CHAPTER-3

An Efficient and Direct Esterification of Uronic Acids using H_2SO_4-SiO_2 at Room Temperature

3.1 Introduction

Carbohydrates are one of the important biomolecules that play a vital role in human health and disease [1]. In this context, the glycosides and glycoconjugates bearing uronic acid units are widespread in nature and involved in diverse biological functions [2]. For example, uronic acids are part of biologically relevant polysaccharides such as glycosaminoglycans (i.e., heparin sulphate, dermatan sulphate, chondroitin sulphate and hyaluronan), bacterial and marine polysaccharides, saponins, homoglycuronans, etc., (Figure 3.1). [2, 3]

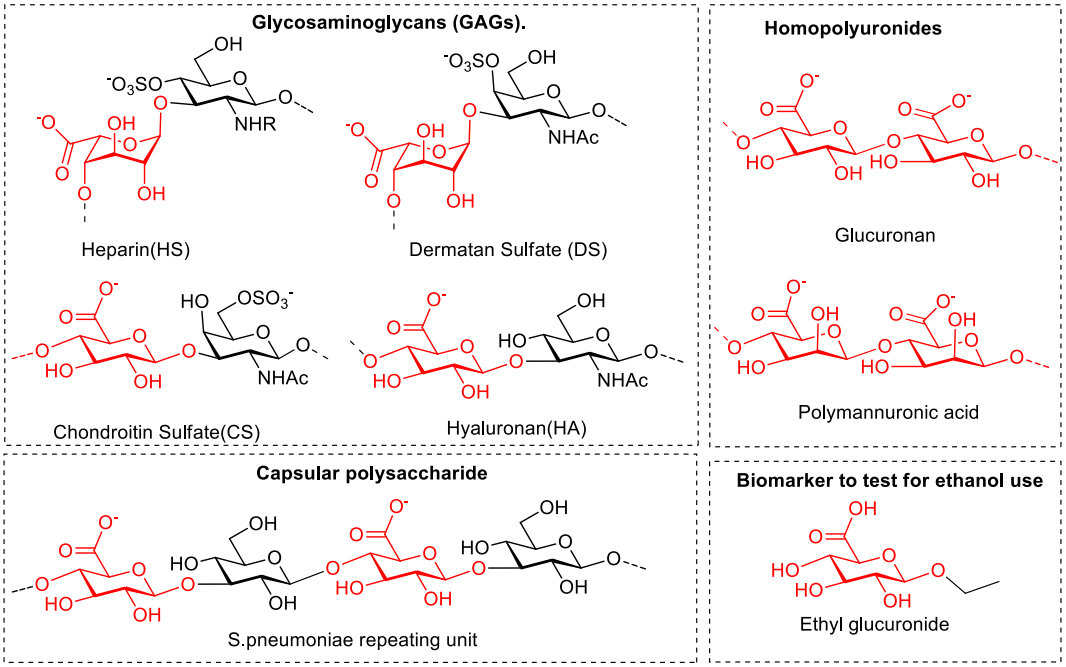
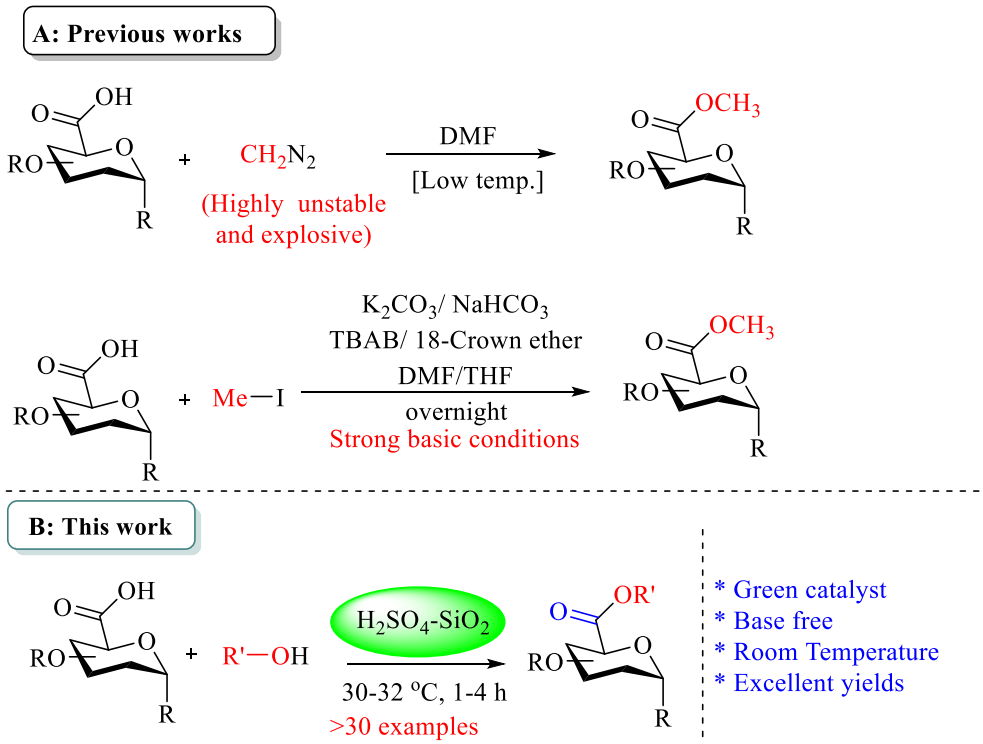


Figure 3.1 Biologically relevant polysaccharides containing uronic acids

Synthesis of uronic acid-containing glycosides is typically achieved using orthogonally protected uronic acid building blocks [2-4]. The carboxylic acid group in uronic acid is usually protected as methyl esters and cleaved at the end of oligosaccharides assembly by

saponification reactions [2-4]. However, the synthesis of uronic methyl esters requires hazardous diazomethane (toxic, carcinogenic and explosive) [5] or methyl iodide with a strong base which usually results in low yield (Scheme 3.1, **A**) [6]. Therefore, it is still desirable to develop simple and mild esterification protocols for the preparation of uronic esters.



Scheme 3.1 Synthesis of uronic esters

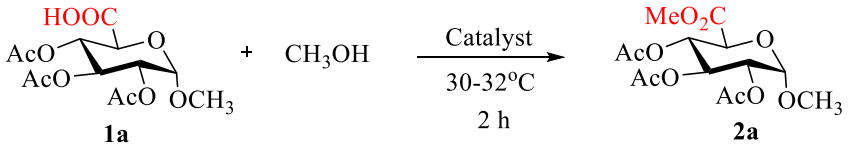
As a part of our ongoing research program in carbohydrate synthesis [7], we have demonstrated an efficient method for the preparation of diverse uronic acids from corresponding alcohols using 1-chloro-1, 2-benziodoxol-3(1H)-one and TEMPO at room temperature [7h]. Also, we have recently explored the photolabile protecting group (2-nitrobenzyl) as a promising masking agent for uronic acids and its proficient deprotection

using a continuous flow photoreactor [7c]. In continuation of these works, here we report a convenient and practical approach for the esterification of uronic acids with alcohols using an eco-friendly catalyst, silica-sulphuric acid (H_2SO_4-SiO_2) at room temperature (Scheme 3.1, **B**).

