Supporting Information
The Royal Society of Chemistry (RSC)

Investigating the Stereo-directing Effect of Remote Participating Groups on the Selectivity in 2-Deoxyglycosylation of Galactal

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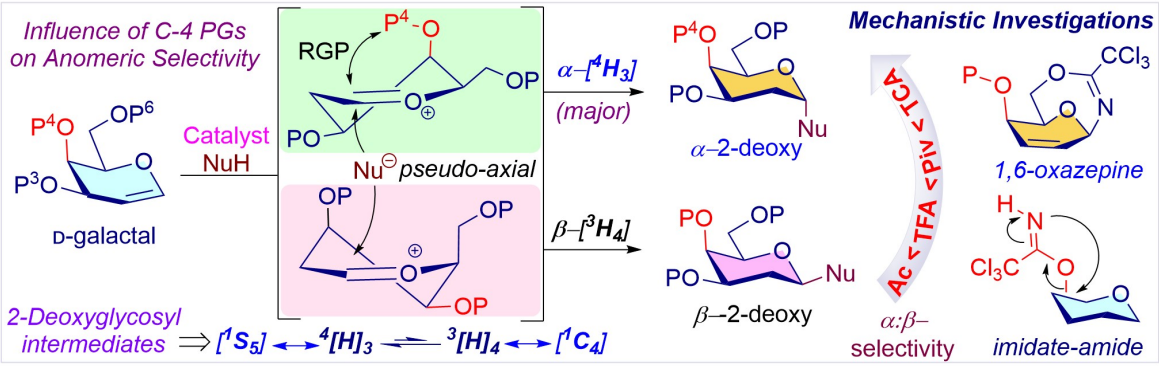

Abstract: Chemical glycosylation arguably is crucial for assembling the structurally defined polysaccharides and glycoconjugates of distinctive biological functions. Predicting and governing the stereochemical outcome in the glycosylation reaction is undoubtedly more challenging and influenced mainly by the configuration of protecting groups and ring conformers. In this paper, we persuaded the direct influence of stereoelectronically diverse protecting groups on the anomeric selectivity in 2-deoxyglycosylation. The galactal donors with C-4 O-pivaloyl as a higher electron density group ensured enhanced α-selectivity; practically, trichloroacetimidate (O-TCA) ensured optimal selectivity, affirming the covalence remote group participation (RGP) featuring a distinctive ring bridging oxazepine structures. Mechanistic investigations, employing Density functional theory (DFT) and experimental studies, revealed the perspective for RGP by distal C-4 PGs facilitating the stabilization of $^{4}H_{3}$ and $^{3}H_{4}$ conformations of oxocarbenium ions via dioxolenium species.

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Supporting Material

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A. General Experimental Information.

General Synthesis Information:

Reactions were run in screw capped glass vials (4 mL) stirred with Teflon®-coated magnetic stir bars. Moisture and air-sensitive reactions were performed in flame-dried round bottom flasks, fitted with rubber septa or glass gas adapters, under a positive pressure of nitrogen. Moisture and air-sensitive liquids or solutions were transferred via nitrogen-flushed syringe. Experiments were monitored by thin layer chromatography (TLC). Melting points were obtained in open capillary tubes using a micro melting point apparatus and were uncorrected.

Materials:

Unless otherwise noted, materials were obtained from commercial suppliers and used without purification. Removal of solvent under reduced pressure refers to distillation with a Büchi rotary evaporator attached to a vacuum pump (~3 mmHg). Products obtained as solids or high boiling oils were dried under vacuum (~1 mmHg).

Chromatography:

Analytical TLC was performed using Whatman 250-micron aluminium backed UV F254 pre-coated silica gel flexible plates. Subsequent to elution, ultraviolet illumination at 254 nm allowed for visualization of UV active materials. Staining with p-anisaldehyde, basic potassium permanganate solution, or Molisch's reagents allowed for further visualization.

Physical Data:

Proton and Carbon nuclear magnetic resonance spectra (^{1}H, ^{13}C NMR) were recorded on Avance 300, 400 or 500 MHz and ECS 400 MHz (JEOL) NMR spectrometers. The proton resonances are annotated as: chemical shift (δ) relative to tetramethylsilane (δ 0.0) using the residual solvent signal as an internal standard or tetramethylsilane itself: chloroform-d (δ 7.26, singlet), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant (J, Hz), and number of protons for a given resonance is indicated by nH. The chemical shifts of ^{13}C NMR are reported in ppm relative to the central line of the triplet at 77.00 ppm for $CDCl_3$.

Mass analyses (ESI-MS) and HRMS were performed on Xevo G2-S QTTOF (Waters, USA) Spectrometer.

Computational Methods:

All calculations in this paper were performed using Gaussian 16 software package. All the structures were visualized using gview 6 software package. All energies discussed are zero point energy (ZPE) corrected Gibbs free energies (GFE). Geometry optimization and frequency analysis were performed using density functional theory (B3LYP) in combination with Pople type basis set (6-31G*). No imaginary frequencies were observed in the optimized conformers. GFE of optimized structure of different conformers are computed and compared with respect to $^4H_3$. The relative GFE is calculated using the following equation:

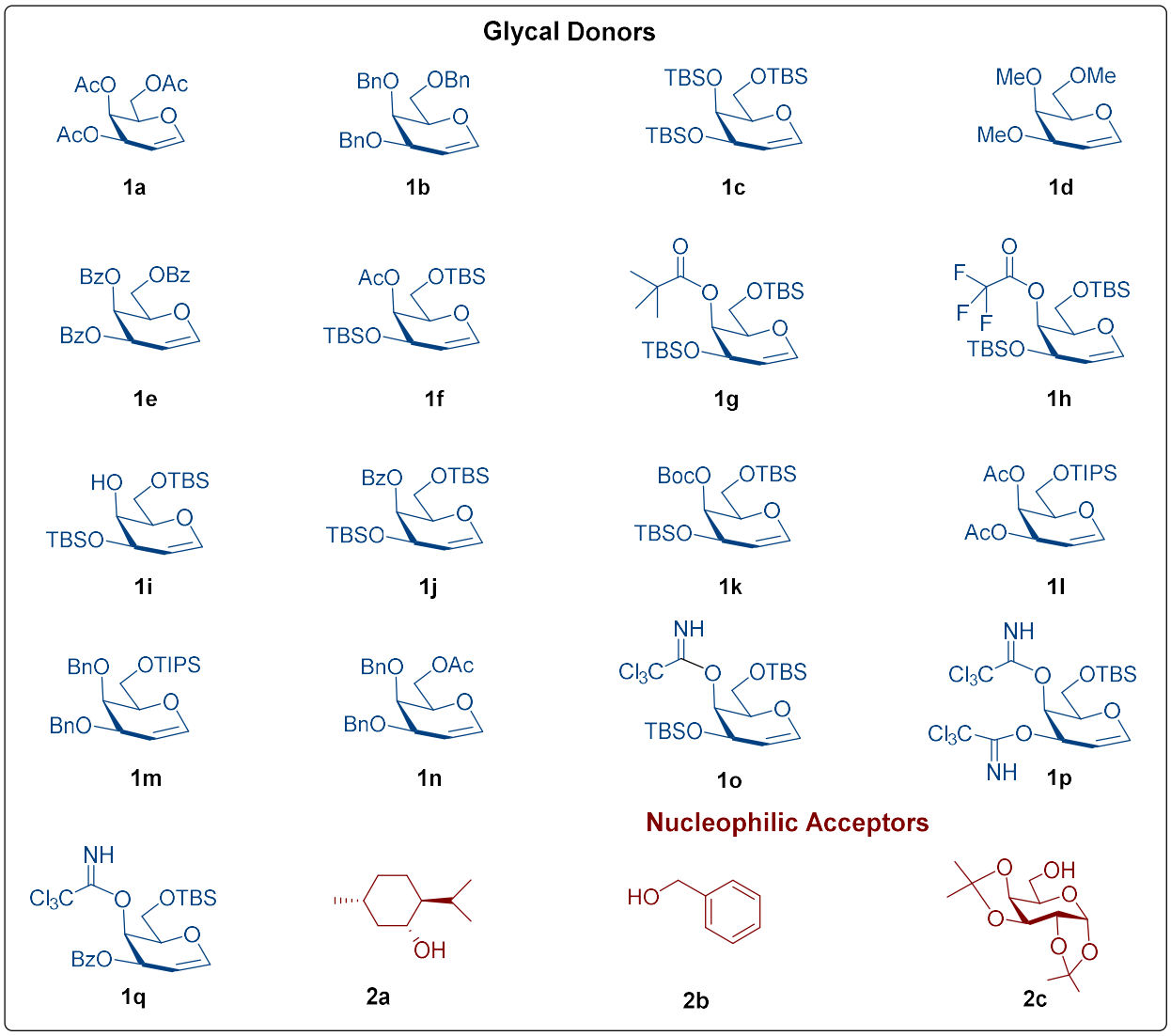
$$\Delta G = G_X - G_{^4H_3}$$

Where, ΔG is the relative GFE, G_X is the GFE of the respective conformer, and $G_{^4H_3}$ is the GFE of $^4H_3$.

Abbreviations used:

MeCN: Acetonitrile, DCE: Dichloroethane, DCM: Dichloromethane, TLC: Thin layer chromatography, $MeNO_2$: Nitromethane EtOAc: Ethylacetate, $CHCl_3$: Chloroform, $Zn(OTf)_2$: Zinc(II) trifluoromethanesulfonate, $Bi(OTf)_3$: Bismuth(III) trifluoromethanesulfonate, TBS: tert-Butyldimethylsilyl, Bn: Benzyl, Bz: Benzoyl, TIPS: Triisopropylsilyl, DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene, $NaHCO_3$: Sodium bicarbonate, $MgSO_4$: Magnesium sulfate, NaOMe: Sodium methoxide, Rf: Retardation factor

B. Glycal Donors and Nucleophilic Acceptors Employed in Glycosylation.



All glycosyl donors and acceptors were prepared by using the following literature procedure **1a,**[1,2] **1b,**[3,4]**, 1c,**[3,5] **1d,**[3,4,5] **1e,**[1] **1i,**[6] **1l,**[5] **1m,**[5] **1n,**[5] **2c.**[7]

1. Zhao, J.; Wei, S.; Maa, X.; Shao, H. *Green Chem.* **2009**, *11*, 1124-1127. **A Mild and Environmentally Benign Method for the Synthesis of Glycals in PEG-600/H_2O.**

2. Chen, H.; Xian, T.; Zhang, W.; Si, W.; Luo, X.; Zhang, B.; Zhang, M.; Wang, Z.; Zhang, J. *Carbohydr. Res*. **2016**, *431*, 42-46. **An Efficient Method for the Synthesis of Pyranoid Glycals.**

3. Pal, K. B.; Guo, A.; Das, M.; Lee, J.; Báti, G.; Peng Yip, B. R.; Loh, T.-P.; Liu, X.-W. *Chem. Sci.* **2021**, *12*, 2209-2216. **Iridium-promoted deoxyglycoside synthesis: stereoselectivity and mechanistic insight.**

4. Wang, B.; Xiong, D.-C.; Ye, X.-S. *Org. Lett.* **2015**, *17*, 5698-5701. **Direct C-H Trifluoromethylation of Glycals by Photoredox Catalysis.**

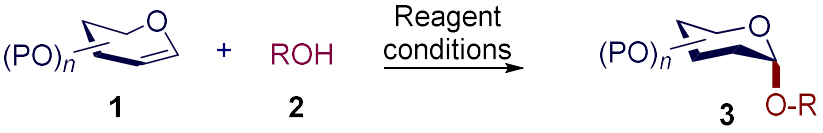
5. Balmond, E. I.; Coe, D. M.; Galan, M. C.; McGarrigle, E. M. *Angew. Chem., Int. Ed*. **2012**, *51*, 9152-9155. **α-Selective Organocatalytic Synthesis of 2-Deoxygalactosides**.

6. Jacquinet, J.-C.; *Carbohydr. Res.* **1990**, *199*, 153-181. **Syntheses of the methyl glycosides of the repeating units of chondroitin 4- and 6-sulfate.**

7. Rokade, S. M.; Bhate, P. M. *J. Carbohydr. Chem*. **2017**, *36*, 20-30. **Practical Preparation of Mono- and Di-*O*-Isopropylidene Derivatives of Monosaccharides and Methyl 4,6-*O*-Benzylidene Glycosides from free Sugars in a Deep Eutectic Solvent.**

C. Optimizations Studies.

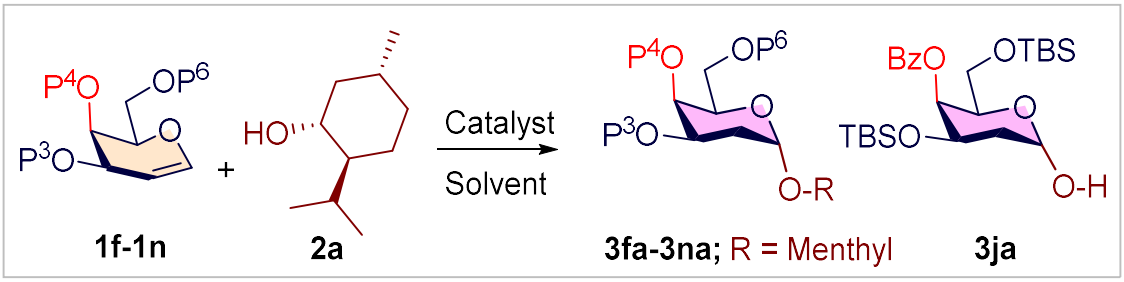
Table 1. Screening and investigating the influence of diverse protecting groups for anomeric selectivity in the 2-deoxyglycosylation of glycals. [a]

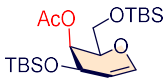
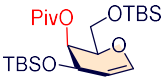
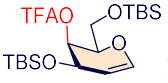
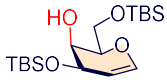
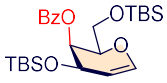
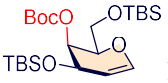
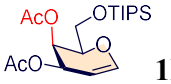
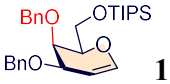
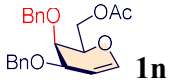


Entry	Glycal donor/ Acceptor	Reagent conditions	Glycoside (yield)[b] α:β selectivity[c]
1	**1a/2a**	$Zn(OTf)_2$, 1,4-dioxane, 50 °C	**3aa** (90%); 90:10
2	**1a/2b**	$Zn(OTf)_2$, 1,4-dioxane, 50 °C	**3ab** (86%); 95:5
3	**1a/2c**	$Zn(OTf)_2$, 1,4-dioxane, 50 °C	**3ac** (84%); 93:7
4	**1b/2a**	$Zn(OTf)_2$, toluene, 25 °C	**3ba** (90%); 95:5
5	**1c/2a**	$Zn(OTf)_2$, toluene, 25 °C	**3ca** (62%); 93:7
6	**1d/2a**	$Zn(OTf)_2$, toluene, 25 °C	**3da** (52%); 85:15
7	**1e/2a**	$Zn(OTf)_2$, 1,4-dioxane, 50 °C	**NA**
8	**1a/2a**	$Bi(OTf)_3$, 1,4-dioxane, 50 °C	**3aa** (94%); 99:1
9	**1b/2a**	$Bi(OTf)_3$, toluene, 25 °C	**3ba** (90%); 95:5
10	**1b/2a**	$CuOTf)_2$, toluene, 50 °C	**3ba** (84%); 95:5
11	**1a/2b**	$C_6F_5B(OH)_2$, $MeNO_2$, 60 °C	**3ab** (88%); α
12	**1a/2c**	Fe_3O_4@C@SO_3H, DCE, 80 °C	**3ac** (87%); 97:3
13	**1a/2c**	Eosin Y, PhSSPh, blue LEDs, DCM	**3ac** (66%); 95:5

[a] Reaction conditions: D-galactal donors **1a-1e** (1.0 equiv), acceptor **2a-2c** (1.2 equiv), and Catalyst (10 mol%), Solvent (2 mL), stirred at 0 °C to rt or 50 °C under the inert atmosphere of nitrogen (entries 1-8). [b] The isolated yields. [c] The α/β ratios were determined by ^{1}H NMR analysis.

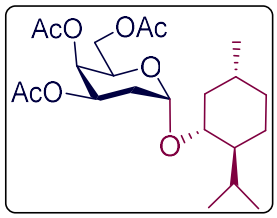
Table 2. Studies of diverse donors and investigating the influence of different protecting groups at C-4 position on selectivity in 2-deoxyglycosylation and possible distal participation.[a]



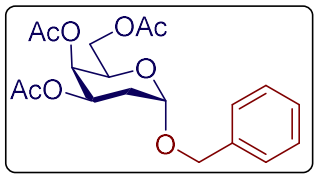
Entry	Glycal donor	Glycoside; Yields[b], Time	α:β selectivity [c]
1	 **1f**	**3fa;** 64%, 2 h	80:20
2	 **1g**	**3ga;** 76%, 1.5 h	92:8
3	 **1h**	**3ha;** 78%, 2 h	90:10
4	 **1i**	**3ia;** 58%, 30 min	85:15
5	 **1j**	**3ja;** 66%, 2 h	88:12
6	 **1k**	**1i;** 76%, 1.5 h	NA
7 [d]	 **1l**	**3la;** 90%, 30 min	88:12
8	 **1m**	**3ma;** 88%, 30 min	84:16
9	 **1n**	**3na;** 92%, 15 min	90:10

[a] Reaction conditions: Glycal donors **1f-1n** (1.0 equiv), L-menthol **2a** (1.2 equiv), and $Zn(OTf)_2$ (10 mol%) in toluene or 1,4-dioxane (2 mL), stirred at 0 °C to rt or 50 °C under the inert atmosphere of nitrogen. [b] The isolated yields. [c] The α/β ratios were determined by ^1H NMR analysis. [d] Reaction was performed in 1,4-dioxane at 50 °C.

D. Chemical Synthesis and Spectroscopic Characterization Data.

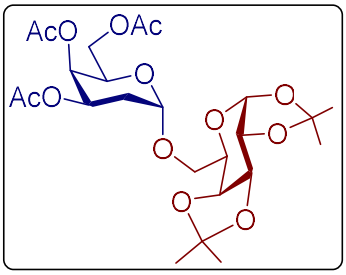


***Menthyl-3,4,6-tri-O-acetyl-2-deoxy-α-D-lyxo-hexapyranoside (3aa)*:** To a preformed solution of 3,4,6-tri-*O*-acetyl-D-galactal (272 mg, 1.0 mmol, 1.0 equiv.) and L-menthol (187 mg, 1.2 mmol, 1.2 equiv.) in 1,4-dioxane (2 mL) was added 10 mol% $Zn(OTf)_2$ and the resulting mixture was stirred at 50 ^{o}C in an oil bath under N_2 atmosphere until the completion of starting material, typically for 30 min. (adjudged by TLC). The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated $NaHCO_3$ (5 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by silica gel column chromatography using hexane/EtOAc as eluent to afford the compound **3aa** as a pale-yellow semi-solid (428 mg, 0.94 mmol, 90% yield, *α:β*; 90:10). Rf (20% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (s, 1H), 5.28-5.24 (m, 1H), 5.03 (d, J = 3.1 Hz, 1H), 4.30 (t, J = 6.4 Hz, 2H), 4.05 (d, J = 6.6 Hz, 2H), 3.30 (td, J = 10.6, 4.4 Hz, 1H), 2.11 (s, 3H), 2.07-2.06 (m, 1H), 2.03 (s, 3H), 2.01-1.99 (m, 1H), 1.96 (s, 3H), 1.84 (dd, J = 12.2, 4.7 Hz, 1H), 1.64-1.57 (m, 2H), 1.41-1.34 (m, 1H), 1.19-1.16 (m, 1H), 1.01-0.95 (m, 2H), 0.90-0.87 (m, 6H), 0.81 (dd, J = 12.2, 2.8 Hz, 1H), 0.73 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 170.4, 170.1, 99.5, 81.2, 67.0, 66.8, 66.4, 63.0, 48.6, 42.8, 34.2, 31.7, 30.8, 25.7, 23.1, 22.3, 21.1, 20.9, 20.7, 16.2; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[1-3]

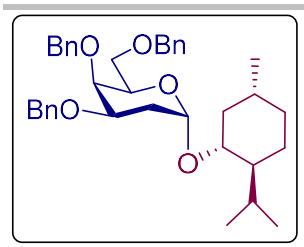


***Benzyl-3,4,6-tri-O-acetyl-2-deoxy-α-D-lyxo-hexapyranoside (3ab)*:** Glycosylation of 3,4,6-tri-*O*-acetyl-D-galactal (100 mg, 0.367 mmol, 1.0 equiv.) with benzyl alcohol (45 µL, 47 mg, 0.441 mmol, 1.2 equiv.) in 1,4-dioxane (2 mL) at 50 ^{o}C for 1 h in oil bath, purified by silica gel column

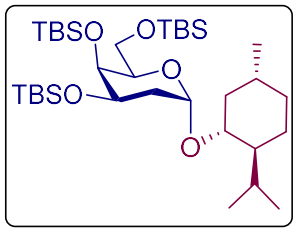
chromatography to obtain glycoside **3ab** as a colorless semi-solid (119 mg, 0.315 mmol, 86% yield, *α:β*; 95:5). Rf (20% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, J = 7.7, 1.9 Hz, 5H), 5.33-5.28 (m, 2H), 5.09 (d, J = 3.0 Hz, 1H), 4.66 (d, J = 11.8 Hz, 1H), 4.47 (d, J = 11.8 Hz, 1H), 4.19 (s, 1H), 4.08 (d, J = 6.5 Hz, 2H), 2.12 (s, 3H), 2.09-2.08 (m, 1H), 2.04 (s, 3H), 1.96 (s, 3H), 1.91-1.87 (m, J = 5.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 170.3, 170.1, 137.1, 128.5, 128.1, 128.0, 127.9, 96.5, 69.2, 66.8, 66.6, 66.2, 62.4, 30.1, 20.9, 20.8, 20.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[1-3]



***1,2,3,4-di-O-isopropylidene-6-O-(3,4,6-tri-O-acetyl-2-deoxy-α-D-lyxo-hexapyranosyl)-α-D-galactopyranoside (3ac)*:** Glycosylation of 3,4,6-tri-*O*-acetyl-D-galactal (100 mg, 0.367 mmol, 1.0 equiv.) with 6-hydroxy-1,2,3,4-di-*O*-isopropylidene-*α*-D-galactopyranoside (107 mg, 0.44 mmol, 1.2 equiv.) in 1,4-dioxane (2 mL) at 50 ^{o}C for 1 h in oil bath, purified by silica gel column chromatography to obtain glycoside **3ac** as a colorless oil (164 mg, 0.308 mmol, 84% yield, *α:β*; 93:7). Rf (30% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (d, J = 5.0 Hz, 1H), 5.30-5.28 (m, 3H), 5.04 (s, 1H), 4.59 (d, J = 7.9 Hz, 1H), 4.30-4.28 (m, 1H), 4.20 (t, J = 7.8 Hz, 1H), 4.07 (t, J = 11.1 Hz, 2H), 3.93 (t, J = 6.3 Hz, 1H), 3.76-3.72 (m, 1H), 3.65-3.61 (m, 1H), 2.10 (s, 3H), 2.08-2.04 (m, 1H), 2.02 (s, 3H), 1.95 (s, 3H), 1.88 (dd, J = 12.7, 5.0 Hz, 1H), 1.52 (s, 3H), 1.41 (s, 3H), 1.31 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 170.3, 170.0, 109.4, 109.3, 108.6, 108.6, 97.3, 96.3, 71.6, 70.9, 70.7, 70.6, 70.5, 68.0, 66.8, 66.7, 66.2, 66.1, 66.0, 62.3, 62.3, 53.4, 30.0, 26.1, 25.9, 25.9, 25.9, 24.9, 24.4, 24.2, 20.8, 20.7, 20.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[1,2,5]

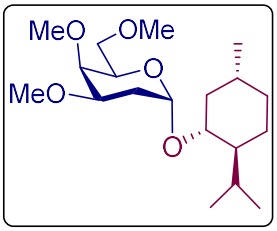


Menthyl-3,4,6-tri-O-benzyl-2-deoxy-α-D-lyxo-hexapyranoside (3ba): Glycosylation of 3,4,6-tri-*O*-benzyl-D-galactal (416 mg, 1.0 mmol, 1.0 equiv.) and L-Menthol (187 mg, 1.2 mmol, 1.2 equiv.) in toluene (2 mL) at 25 °C for 15 min., purified by silica gel column chromatography to obtain glycoside **3ba** as a colourless syrup (514 mg, 0.90 mmol, 90% yield, *α:β* ; 95:5). Rf (15% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 15H), 5.03 (d, J = 2.9 Hz, 1H), 4.94 (d, J = 11.7 Hz, 1H), 4.63-4.57 (m, 3H), 4.52-4.42 (m, 3H), 4.06 (t, J = 6.4 Hz, 1H), 3.93 (d, J = 9.0 Hz, 2H), 3.57 (d, J = 6.4 Hz, 2H), 3.30 (td, J = 10.5, 4.2 Hz, 1H), 2.19 (td, J = 12.3, 3.4 Hz, 1H), 2.10-1.97 (m, 3H), 1.61-1.57 (m, 3H), 1.17 (s, 1H), 0.99-0.93 (m, 1H), 0.91-0.88 (m, 3H), 0.87-0.84 (m, 1H), 0.81 (d, J = 6.5 Hz, 3H), 0.75 (d, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 138.6, 138.2, 128.3, 128.3, 128.1, 127.6, 127.5, 127.4, 127.4, 127.3, 99.7, 79.9, 74.9, 74.2, 73.3, 73.1, 70.3, 69.8, 69.6, 48.8, 42.8, 34.3, 31.6, 25.6, 23.2, 22.2, 21.1, 16.3; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[3]

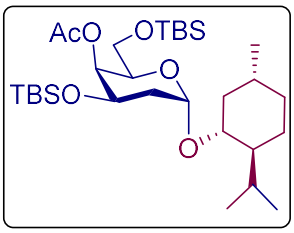


Menthyl-3,4,6-tri-O-(tert-butyldimethylsilyl)-α-D-lyxo-hexapyranoside (3ca): Glycosylation of 3,4,6-tri-*O*-TBS-D-galactal (100 mg, 0.204 mmol, 1.0 equiv.) with L-Menthol (38 mg, 0.245 mmol, 1.2 equiv.) in toluene (2 mL) at 25 °C for 20 min., purified by silica gel column chromatography to obtain glycoside **3ca** as a pale-yellow semi solid (81 mg, 0.126 mmol, 62% yield, *α:β*; 93:7). Rf (5% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (d, J = 3.6 Hz, 1H), 4.07 (ddd, J = 11.5, 5.2, 3.1 Hz, 1H), 3.91-3.83 (m, 2H), 3.78-3.72 (m, 2H), 3.28 (td, J = 10.6, 4.4 Hz, 1H), 2.11 (dd, J = 12.0, 4.5 Hz, 1H), 1.91 (ddd, J = 12.8, 11.4, 3.8 Hz, 1H), 1.75-

1.52 (m, 7H), 1.19 (td, *J* = 13.1, 11.6, 3.0 Hz, 2H), 1.05-0.93 (m, 3H), 0.89 (dd, *J* = 6.4, 4.0 Hz, 30H), 0.82 (dd, *J* = 7.0, 2.8 Hz, 2H), 0.76 (d, *J* = 6.9 Hz, 4H), 0.14-0.05 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 99.7, 80.4, 70.2, 68.1, 66.7, 62.7, 48.8, 42.9, 34.4, 33.9, 31.6, 29.7, 25.9, 25.7, 23.5, 22.3, 21.0, 18.4, 18.0, 16.5, 1.0, -4.6, -4.8, -5.3, -5.4; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{34}H_{71}O_5Si_3]^+$: 645.4760; found 645.4761.

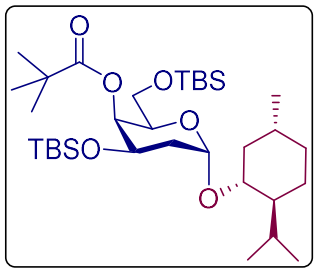


Menthyl-3,4,6-tri-O-methyl-α-D-lyxo-hexapyranoside (3da): Glycosylation of 3,4,6-tri-*O*-methyl-D-galactal (100 mg, 0.532 mmol, 1.0 equiv.) with L-Menthol (99 mg, 0.638 mmol, 1.2 equiv.) in toluene (2 mL) at 25 °C for 3 h, purified by silica gel column chromatography to obtain glycoside **3da** as a white semi solid (95 mg, 0.277 mmol, 52% yield, *α:β*; 85:15). Rf (20% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (d, *J* = 3.0 Hz, 1H), 4.96 (d, *J* = 3.6 Hz, 1H), 4.23 (ddd, *J* = 6.8, 5.6, 2.7 Hz, 1H), 3.95 (t, *J* = 6.6 Hz, 1H), 3.58 (d, *J* = 3.7 Hz, 2H), 3.52 (s, 3H), 3.38 (s, 6H), 3.27 (td, *J* = 10.6, 4.4 Hz, 1H), 2.01 (dd, *J* = 7.0, 2.4 Hz, 1H), 1.93 (dd, *J* = 11.2, 3.7 Hz, 1H), 1.58 (ddd, *J* = 10.2, 7.5, 3.1 Hz, 4H), 0.99-0.94 (m, 2H), 0.87 (d, *J* = 6.2 Hz, 8H), 0.80 (d, *J* = 4.0 Hz, 1H), 0.72 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 99.8, 80.1, 75.9, 74.4, 71.6, 69.2, 60.7, 59.1, 55.9, 48.8, 42.9, 34.2, 31.6, 31.2, 25.6, 23.1, 22.2, 21.1, 16.2; HRMS (ESI) m/z $[M + Na]^+$ calculated for $[C_{19}H_{36}O_5Na]^+$: 367.2455; found 367.2456.

