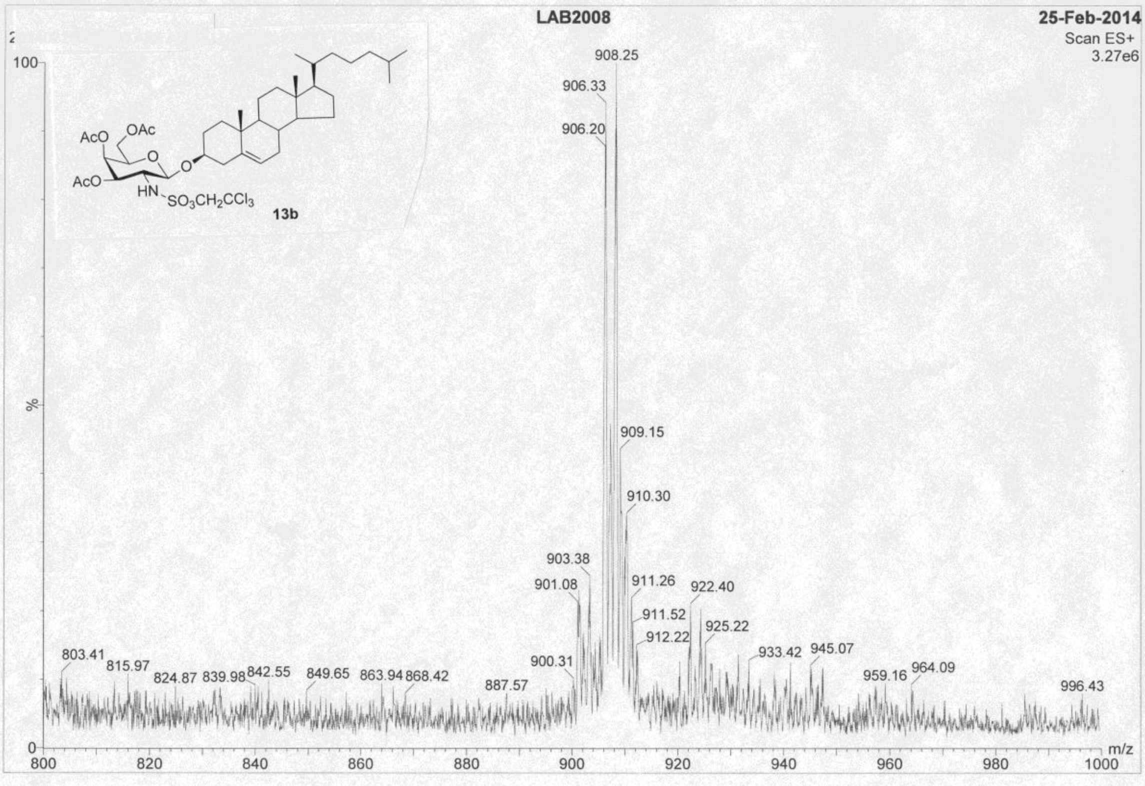


LAB2008
27-Jan-2014
20140
ENZYL 1 (2.005)
Scan ES+
4.47e6
AcO
OAc
OCH2Ph
HN
SO3CH2CCl3
7b
629.94
627.96
631.93
632.95
588.06
687.97
685.92
689.96
633.85
622.07
653.96
645.83
654.92
589.15
583.39
681.25
691.36
501.35
%
m/z



LAB2008
17-Jan-2014
20130
008)
Scan ES+
7.12e7
AcO
OAc
NH
Cl3CCH2OSO2
9b
622.00
620.02
623.99
617.07
571.99
578.01
615.09
569.87
625.97
566.03
627.00
690.02
511.85
529.85
581.98
692.01
562.12
628.98
604.97
647.94
500.01
518.90
533.75
587.87
597.92
651.91
679.07
699.05
661.07
%
m/z


LAB2008
20-Jan-2014
Scan ES+
7.67e6
20140
10c
966.27
964.26
967.27
969.21
973.23
961.44
982.20
988.47
1024.34
922.30
902.66
803.61
m/z


LAB2008
25-Feb-2014
Scan ES+
3.27e6
13b
908.25
906.33
906.20
909.15
910.30
903.38
901.08
911.26
922.40
911.52
912.22
925.22
933.42
945.07
959.16
964.09
996.43
900.31
887.57
803.41
815.97
824.87
839.98
842.55
849.65
863.94
868.42
m/z