3.2 Results and Discussion

At the outset, various homogeneous Bronsted acids were used as catalysts for the esterification reaction of uronic acid **1a** with methanol at room temperature (30-32 ^oC). It was observed that the reactions with sulphuric acid, triflic acid and perchloric acid were found to be incompetent due to their intolerance towards sensitive acetyl group resulting in the formation of deprotected product in a major amount (Table 3.1, entries 1-3). Solid supported catalysts play very important roles in organic synthesis [8]. In particular, silica-supported Bronsted acids are well explored as catalysts in many transformations to achieve high selectivity and yields [9]. More importantly, silica-supported sulphuric acid has been previously used in carbohydrate chemistry to synthesize *O*-isopropylidene and per-*O*-acetyl sugar derivatives, deprotection of the terminal *O*-isopropylidene group, the Fischer or Ferrier-type glycosylation reactions, etc [10]. In light of these reports, we have investigated the esterification of uronic acid **1a** with methanol in the presence of different silica-supported acid catalysts. To our delight, SiO_2-HBF_4, SiO_2-TfOH, SiO_2-$HClO_4$ and SiO_2-H_2SO_4 proved to be better catalysts for the esterification reaction when compared with parent acids (Table 3.1, entries 4-7). Among them, H_2SO_4-SiO_2 gave the most satisfactory result by providing the desired ester **2a** in 90% yield (Table 3.1, entry 7).

Table 3.1 Optimization of the reaction condition.[a]



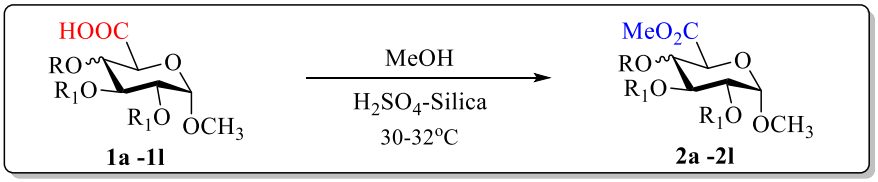
Entry	Catalyst	Loading of acid (mmol g^{-1})	Yield (%)[b]
1	[c]H_2SO_4	-	10
2	[c]TfOH	-	>5
3	[c]$HClO_4$	-	Trace
4	HBF4-SiO_2	5.0	40
5	TfOH-SiO_2	5.0	62
6	$HClO_4$-SiO_2	5.0	79
7	H_2SO_4-SiO_2	5.0	90
8	H_2SO_4-SiO_2	6.0	90
9	H_2SO_4-SiO_2	3.0	61
10	H_2SO_4-SiO_2	1.0	52
11	SiO_2	-	0
12	Amberlite-H^+	-	25
13	Dowex-H^+	-	34

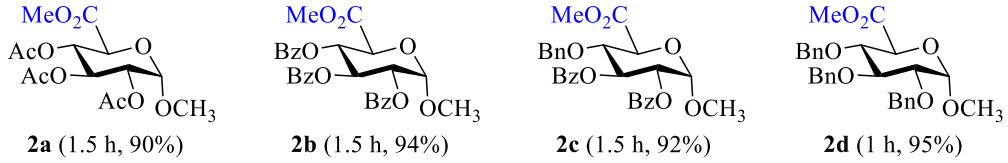
[a]Reaction Conditions: Uronic acid (67 mg, 0.2 mmol, 1 equiv.), methanol (1 mL) and catalyst (30 mg, containing 0.15 mmol of H_2SO_4) were stirred together for 2 hours at 30-32 °C. [b]Isolated yields. [c]20µL of protic acids were used.

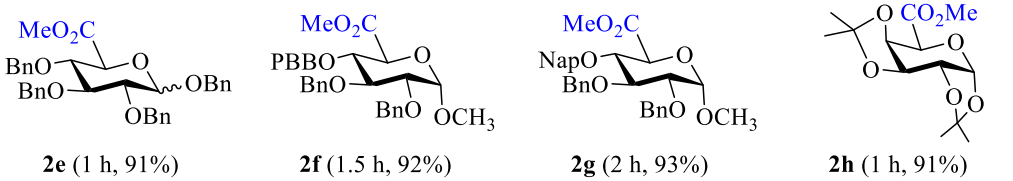
Further, the catalysts with different loading of sulphuric acid (on SiO_2) were examined for the esterification reaction. The yield of **2a** did not increase with a high-loaded silica-sulphuric acid, while a subsequent decrease was observed with low-loaded catalysts (Table

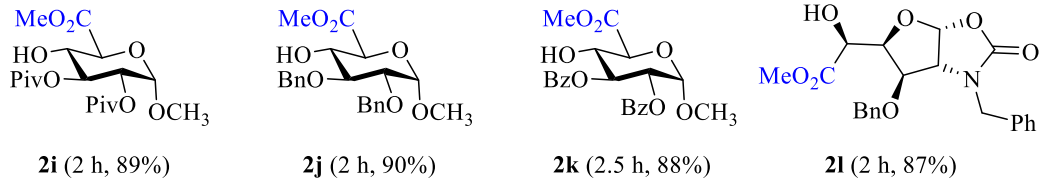
3.1, entries 8-10). Also, it is worth noting that no product was observed with silica alone at room temperature (Table 3.1, entry 11). Also, acidic resins such as Amberlite and Dowex were found to be less efficient for the esterification reaction in comparison to silica-supported acid catalysts (Table 3.1, entries 12 and 13).

Table 3.2 Esterification of various protected monosaccharide uronic acids.[a,b]







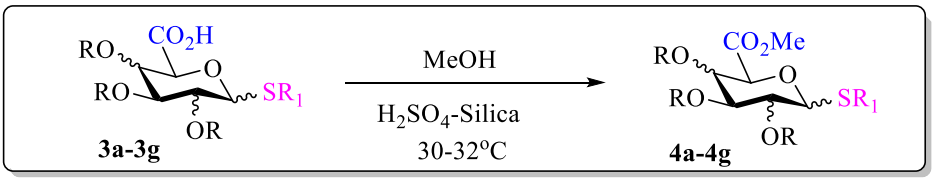


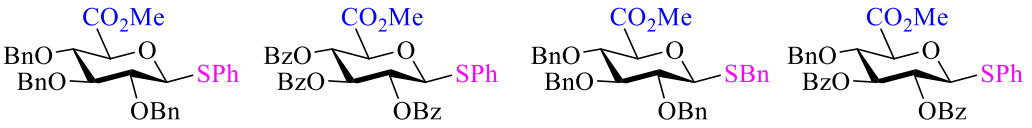
[a]Reaction Conditions: Uronic acid (0.2 mmol, 1 equiv.), methanol (1mL) and catalyst (30 mg, containing 0.15 mmol of H_2SO_4) were stirred together for 2 hours at 30-32 °C. [b]Isolated yield.