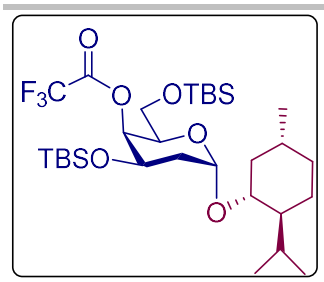


Menthyl-4-O-acetyl-3,6-di-O-(tert-butyldimethylsilyl)-α-D-lyxo-hexapyranoside (3fa): Glycosylation of 4-*O*-acetyl-3,6-di-*O*-TBS-D-galactal (100 mg, 0.249 mmol, 1.0 equiv.) with L-Menthol (47 mg, 0.299 mmol, 1.2 equiv.) in toluene (2 mL) at 25 °C for 2 h, purified by silica

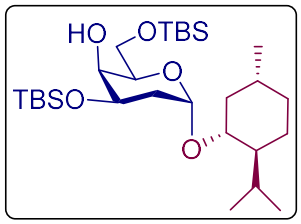
gel column chromatography to obtain glycoside **3fa** as a colorless semi solid (91 mg, 0.159 mmol, 64% yield, *α:β*; 80:20). Rf (5% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (d, J = 3.2 Hz, 1H), 4.98 (d, J = 3.6 Hz, 1H), 4.13 (ddd, J = 11.6, 4.9, 3.2 Hz, 1H), 4.09-4.00 (m, 1H), 3.58 (dd, J = 6.7, 2.4 Hz, 2H), 3.28 (td, J = 10.5, 4.3 Hz, 1H), 2.08 (s, 3H), 1.91 (td, J = 12.1, 3.7 Hz, 1H), 1.74 (ddt, J = 12.6, 5.0, 1.3 Hz, 1H), 1.60 (d, J = 20.6 Hz, 6H), 1.43 (s, 3H), 0.91 (d, J = 10.3 Hz, 7H), 0.88 (d, J = 1.2 Hz, 8H), 0.85 (d, J = 1.1 Hz, 5H), 0.77 (d, J = 6.9 Hz, 3H), 0.07 (d, J = 1.9 Hz, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 99.8, 80.5, 69.9, 69.5, 65.1, 62.1, 48.8, 42.8, 35.0, 34.4, 31.6, 30.3, 29.7, 29.4, 26.0, 25.9, 25.8, 25.7, 25.6, 23.5, 22.7, 22.3, 21.0, 20.9, 18.3, 18.0, 16.5, 14.1, 1.0, -4.9, -5.1, -5.5; HRMS (ESI) m/z [M + Na]$^{+}$ calculated for $[C_{30}H_{60}O_6Si_2Na]^{+}$: 595.3821; found 595.3822.



Menthyl-4-(2,2-dimethylpropanoate)-3,6-di-O-(tert-butyldimethylsilyl)-α-D-lyxo-hexapyranoside (3ga): Glycosylation of 4-*O*-Piv-3,6-di-*O*-TBS-D-galactal (100 mg, 0.172 mmol, 1.0 equiv.) with L-Menthol (32 mg, 0.206 mmol, 1.2 equiv.) in toluene (2 mL) at 25 ^{o}C for 1.5 h, purified by silica gel column chromatography to obtain glycoside **3ga** as a colourless liquid (80 mg, 0.131 mmol, 76% yield, *α:β*; 92:8). Rf (5% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (d, *J* = 3.1 Hz, 1H), 4.99 (d, *J* = 3.6 Hz, 1H), 4.13 (ddd, *J* = 11.7, 5.0, 3.2 Hz, 1H), 4.03 (t, *J* = 6.9 Hz, 1H), 3.55 (dd, *J* = 6.6, 3.4 Hz, 2H), 3.27 (td, *J* = 10.5, 4.3 Hz, 1H), 1.91 (td, *J* = 12.0, 3.6 Hz, 1H), 1.74 (ddt, *J* = 12.5, 5.0, 1.2 Hz, 1H), 1.42 (d, *J* = 1.0 Hz, 1H), 1.35-1.24 (m, 7H), 1.21 (d, *J* = 0.9 Hz, 10H), 1.06-0.94 (m, 2H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 9H), 0.84 (s, 9H), 0.80-0.75 (m, 3H), 0.07-0.02 (m, 13H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 99.9, 80.7, 70.3, 68.9, 65.3, 62.3, 48.7, 42.8, 39.0, 35.2, 34.4, 31.7, 29.7, 27.3, 26.0, 25.9, 25.8, 25.7, 23.6, 22.3, 20.9, 18.3, 18.0, 16.6, 1.0, -4.9, -5.1, -5.5; HRMS (ESI) m/z [M + Na]$^{+}$ calculated for $[C_{33}H_{66}NaO_6Si_2]^{+}$: 637.4290; found 637.4291.

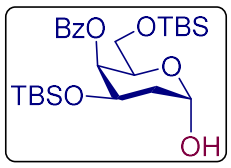


Menthyl-4-(trifluoroacetate)-3,6-di-O-(tert-butyldimethylsilyl)-α-D-lyxo-hexapyranoside (3ha): Glycosylation of 4-*O*-TFA-3,6-di-*O*-TBS-D-galactal (100 mg, 0.212 mmol, 1.0 equiv.) with L-Menthol (40 mg, 0.254 mmol, 1.2 equiv.) in toluene (2 mL) at 25 °C for 2 h, purified by silica gel column chromatography to obtain glycoside **3ha** as a colourless liquid (103 mg, 0.165 mmol, 78% yield, *α:β*; 90:10). Rf (5% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42-5.37 (m, 1H), 4.98 (d, J = 3.5 Hz, 1H), 4.22 (dt, *J* = 11.7, 4.3 Hz, 1H), 4.09 (dd, *J* = 8.6, 6.3 Hz, 1H), 3.62 (dd, *J* = 9.8, 5.9 Hz, 1H), 3.53 (q, *J* = 9.5 Hz, 1H), 3.27 (td, *J* = 10.6, 4.4 Hz, 1H), 1.90 (td, *J* = 12.2, 3.6 Hz, 1H), 1.78 (dd, *J* = 12.9, 5.3 Hz, 1H), 1.68-1.51 (m, 4H), 1.08-0.95 (m, 3H), 0.89 (d, *J* = 8.0 Hz, 16H), 0.84 (s, 8H), 0.77 (d, *J* = 7.0 Hz, 3H), 0.10-0.01 (m, 14H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 99.7, 81.0, 73.5, 68.6, 64.7, 60.8, 48.6, 42.8, 34.9, 34.3, 31.6, 29.7, 26.1, 25.8, 25.5, 23.6, 22.3, 20.9, 18.2, 17.9, 16.6, 1.0; HRMS (ESI) m/z $[M + Na]^+$ calculated for $[C_{30}H_{57}F_3O_6Si_2Na]^+$: 649.3538; found 649.3537.

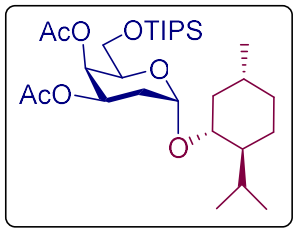


Menthyl-4-OH-3,6-di-O-(tert-butyldimethylsilyl)-α-D-lyxo-hexapyranoside (3ia): Glycosylation of 4-OH-3,6-di-*O*-TBS-D-galactal (100 mg, 0.267 mmol, 1.0 equiv.) with L-Menthol (50 mg, 0.32 mmol, 1.2 equiv.) in toluene (2 mL) at 25 °C for 30 min., purified by silica gel column chromatography to obtain glycoside **3ia** as a colourless liquid (82 mg, 0.155 mmol, 58% yield, *α:β*; 85:15). Rf (5% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (d, *J* = 3.6 Hz, 1H), 4.07 (ddd, *J* = 11.4, 5.1, 3.2 Hz, 1H), 3.90-3.84 (m, 2H), 3.75 (d, *J* = 4.0 Hz, 1H), 3.28 (td, *J* = 10.6, 4.3 Hz, 1H), 1.90 (td, *J* = 12.2, 3.8 Hz, 1H), 1.72 (dd, *J* = 12.8, 5.1 Hz, 1H), 1.66-1.54 (m, 5H), 1.04-0.95 (m, 2H), 0.90 (dd, *J* = 5.7, 1.3 Hz, 28H), 0.76 (dd, *J* = 7.0, 1.2 Hz, 3H), 0.08

(d, J = 7.2 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 99.7, 80.4, 70.2, 68.1, 66.7, 62.7, 48.8, 42.9, 34.4, 33.9, 31.6, 29.7, 25.9, 25.7, 23.5, 22.3, 21.0, 18.4, 18.0, 16.5, -4.6, -4.8, -5.3, -5.4; HRMS (ESI) m/z $[M + Na]^+$ calculated for $[C_{28}H_{58}NaO_5Si_2]^+$: 553.3715; found 553.3716.

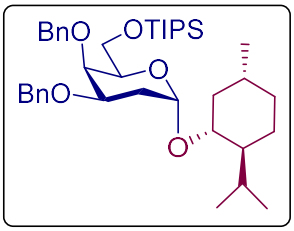


Menthyl-4-benzoyl-3,6-di-O-(tert-butyldimethylsilyl)-α-D-lyxo-hexapyranoside (3ja): Glycosylation of 4-*O*-benzoyl-3,6-di-*O*-TBS-D-galactal (100 mg, 0.209 mmol, 1.0 equiv.) with L-Menthol (39 mg, 0.25 mmol, 1.2 equiv.) in toluene (2 mL) at 25 °C for 2 h, purified by silica gel column chromatography to obtain glycoside **3ja** as a colourless liquid (69 mg, 0.138 mmol, 66% yield, α:β; 88:12). Rf (10% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.04 (m, 2H), 7.60-7.55 (m, 1H), 7.46 (d, J = 7.9 Hz, 2H), 5.59 (d, J = 2.0 Hz, 1H), 5.18-5.12 (m, 1H), 4.78 (d, J = 6.8 Hz, 1H), 4.50 (t, J = 4.6 Hz, 1H), 4.48-4.45 (m, 1H), 3.78 (ddd, J = 6.6, 5.3, 1.1 Hz, 1H), 2.01 (dt, J = 3.9, 1.9 Hz, 2H), 1.59 (s, 1H), 0.85 (s, 16H), 0.04 (d, J = 25.2 Hz, 10H), -0.20 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 133.3, 129.8, 128.4, 100.6, 72.8, 70.6, 65.4, 65.1, 39.3, 29.7, 25.6, 17.7, 1.0, -5.0, -5.4; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{25}H_{45}O_6Si_2]^+$: 497.2749; found 497.2748.

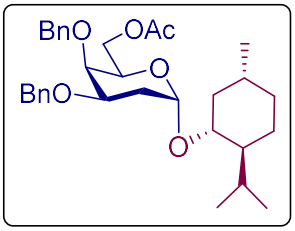


Menthyl-6-O-TIPS,3,4-di-O-acetyl-α-D-lyxo-hexapyranoside (3la): Glycosylation of 6-*O*-TIPS,3,4-di-*O*-acetyl-D-galactal (100 mg, 0.259 mmol, 1.0 equiv.) with L-Menthol (48 mg, 0.310 mmol, 1.2 equiv.) in 1,4-dioxane (2 mL) at 50 °C for 30 min., purified by silica gel column chromatography to obtain glycoside **3la** as a pale-yellow semi solid (126 mg, 0.233 mmol, 90% yield, α:β; 88:12). Rf (20% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (d, J = 3.0 Hz, 1H), 5.36-5.28 (m, 1H), 5.02 (d, J = 3.5 Hz, 1H), 4.14 (t, J = 7.0 Hz, 1H), 3.66 (p, J = 9.2 Hz, 2H), 3.30 (td, J = 10.5, 4.5 Hz, 1H), 2.11 (s, 3H), 2.06-2.02 (m, 1H), 1.98 (s, 3H), 1.86 (dd, J

= 12.0, 5.3 Hz, 1H), 1.05-1.02 (m, 28H), 0.88 (t, *J* = 7.4 Hz, 8H), 0.74 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 170.0, 99.4, 80.5, 69.1, 66.7, 66.6, 61.2, 48.6, 42.9, 34.2, 31.6, 31.0, 25.6, 23.1, 22.1, 21.1, 20.9, 20.7, 17.9, 17.8, 17.6, 16.1, 12.2, 11.8, 11.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[3]

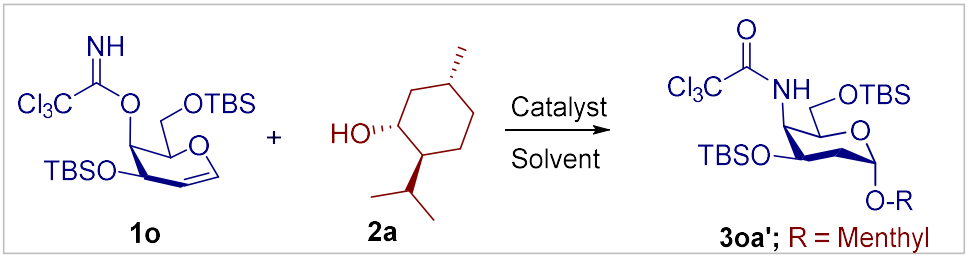


Menthyl-6-O-TIPS,3,4-di-O-benzyl-α-D-lyxo-hexapyranoside (3ma): Glycosylation of 6-*O*-TIPS,3,4-di-*O*-benzyl-D-galactal (100 mg, 0.207 mmol, 1.0 equiv.) with L-Menthol (38 mg, 0.248 mmol, 1.2 equiv.) in toluene (2 mL) at 25 °C for 30 min., purified by silica gel column chromatography to obtain glycoside **3ma** as a pale-yellow semi solid (116 mg, 0.182 mmol, 88% yield, *α:β*; 84:16). Rf (20% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 10H), 5.00 (d, *J* = 3.6 Hz, 1H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.61 (s, 2H), 4.03 (s, 1H), 3.95-3.86 (m, 3H), 3.72 (d, *J* = 4.2 Hz, 1H), 3.35-3.21 (m, 1H), 2.18 (td, *J* = 12.3, 3.9 Hz, 1H), 2.04-2.01 (m, 1H), 1.62 (t, *J* = 10.8 Hz, 4H), 1.07 (dd, *J* = 7.8, 3.7 Hz, 21H), 0.92-0.85 (m, 11H), 0.74 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.7, 128.3, 128.1, 128.0, 127.4, 127.3, 99.9, 74.9, 74.5, 72.9, 71.4, 70.3, 61.8, 48.9, 43.1, 34.3, 31.6, 25.7, 23.2, 22.2, 21.1, 18.1, 18.0, 17.6, 16.2, 11.8; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[3]



Menthyl-6-O-acetyl-3,4-di-O-benzyl-α-D-lyxo-hexapyranoside (3na): Glycosylation of 6-*O*-Ac,3,4-di-*O*-benzyl-D-galactal (100 mg, 0.217 mmol, 1.0 equiv.) with L-Menthol (50 mg, 0.326 mmol, 1.2 equiv.) in toluene (2 mL) at 25 °C for 15 min., purified by silica gel column

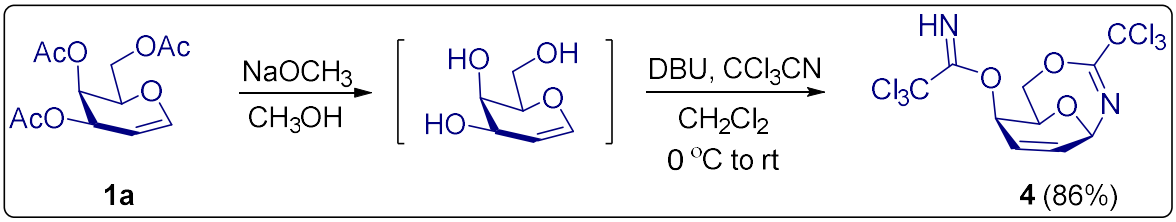
chromatography to obtain glycoside **3na** as a pale-yellow semi solid (104 mg, 0.199 mmol, 92% yield, α:β ; 90:10). Rf (20% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 10H), 5.04 (s, 1H), 4.96 (dd, J = 11.9, 3.8 Hz, 1H), 4.66-4.63 (m, 3H), 4.20-4.15 (m, 1H), 4.11-4.08 (m, 1H), 4.03 (d, J = 3.9 Hz, 1H), 3.93 (d, J = 11.8 Hz, 1H), 3.81 (s, 1H), 3.34-3.29 (m, 1H), 2.23-2.16 (m, 1H), 2.11-2.06 (m, 1H), 2.00 (s, 3H), 1.64-1.58 (m, 3H), 1.26 (d, J = 3.6 Hz, 3H), 0.92-90 (m, 9H), 0.77-0.75 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 138.5, 138.4, 128.3, 128.2, 127.5, 127.5, 127.2, 99.8, 80.3, 74.8, 73.9, 72.9, 70.4, 69.1, 64.7, 48.7, 42.8, 34.3, 31.5, 31.4, 29.6, 25.7, 23.2, 22.3, 21.1, 20.8, 16.2; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[3]



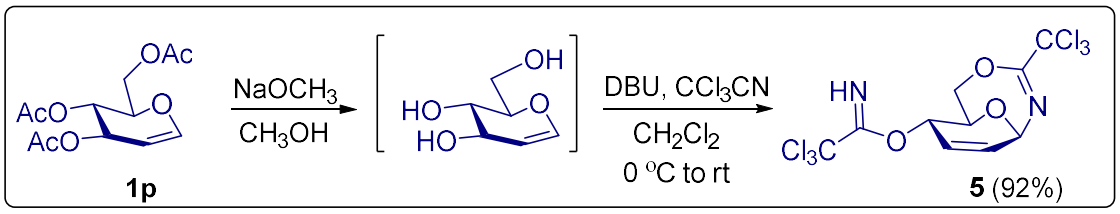
Menthyl-4-O-trichloroacetamidoyl-3,6-di-O-(tert-butyldimethylsilyl)-α-D-lyxo-hexapyranoside (3oa'): Glycosylation of 4-*O*-trichloroacetamidoyl-3,6-di-*O*-TBS-D-galactal (100 mg, 0.193 mmol, 1.0 equiv.) with L-Menthol (36 mg, 0.232 mmol, 1.2 equiv.) at 25 ^{o}C for 2 h, purified by silica gel column chromatography to obtain glycoside **3oa'** as a pale-yellow semi solid (112 mg, 0.166 mmol, 86% yield, α:β ; 95:5). Rf (5% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (d, J = 3.0 Hz, 1H), 4.99 (d, J = 3.5 Hz, 1H), 4.23 (ddd, J = 11.8, 5.1, 3.1 Hz, 1H), 4.12-4.07 (m, 1H), 3.67-3.56 (m, 2H), 3.26 (td, J = 10.6, 4.3 Hz, 1H), 1.96 (dd, J = 11.9, 3.5 Hz, 1H), 1.77 (ddd, J = 11.9, 4.7, 1.5 Hz, 1H), 1.66-1.51 (m, 4H), 1.07-0.94 (m, 2H), 0.90 (s, 5H), 0.87 (s, 13H), 0.84 (s, 9H), 0.76 (d, J = 7.0 Hz, 3H), 0.06 (d, J = 2.2 Hz, 7H), 0.03 (d, J = 4.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 99.8, 90.5, 81.1, 74.7, 69.2, 65.2, 61.1, 48.6, 42.8, 34.9, 34.3, 31.6, 29.7, 26.1, 25.8, 25.6, 23.6, 22.3, 20.9, 18.2, 17.9, 16.6, 1.0, -5.0, -5.1, -5.6, -5.6; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{30}H_{59}Cl_3NO_5Si_2]^+$: 674.2992; found 674.2991.

E. Mechanistic Studies and Spectroscopic Data

Traping the intermediate with Participating group

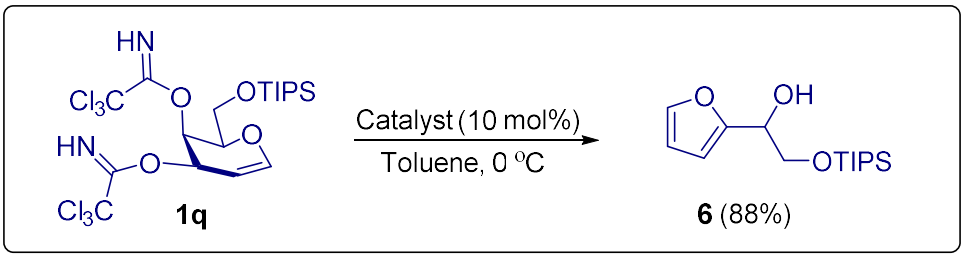


α-Amino-4-O-trichloroacetimidoyl-6-O,1-N-[(trichloromethyl)-oxazolino]-2,3-dideoxy-D-threo-hex-2-enopyranoside (4): To a preformed solution of tri-*O*-acetyl-D-galactal (100 mg, 0.368 mmol, 1.0 equiv.) in CH_3OH at room temperature was added sodium methanolate, the mixture was kept stirring for 12 h and solvent was evaporated. The residue was dissolved in anhydrous DCM containing DBU (109 µL, 0.735 mmol, 2.0 equiv.) and trichloro-acetonitrile (221 µL, 2.206 mmol, 6.0 equiv.), the reaction mixture was kept stirring at 0 °C to rt for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **4** as a colorless oil (174 mg, 0.316 mmol, 86% yield). Rf (15% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 6.35 (ddd, J = 10.5, 3.2, 2.1 Hz, 1H), 5.99 (dq, J = 10.4, 1.6 Hz, 1H), 5.89 (dq, J = 6.1, 2.0 Hz, 1H), 5.68 (dd, J = 3.4, 1.8 Hz, 1H), 4.93-4.82 (m, 1H), 4.73 (dd, J = 12.8, 10.0 Hz, 1H), 4.40 (dd, J = 12.8, 6.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 156.3, 130.4, 124.1, 92.6, 90.6, 81.9, 72.5, 71.5, 65.9; HRMS (ESI) m/z $[M + Na]^+$ calculated for $[C_{10}H_8N_2O_3Cl_6Na]^+$: 436.8558; found 436.8559.

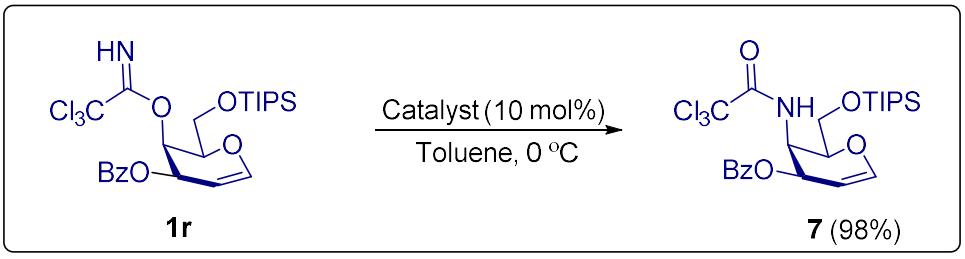


α-Amino-4-O-trichloroacetimidoyl-6-O,1-N-[(trichloromethyl)-oxazolino]-2,3-dideoxy-D-erythreo-hex-2-enopyranoside (5): To a preformed solution of tri-*O*-acetyl-D-glucal (100 mg, 0.368 mmol, 1.0 equiv.) in CH_3OH at room temperature was added sodium methanolate, the mixture was kept stirring for 12 h and solvent was evaporated. The residue was dissolved in anhydrous DCM containing DBU (109 µL, 0.735 mmol, 2.0 equiv.) and trichloro-acetonitrile

(221 µL, 2.206 mmol, 6.0 equiv.), the reaction mixture was kept stirring at 0 °C to rt for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **5** as colorless oil (186 mg, 0.338 mmol, 92% yield. Rf (15% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 6.42 (ddd, J = 10.2, 3.7, 1.1 Hz, 1H), 6.24-6.16 (m, 1H), 5.82 (dd, J = 3.7, 1.8 Hz, 1H), 5.12 (d, J = 5.1 Hz, 1H), 4.68-4.59 (m, 1H), 4.39 (d, J = 5.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 155.8, 130.9, 121.2, 92.8, 90.9, 80.8, 74.7, 71.5, 67.7; HRMS (ESI) m/z [M + Na]$^+$ calculated for $[C_{10}H_8N_2O_3Cl_6Na]^+$: 436.8558;found 436.8557.

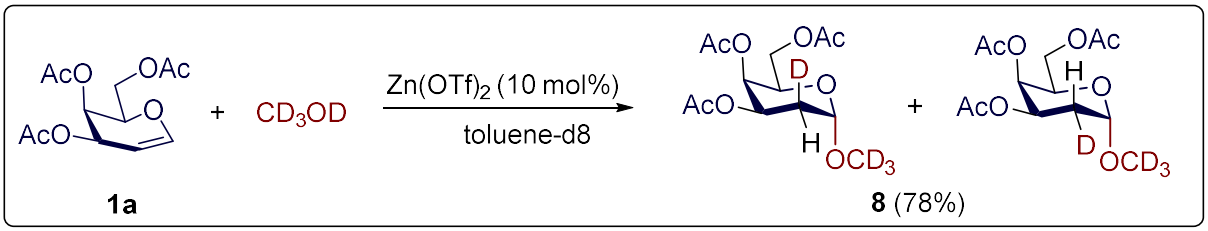


1-(furan-2-yl)-2-((triisopropylsilyl)oxy)ethan-1-ol (6): To a preformed solution of 6-*O*-TIPS,3,4-di-*O*-trichloroacetamidoyl-D-galactal (100 mg, 0.169 mmol, 1.0 equiv.) in toluene (2 mL) was added 10 mol% catalyst ($Bi(OTf)_3$, $Zn(OTf)_2$, CSA, TfOH) and the resulting mixture was stirred at 0 °C for 15 to 30 min. and reaction progress was monitored by TLC. After completion, reaction was purified by silica gel column chromatography to obtain **6** as a pale-yellow semi solid (42 mg, 0.149 mmol, 88% yield. Rf (15% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 1.9, 0.9 Hz, 1H), 6.38-6.26 (m, 2H), 4.83-4.72 (m, 1H), 3.97-3.90 (m, 2H), 2.96 (d, J = 3.9 Hz, 1H), 1.08-1.05 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 142.1, 110.2, 107.1, 68.4, 65.9, 17.9, 11.9; HRMS (ESI) m/z [M + H]$^+$ calculated for $[C_{15}H_{29}O_3Si]^+$: 285.1880; found 285.1881.

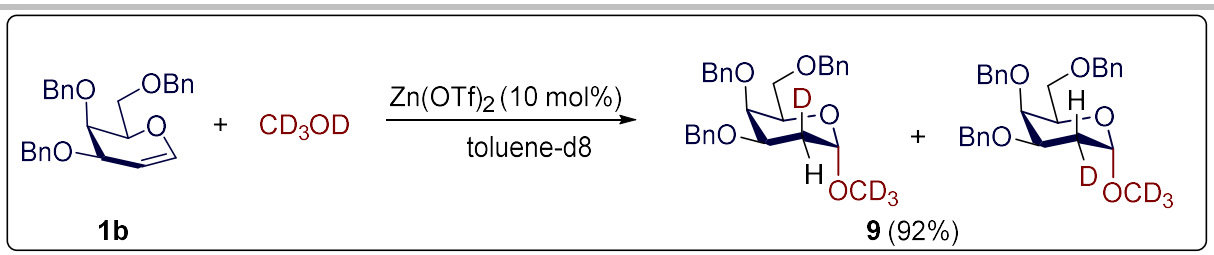


1,5-Anhydro-2,3-dideoxy-3-(benzoyl)-4-(trichloroacetamido)-6-O-(triisopropylsilyl)-D-threo-hex-1-enopyranose (7): To a preformed solution of 6-*O*-TIPS,3-*O*-benzoyl-4-di-*O*-trichloroacetamidoyl-D-galactal (100 mg, 0.181 mmol, 1.0 equiv.) in toluene (2 mL) was added 10 mol% catalyst ($Bi(OTf)_3$, $Zn(OTf)_2$, CSA, TfOH) and the resulting mixture was stirred at 0 °C for 30 min. and reaction progress was monitored by TLC. After completion, reaction was purified by silica gel column chromatography to obtain **7** as a pale-yellow semi solid (98 mg, 0.177 mmol, 98% yield. Rf (5% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.85 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 6.52 (dd, J = 6.3, 2.0 Hz, 1H), 5.96 (dd, J = 4.2, 2.0 Hz, 1H), 5.88-5.76 (m, 1H), 4.85 (dt, J = 6.2, 2.0 Hz, 1H), 4.31 (dd, J = 8.5, 6.0 Hz, 1H), 3.97 (dd, J = 9.9, 6.0 Hz, 1H), 3.88 (dd, J = 9.9, 8.5 Hz, 1H), 1.12-0.97 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 161.2, 145.5, 133.3, 129.8, 129.3, 128.3, 98.7, 89.8, 75.2, 68.2, 65.3, 60.6, 29.7, 17.9, 11.8; HRMS (ESI) m/z $[M + Na]^+$ calculated for $[C_{24}H_{35}Cl_3NO_5Si]^+$: 550.1345; found 550.1346.

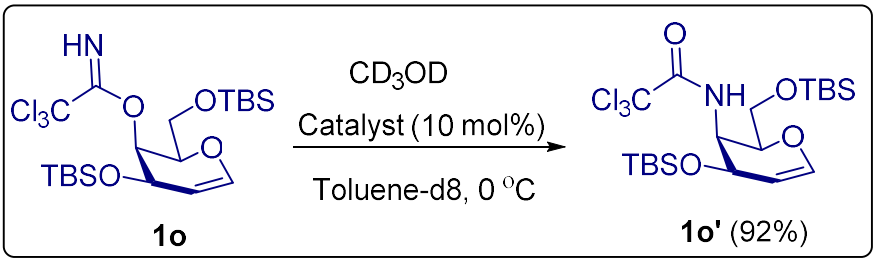
Trapping the glycosyl cation with Deuterated and Silane acceptors



Methanol-d4-3,4,6-tri-O-acetyl-2-deoxy-α-D-lyxo-hexapyranoside (8): Glycosylation of 3,4,6-tri-*O*-acetyl-D-galactal (100 mg, 0.367 mmol, 1.0 equiv.) with Methanol-d4 (13 µL, 16 mg, 0.44 mmol, 1.2 equiv.) in toluene-d8 (2 mL) was added 10 mol% $Zn(OTf)_2$ and the resulting mixture was stirred at 0 °C to rt for 30 min. and reaction progress was monitored by TLC. After completion, reaction was purified by silica gel column chromatography to obtain glycoside **8** as a white semi solid (88 mg, 0.286 mmol, 78% yield. Rf (20% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (d, J = 3.0 Hz, 1H), 5.27 (ddd, J = 12.4, 5.1, 3.1 Hz, 1H), 4.90 (d, J = 2.9 Hz, 1H), 4.15-4.08 (m, 3H), 2.13 (s, 3H), 2.09 (q, J = 2.9, 2.4 Hz, 1H), 2.05 (s, 3H), 1.98 (s, 3H), 1.87 (ddt, J = 12.7, 5.1, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 170.4, 170.0, 98.4, 66.7, 66.6, 66.2, 62.5, 29.7, 20.8, 20.7; HRMS (ESI) m/z $[M + N_a]^+$ calculated for $[C_{13}H_{17}D_3NaO_8]^+$: 330.1239; found 330.1238.



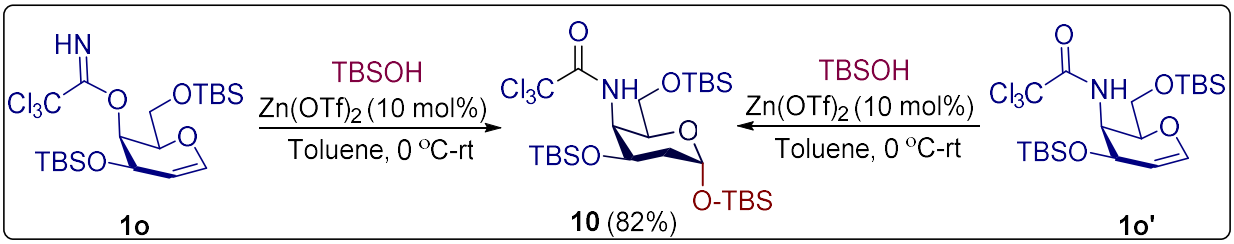
Methanol-d4-3,4,6-tri-O-benzyl-2-deoxy-α-D-lyxo-hexapyranoside (9): Glycosylation of 3,4,6-tri-*O*-benzyl-D-galactal (100 mg, 0.240 mmol, 1.0 equiv.) with methanol-d4 (11 µL, 10 mg, 0.288 mmol, 1.2 equiv.) in toluene-d8 (2 mL) was added 10 mol% $Zn(OTf)_2$ and the resulting mixture was stirred at 0 °C to rt for 1 h and reaction progress was monitored by TLC. After completion, reaction was purified by silica gel column chromatography to obtain glycoside **9** as an oil (100 mg, 0.22 mmol, 92% yield). Rf (20% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 15H), 4.93 (d, J = 11.6 Hz, 1H), 4.87 (m, 1H), 4.66-4.55 (m, 4H), 4.51 (d, J = 11.8 Hz, 1H), 4.43 (s, 1H), 3.94-3.85 (m, 2H), 3.59 (d, J = 6.1 Hz, 2H), 2.22 (m, 1H), 2.08-1.94 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.5, 138.1, 129.0, 128.4, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.2, 98.8, 74.7, 74.6, 74.2, 73.4, 72.9, 70.4, 69.7, 69.6, 31.1; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{28}H_{30}D_3O_5]^+$: 452.2511; found 452.2510.



1,5-Anhydro-2,3-dideoxy-4-(trichloroacetimido)-3,6-di-O-(tert-butyldimethylsilyl)-D-threo-hex-1-enopyranose (1o): Following the slightly modified procedure,[6] to a solution of 4-*OH*-3,6-di-*O*-TBS-D-galactal (100 mg, 0.267 mmol, 1.0 equiv.) in CH_2Cl_2 (4 mL) was added DBU (79 µL, 0.535 mmol, 2.0 equiv.) followed by the addition of trichloro-acetonitrile (53 µL, 0.535 mmol, 2.0 equiv.) at 0 °C and stirred for 1 h or till the complete conversion of starting material as observed by TLC. The reaction mixture was diluted with DCM (10 mL), quenched with saturated $NaHCO_3$ (5 mL) and extracted with DCM (3 × 30 mL). The combined organic layers

were washed with brine solution, dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by silica gel column chromatography using hexane-EtOAc gradient to afford the title compound **1o** (130 mg, 0.251 mmol, 94%) as a colorless oil. Rf (5% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 6.33 (dd, J = 6.2, 1.4 Hz, 1H), 5.47 (t, J = 3.5 Hz, 1H), 4.69 (ddd, J = 6.3, 3.2, 1.1 Hz, 1H), 4.60-4.56 (m, 1H), 4.27-4.21 (m, 1H), 3.98 (dd, J = 11.0, 7.5 Hz, 1H), 3.82 (dd, J = 11.1, 4.9 Hz, 1H), 0.87 (d, J = 10.2 Hz, 18H), 0.12-0.01 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 143.3, 102.9, 91.6, 71.6, 62.9, 61.3, 29.7, 25.9, 25.7, 18.4, 17.9, -4.8, -5.1, -5.3, -5.4; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{20}H_{39}Cl_3NO_4Si_2]^+$: 518.1478; found 518.1477.

1,5-Anhydro-2,3-dideoxy-4-(trichloroacetamido)-3,6-di-O-(tert-butyldimethylsilyl)-D-threo-hex-1-enopyranose (1o'): To a preformed solution of 4-*O*-trichloroacetimidoyl-3,6-di-*O*-TBS-D-galactal (100 mg, 0.193 mmol, 1.0 equiv.) and methanol-d4 (12 µL, 11 mg, 0.290 mmol, 1.5 equiv.) in toluene-d8 (2 mL) was added 10 mol% catalyst ($Bi(OTf)_3$, $Zn(OTf)_2$, CSA, TfOH) and the resulting mixture was stirred at 0 °C for 10 to 15 min. and reaction progress was monitored by TLC. After completion, reaction was purified by silica gel column chromatography to obtain **1o'** as a colorless semisolid (92 mg, 0.177 mmol, 92% yield). Rf (5% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (dd, J = 6.1, 1.6 Hz, 1H), 5.43 (dt, J = 3.3, 1.6 Hz, 1H), 4.67-4.58 (m, 2H), 4.13 (dd, J = 8.2, 6.1 Hz, 1H), 3.81 (dd, J = 10.0, 6.1 Hz, 1H), 3.70 (dd, J = 10.0, 8.2 Hz, 1H), 0.88 (d, J = 5.1 Hz, 18H), 0.10 (d, J = 7.5 Hz, 6H), 0.05 (d, J = 2.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 143.3, 103.2, 90.1, 75.2, 70.6, 63.6, 60.5, 29.7, 25.8, 25.7, 18.2, 18.1, -5.2, -5.1, -5.6, -5.6; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{20}H_{39}Cl_3NO_4Si_2]^+$: 518.1478; found 518.1477.



tert-butyldimethylsilyl-4-O-trichloroacetamidoyl-3,6-di-O-(tert-butyldimethylsilyl)-α-D-lyxo-hexapyranoside (10): Glycosylation of 4-*O*-trichloroacetamidoyl-3,6-di-*O*-TBS-D-galactal (100 mg, 0.193 mmol, 1.0 equiv.) with *tert*-Butyldimethylsilanol (30 mg, 0.232 mmol, 1.2 equiv.) in

toluene (2 mL) was added 10 mol% $Zn(OTf)_2$ and the resulting mixture was stirred at 0 ^{o}C to rt for 30 min. and reaction progress was monitored by TLC. After completion, reaction was purified by silica gel column chromatography to obtain glycoside **10** as a colorless semisolid (103 mg, 0.158 mmol, 82% yield). Rf (5% EtOAc/Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (dt, J = 3.4, 2.0 Hz, 2H), 4.32 (ddd, J = 11.6, 4.9, 2.9 Hz, 1H), 4.10 (ddd, J = 7.5, 6.1, 1.2 Hz, 1H), 3.62 (dd, J = 7.1, 2.8 Hz, 2H), 2.03 (ddd, J = 12.7, 11.6, 3.0 Hz, 1H), 1.70 (ddt, J = 12.8, 5.0, 1.5 Hz, 1H), 0.90 (s, 9H), 0.88 (s, 9H), 0.86 (s, 9H), 0.11 (d, J = 1.7 Hz, 6H), 0.07 (d, J = 1.1 Hz, 6H), 0.03 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 92.7, 90.4, 74.8, 69.2, 64.9, 61.2, 36.5, 31.9, 25.8, 25.6, 25.6, 22.7, 18.2, 18.0, 17.9, 14.1, 1.0, -4.5, -5.1, -5.1, -5.6, -5.9; HRMS (ESI) m/z $[M + Na]^+$ calculated for $[C_{26}H_{54}Cl_3NNaO_5Si_3]^+$:672.2268; found 672.2269.

F. References for Supporting Information.

(1) Jiang, N.; Dong, Y.; Sun, G.; Yang, G.; Wang, Q.; Zhang, J. *Chemistry Select* **2020**, *5*, 1592-1596. **Core-Shell Fe_3O_4@Carbon@SO_3H: A Powerful Recyclable Catalyst for the Synthesis of α-2-Deoxygalactosides**.

(2) Kumar, N.; Gurawa, A.; Yadav, A.; Kashyap, S. *Org. Lett.* **2024**, *26*, 7072-7077. **Influence of C-4 Axial/Equatorial Configuration and Neighboring Group/Remote Group Participation (NGP/RGP) Driven Conformational Evidence in Chemoselective Activation of Glycals.**

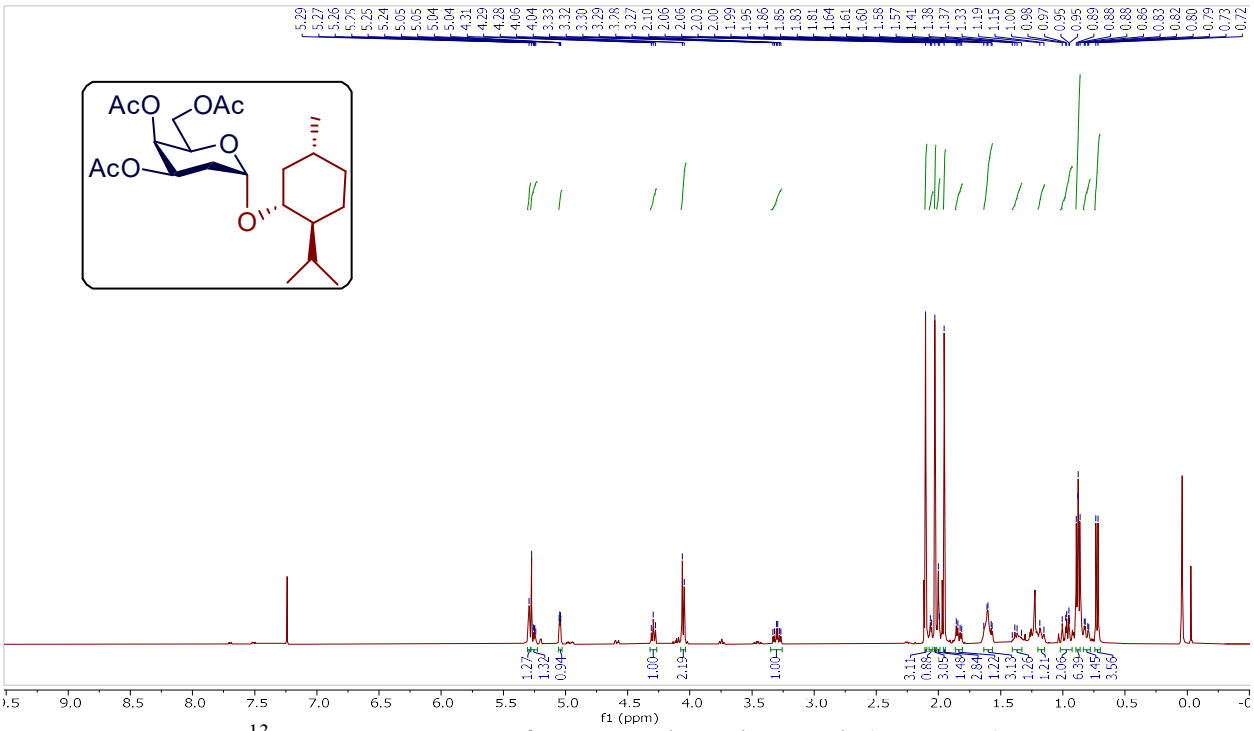
(3) Kumar, M.; Gurawa, A.; Kumar, N.; Kashyap, S. *Org. Lett.* **2022**, *24*, 575. **Bismuth-Catalyzed Stereoselective 2-Deoxyglycosylation of Disarmed/Armed Glycal Donors.**

(4) Judeh, Z. M. A.; Tatina, M. B.; Moussa, Z.; Xia, M. *Chem. Commun.* **2019**, *55*, 12204-12207. **Perfluorophenylboronic Acid-Catalyzed Direct α-Stereoselective Synthesis of 2-Deoxygalactosides from Deactivated Peracetylated D-Galactal**.

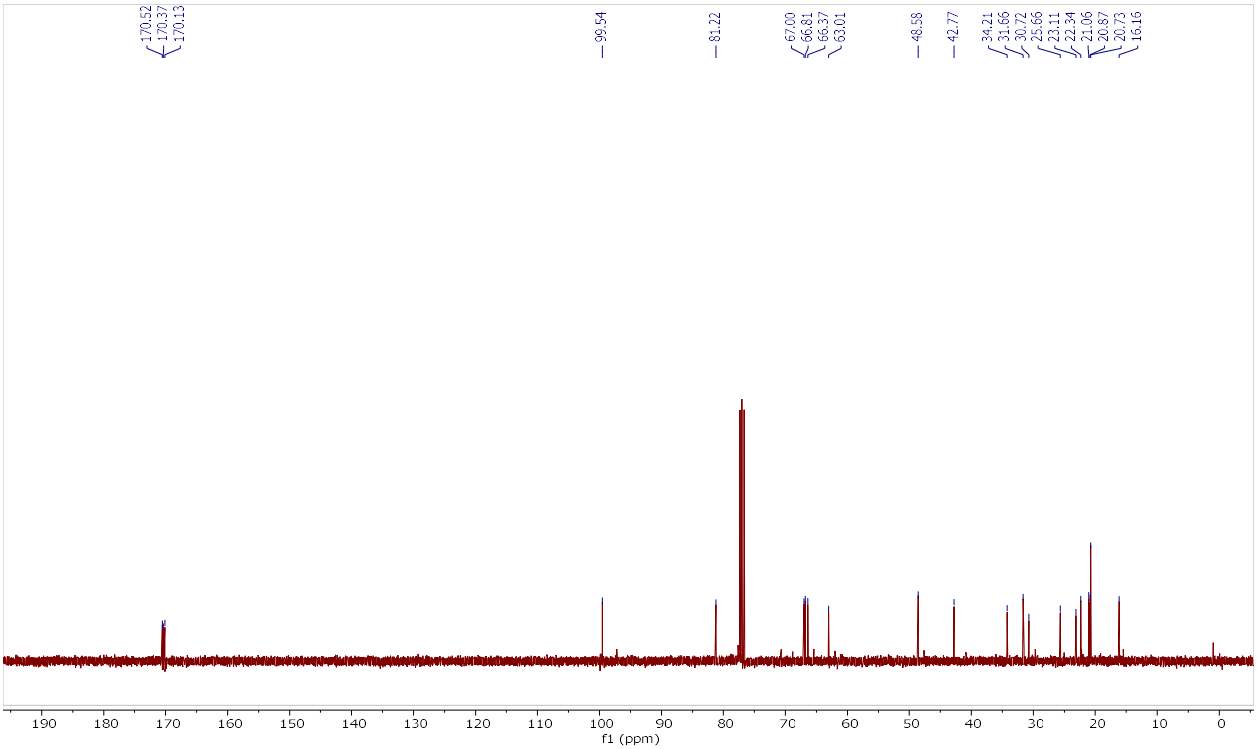
(5) Zhao, G.; Wang, T. *Angew. Chem., Int. Ed.* **2018**, *57*, 1-6. **Stereoselective Synthesis of 2-Deoxyglycosides from Glycals by Visible-Light-Induced Photoacid Catalysis.**

G. ^{1}H and ^{13}C NMR Spectra of Glycosides.

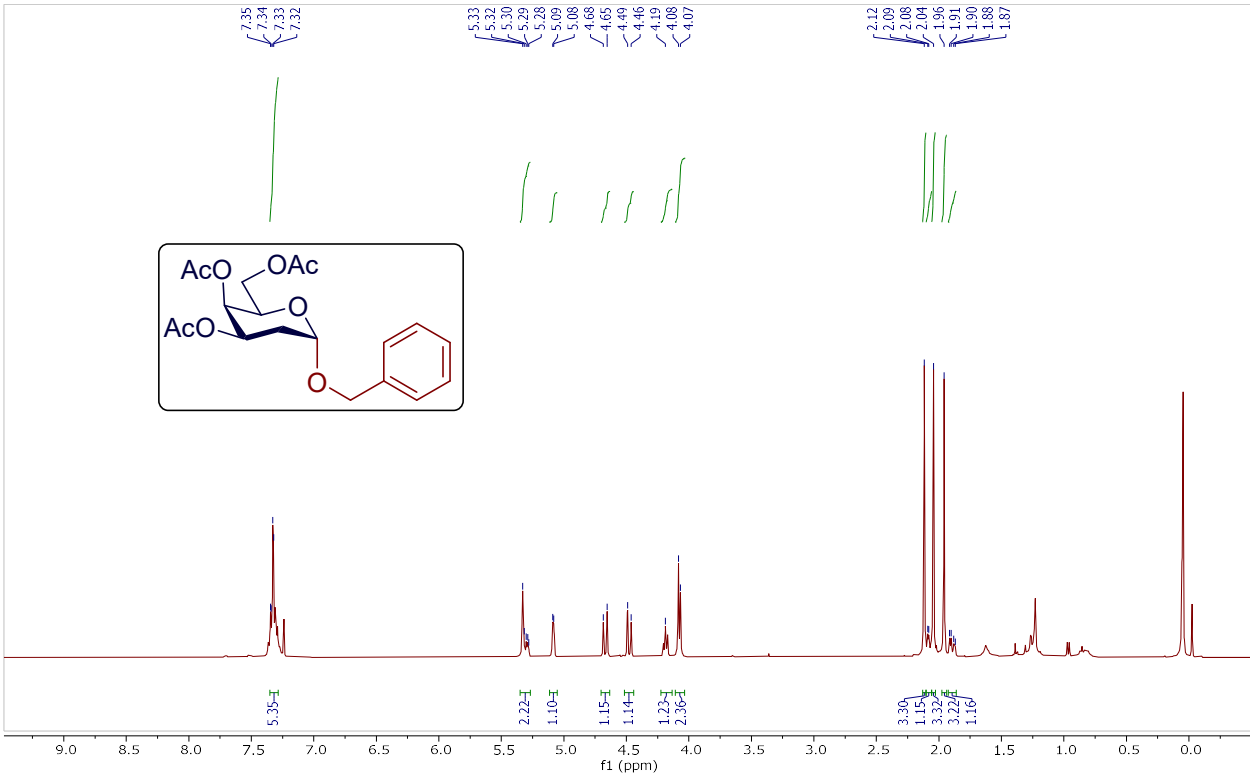
^{1}H NMR spectrum of compound **3aa** in $CDCl_3$ (400 MHz)



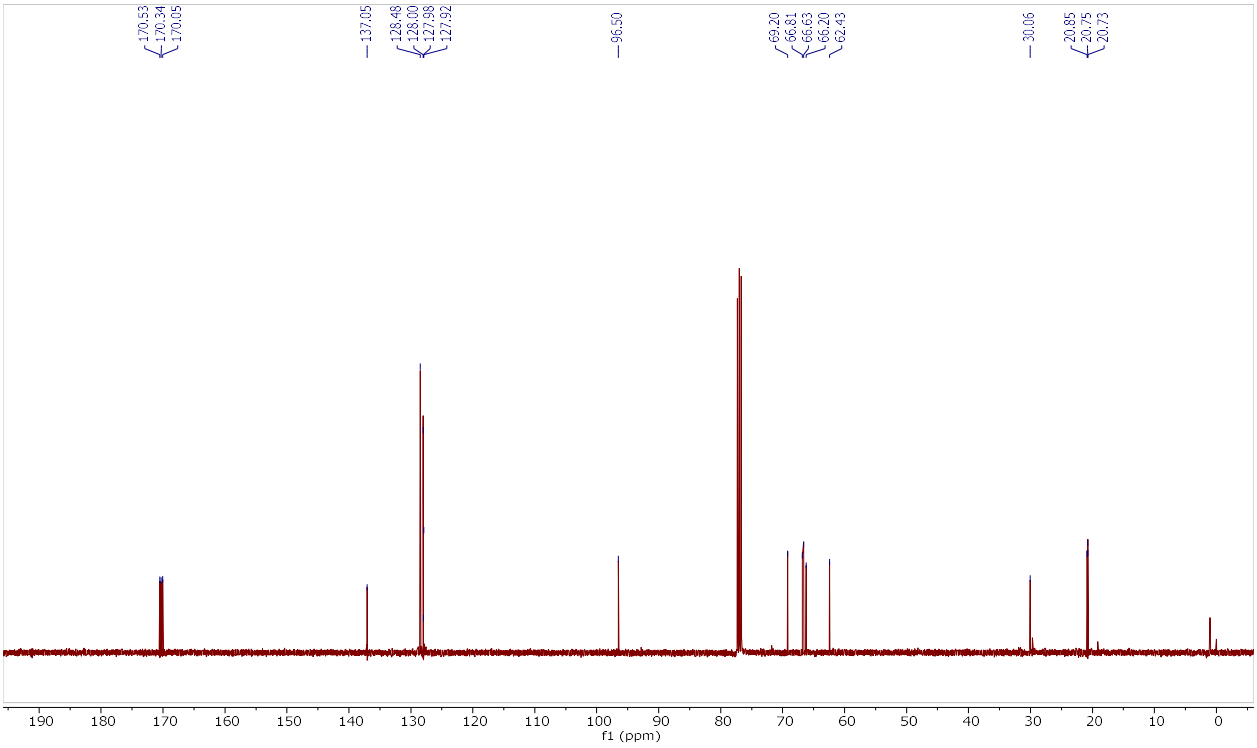
^{13}C NMR spectrum of compound **3aa** in $CDCl_3$ (101 MHz)



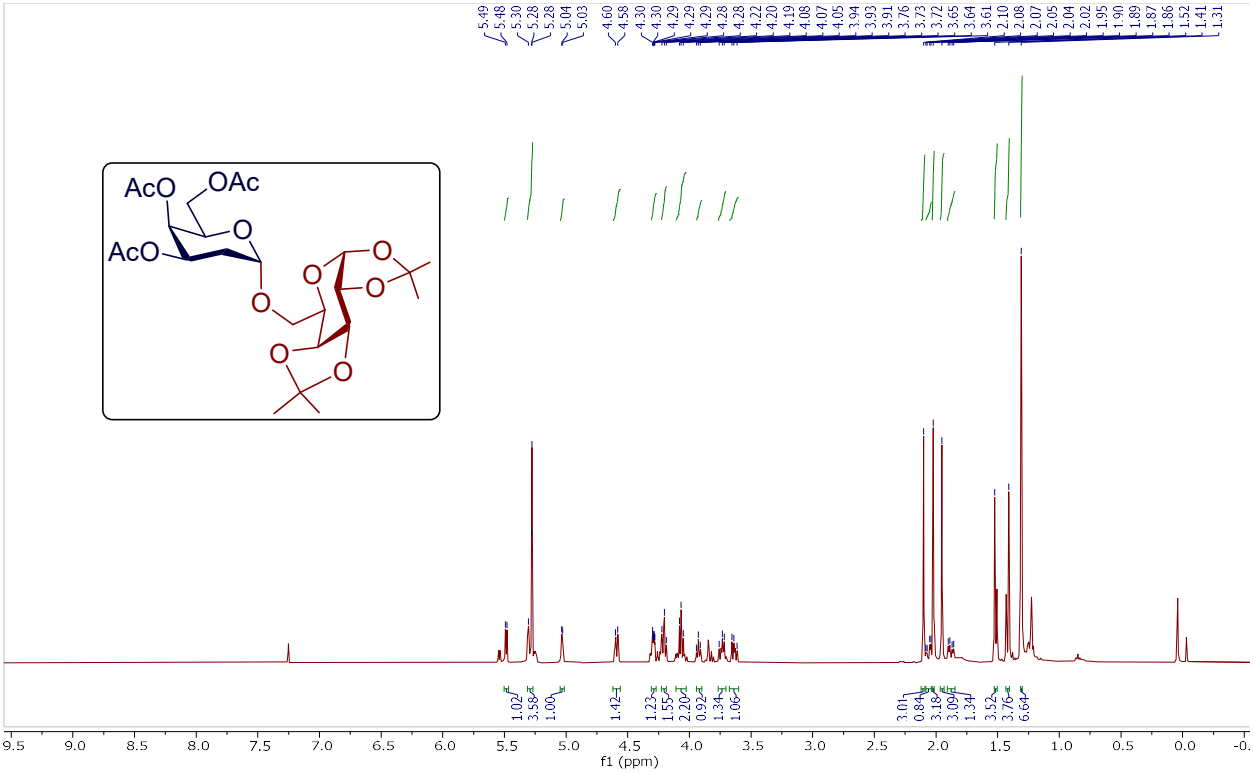
^{1}H NMR spectrum of compound **3ab** in $CDCl_3$ (400 MHz)



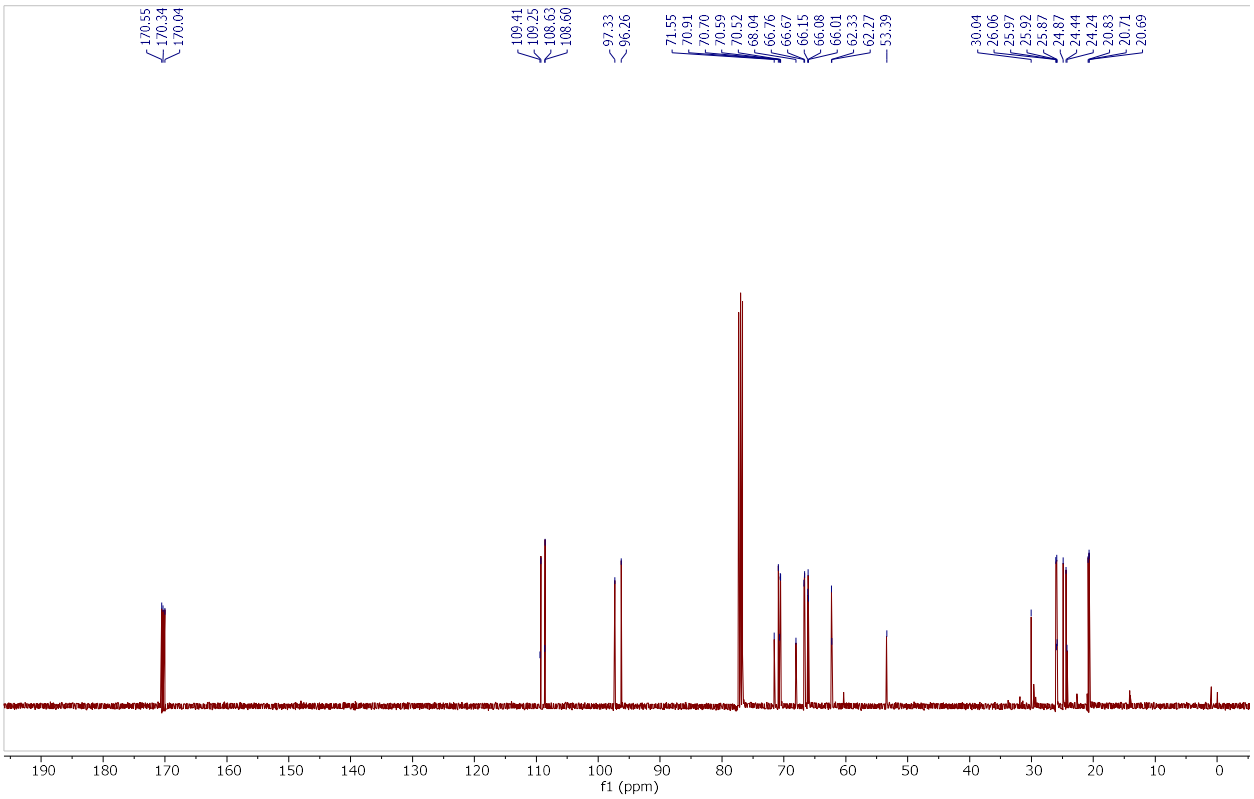
^{13}C NMR spectrum of compound **3ab** in $CDCl_3$ (101 MHz)



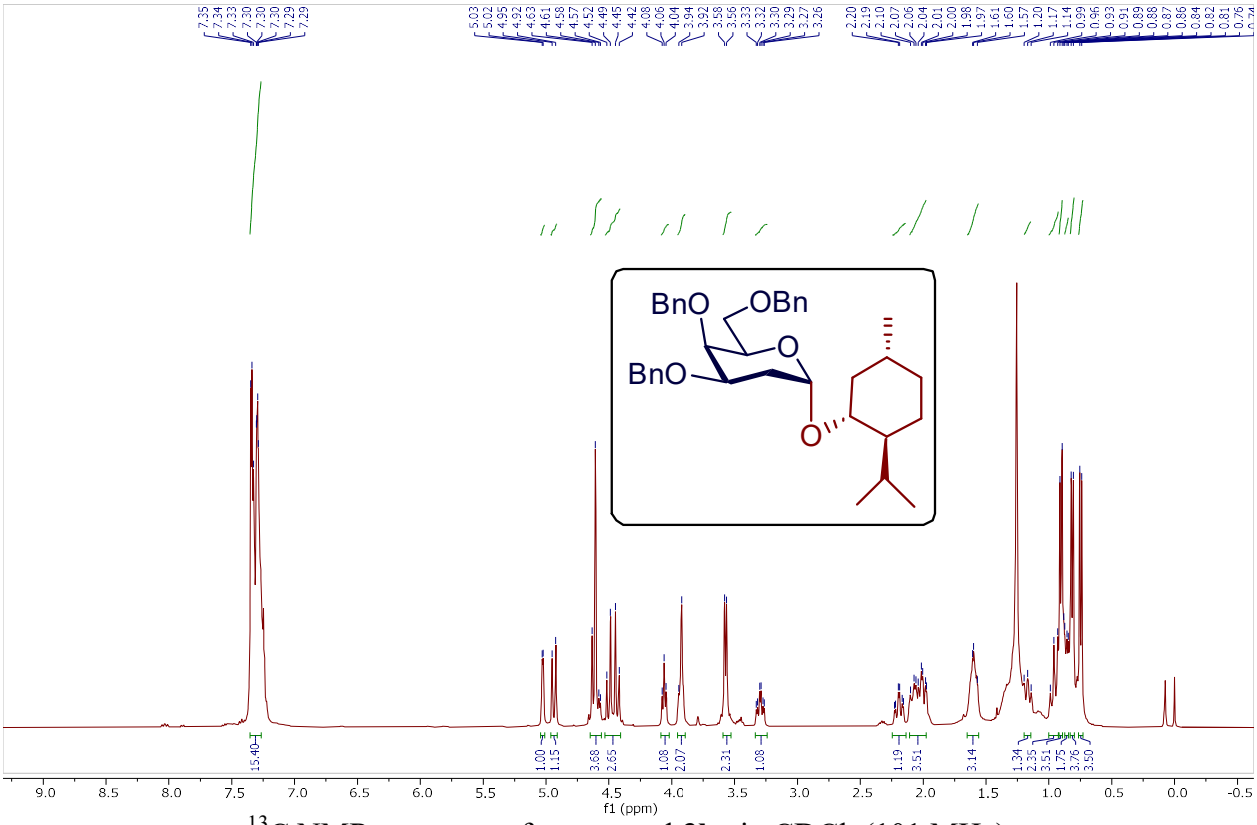
^{1}H NMR spectrum of compound **3ac** in $CDCl_3$ (400 MHz)