After establishing the optimized conditions, the applicability of the developed protocol was investigated with differently protected uronic acids (**1a-1l**) in the presence of methanol and silica-sulphuric acid (Table 3.2). The uronic acids bearing acetyl, benzoyl, benzyl, pivaloyl,

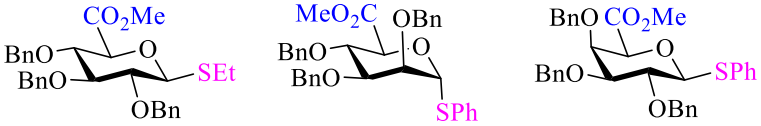
p-bromobenzyl and 2-naphthyl underwent esterification with methanol and provided corresponding methyl esters **2a-2g** in 90-95% yields without any side-product formation. Interestingly, the acid-labile isopropylidene group protected uronic acid also underwent esterification and provided the corresponding methyl ester **2h** in 91% yield. Moreover, partially protected uronic acids were also successfully converted into the corresponding methyl esters **2i-2l** in good yields without forming self-condensation products.

Table 3.3 Esterification of various thioglycoside uronic acids.[a,b]





4a (1.5 h, 95%) **4b** (2 h, 91%) **4c** (2 h, 91%) **4d** (1.5 h, 90%)

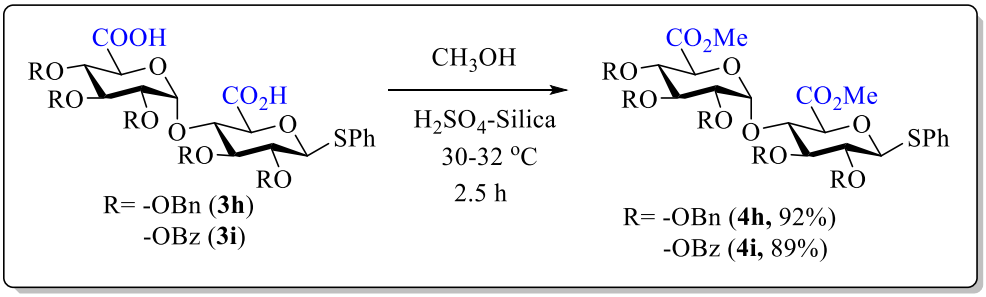


4e (1.5 h, 96%) **4f** (1.5 h, 95%) **4g** (1.5 h, 95%)

[a]Reaction Conditions: Uronic acid (0.2 mmol, 1 equiv.), methanol (1 mL) and catalyst (30 mg, containing 0.15 mmol of H_2SO_4) were stirred together for 2 hours at 30-32°C. [b]Isolated yields.

Thioglycosides are the most important glycosyl donors frequently used in the oligosaccharide assembly. Given this fact, various thioglycoside uronic acids of glucose, mannose and galactose bearing different protecting groups (**3a-3g**) were subjected to the

esterification reaction with methanol in the presence of silica-sulphuric acid (Table 3.3). To our delight, these reactions gave the corresponding methyl esters **4a-4g** in 90-96% yields within two hours.



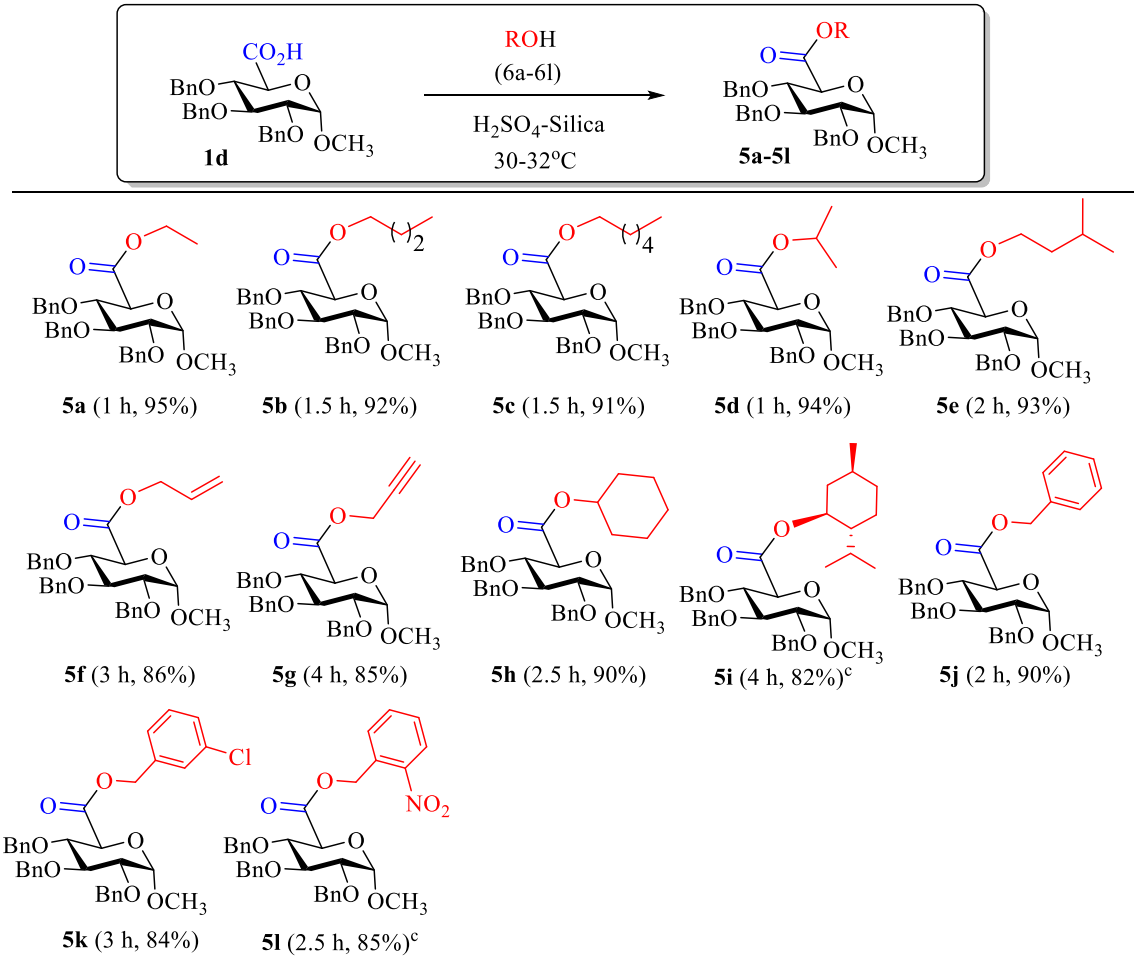
Scheme 3.2 Esterification of maltose uronic acids using H_2SO_4-SiO_2

Having explored the scope of monosaccharides esterification, we investigated the esterification of disaccharides bearing different protecting groups (i.e., **3h** and **3i**) under optimized conditions (Scheme 3.2). To our delight, these reactions gave the corresponding disaccharide methyl esters **4h** and **4i** in 92% and 89% yields, respectively, within 2.5 hours at room temperature.