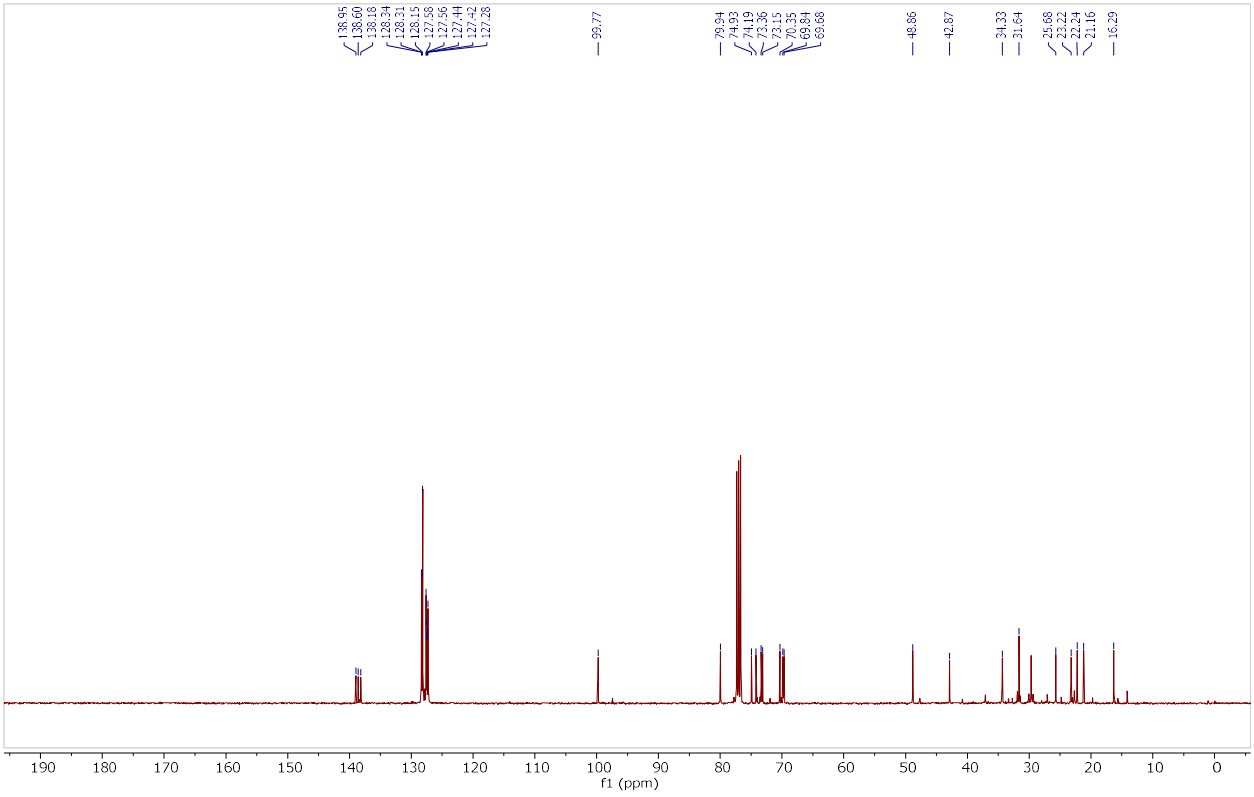
^{13}C NMR spectrum of compound **3ac** in $CDCl_3$ (101 MHz)



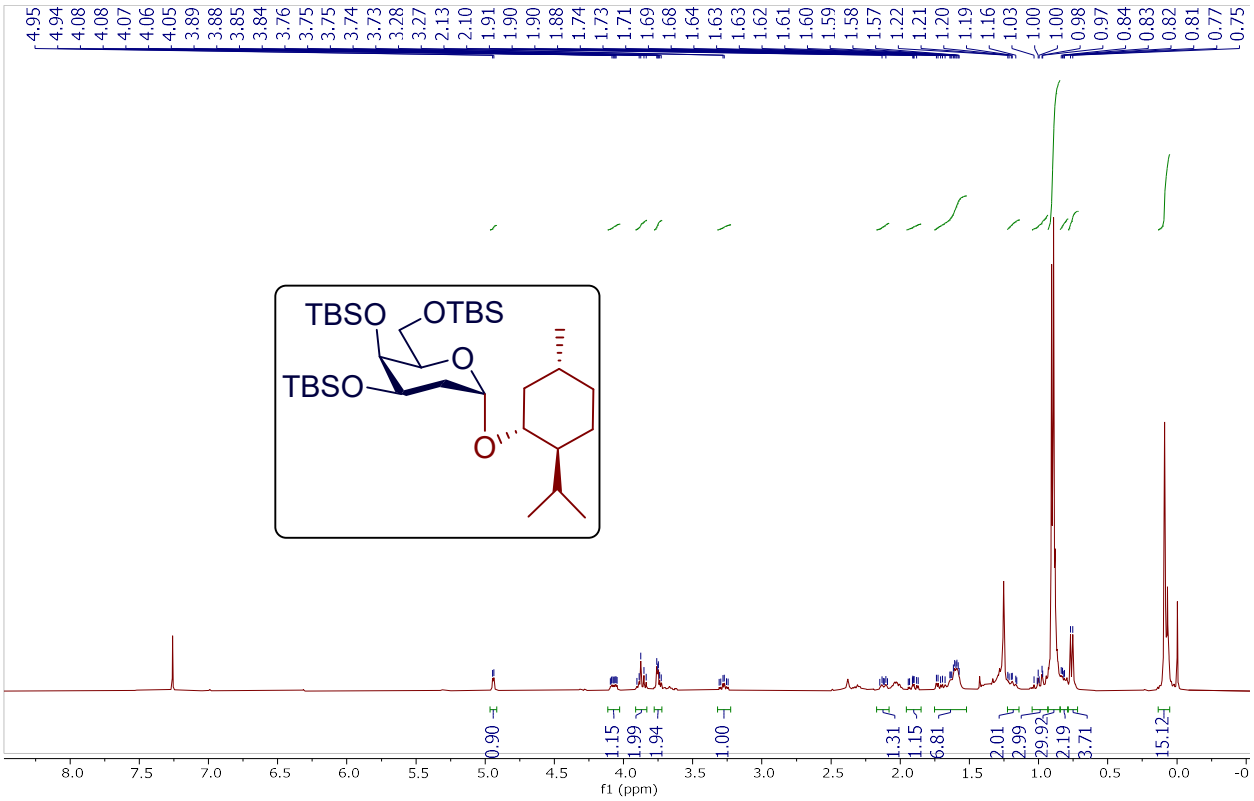
^{1}H NMR spectrum of compound **3ba** in $CDCl_3$ (400 MHz)



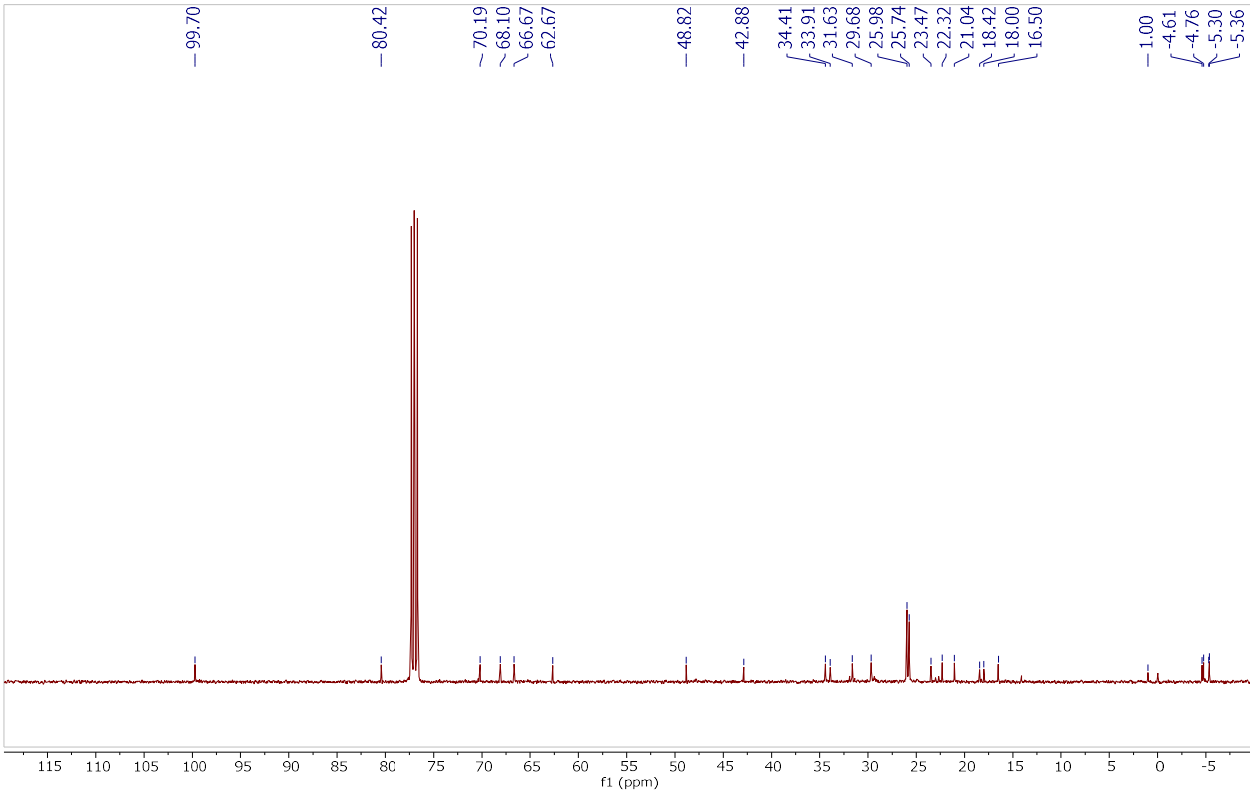
^{13}C NMR spectrum of compound **3ba** in $CDCl_3$ (101 MHz)



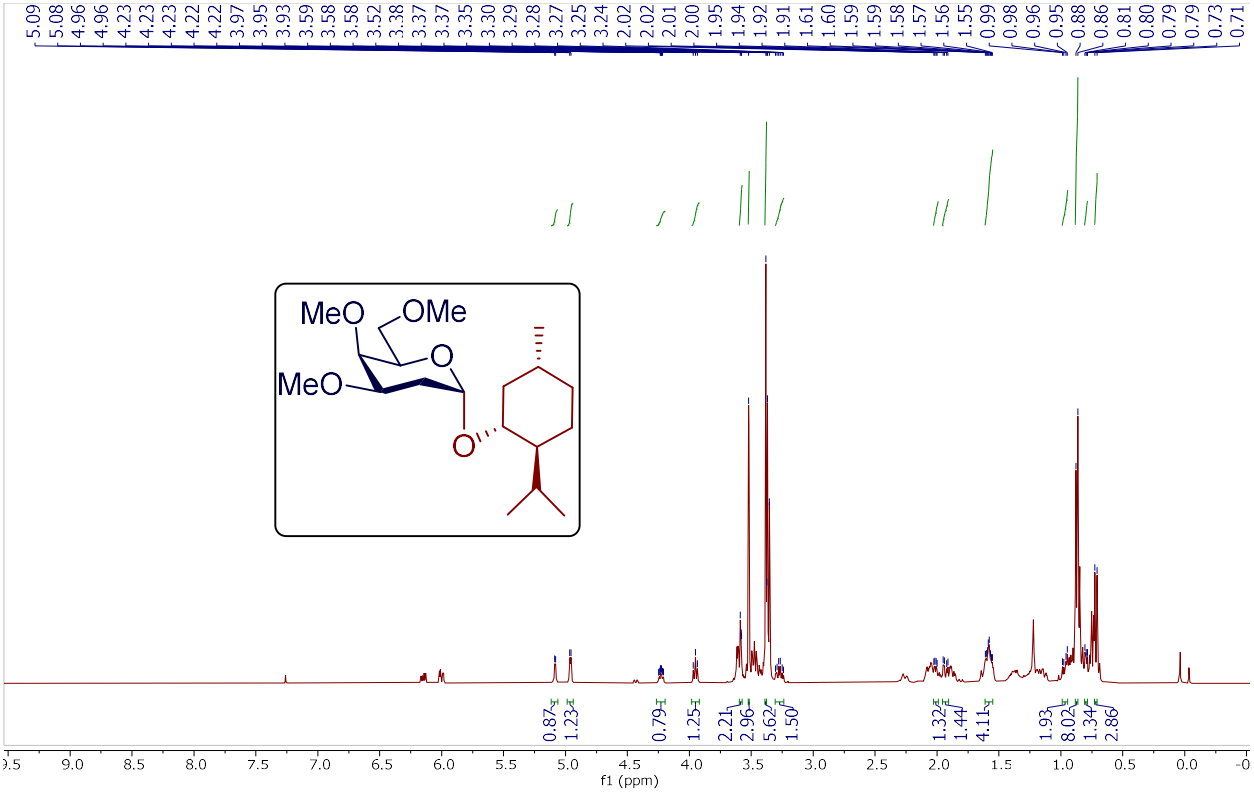
^{1}H NMR spectrum of compound **3ca** in $CDCl_3$ (400 MHz)



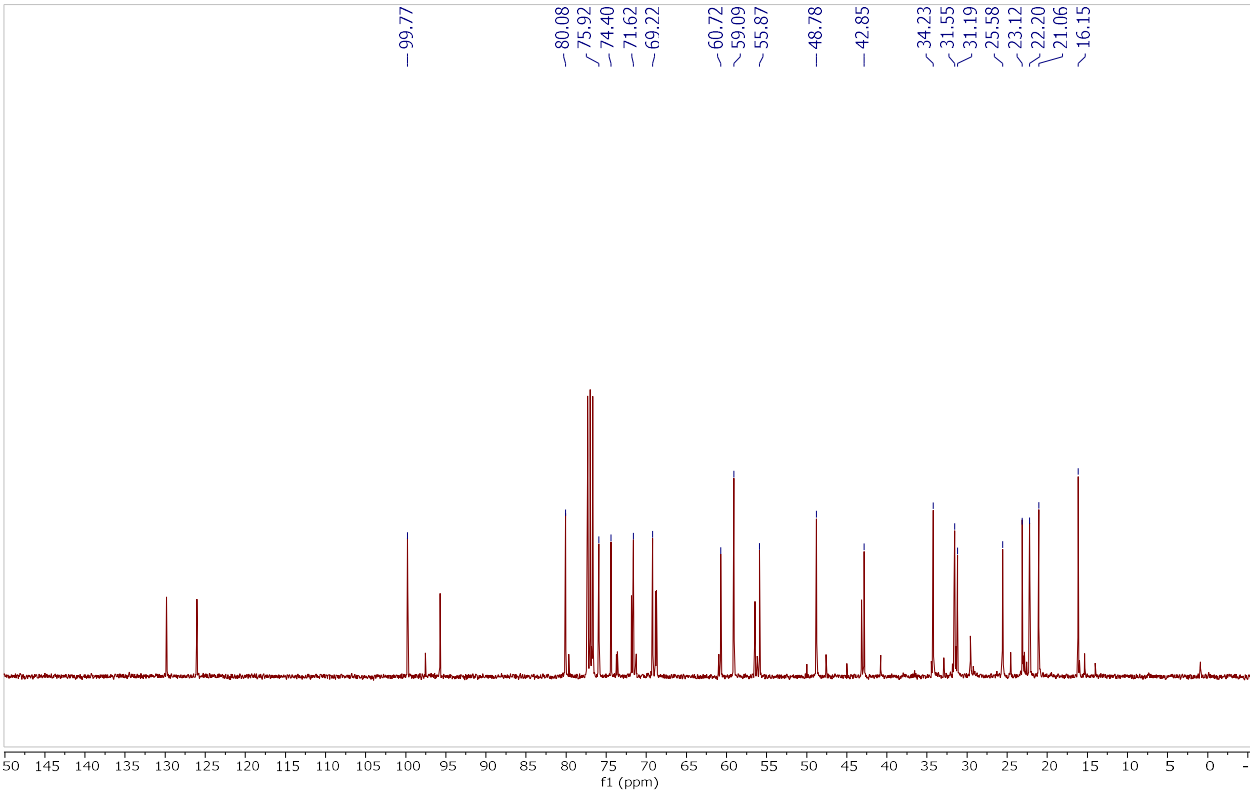
^{13}C NMR spectrum of compound **3ca** in $CDCl_3$ (101 MHz)



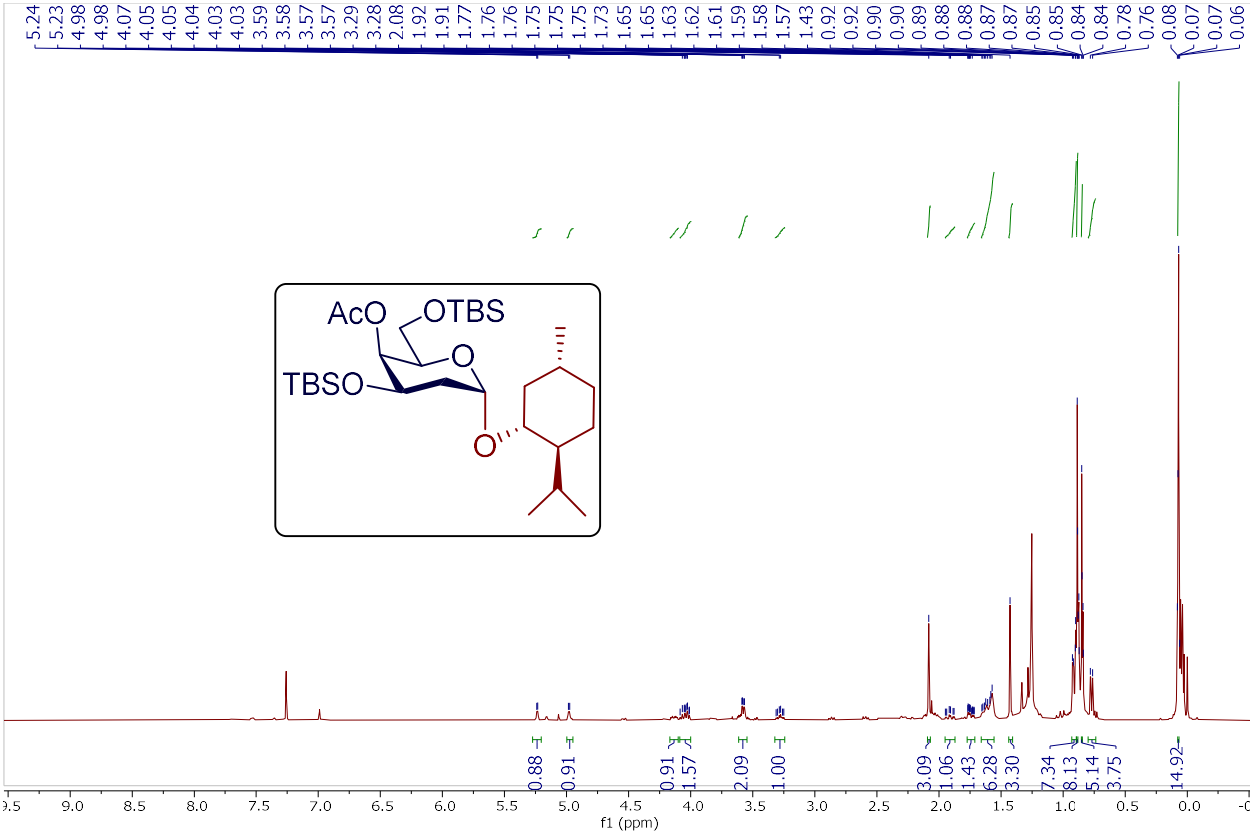
^{1}H NMR spectrum of compound **3da** in $CDCl_3$ (400 MHz)



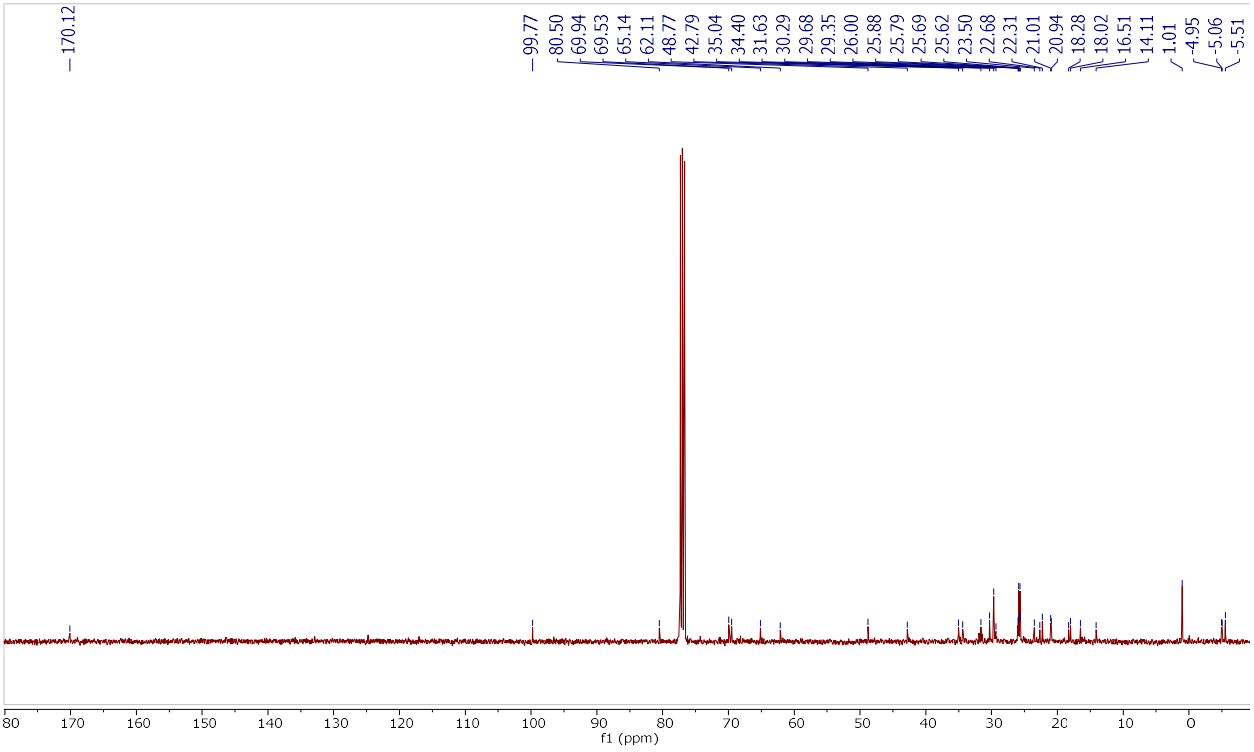
^{13}C NMR spectrum of compound **3da** in $CDCl_3$ (101 MHz)



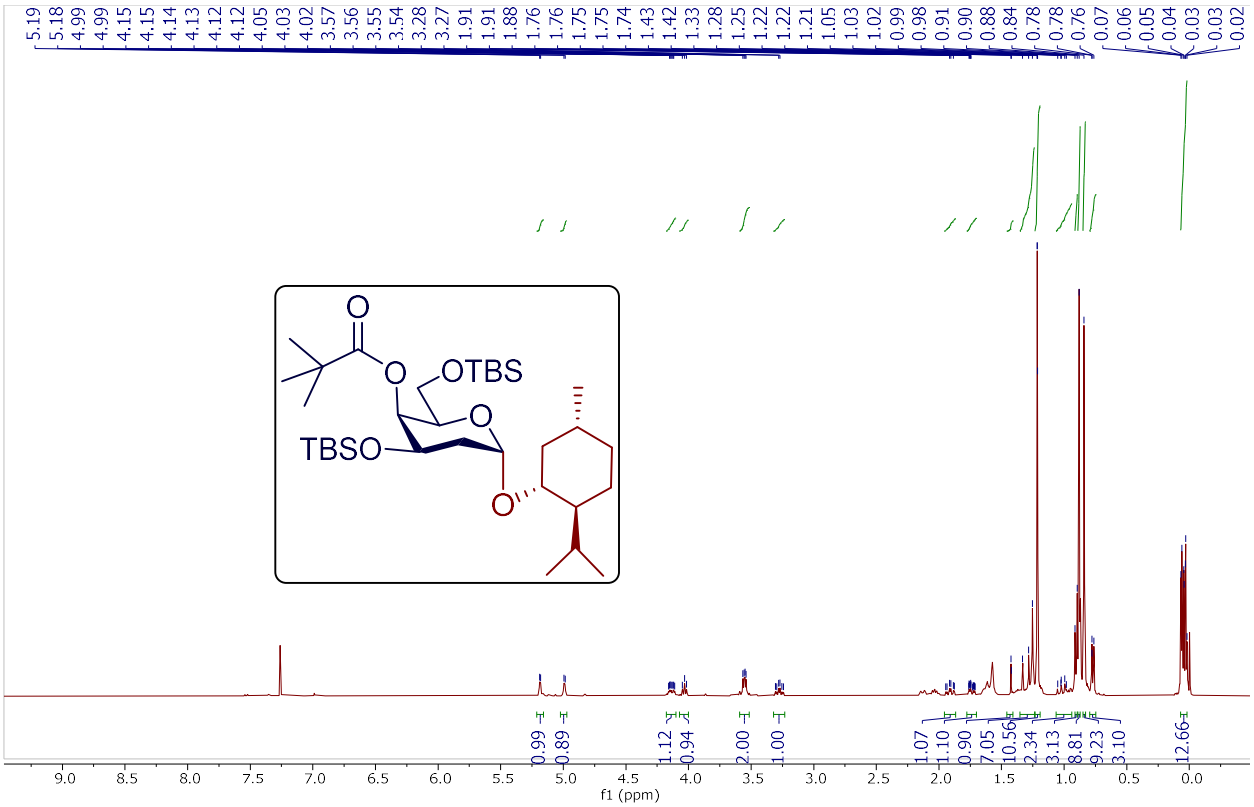
^{1}H NMR spectrum of compound **3fa** in $CDCl_3$ (400 MHz)



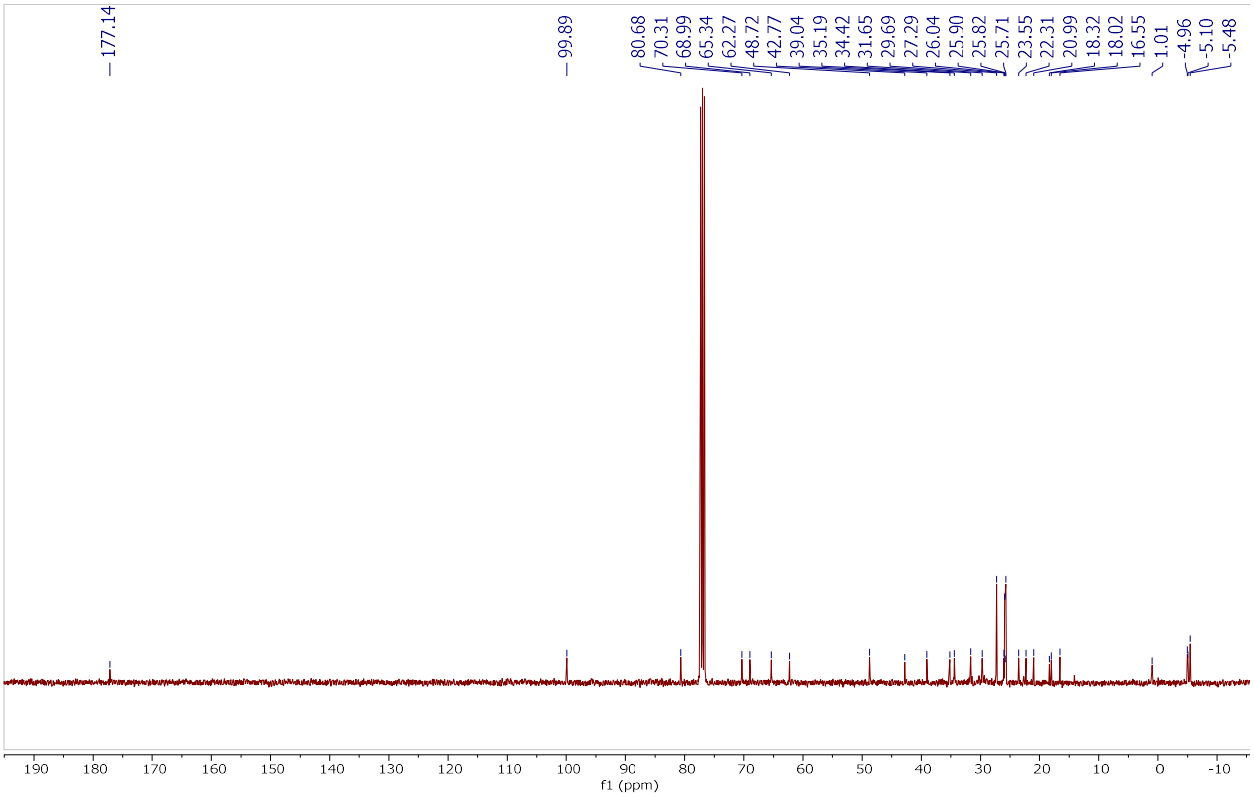
^{13}C NMR spectrum of compound **3fa** in $CDCl_3$ (101 MHz)



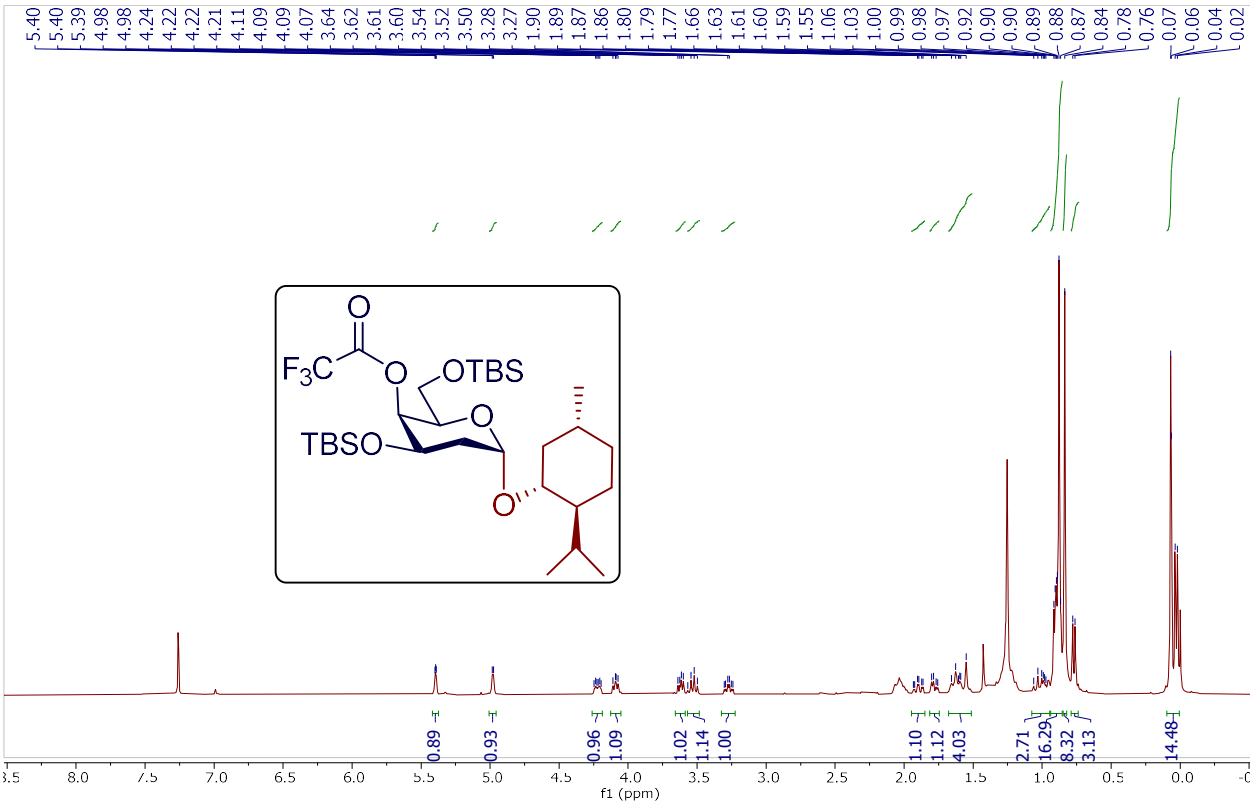
^{1}H NMR spectrum of compound **3ga** in $CDCl_3$ (400 MHz)



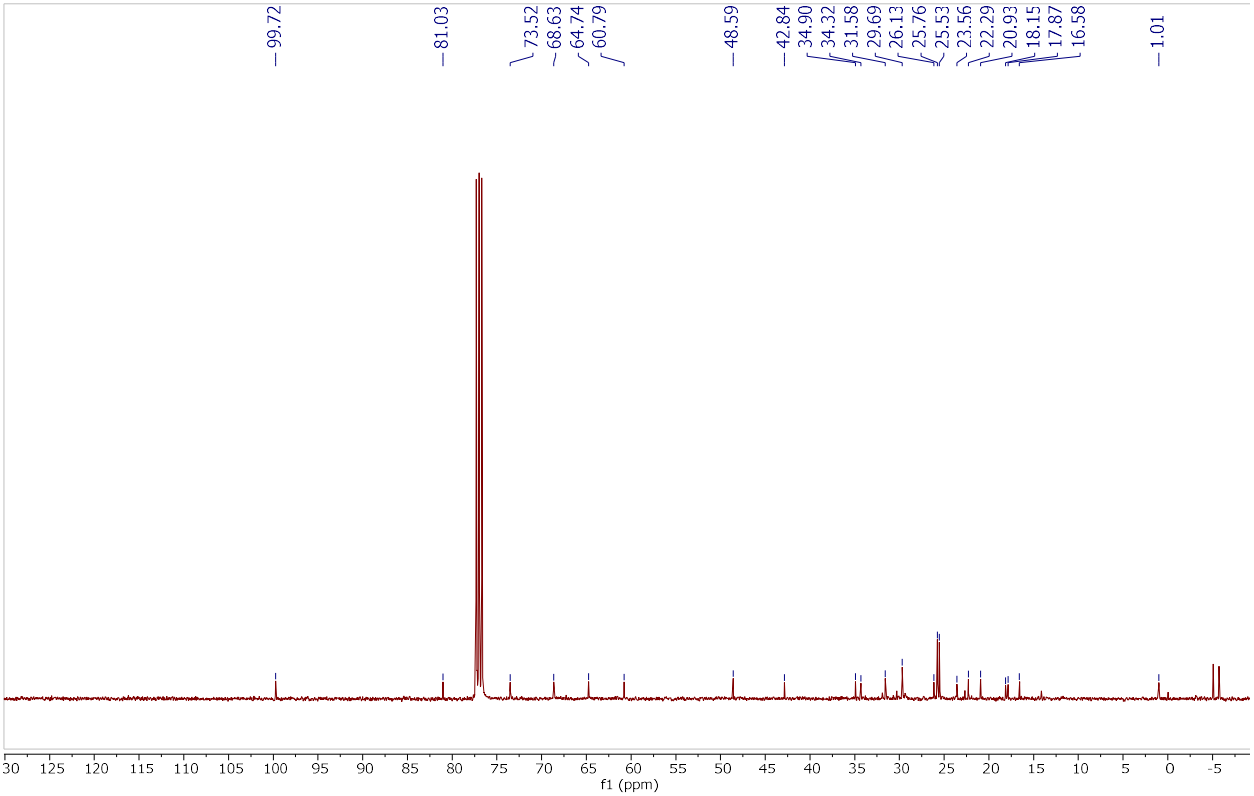
^{13}C NMR spectrum of compound **3ga** in $CDCl_3$ (101 MHz)



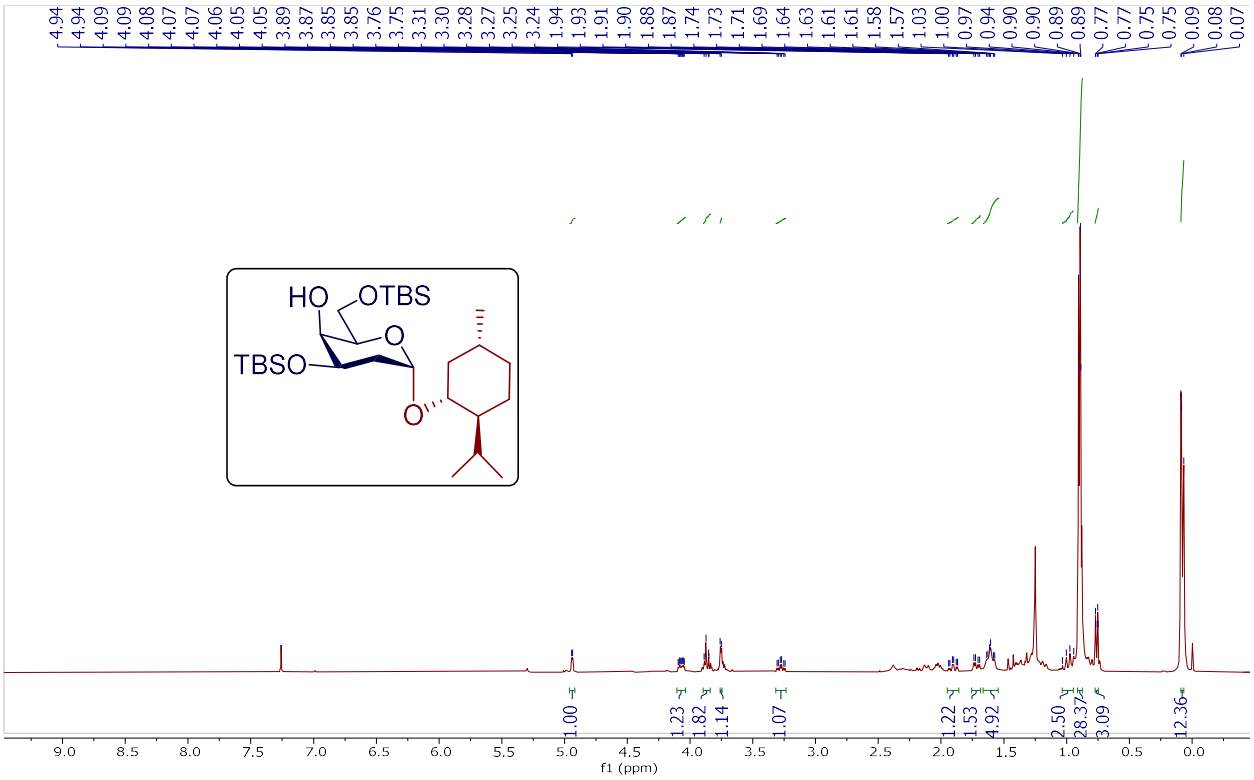
^{1}H NMR spectrum of compound **3ha** in $CDCl_3$ (400 MHz)



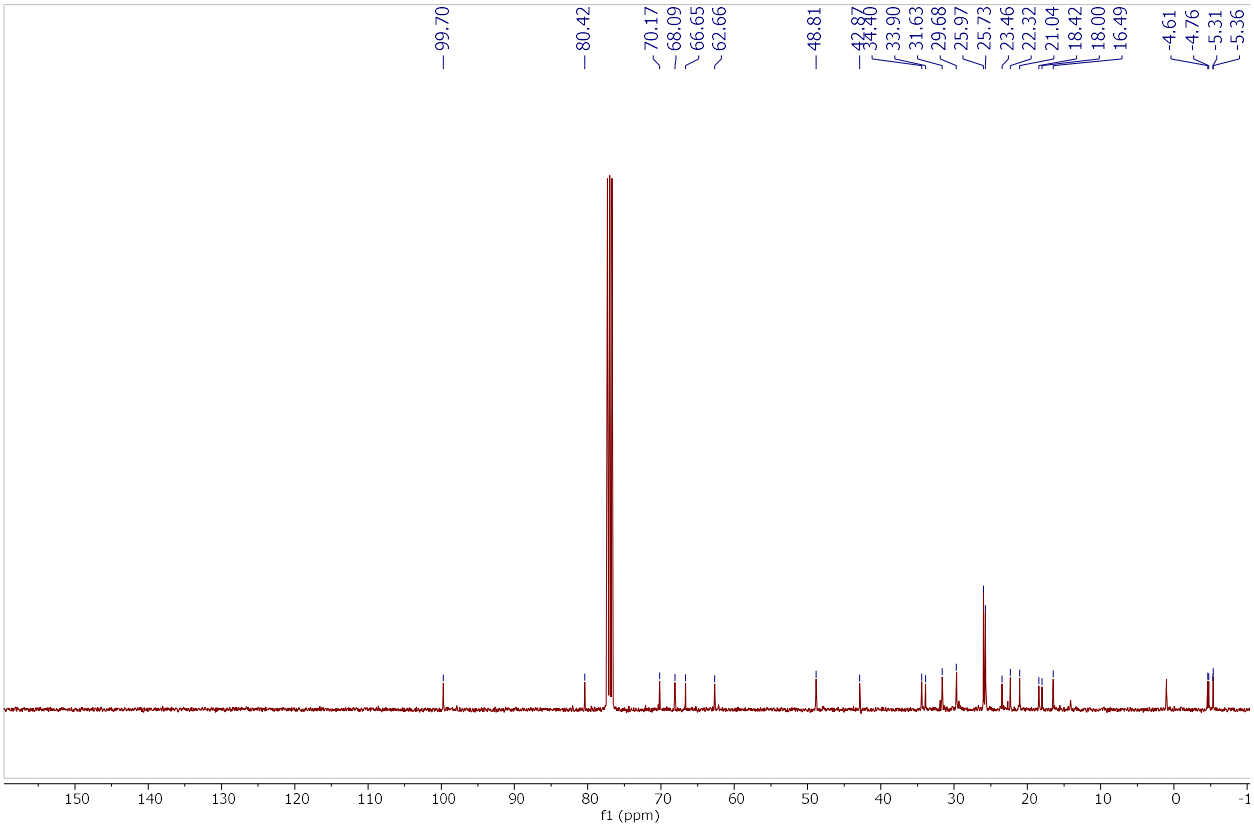
^{13}C NMR spectrum of compound **3ha** in $CDCl_3$ (101 MHz)



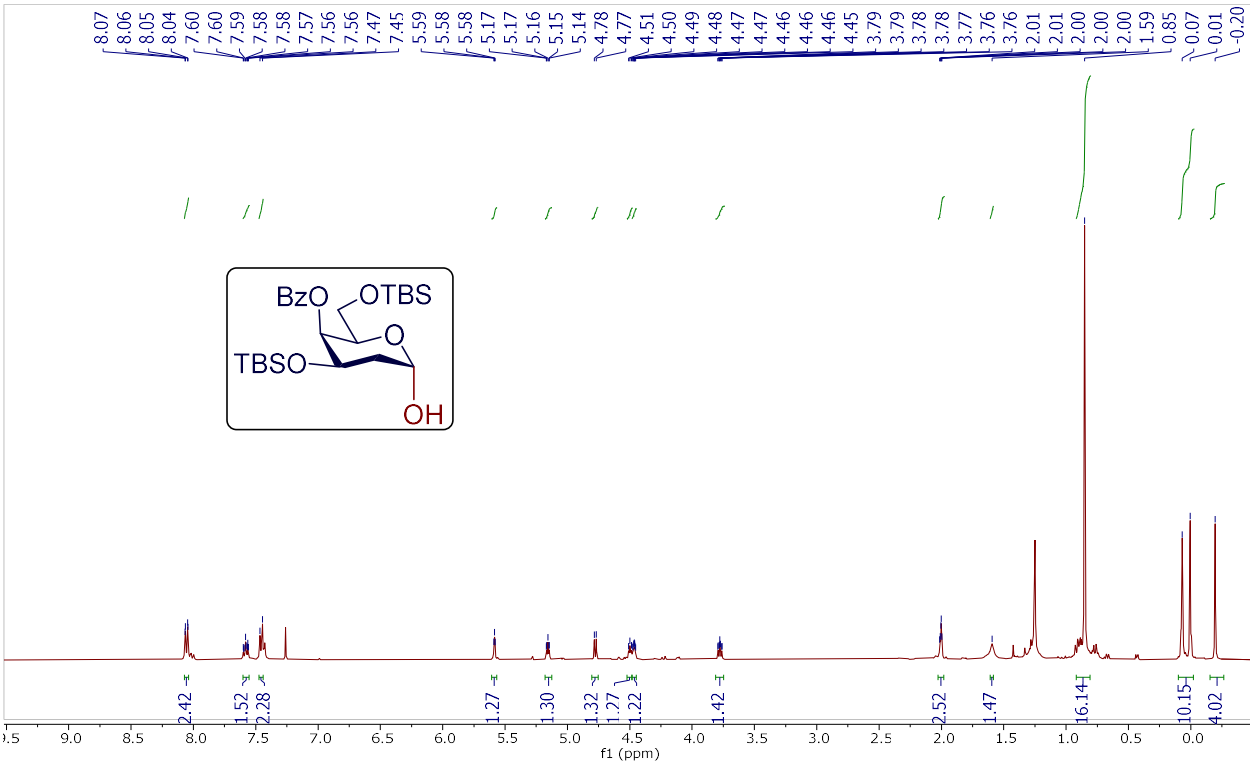
^{1}H NMR spectrum of compound **3ia** in $CDCl_3$ (400 MHz)



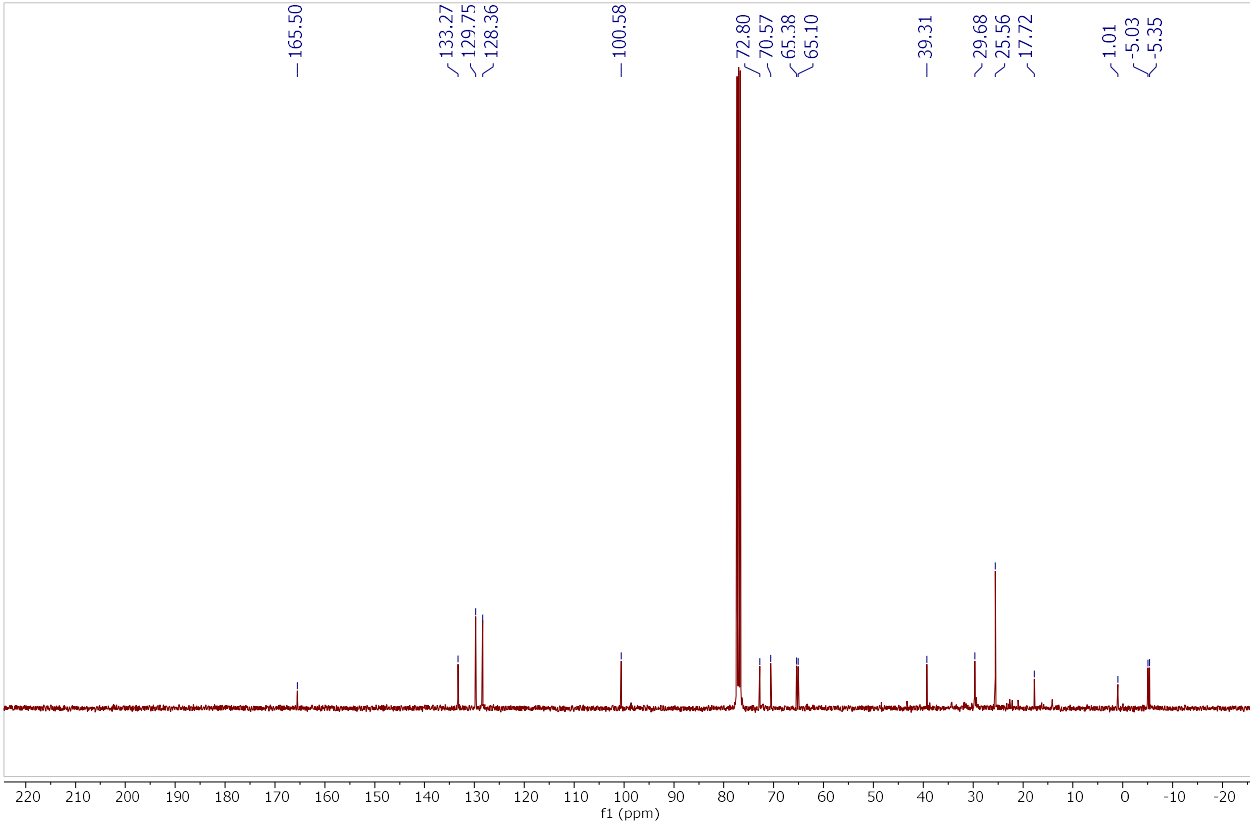
^{13}C NMR spectrum of compound **3ia** in $CDCl_3$ (101 MHz)



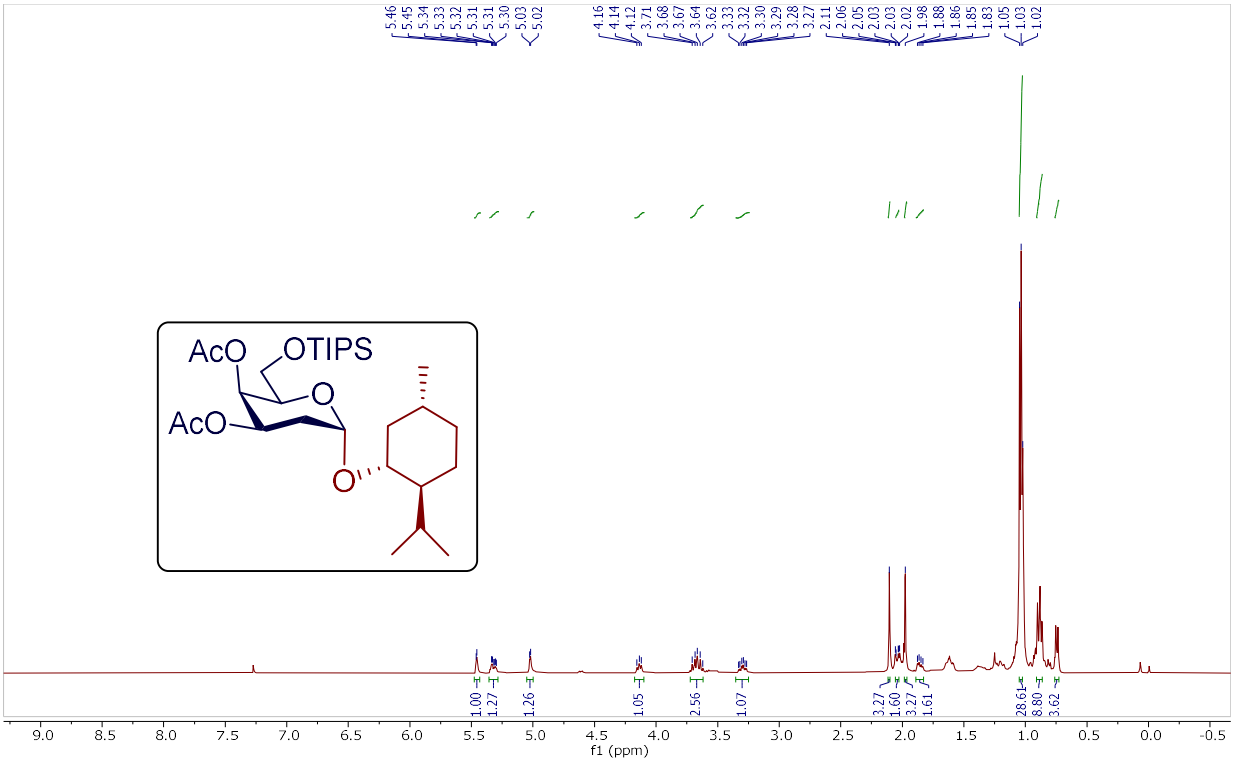
^{1}H NMR spectrum of compound **3ja** in $CDCl_3$ (400 MHz)



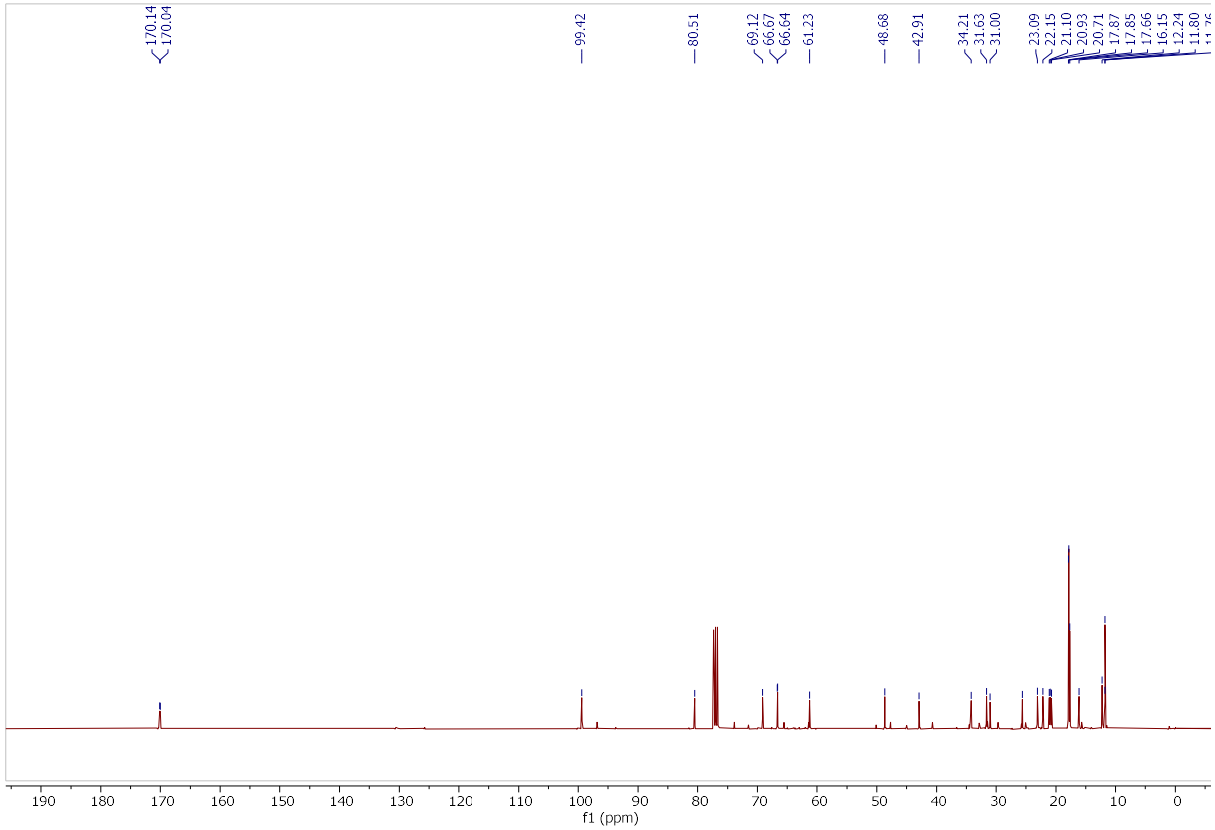
^{13}C NMR spectrum of compound **3ja** in $CDCl_3$ (101 MHz)



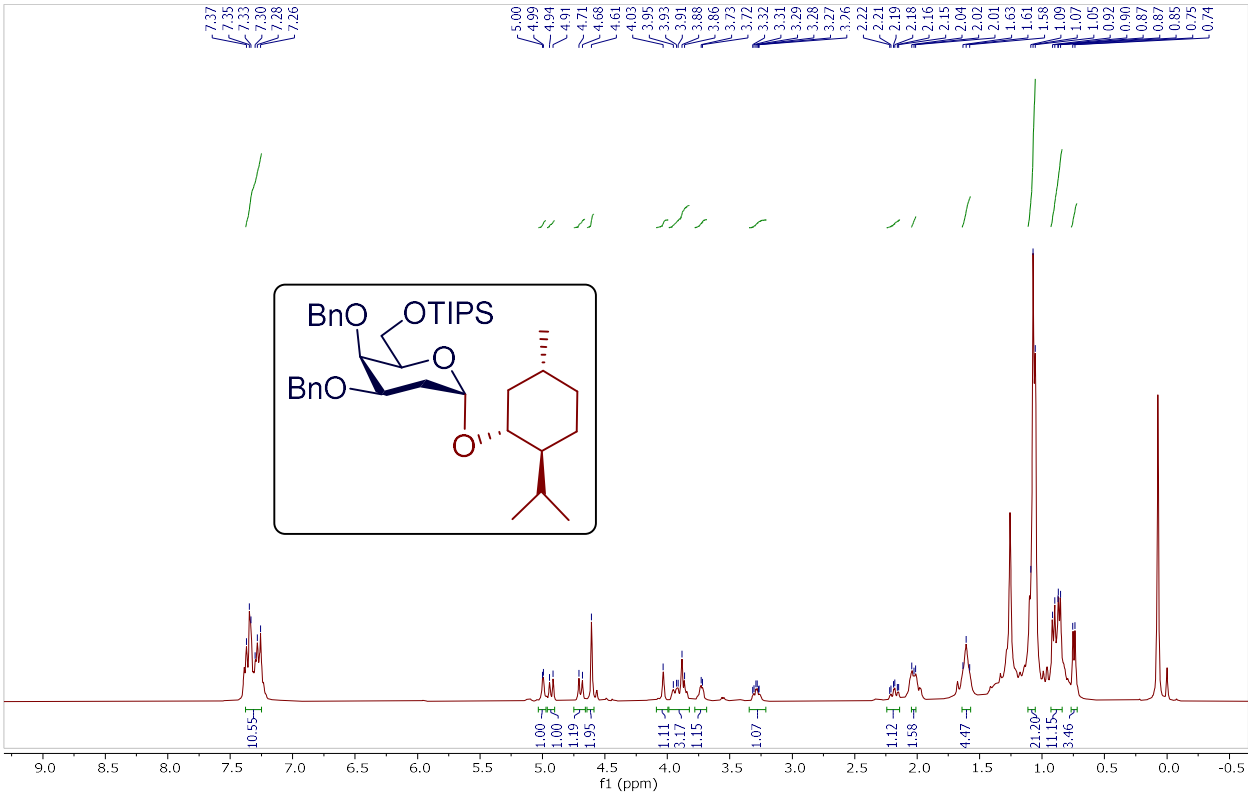
^{1}H NMR spectrum of compound **3la** in $CDCl_3$ (400 MHz)



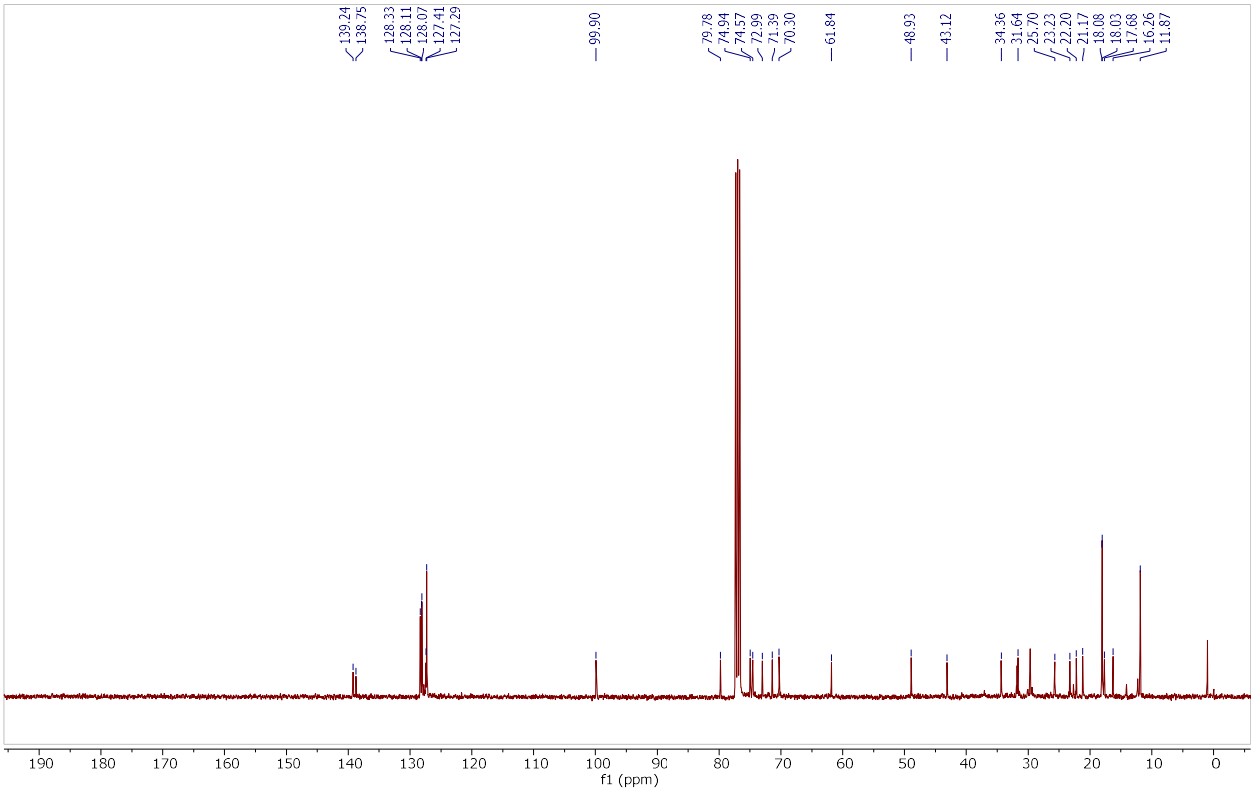
^{13}C NMR spectrum of compound **3la** in $CDCl_3$ (101 MHz)