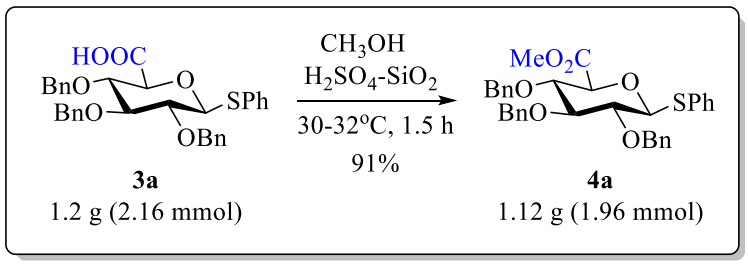
Further, to understand the broad applicability of the developed method, esterification of uronic acid **1d** was investigated with different alcohols, including alkyl, benzyl, cyclohexyl, allyl and propargyl alcohol (**6a-6l**) in the presence of H_2SO_4-SiO_2 (Table 3.4). These reactions gave desired esters **5a-5l** in 82-95 % yields under optimized conditions.

Further, a gram scale esterification was performed with uronic acid **3a** under optimized conditions (Scheme 3.3). This reaction gave the corresponding ester **4a** in 91% yield, demonstrating the practical utility of the developed protocol.

Table 3.4 Esterification of **1d** using various aliphatic and aromatic alcohols.[a,b]



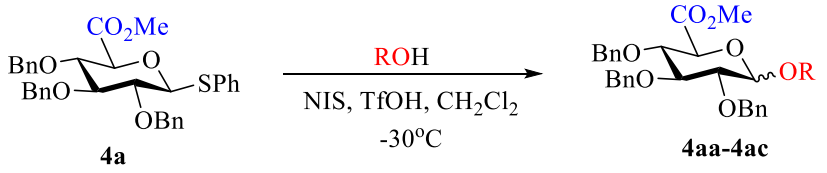
[a]Reaction Conditions: Uronic acid (96 mg, 0.2 mmol, 1 equiv.), alcohol (2 equiv.) and catalyst (30 mg, containing 0.15 mmol of H_2SO_4) were stirred together for 2 hours at 30-32°C. [b]Isolated yields. [c]DCM (1mL) was used as solvent.

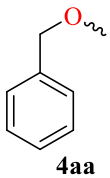
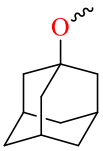
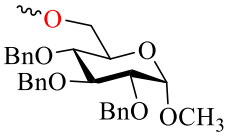


Scheme 3.3 Gram scale preparation of **4a** under optimized reaction conditions

After exploring the synthesis of uronic esters, their synthetic applications were investigated in glycosylation reactions. Glycosylation of thioglycoside uronic ester **4a** with different acceptors in the presence of NIS/TfOH gave the corresponding *O*-glycosides **4aa-4ac** in 85-89% yields (Table 3.5).

Table 3.5 Glycosylation of **4a** with acceptors **a**, **b** and **c**.[a,b]



R=			
	4aa	**4ab**	**4ac**
	89%, 1.5 h	87%, 2 h	85%, 2.5 h
	a:b = 1:1	a:b = 3:1	a:b = 1:1.5

[a]Reaction conditions: Donor **4a** (99 mg, 0.2 mmol, 1 equiv.), acceptor: **a** and **b** (3 equiv.), **c** (1.2 equiv.), CH_2Cl_2 (5 mL), NIS/TfOH. [b]Isolated yields.

3.3 Summary

In summary, a highly efficient and convenient protocol for the preparation of uronic esters from corresponding uronic acids and alcohols was reported using an eco-friendly solid-supported catalyst, silica-sulphuric acid (H_2SO_4-SiO_2). The reactions proceeded at room temperature and provided various monosaccharide and disaccharide uronic esters of glucose, mannose and galactose bearing different protecting groups and anomeric functional groups. The developed protocol is much more tolerant towards commonly used protecting groups including acetyl, benzoyl, pivaloyl, isopropylidene, benzyl, 2-naphthyl,

etc. and gave the products in excellent yields within 4 hours. This protocol should prove helpful in the synthesis of complex oligosaccharides.

3.4 Experimental Section

3.4.1 Procedure for preparation of H_2SO_4–Silica [11]:

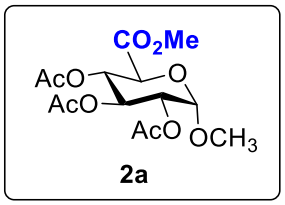
To silica gel (10 g, 100–200 mesh) in Et_2O (50 mL) was added commercially available conc. H_2SO_4 (4.91 g, 50.0 mmol) and shaken for 5 minutes. After that, the solvent was evaporated in vacuo to get free-flowing H_2SO_4–silica. The resulting slurry was then dried at 100 °C for 3 hours to obtain the desired silica-supported sulphuric acid catalyst.

3.4.2 Experimental procedure for preparation of various uronic methyl esters (2a-2l) using silica-supported sulphuric acid:

To a solution of uronic acid (0.2 mmol, 1.0 equiv.) in methanol (0.4 mmol, 2 equiv.) was added silica-supported sulphuric acid (30 mg, 0.15 mmol) and stirred until the completion of reaction. The reaction mixture was then filtered and rinsed using methanol. The filtrate was neutralized with 0.5 mL of Et_3N and was concentrated under reduced pressure. The crude residue was further purified by column chromatography (SiO_2:100-200 mesh) to obtain the desired product using ethyl acetate/hexane as eluent.

3.5 Analytical data of uronic methyl esters

3.5.1 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-acetyl methyl ester (2a) [12]

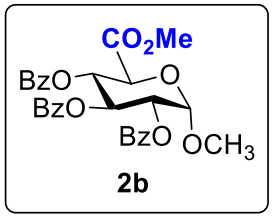


2a

Viscous liquid (63 mg, 90%), R_f value =0.5 in 50% EtOAc/ Hexane. IR υ_{max} (neat): 1745, 1735, 1215 cm^{-1} $[\alpha]_D^{20}$= +70.0 [c 0.1, CH_3OH]. ^1H NMR (500 MHz, $CDCl_3$) δ 5.51 (t, J = 9.8 Hz, 1H), 5.16 (t, J = 9.8 Hz, 1H), 5.02 (d, J = 3.6 Hz,

1H), 4.89 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.29 (d, *J* = 10.1 Hz, 1H), 3.74 (s, 3H), 3.43 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.9, 169.5, 168.0, 97.0, 70.4, 69.6, 69.2, 68.1, 55.9, 52.8, 20.6 (2C), 20.5.