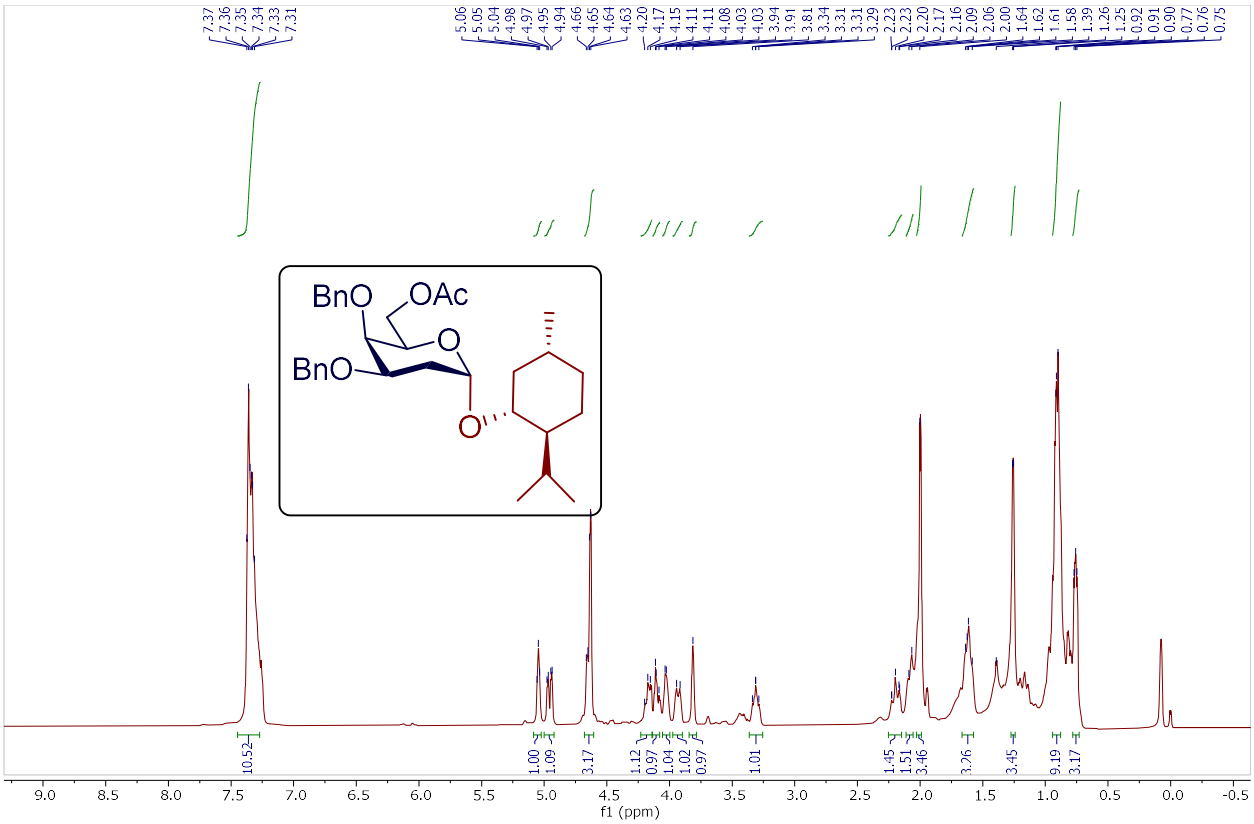
^{1}H NMR spectrum of compound **3ma** in $CDCl_3$ (400 MHz)



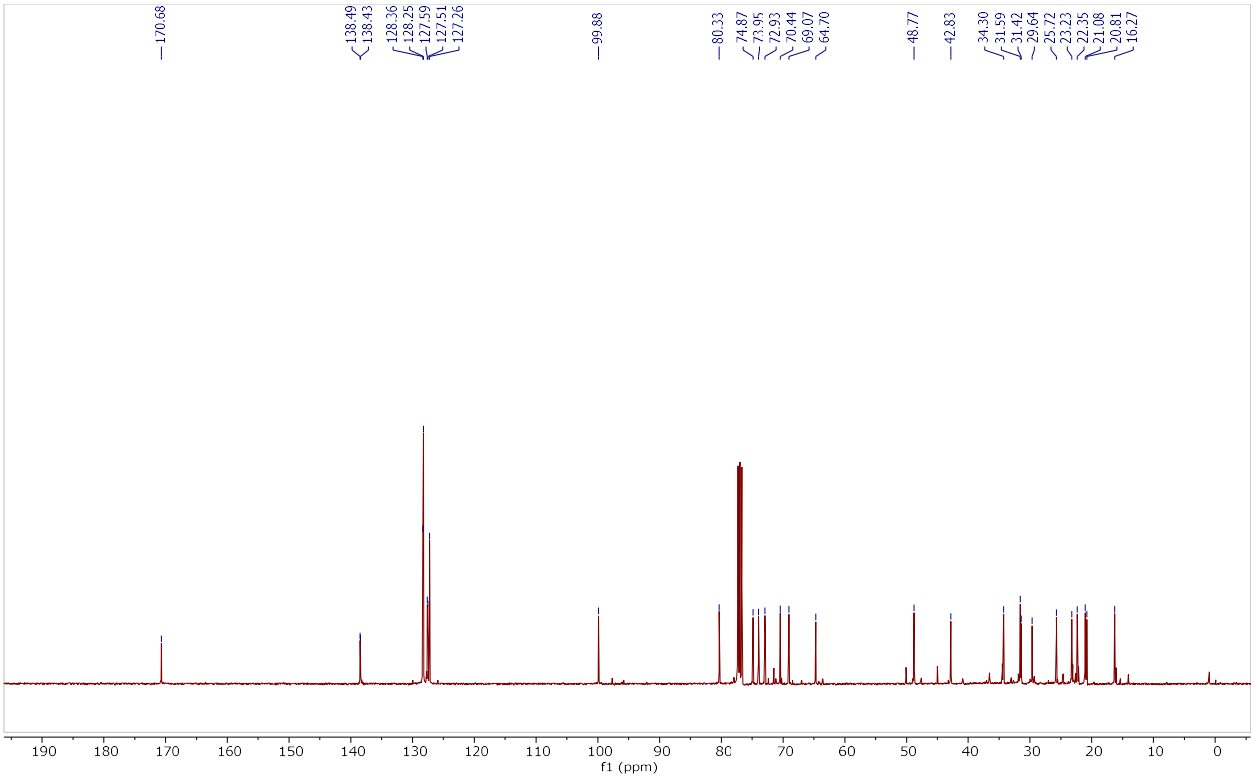
^{13}C NMR spectrum of compound **3ma** in $CDCl_3$ (101 MHz)



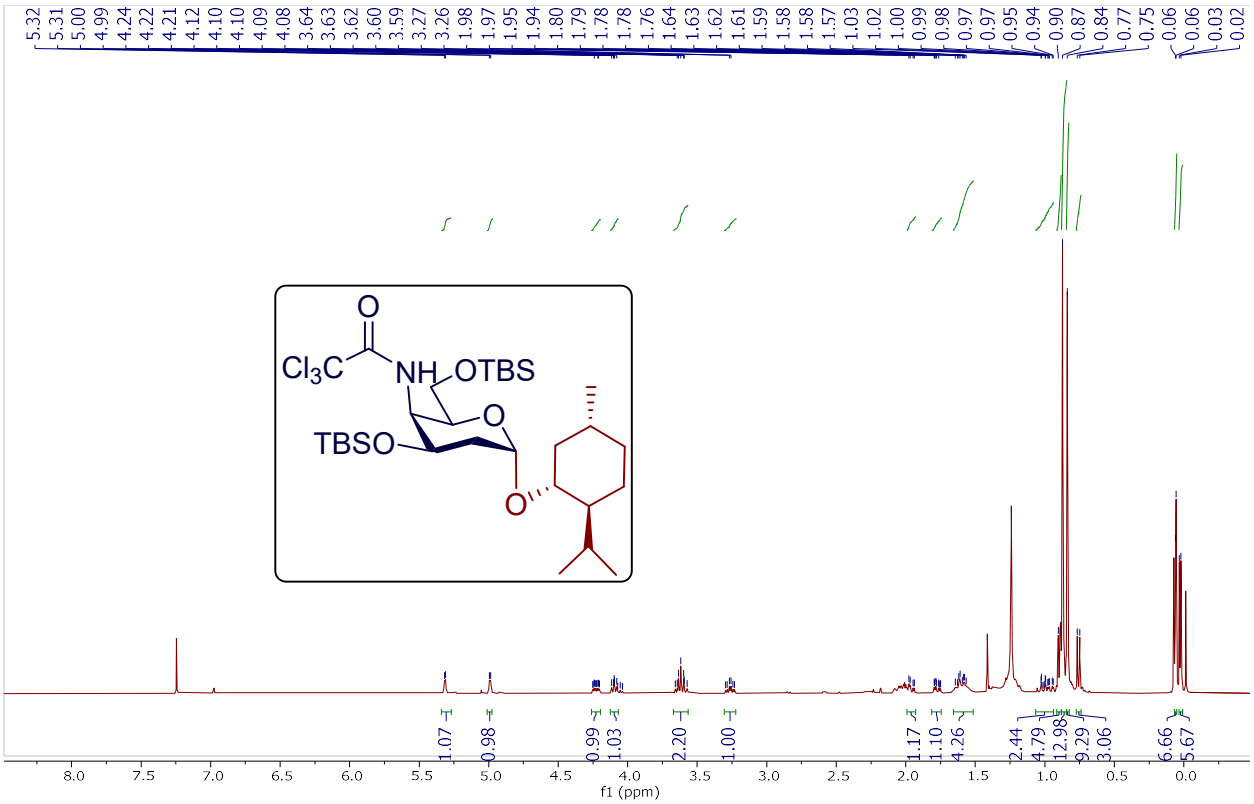
^{1}H NMR spectrum of compound **3na** in $CDCl_3$ (400 MHz)



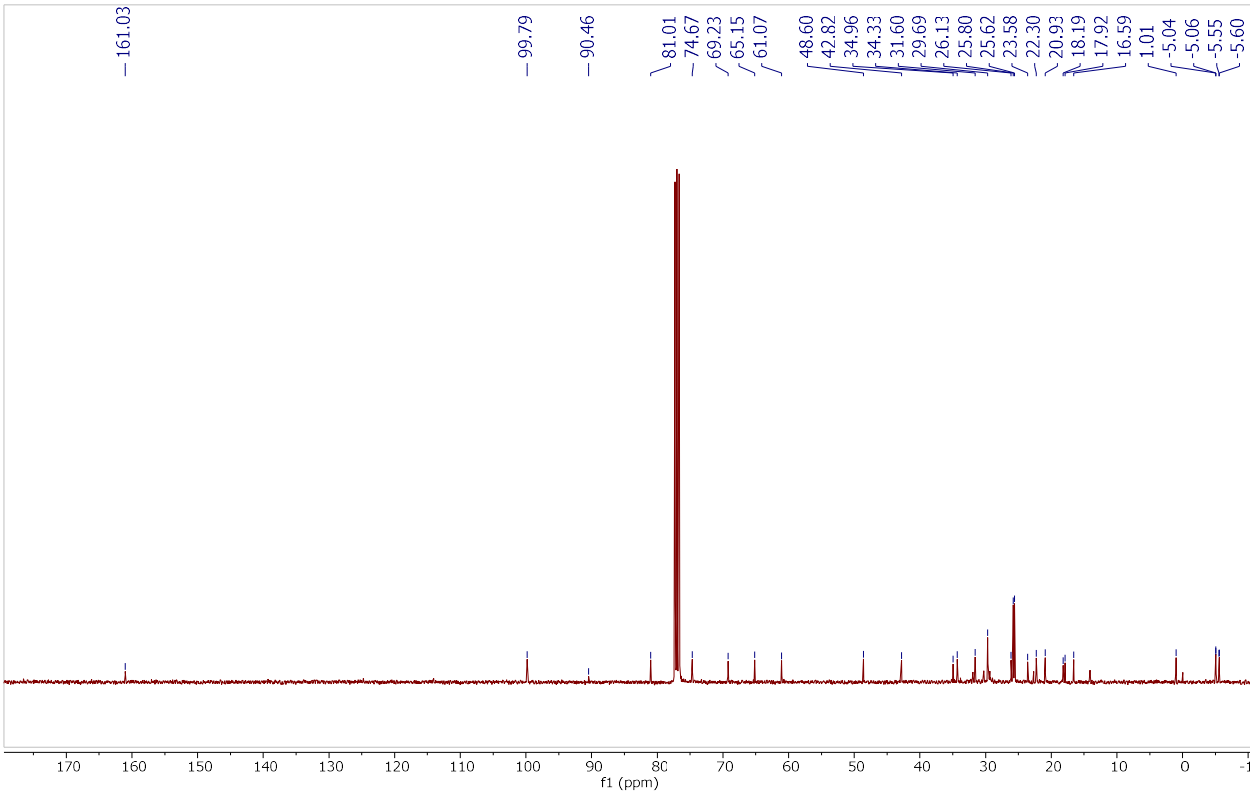
^{13}C NMR spectrum of compound **3na** in $CDCl_3$ (101 MHz)



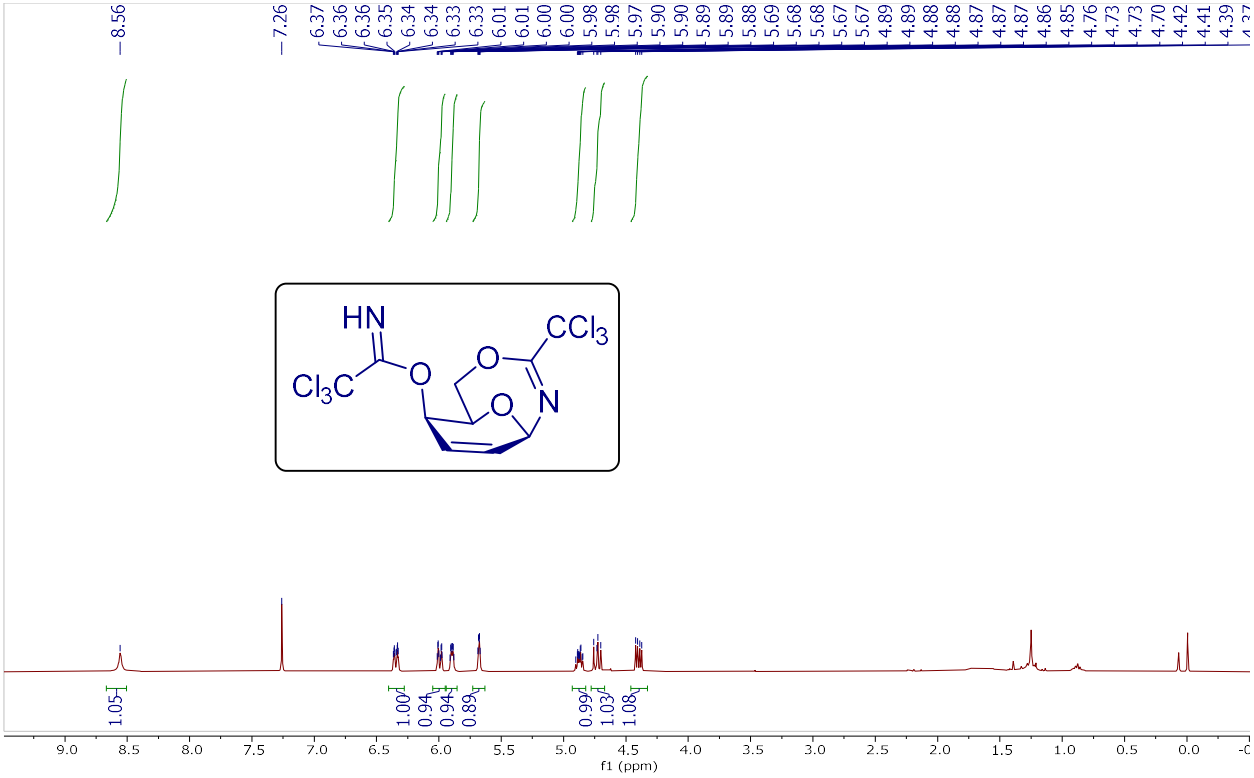
^{1}H NMR spectrum of compound **3oa'** in $CDCl_3$ (400 MHz)



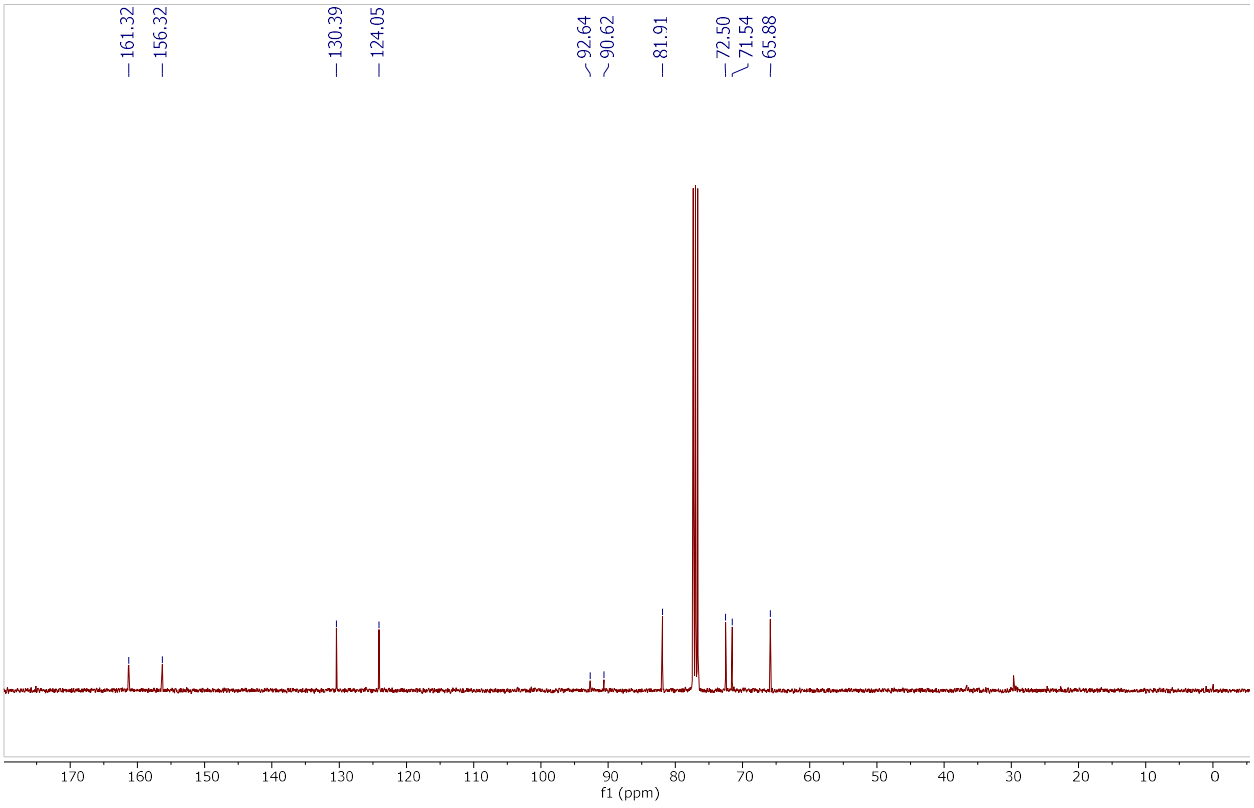
^{13}C NMR spectrum of compound **3oa'** in $CDCl_3$ (101 MHz)



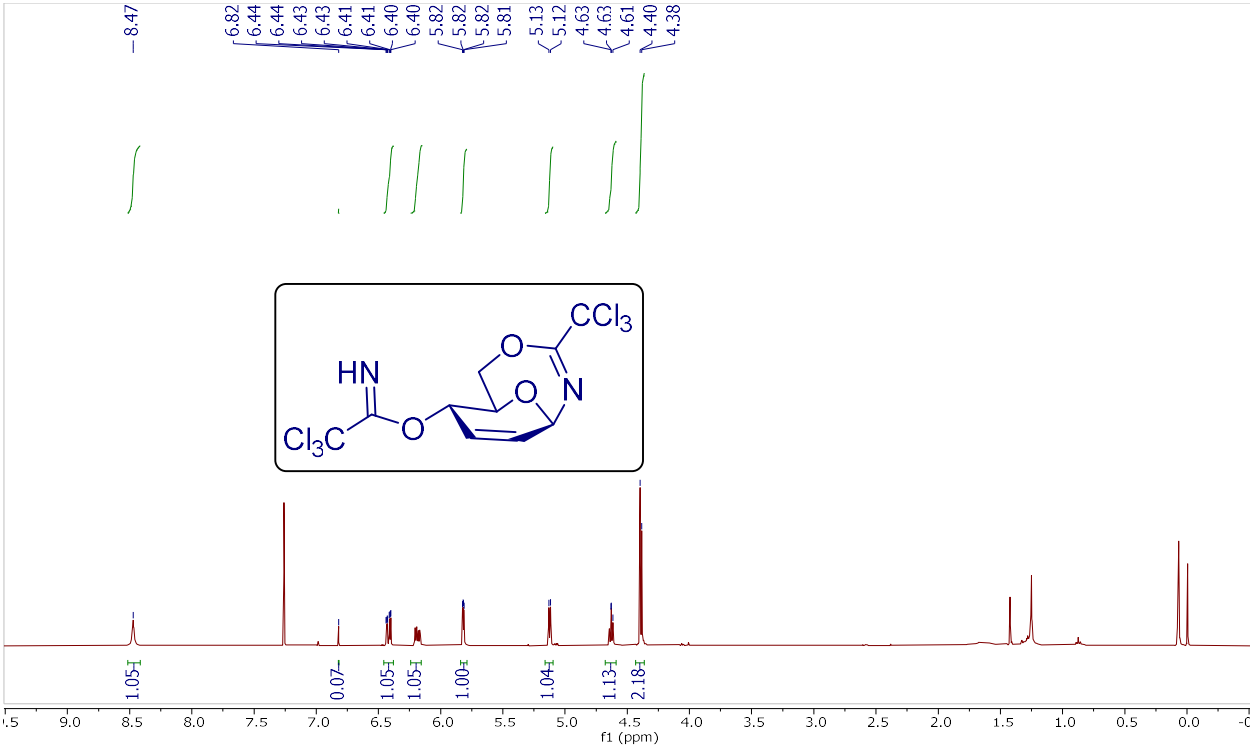
^{1}H NMR spectrum of compound **4** in $CDCl_3$ (400 MHz)



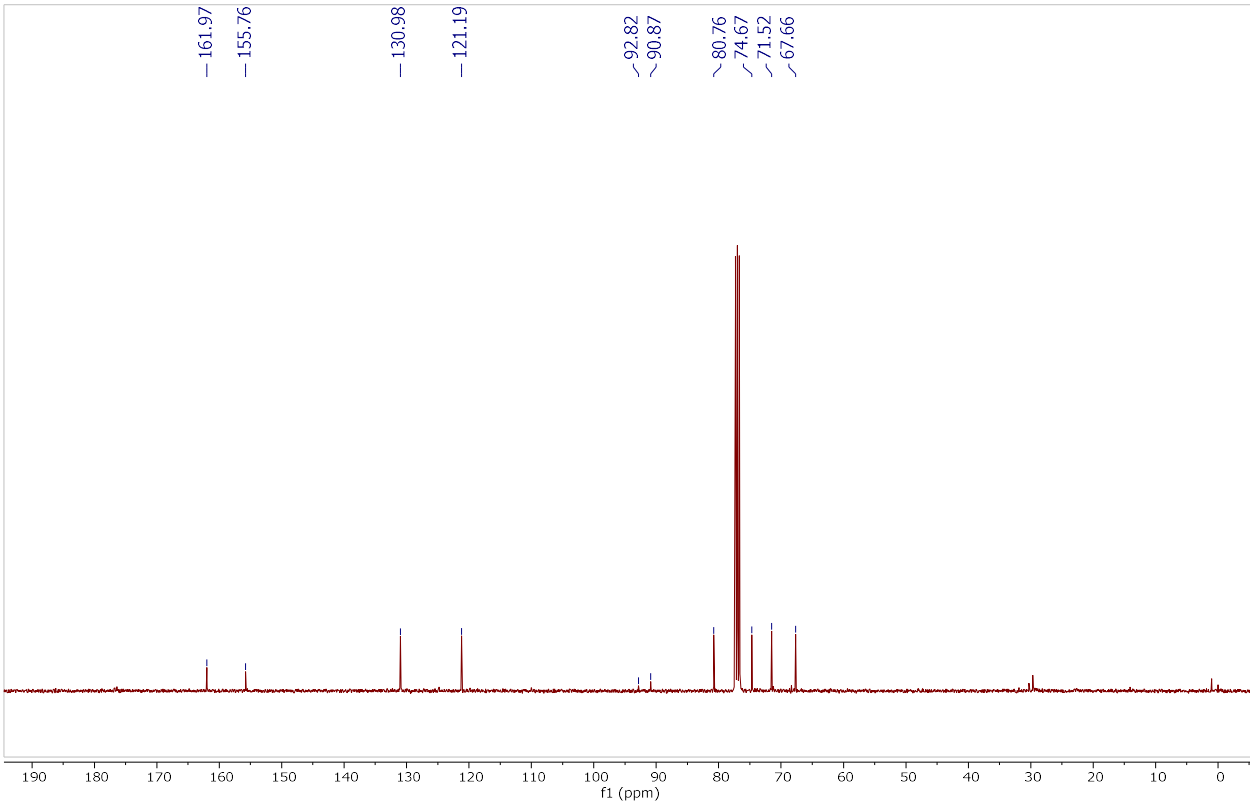
^{13}C NMR spectrum of compound **4** in $CDCl_3$ (101 MHz)



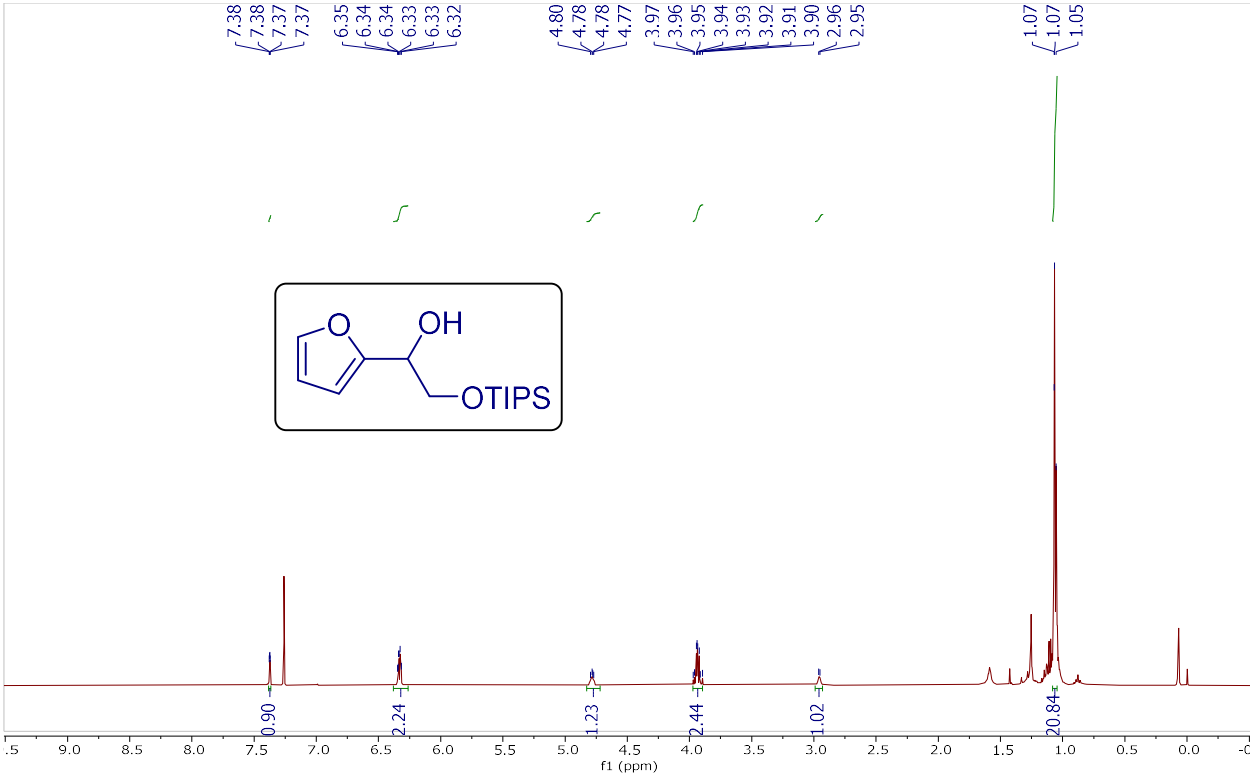
^{1}H NMR spectrum of compound **5** in $CDCl_3$ (400 MHz)