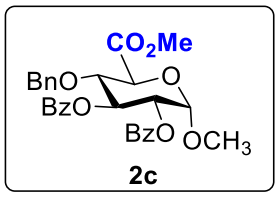
3.5.2 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzoyl-methyl ester (2b) [13a, b]



2b

Colourless viscous oil (101 mg, 94%), R_f value =0.5 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1748, 1726, 1220 cm^{-1} $[\alpha]_D^{20}$= -123.5 [c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.11 (m, 2H), 8.01–8.00 (m, 2H), 7.88–7.87 (m, 2H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.55–7.38 (m, 6H), 7.30–7.28 (m, 2H), 6.01–5.95 (m, 2H), 5.71–5.70 (m, 1H), 5.16 (s, 1H), 4.67 (d, *J* = 9.0 Hz, 1H), 3.71 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 165.5, 165.4, 165.2, 133.5, 133.4, 133.3, 129.9, 129.7, 129.7, 129.2, 129.0, 129.0, 128.6, 128.4, 128.3, 98.9, 69.9, 69.8, 69.2, 67.9, 56.1, 52.8.

3.5.3 *α*-D-Glucopyranosiduronic acid, methyl 2-*O*-(phenylmethyl)-3, 4-tris-*O*-benzoyl-methyl ester (2c)

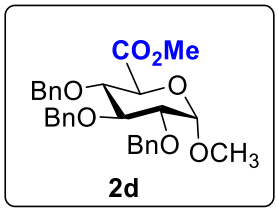


2c

Colourless viscous oily syrup (96 mg, 92%), R_f value =0.6 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1736, 1716, 1290 cm^{-1} $[\alpha]_D^{20}$= +90.5 [c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.99–7.97 (m, 4H), 7.55–7.50 (m, 2H), 7.41–7.37 (m, 4H), 7.21–7.18 (m, 3H), 7.16–7.13 (m, 2H), 6.05 (t, *J* = 9.5 Hz, 1H), 5.22–5.19 (m, 2H), 4.63 (d, *J* = 11.0 Hz, 1H), 4.59 (d, *J* = 11.0 Hz, 1H), 4.43 (d, *J* = 9.9 Hz, 1H), 4.15 (t, *J* = 9.5 Hz, 1H), 3.81 (s, 3H), 3.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 165.9, 165.5, 137.1, 133.3, 133.1, 129.9, 129.7, 129.5, 129.0, 128.4, 128.3, 128.0, 127.9, 97.5, 77.7, 74.6, 71.9, 71.8, 70.0, 55.8, 52.7. HRMS: Calc. for $C_{29}H_{28}O_9$ $[M+H]^+$: 521.1812, Obser. 521.1813.

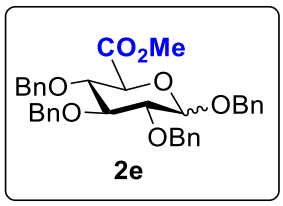
3.5.4 *α*-D-Glucopyranosiduronic acid, methyl-2,3,4-tris-*O*-(phenylmethyl)-methyl ester (2d) [14a, b]



2d

Viscous colourless oil (94 mg, 95%), R_f value =0.7 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1742 cm^{-1}. $[\alpha]_D^{20}$= -0.3 [c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 13H), 7.24–7.23 (m, 2H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.84–4.79 (m, 3H), 4.66–4.57 (m, 3H), 4.20 (d, *J* = 10.0 Hz, 1H), 4.00 (t, *J* = 9.3 Hz, 1H), 3.75–3.71 (m, 4H), 3.58 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 138.5, 137.9, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 98.7, 81.4, 79.5, 79.3, 75.9, 75.1, 73.6, 70.1, 55.6, 52.4.

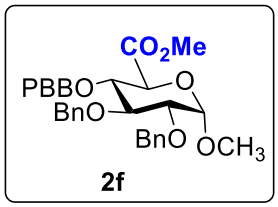
3.5.5 D-Glucopyranosiduronic acid, methyl-1, 2,3,4-tetra-*O*-(phenylmethyl)-methyl ester (2e) [*α/β* mixture, ratio: 1: 5.5]



2e

White solid (104 mg, 91%), R_f value =0.7 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1775, 1230 cm^{-1} M.P. 110-112 °C, $[\alpha]_D^{20}$= -15.6 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.40–7.24 (m, 20H), 5.91–4.86 (m, 3H), 4.84–4.70 (m, 3H), 4.67–4.54 (m, 3H), 4.31-3.88 (m, 2H), 3.78-3.74 (m, 3H), 3.70-3.67 (m, 1H), 3.61-3.57 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 138.4, 138.1, 137.8, 137.0, 128.4, 128.3, 128.3, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 102.7, 83.8, 81.8, 79.2, 75.7, 75.0, 74.9, 74.5, 71.4, 52.4 (*In 13C NMR, minor peaks of α-Isomer are excluded)*. HRMS: Calc. for $C_{35}H_{36}O_7$ $[M+Na]^+$: 591.2359, Obser. 591.2362.

3.5.6 *α*-D-Glucopyranosiduronic acid, methyl 2, 3-bis-*O*-phenylmethyl-4-*O*-(4-bromobenzyl) methyl ester (2f)

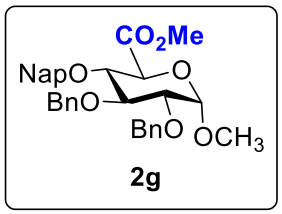


2f

Pale yellow viscous liquid (105 mg, 92%), R_f value =0.6 in 30% EtOAc/ Hexane. IR υ_{max} (neat): 1730, 1235, 1185 cm^{-1} $[\alpha]_D^{20}$= -12.3 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.36–7.31 (m, 10H), 7.10 (d, *J* = 8.4 Hz, 2H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.83–4.73 (m, 3H), 4.67 (d, *J* = 7.0 Hz, 1H), 4.63 (d, *J* = 3.5 Hz, 1H), 4.55 (d, *J* =

11.2 Hz, 1H), 4.20 (d, *J* = 10.0 Hz, 1H), 4.00 (t, *J* = 9.3 Hz, 1H), 3.76–3.70 (m, 4H), 3.59 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 138.5, 137.8, 137.0, 131.4, 129.4, 128.5, 128.4, 128.1, 127.8, 121.6, 98.7, 81.3, 79.5, 79.3, 75.85, 74.2, 73.5, 70.0, 55.7, 52.4. HRMS: Calc. for $C_{29}H_{31}BrO_7$ $[M+Na]^+$: 593.1151, Obser. 593.1140.