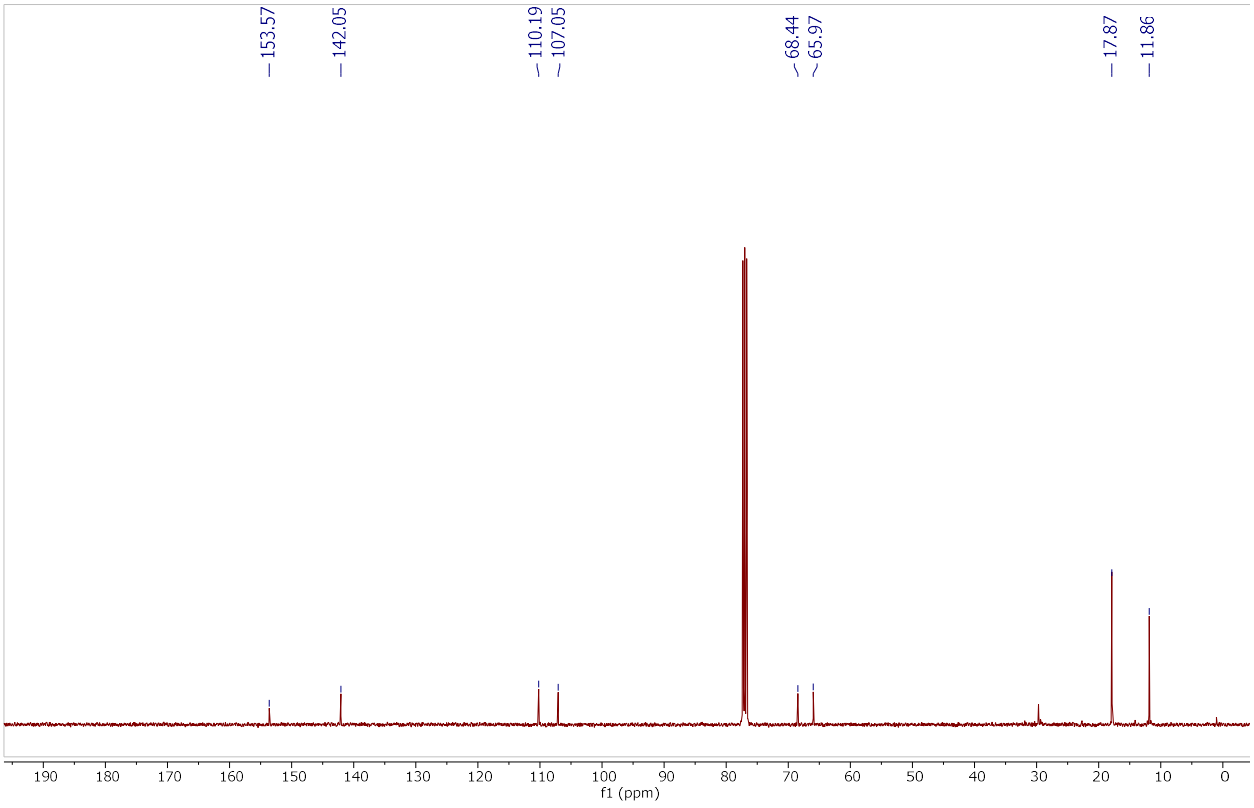
^{13}C NMR spectrum of compound **5** in $CDCl_3$ (101 MHz)



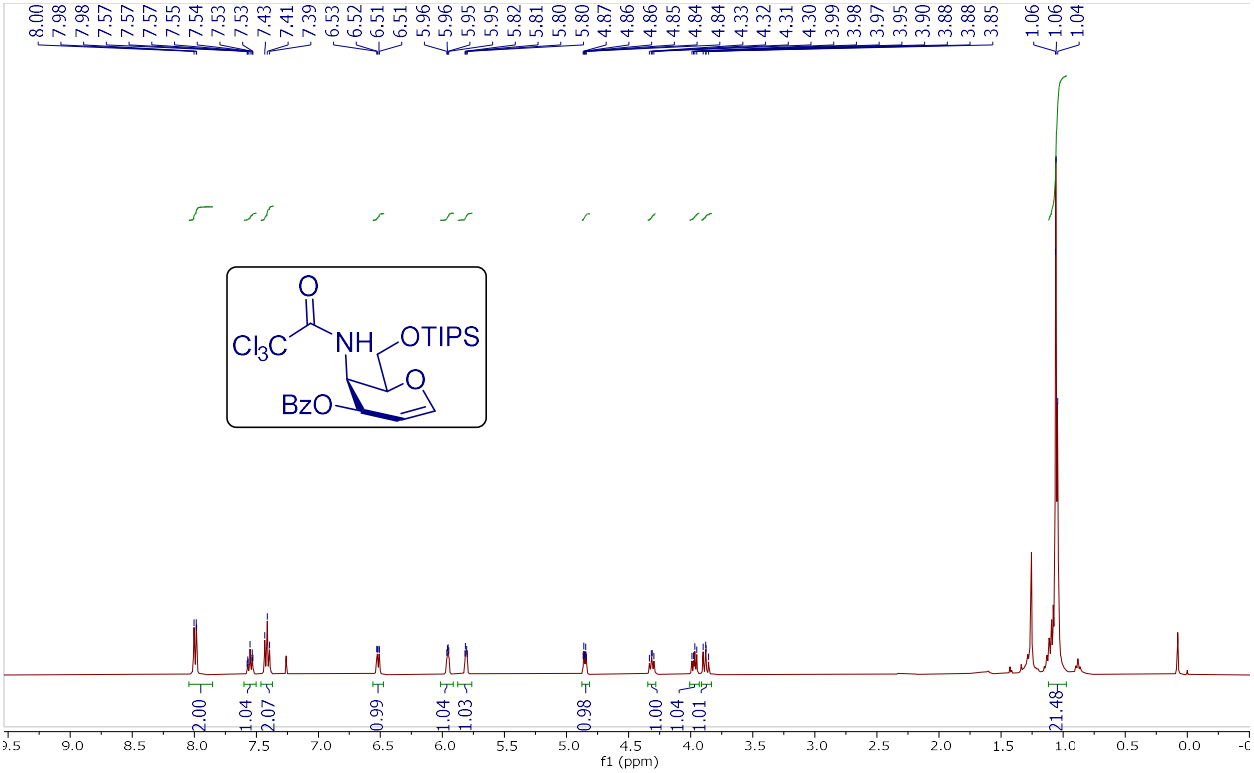
^{1}H NMR spectrum of compound **6** in $CDCl_3$ (400 MHz)



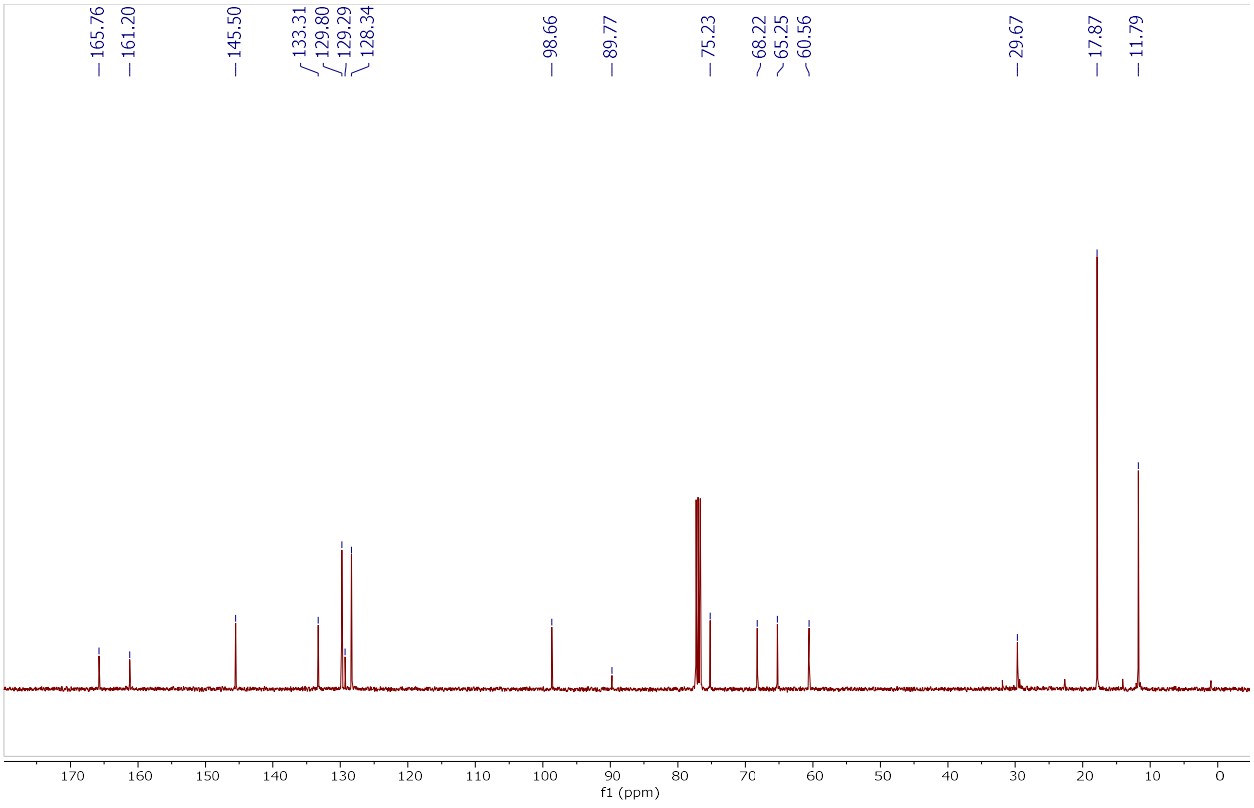
^{13}C NMR spectrum of compound **6** in $CDCl_3$ (101 MHz)



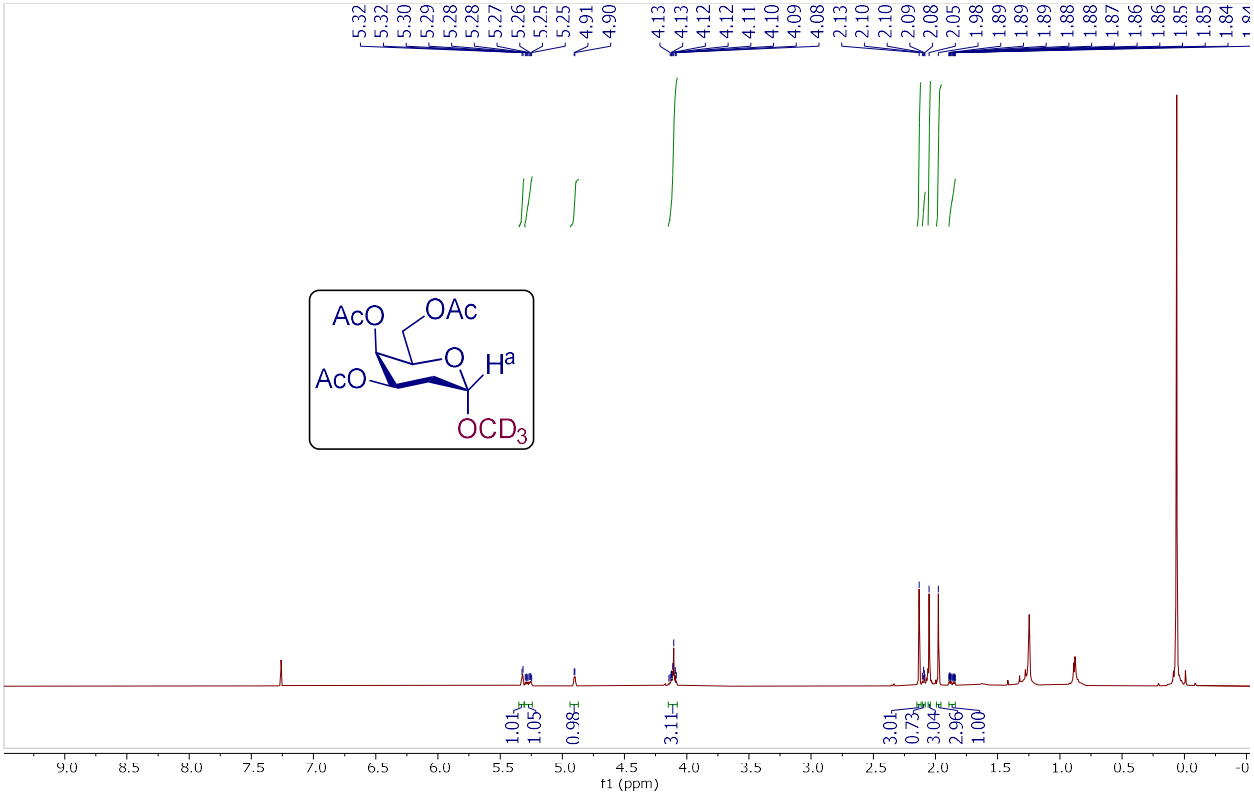
^{1}H NMR spectrum of compound **7** in $CDCl_3$ (400 MHz)



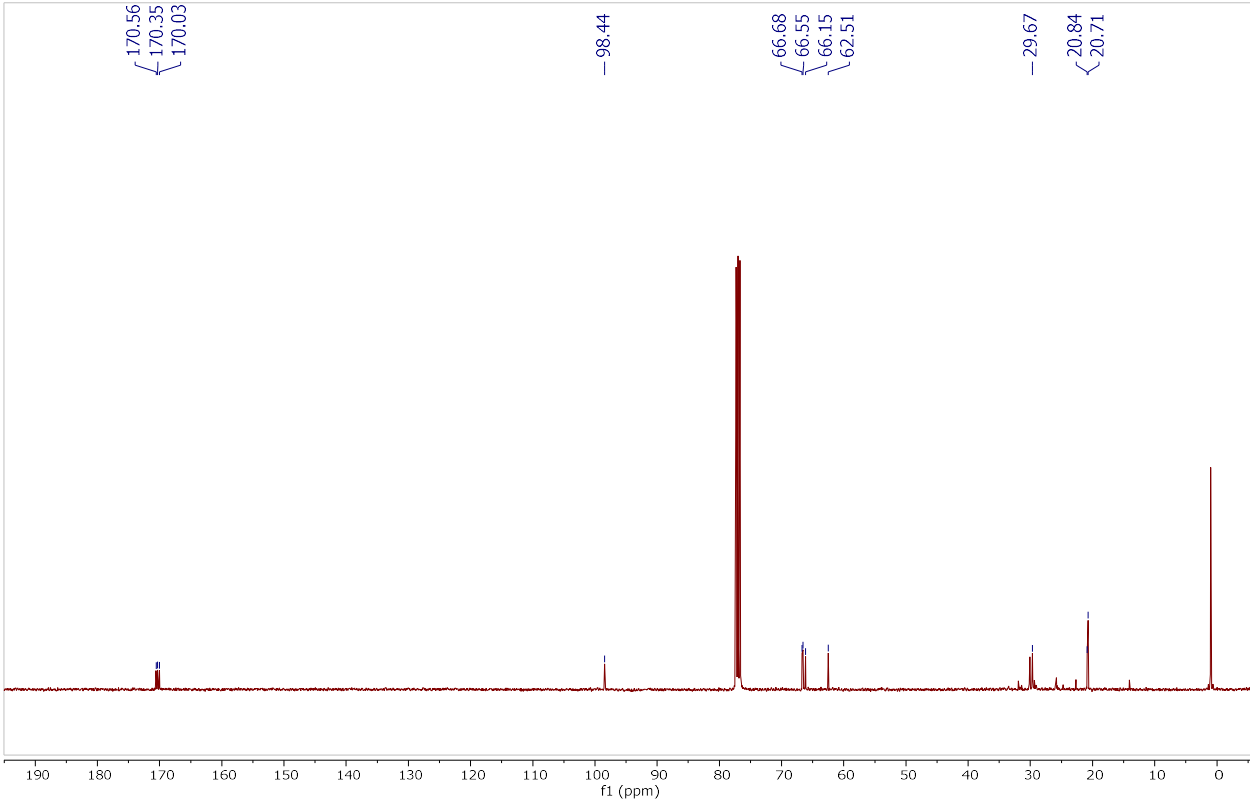
^{13}C NMR spectrum of compound **7** in $CDCl_3$ (101 MHz)



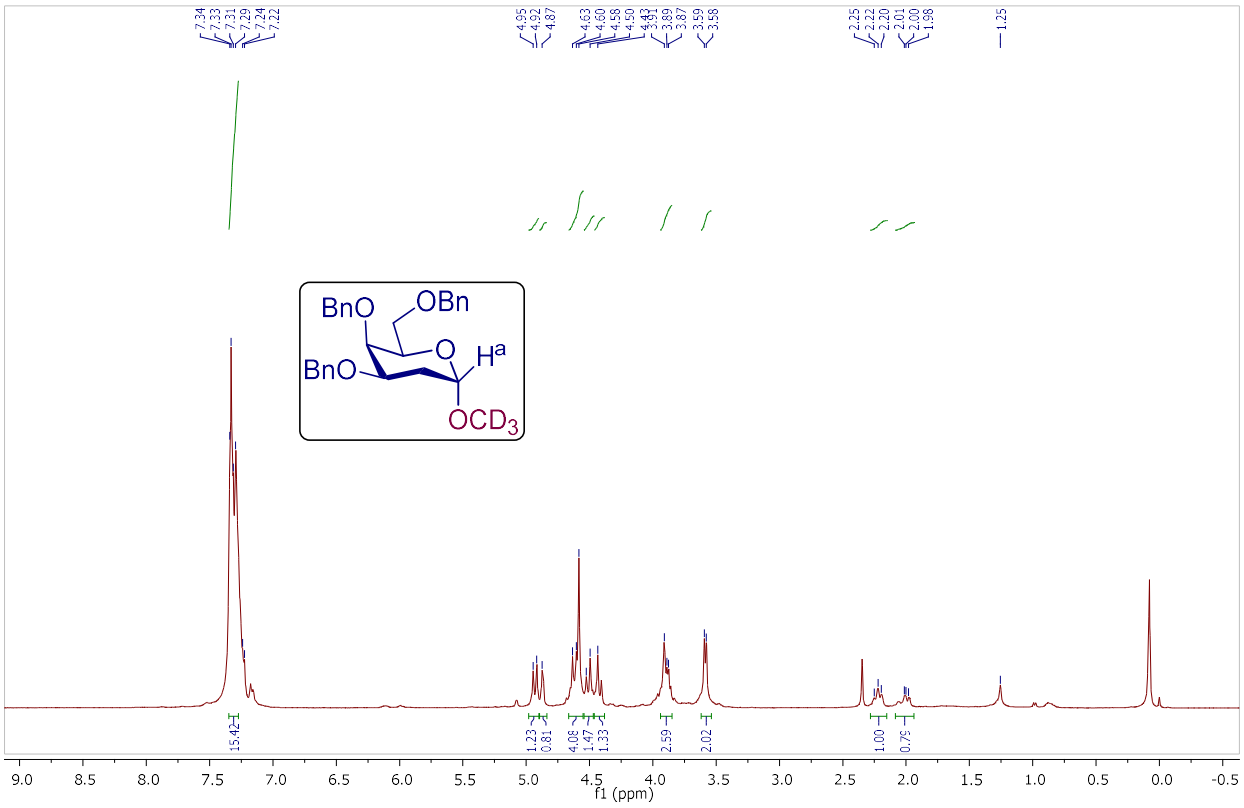
^{1}H NMR spectrum of compound **8** in $CDCl_3$ (400 MHz)



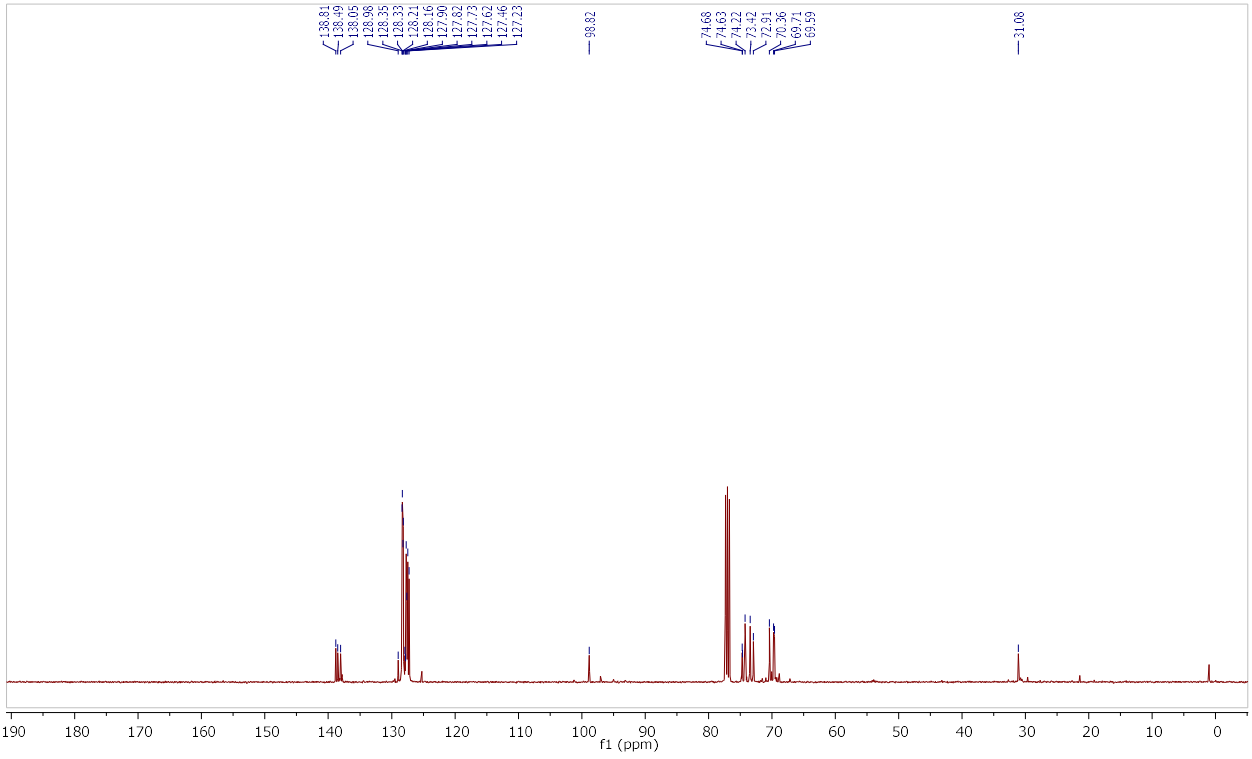
^{13}C NMR spectrum of compound **8** in $CDCl_3$ (101 MHz)



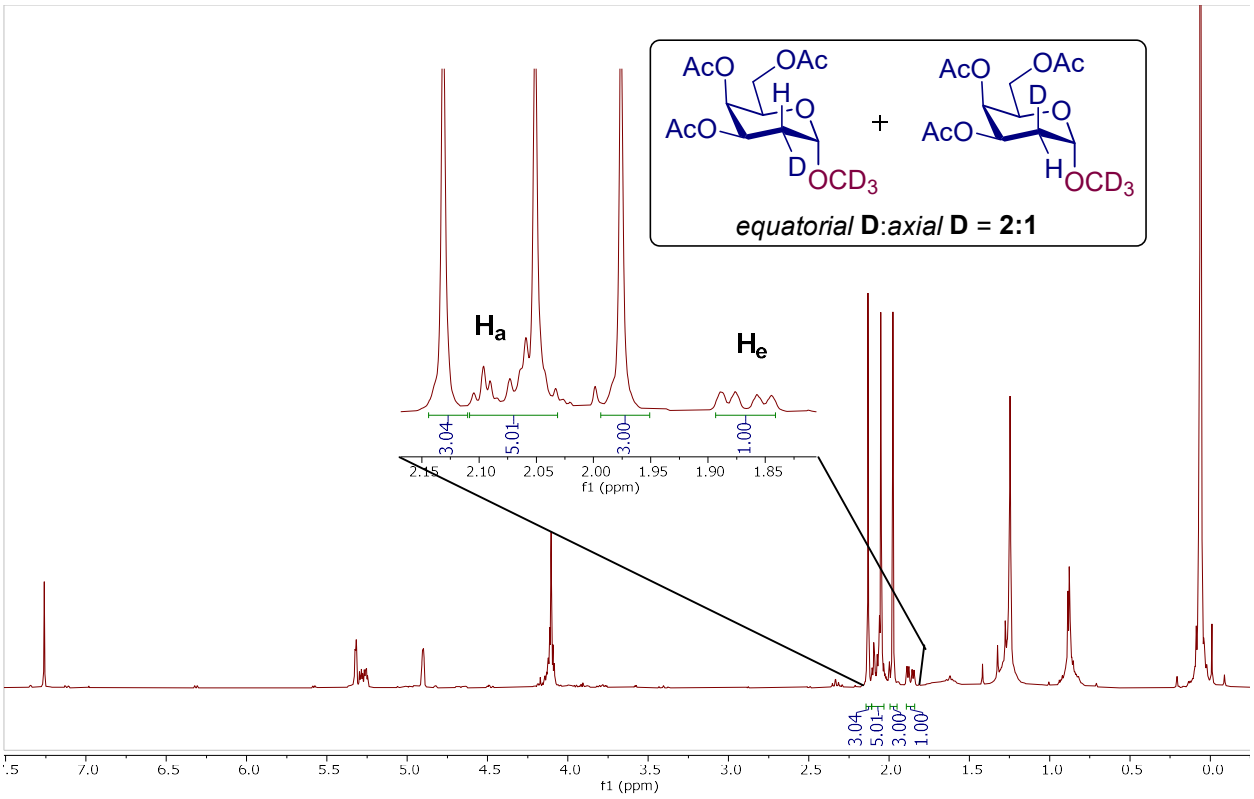
^{1}H NMR spectrum of compound **9** in $CDCl_3$ (400 MHz)



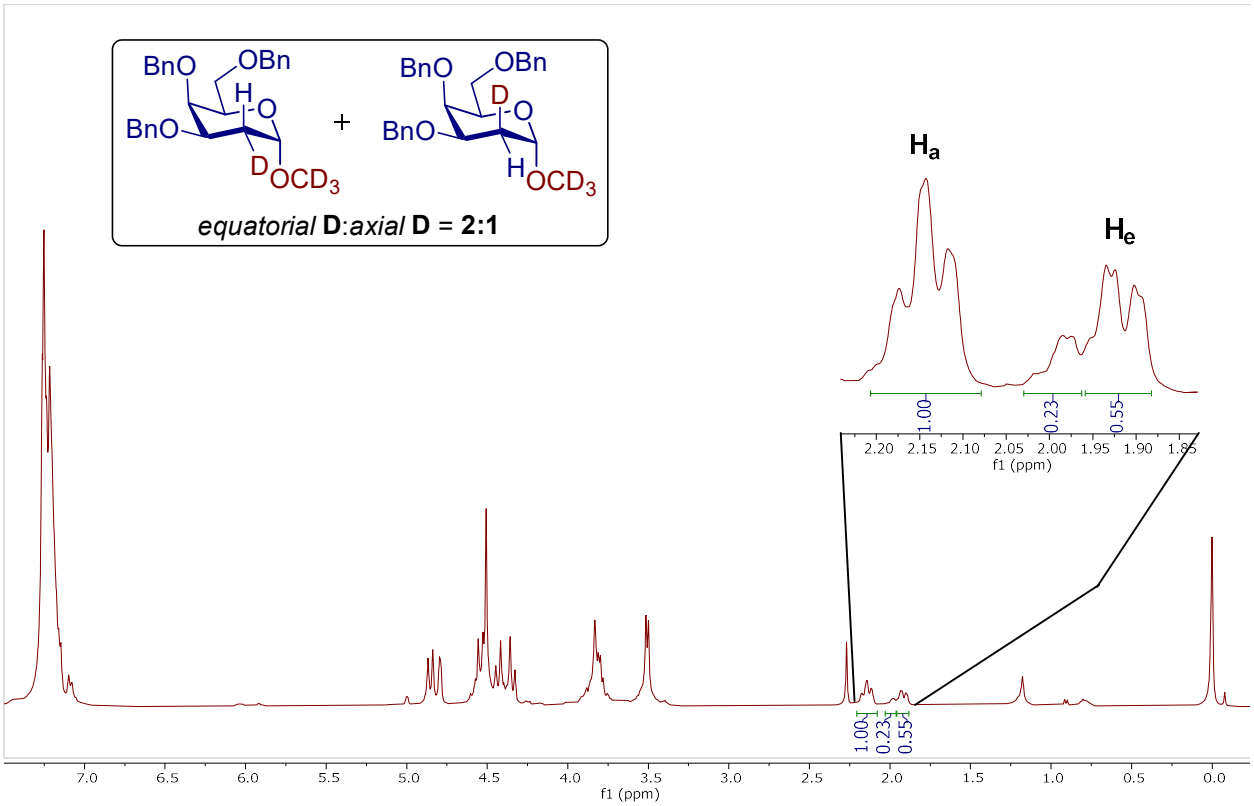
^{13}C NMR spectrum of compound **9** in $CDCl_3$ (101 MHz)



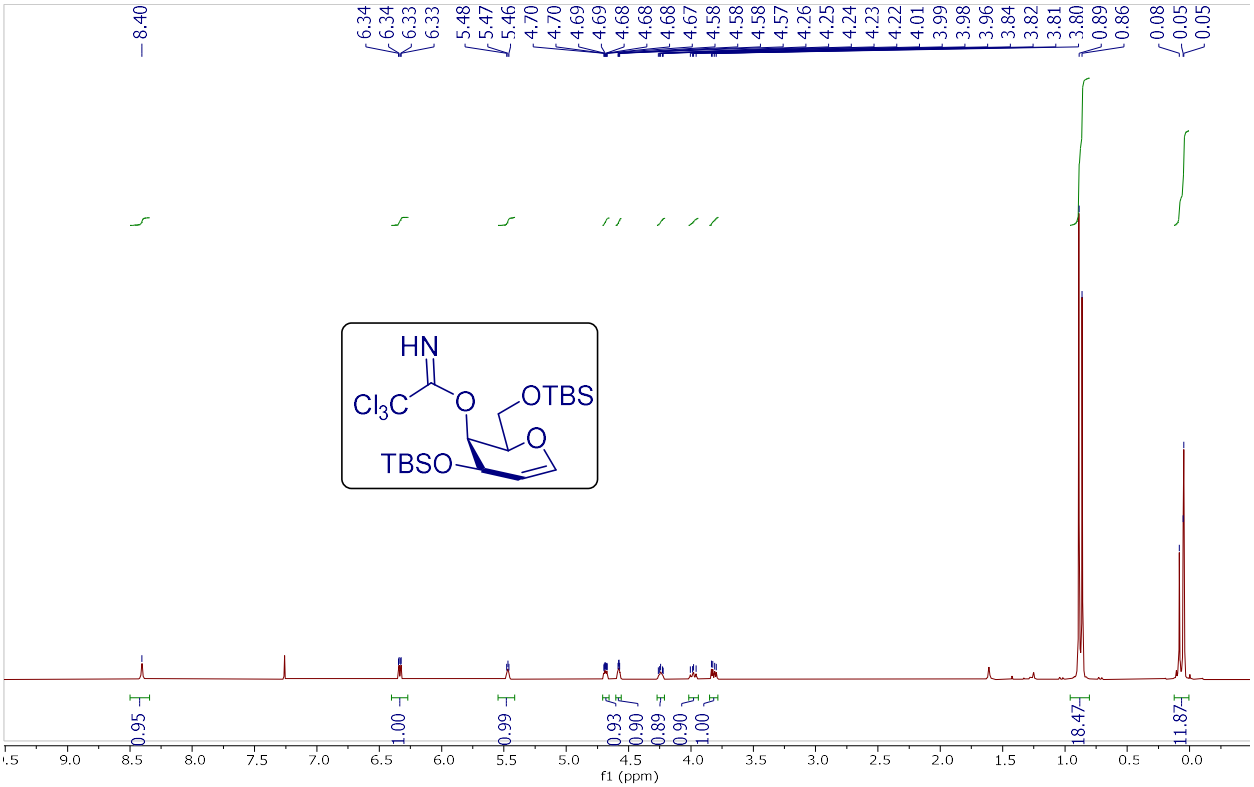
^{1}H NMR spectrum of compound **8 (*equatorial*-D:*axial*-D)** in $CDCl_3$ (400 MHz)