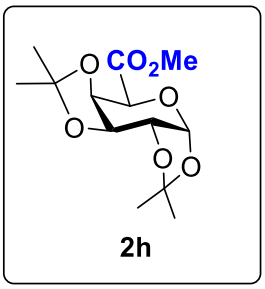
3.5.7 *α*-D-Glucopyranosiduronic acid, methyl 2, 3-bis-*O*-phenylmethyl-4-*O*-(2-naphthyl) methyl ester (2g)



2g

Transparent viscous liquid (101 mg, 93%), R_f value =0.62 in 30% EtOAc/ Hexane. IR υ_{max} (neat): 1735, 1265 cm^{-1} $[\alpha]_D^{20}$= -7.7 [c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85–7.81 (m, 3H), 7.70 (s, 1H), 7.50–7.48 (m, 2H), 7.39–7.34 (m, 11H), 5.03 (d, *J* = 10.9 Hz, 1H), 4.99 (d, *J* = 11.2 Hz, 1H), 4.89 (d, *J* = 11 Hz, 1H), 4.85 (d, *J* = 12.1 Hz, 1H), 4.79 (d, *J* = 11.1 Hz, 1H), 4.70–4.66 (m, 2H), 4.27 (d, *J* = 9.9 Hz, 1H), 4.07 (t, *J* = 9.3 Hz, 1H), 3.83 (t, *J* = 9.5 Hz, 1H), 3.71 (s, 3H), 3.65-3.63 (m, 1H), 3.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 138.6, 137.9, 135.4, 133.2, 133.0, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.9, 127.6, 127.6, 126.6, 126.0, 125.9, 125.8, 98.8, 81.4, 79.6, 79.4, 75.9, 75.1, 73.6, 70.2, 55.7, 52.4. HRMS: Calc. for $C_{33}H_{34}O_7$ $[M+Na]^+$: 565.2202, Obser. 565.2208.

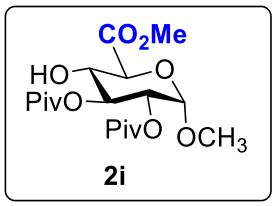
3.5.8 *α*-D-galactopyranosiduronic acid- 1, 2, 3, 4-di-*O*-isopropylidene methyl ester (2h) [15]



2h

Viscous liquid (53 mg, 91%), R_f value =0.5 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1747, 1242 cm^{-1} $[\alpha]_D^{20}$= -87.8 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 5.60 (d, J = 4.6 Hz, 1H), 4.61 (dd, J = 7.6, 1.5 Hz, 1H), 4.53–4.51 (m, 1H), 4.39 (s, 1H), 4.33–4.31 (m, 1H), 3.76 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H), 1.28 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 109.8, 108.7, 96.3, 71.8, 70.4, 70.0, 68.2, 52.0, 25.7, 25.6, 24.5, 24.4.

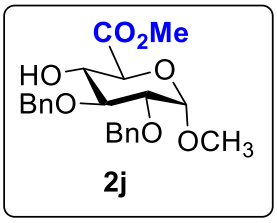
3.5.9 *α*-D-Glucopyranosiduronic acid, methyl- 3, 4-bis-*O*-pivolyl-methyl ester (2i)



2i

Viscous oil (70 mg, 89%), R_f value =0.4 in 30% EtOAc/ Hexane. IR υ_{max} (neat): 3250, 1775, 1745, 1230 cm^{-1} $[\alpha]_D^{20}$= +91.5 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 5.41 (t, J = 9.7 Hz, 1H), 5.01 (d, J = 3.6 Hz, 1H), 4.82 (dd, J = 10.2, 3.7 Hz, 1H), 4.23 (d, J = 9.9 Hz, 1H), 3.91 (t, J = 9.6 Hz, 1H), 3.85 (s, 3H), 3.44 (s, 3H), 1.20 (s, 9H), 1.18 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 177.8, 170.2, 97.2, 71.3, 70.8, 70.2, 56.0, 52.9, 38.8, 38.7, 27.1, 26.9. HRMS: Calc. for $C_{18}H_{30}O_9$ $[M+H]^+$: 391.1968, Obser. 391.1974.

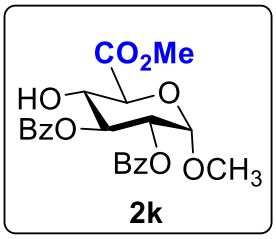
3.5.10 *α*-D-Glucopyranosiduronic acid, methyl 3, 4-bis-*O*-(phenylmethyl)-methyl ester (2j) [16]



2j

Colourless viscous oil (73 mg, 90%), R_f value =0.5 in 30% EtOAc/ Hexane. IR υ_{max} (neat): 3355, 1745, 1245 cm^{-1} $[\alpha]_D^{20}$= -7.8 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.41–7.28 (m, 10H), 4.94 (d, J = 11.3 Hz, 1H), 4.85–4.80 (m, 2H), 4.68–4.65 (m, 2H), 4.18 (d, J = 9.2 Hz, 1H), 3.88–3.81 (m, 2H), 3.80 (s, 3H), 3.56 (dd, J = 9.0, 3.4 Hz, 1H), 3.45 (s, 3H), 2.92 (s, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 138.6, 137.9, 128.5, 128.5, 128.1, 128.0, 127.9, 127.8, 98.7, 80.4, 78.4, 75.4, 73.6, 71.8, 70.5, 55.9, 52.7.

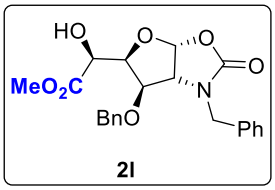
3.5.11 *α*-D-Glucopyranosiduronic acid, methyl 3, 4-bis-*O*-benzoyl- methyl ester (2k) [17]



2k

Colourless viscous oil (76 mg, 88%), R_f value =0.3 in 30% EtOAc/ Hexane. IR υ_{max} (neat): 3250, 1756, 1718 cm^{-1} $[\alpha]_D^{20}$= +138.3 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 8.01–7.98 (m, 4H), 7.53–7.49 (m, 2H), 7.39–7.36 (m, 4H), 5.89–5.84 (m, 1H), 5.26–5.23 (m, 2H), 4.39 (d, J = 9.8 Hz, 1H), 4.18 (t, J = 9.5 Hz, 1H), 3.88 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 166.6, 165.9, 133.4, 133.3, 129.9, 129.8, 129.3, 128.9, 128.4, 128.3, 97.5, 72.4, 71.1, 70.7, 70.4, 55.9, 52.9.

3.5.12 Methyl-(S)-2-((3aR,5R,6R,6aR)-1-benzyl-6-(benzyloxy)-2-oxohexahydro furo[3,2d]oxazol-5-yl)-2-hydroxyacetate (2l)

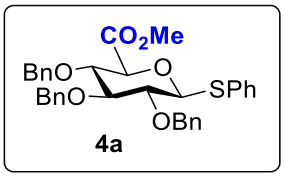


2l

Viscous oil (72 mg, 87%), R_f value =0.42 in 30% EtOAc/ Hexane. IR υ_{max} (neat): 3355, 1762, 1751, 1290 cm^{-1} $[\alpha]_D^{20}$= -31.2 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.32 (m, 6H), 7.23–7.18 (m, 4H), 6.09 (d, *J* = 5.6 Hz, 1H), 4.64 (d, *J* = 15.2 Hz, 1H), 4.54 (d, *J* = 7.1 Hz, 1H), 4.41 (d, *J* =11.5 Hz, 1H), 4.34 (d, *J* =11.5 Hz, 1H), 4.21 (dd, *J* = 7.2, 3.3 Hz, 1H), 4.14 (d, *J* = 15.2 Hz, 1H), 4.03 (d, *J* = 5.7 Hz, 1H), 3.98 (d, *J* = 3.3 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 156.7, 136.3, 135.1, 129.1, 129.0, 128.7, 128.6, 128.5, 128.5, 128.4, 128.2, 128.0, 101.0, 80.3, 79.5, 72.8, 68.6, 64.1, 52.8, 47.5. HRMS: Calc. for $C_{22}H_{23}NO_7$ $[M+H]^+$: 414.1553, Obser. 414.1551.

3.6 Analytical data of various thioglycosides methyl esters

3.6.1 *β*-D-Glucopyranosiduronic acid, phenyl-2, 3, 4-tris-*O*-(phenylmethyl)-1-thio, methyl ester (4a) [19]

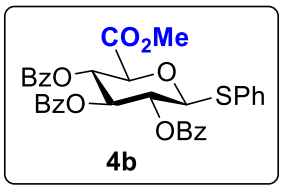


4a

Viscous liquid (109 mg, 95%), R_f value =0.6 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1743 cm^{-1} $[\alpha]_D^{20}$= -21.0 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.60–7.58 (m, 2H), 7.42–7.40 (m, 2H), 7.39–7.30 (m, 14H), 7.27–7.25 (m, 2H), 4.94–4.87 (m, 3H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.77 (d, *J* = 10.3 Hz, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.65 (d, *J* = 10.8 Hz, 1H), 3.96 (d, *J* = 9.7 Hz, 1H),

3.88 (t, *J* = 9.4 Hz, 1H), 3.77 (s, 3H), 3.75–3.73 (m, 1H), 3.58-3.54 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 138.1, 137.8, 137.7, 133.2, 132.2, 129.0, 128.4, 128.4, 128.4, 128.2, 127.9, 127.9, 127.9, 127.8, 88.3, 85.8, 80.3, 79.2, 78.0, 75.8, 75.5, 75.1, 52.5.

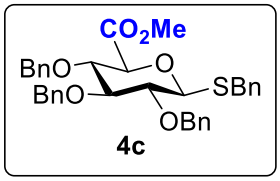
3.6.2 *β*-D-Glucopyranosiduronic acid, phenyl-2, 3, 4-tris-*O*-benzyl-1-thio, methyl ester (4b)



4b

Viscous liquid (112 mg, 91%), R_f value =0.45 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1748, 1718, 1275 cm^{-1} $[\alpha]_D^{20}$= +3.2 [c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–7.93 (m, 4H), 7.85 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.57–7.52 (m, 4H), 7.46–7.30 (m, 10H), 5.94 (t, *J* = 9.4 Hz, 1H), 5.66 (t, *J* = 9.7 Hz, 1H), 5.52 (t, *J* = 9.6 Hz, 1H), 5.08 (d, *J* = 9.9 Hz, 1H), 4.38 (d, *J* = 9.8 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 165.6, 165.1, 164.9, 133.5, 133.4, 133.4, 133.3, 131.2, 129.8, 129.8, 129.1, 129.0, 128.7, 128.6, 128.4, 128.4, 128.3, 86.5, 77.2, 76.5, 73.4, 70.0, 52.9. HRMS: Calc. for $C_{34}H_{28}O_9S$ $[M+H]^+$: 613.1532, Obser. 613.1538.

3.6.3 *β*-D-Glucopyranosiduronic acid, benzyl-2, 3, 4-tris-*O*-benzyl-1-thio, methyl ester (4c)

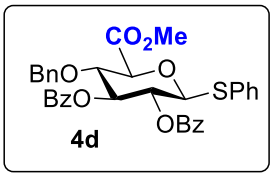


4c

Viscous liquid (107 mg, 91%), R_f value =0.4 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1750, 1232 cm^{-1} $[\alpha]_D^{20}$= -55.2 [c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.30 (m, 18H),

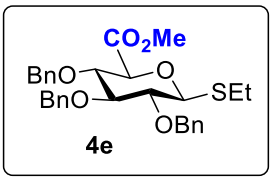
7.28–7.22 (m, 2H), 4.90–4.80 (m, 4H), 4.71 (d, *J* = 10.3 Hz, 1H), 4.65 (d, *J* = 10.8 Hz, 1H), 4.34 (d, *J* = 9.7 Hz, 1H), 4.02–3.99 (m, 1H), 3.92–3.82 (m, 3H), 3.79 (s, 3H), 3.65 (t, *J* = 8.8 Hz, 1H), 3.55–3.51 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 138.2, 137.8, 137.7, 137.2, 129.1, 128.6, 128.4, 128.4, 128.4, 128.2, 127.9, 127.9, 127.9, 127.7, 127.7, 127.2, 85.8, 84.1, 81.0, 79.2, 77.9, 75.8, 75.4, 75.1, 52.5, 34.6. HRMS: Calc. for $C_{35}H_{36}O_6S$ $[M+H]^+$: 585.2311, Obser. 585.2312.

3.6.4 *β*-D-Glucopyranosiduronic acid, phenyl-2, 3-bis-*O*-phenylmethyl-4-*O*-benzoyl-1-thio, methyl ester (4d) [20]



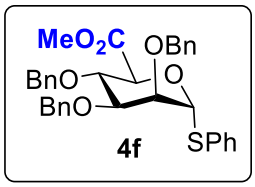
Viscous liquid (108 mg, 90%), R_f value =0.5 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1746, 1725, 1234 cm^{-1} $[\alpha]_D^{20}$= -64.9 [c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.07 (m, 4H), 7.98 (d, *J* = 7.4 Hz, 2H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.63–7.58 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45–7.37 (m, 7H), 7.30–7.27 (m, 2H), 6.13 (t, *J* = 10.1 Hz, 1H), 5.95–5.92 (m, 1H), 5.73–5.72 (m, 1H), 5.03 (s, 1H), 4.75–4.72 (m, 1H), 4.55–4.51 (m, 1H), 4.46–4.43 (m, 1H), 3.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 165.4, 165.4, 133.4, 133.4, 133.1, 133.0, 129.8, 129.8, 129.7, 129.7, 129.3, 129.1, 129.0, 128.5, 128.4, 128.2, 98.7, 70.4, 70.0, 68.7, 66.9, 62.9, 55.6.