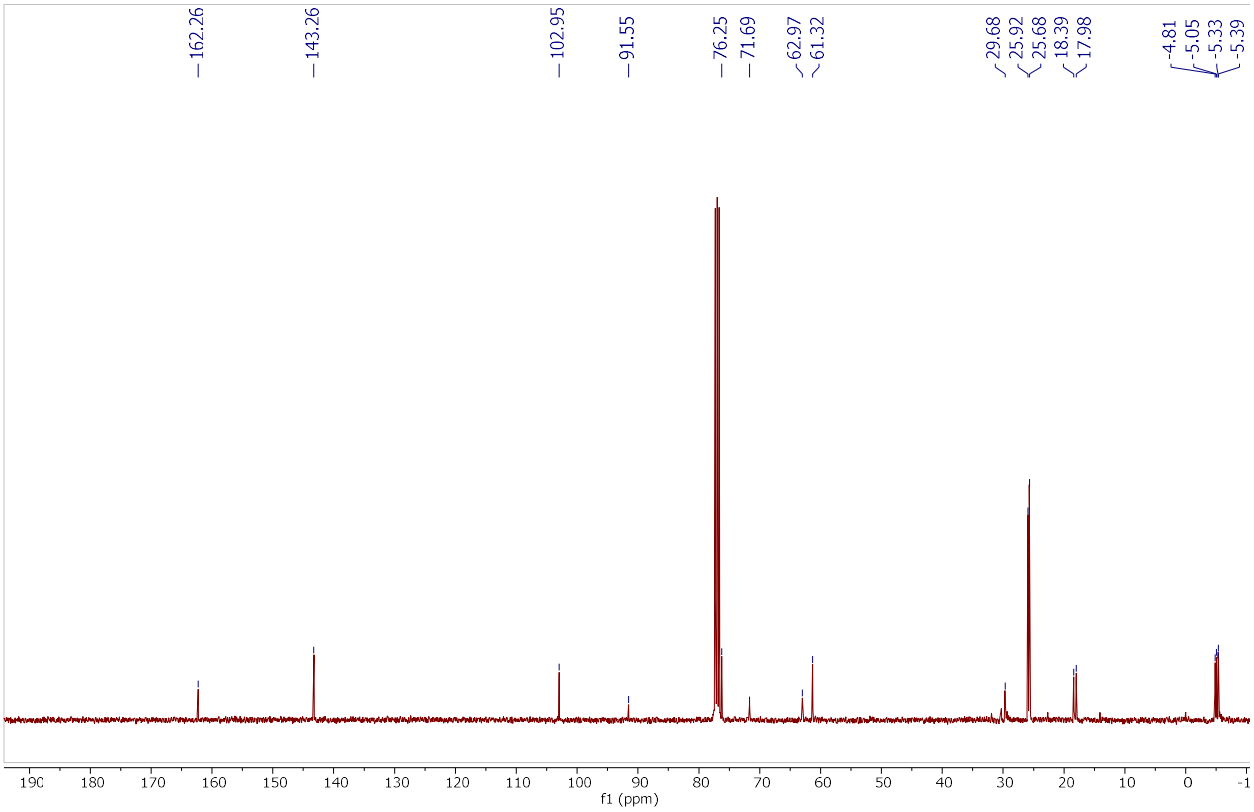
^{1}H NMR spectrum of compound **9 (*equatorial*:*axial*-D)** in $CDCl_3$ (400 MHz)



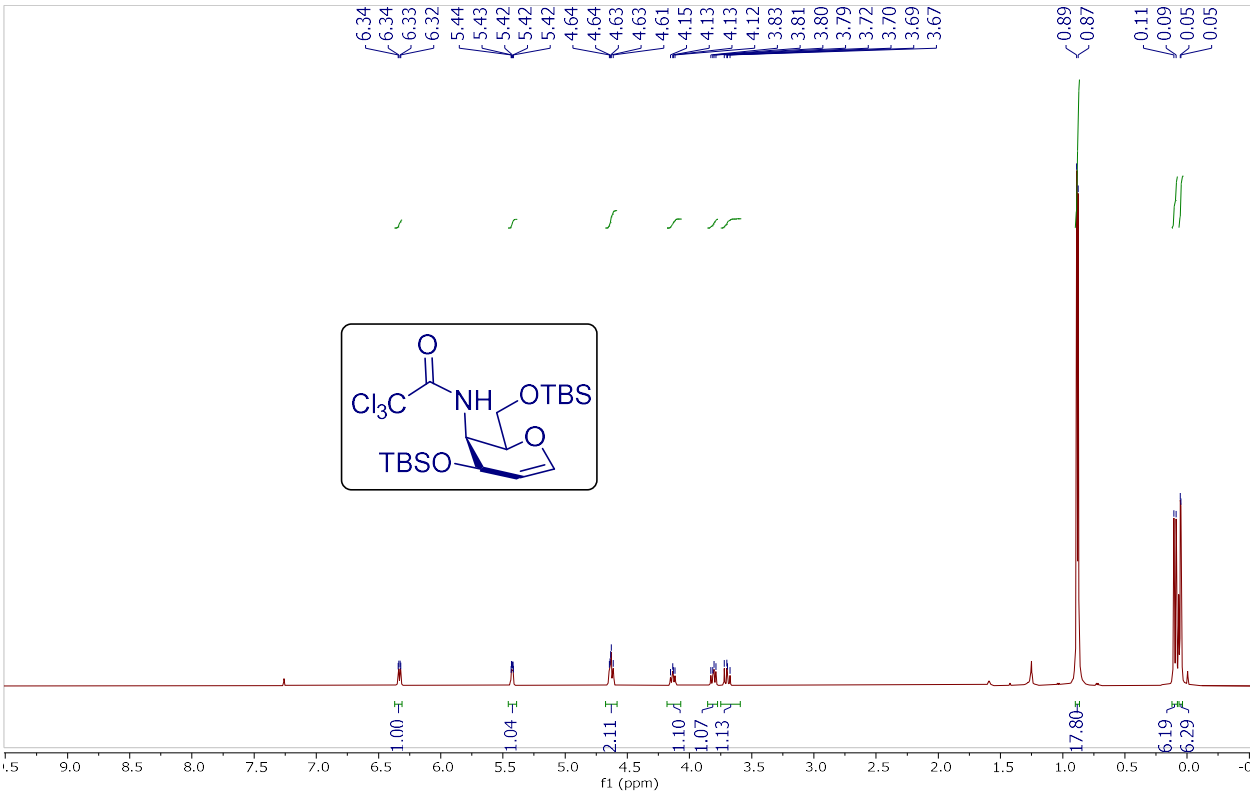
^{1}H NMR spectrum of compound **1o** in $CDCl_3$ (400 MHz)



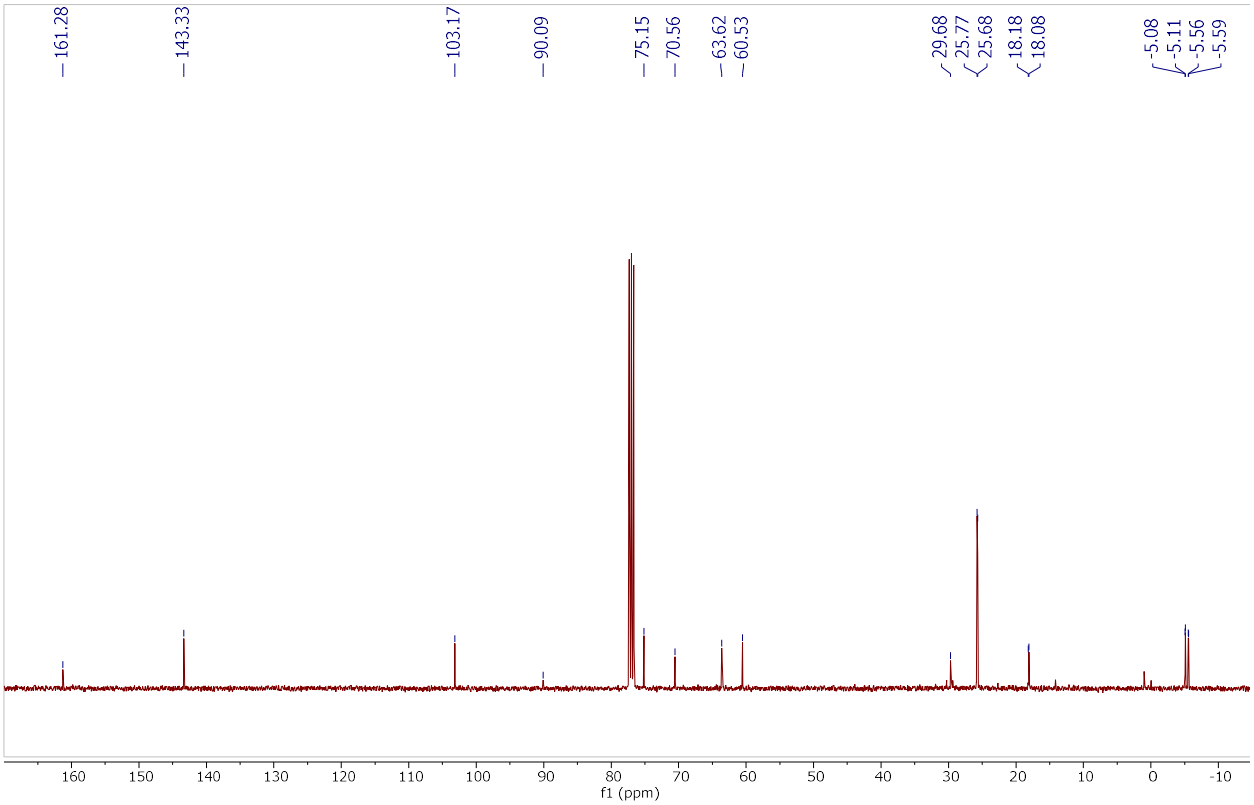
^{13}C NMR spectrum of compound **1o** in $CDCl_3$ (101 MHz)



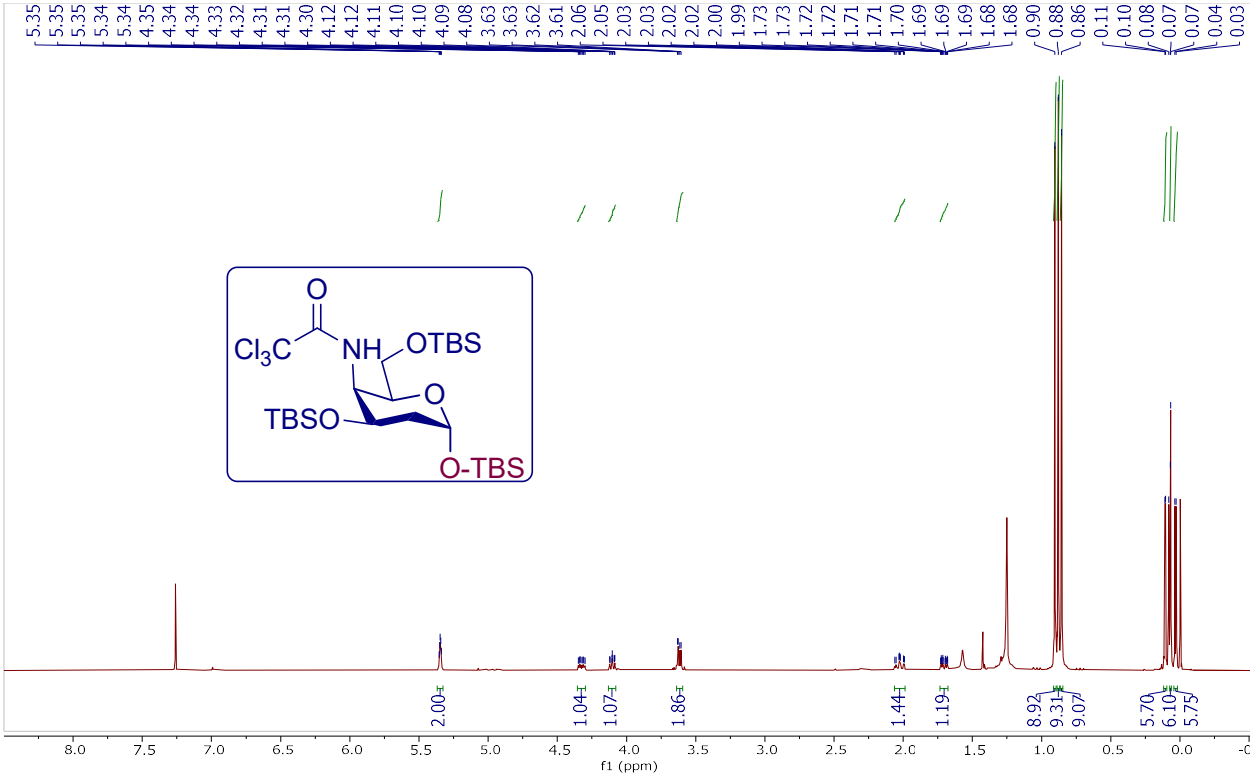
^{1}H NMR spectrum of compound **1o'** in $CDCl_3$ (400 MHz)



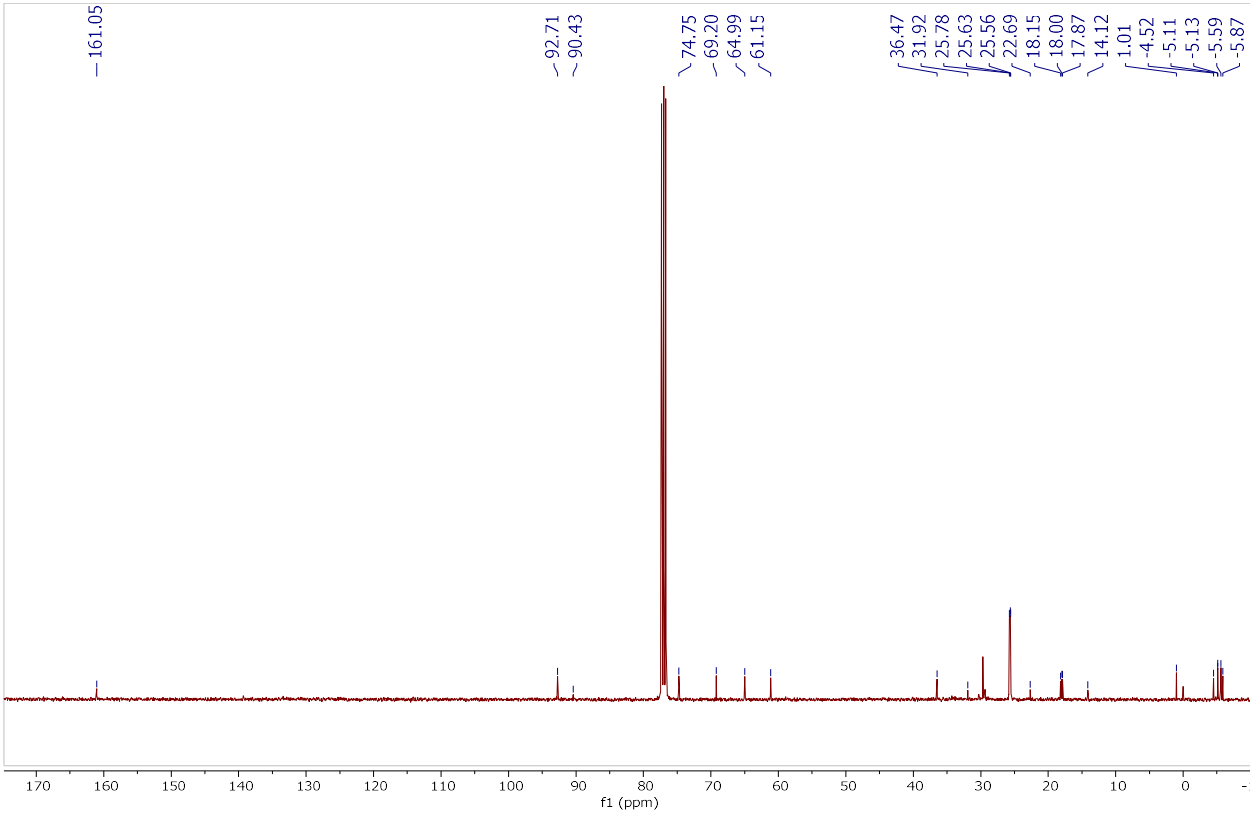
^{13}C NMR spectrum of compound **1o'** in $CDCl_3$ (101 MHz)



^{1}H NMR spectrum of compound **10** in $CDCl_3$ (400 MHz)

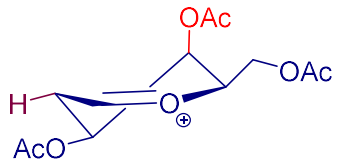


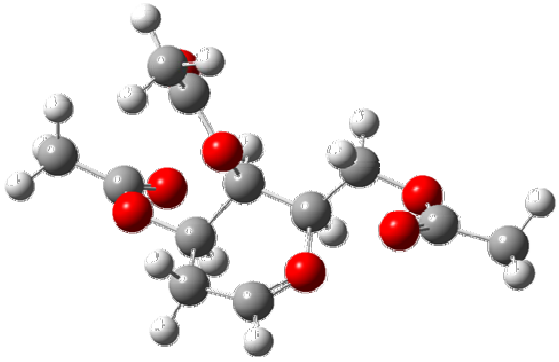
^{13}C NMR spectrum of compound **10** in $CDCl_3$ (101 MHz)



H. Computational Data

$^4H_3$-1a





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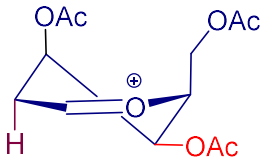
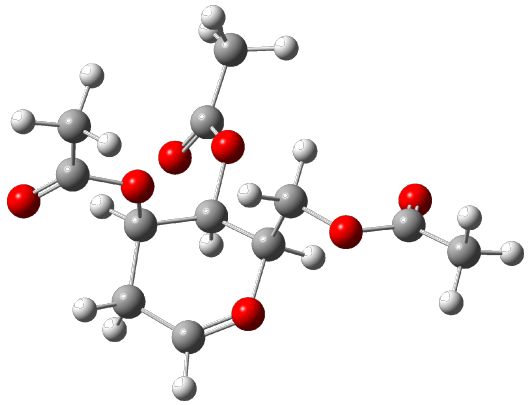
C	-1.30579100	-1.20320200	0.29193800
C	0.94905500	-0.52866200	-0.57226100
C	-0.49185700	-0.08488100	-0.38143200
O	1.48854000	-1.16591900	0.70719800
C	-0.71193700	-1.49251800	1.67118200
H	-1.26948100	-2.09214800	-0.34687900
H	1.02834100	-1.35281400	-1.28550200
H	-0.98466900	-0.69168600	2.38207300
H	-0.92616500	0.14714400	-1.35855300
O	-0.49634100	1.08078400	0.45057000
O	-2.65393200	-0.81640100	0.49507900
C	1.93611500	0.57895400	-0.91703900
H	1.56786900	1.06570700	-1.82608100
H	1.99404200	1.30351500	-0.10403300
O	3.21974000	0.04948400	-1.21846900
H	1.32502700	-1.91406500	2.51485400
C	-3.47304200	-0.96160700	-0.62199000
C	-1.41149500	2.07522900	0.11194700
C	4.15428400	0.10255300	-0.20131000
O	3.87276100	0.47168900	0.91307300
O	-2.14485300	1.96947500	-0.83579500
O	-3.05223300	-1.43687100	-1.64609400
C	5.50021000	-0.34024400	-0.69872500
H	6.18279700	-0.44503900	0.14468300
H	5.89447700	0.40774600	-1.39568600
H	5.41940900	-1.28390700	-1.24611800
C	-1.32079500	3.22403500	1.07423200
H	-0.29197500	3.59165200	1.13821100
H	-1.61591300	2.89552800	2.07673800
H	-1.98384500	4.02294300	0.74234200
C	-4.84781000	-0.43161900	-0.35078200
H	-5.53412600	-0.80317000	-1.11223300
H	-4.81279300	0.66287500	-0.40535800
H	-5.19124800	-0.71104000	0.64844000
H	-1.08998700	-2.41803300	2.12596100

Energy: -993.3128267 Hartree
No. of Imaginary frequencies: 0

$^3H_4$-1a





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C	-0.43450700	0.68778600	-0.80225400
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C	-1.50363800	-1.33473000	-1.78806800
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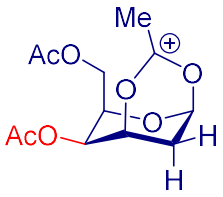
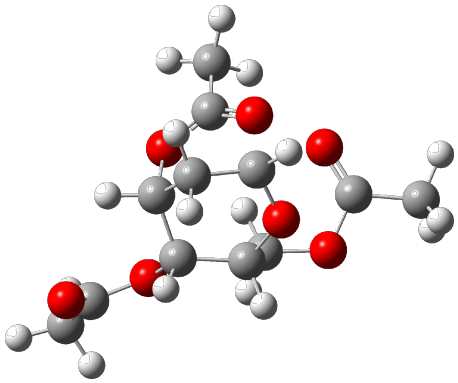
H	1.70506500	0.57532200	-1.20657200
H	-2.16402700	-2.19161500	-1.60025300
H	-0.52370100	1.16847100	-1.78383600
O	-0.43339400	1.68913300	0.20320400
O	-1.57247800	-0.88754900	0.61378600
C	1.43350000	-0.42759200	0.67128300
H	1.43706900	0.47819900	1.28262700
H	0.78288300	-1.17496600	1.12284200
O	2.73284900	-1.00970800	0.60619600
H	0.07270100	-2.69636800	-2.61539900
C	-2.74269500	-1.51304500	1.01321000
C	-1.16906500	2.83191800	-0.09899400
C	3.77457400	-0.12120900	0.45444900
O	3.58133600	1.05689200	0.26235100
O	-1.80093500	2.91822000	-1.12074100
O	-3.67271900	-1.64236500	0.25587300
C	5.10064700	-0.81667100	0.56690500
H	5.89652100	-0.12761900	0.28400200
H	5.12403600	-1.70820300	-0.06665800
H	5.25373000	-1.14623600	1.60065400
C	-1.03632600	3.85127200	0.99294700
H	-1.67330300	4.70605200	0.76593200
H	0.00664600	4.17630100	1.07242200
H	-1.31902100	3.41564300	1.95638300
C	-2.65793200	-1.96697500	2.44168600
H	-1.76895700	-2.58614100	2.59884400
H	-3.55558900	-2.53210400	2.69259100
H	-2.57382400	-1.09738400	3.10239000
H	-1.84937400	-0.94422700	-2.76326600

Energy: -993.3086813 Hartree
No. of Imaginary frequencies: 0

P3-1a

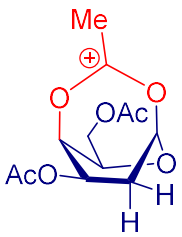


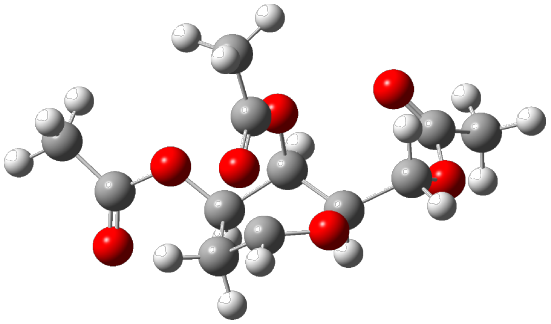


C	-0.76734100	1.56604600	-1.43344200
C	1.36227100	1.31309500	-0.34515900
C	0.04892000	-0.75709500	-1.12843500
C	1.43273600	-0.15289800	-0.78162200
O	-0.89007100	0.23275600	-1.65117700
C	0.64358100	2.11719100	-1.41227100
H	2.35685000	1.68013300	-0.10013000
H	0.16052900	-1.44282200	-1.97082700
H	0.64095500	3.19010900	-1.20002800
H	2.06795600	-0.13657200	-1.67406400
O	2.03998400	-0.98775300	0.20095100
O	0.62772500	1.44610300	0.94666700
C	-0.57968300	-1.54412500	0.03476000
H	0.01451700	-2.44421500	0.19667400
H	-0.61447000	-0.97667600	0.96419400
O	-1.89267500	-1.97164600	-0.32348600
H	-1.46858300	2.08214300	-2.08501400
C	-0.61890300	1.79455900	0.99193400
C	3.42444200	-0.93292000	0.25888800
C	-2.93600800	-1.31616800	0.25803500
O	-2.78653600	-0.40246300	1.04330100
O	4.05245900	-0.16139200	-0.42322900
O	-1.34774000	1.93468500	-0.04961500
C	-4.24968100	-1.88926100	-0.19235400
H	-5.06795300	-1.32662000	0.25686400
H	-4.31609900	-2.94155300	0.10336100
H	-4.32108400	-1.85368700	-1.28401800
C	3.96058200	-1.93075200	1.24312600
H	3.46566700	-1.81706500	2.21245800
H	5.03601200	-1.78864700	1.34958800
H	3.75858400	-2.94716200	0.88764800
C	-1.22940100	2.03060100	2.32113300
H	-1.75632400	2.99021000	2.31290300
H	-0.47315300	2.00936100	3.10552000
H	-1.97881000	1.24459400	2.47504200
H	1.12113700	1.96651700	-2.38502200

Energy: -993.3188454 Hartree
No. of Imaginary frequencies: 0

P4-1a

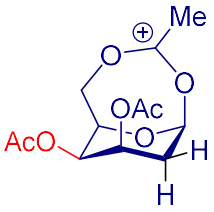


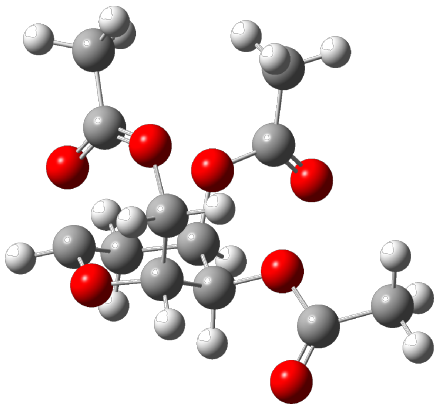


C	0.84578300	1.78238900	-1.39103400
C	1.09020500	-0.62535600	-0.72792900
C	-1.14254700	0.48932400	-1.03106800
C	-0.22619800	-0.23071000	-0.04852500
O	-0.51174000	1.73717700	-1.43336400
C	1.56858500	0.48928700	-1.68868200
H	0.90917400	-1.54094000	-1.29803400
H	-1.26166800	-0.14823400	-1.91720100
H	2.64858000	0.63025500	-1.61452200
H	-0.72217500	-1.07506500	0.42360600
O	0.02327700	0.65551100	1.12362100
O	2.03680800	-0.89925200	0.30686700
C	-2.53803000	0.88055100	-0.52718100
H	-2.49917800	1.25706200	0.49743100
H	-2.92413900	1.65536600	-1.19203700
O	-3.45819700	-0.20875200	-0.62635500
H	1.18744500	2.65287500	-1.94640000
C	3.06549800	-1.75618000	-0.06193000
C	0.80184600	1.68256500	1.10376800
C	-3.55295900	-1.04337400	0.45415700
O	-2.78337600	-0.98203800	1.38901300
O	1.29103700	2.21943600	0.05430600
O	3.15451400	-2.18133400	-1.18518900
C	-4.70885600	-1.99115000	0.30579800
H	-4.71518300	-2.44043600	-0.69142200
H	-5.64784800	-1.43758100	0.41929200
H	-4.64909200	-2.76269000	1.07354500
C	1.15349400	2.26575200	2.42695400
H	0.28281600	2.23848600	3.08736100
H	1.53084100	3.28177800	2.31170600
H	1.93073400	1.63681100	2.87949900
C	3.97336300	-2.03916800	1.10033500
H	3.41247900	-2.52836300	1.90365000
H	4.38126000	-1.10618300	1.50263700
H	4.78609300	-2.68634500	0.77078300
H	1.35016700	0.22363500	-2.72907100

Energy: -993.3194285 Hartree
No. of Imaginary frequencies: 0

P6-1a





C	1.63453400	-1.57034700	1.23385600
C	-0.10745200	0.28506200	1.38842500
C	-0.25551900	-1.74916500	-0.20662700
C	-1.00929900	-0.69030600	0.62953200
O	0.79224600	-2.38887000	0.54923700
C	0.98945600	-0.50389000	2.10659400
H	-0.71152700	0.84674900	2.10343500
H	-0.97517800	-2.54667100	-0.41742700
H	1.75318200	0.16646200	2.50926000
H	-1.58855100	-1.25461900	1.36823700
O	-1.90118900	0.05028700	-0.19962300
O	0.50308800	1.22848600	0.48644100
C	0.29124800	-1.37083700	-1.57148600
H	0.65357500	-2.26761600	-2.07900900
H	-0.46702000	-0.88159900	-2.18097500
O	1.42730600	-0.43483000	-1.63681200
H	2.34092600	-2.19765300	1.77385900
C	-0.06085800	2.49877000	0.46097500
C	-3.15825400	-0.50533400	-0.38283300
C	2.43266400	-0.29737000	-0.84995500
O	2.62093900	-0.83333800	0.29335800
O	-3.42161900	-1.61692700	0.00334800
O	-0.96972700	2.82012400	1.17821200
C	3.51751100	0.60364600	-1.34024600
H	3.41778900	1.56535400	-0.82285000
H	3.43688600	0.76029500	-2.41580200
H	4.49184300	0.18441900	-1.07739600
C	-4.06841100	0.45628800	-1.09047100
H	-5.01030200	-0.04082600	-1.32225800
H	-3.60102100	0.82792000	-2.00760700
H	-4.25546800	1.32225100	-0.44600900
C	0.64262500	3.37310800	-0.54185100
H	0.74891900	2.85906500	-1.50169800
H	1.64458000	3.62554600	-0.17529500
H	0.07547100	4.29504100	-0.67207300
H	0.54806100	-1.04132700	2.95484000

Energy: -993.3133449 Hartree
No. of Imaginary frequencies: 0