3.6.5 *β*-D-Glucopyranosiduronic acid, ethyl-2, 3, 4-tris-*O*-benzyl-1-thio, methyl ester (4e) [21]



Viscous liquid (101 mg, 96%), R_f value =0.8 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1752, 1218 cm^{-1} $[\alpha]_D^{20}$= -16.5 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.40–7.38 (m, 2H), 7.37–7.30 (m, 11H), 7.25–7.24 (m, 2H), 4.94–4.92 (m, 2H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.77 (d, *J* = 10.2 Hz, 1H), 4.64 (d, *J* = 10.8 Hz, 1H), 4.53 (d, *J* = 9.7 Hz, 1H), 3.93–3.85 (m, 2H), 3.75 (s, 3H), 3.71 (d, *J* = 8.8 Hz, 1H), 3.50 (m, 1H), 2.84–2.71 (m, 2H), 1.34 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 138.2, 137.8, 137.7, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.7, 85.8, 85.8, 81.2, 79.3, 78.1, 75.8, 75.5, 75.1, 52.4, 25.1, 14.9.

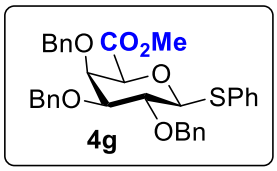
3.6.6 *α*-D-Mannopyranosiduronic acid, phenyl-2, 3, 4-tris-*O*-benzyl-1-thio, methyl ester (4f) [22]



Viscous liquid (109 mg, 95%), R_f value =0.5 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1746, 1222 cm^{-1} $[\alpha]_D^{20}$= +33.3 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.9 Hz, 2H), 7.39–7.30 (m, 18H), 5.73 (d, *J* = 5.2 Hz, 1H), 4.72–4.67 (m, 4H), 4.62–4.56 (m, 3H), 4.32 (t, *J* = 6.6 Hz, 1H), 3.96 (s, 1H), 3.87 (dd, *J* = 6.5, 2.2 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 137.9, 137.8, 133.9, 131.4, 128.9, 128.9, 128.4,

128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.3, 84.3, 76.0, 74.9, 74.97, 73.8, 72.9, 72.5, 72.4, 52.2.

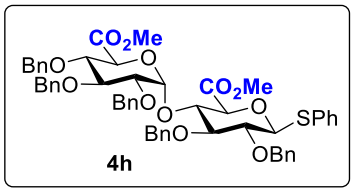
3.6.7 *β*-D-galactopyranosiduronic acid, phenyl-2, 3, 4-tris-*O*-benzyl-1-thio, methyl ester (4g) [19]



4g

Viscous liquid (109 mg, 95%), R_f value =0.55 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1754, 1236 cm^{-1} $[\alpha]_D^{20}$= -5.9 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.69–7.67 (m, 2H), 7.43–7.42 (m, 2H), 7.38–7.30 (m, 13H), 7.25–7.23 (m, 3H), 4.94 (d, *J* = 11.6 Hz, 1H), 4.85 (d, *J* = 10.2 Hz, 1H), 4.80–4.74 (m, 3H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 9.7 Hz, 1H), 4.35–4.34 (m, 1H), 4.09 (s, 1H), 3.97 (t, *J* = 9.4 Hz, 1H), 3.73 (s, 3H), 3.68 (dd, *J* = 9.2, 2.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 138.2, 138.2, 137.9, 133.5, 132.4, 128.8, 128.5, 128.3, 128.3, 128.2, 127.8, 127.8, 127.6, 127.5, 127.5, 87.8, 83.3, 77.2, 76.7, 75.7, 75.1, 74.4, 72.8, 52.4.

3.6.8 *β*-D-Glucopyranosiduronic acid, phenyl-4-*O*-[6-methyl-2, 3, 4-*tris*-*O*-(phenyl methyl)-*β*-D glucopyranosiduronyl]-2, 3-*bis*-*O*-(phenylmethyl)-1-thio, methyl ester (4h)

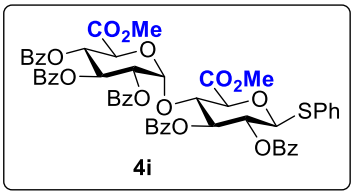


4h

Viscous liquid (174 mg, 92%), R_f value =0.6 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1752, 1735 cm^{-1} $[\alpha]_D^{20}$= +29.2 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.20 (m, 30H), 5.40 (d, *J* = 3.4 Hz, 1H), 5.18 (d, *J* = 3.3 Hz, 1H), 4.95–4.86 (m, 3H), 4.79 (dd, *J* = 12.9, 11.0 Hz, 2H), 4.70 (d,

J = 11.7 Hz, 1H), 4.61–4.54 (m, 5H), 4.18–4.11 (m, 3H), 3.98 (t, *J* = 9.4 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.69 (d, *J* = 9.1 Hz, 1H), 3.62 (dd, *J* = 8.5, 3.4 Hz, 1H), 3.56 (dd, *J* = 9.8, 3.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.7, 138.6, 138.4, 137.9, 137.7, 137.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.3, 127.1, 127.1, 98.0, 91.1, 80.7, 79.8, 79.2, 78.9, 78.5, 77.2, 75.6, 75.0, 74.6, 73.5, 73.0, 70.9, 70.8, 52.6, 52.4. HRMS: Calc. for $C_{55}H_{56}O_{12}S$ $[M+H]^+$: 941.3571, Obser. 941.3560.

3.6.9 *β*-D-Glucopyranosiduronic acid, phenyl-4-*O*-[6-methyl-2, 3, 4-*tris*-*O*-benzoyl-*β*-D-glucopyranosiduronyl]-2, 3-*bis*-*O*-benzoyl- 1-thio, methyl ester (4i)



4i

Viscous liquid (180 mg, 89%), R_f value =0.4 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1752, 1735, 1718 cm^{-1} $[\alpha]_D^{20}$= +64.5[c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, MeOD) δ 8.00–7.29 (m, 30H), 5.89 (m, 1H), 5.72 (t, *J* = 9.8 Hz, 1H), 5.21 (dd, *J* = 10.3, 3.7 Hz, 1H), 5.07 (d, *J* = 10.0 Hz, 1H), 5.00-4.97 (m, 1H), 4.31 (d, *J* = 9.5 Hz, 1H), 4.24 (d, *J* = 10.0 Hz, 1H), 4.07–4.01 (m, 2H), 3.97 (t, *J* = 8.8 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, MeOD) δ 169.7, 168.7, 166.1, 165.8, 165.7, 165.6, 165.5, 133.0, 132.9, 132.9, 132.3, 131.9, 129.8, 129.5, 129.4, 129.3, 129.3,

129.2, 129.2, 128.6, 128.1, 128.0, 127.9, 127.6, 96.8, 86.1, 77.5, 77.3, 75.4, 72.6, 72.1, 72.0, 71.0, 69.8, 52.2, 51.5. HRMS: Calc. for $C_{55}H_{46}O_{17}S$ $[M+H]^+$: 1011.2534, Obser. 1011.2523.

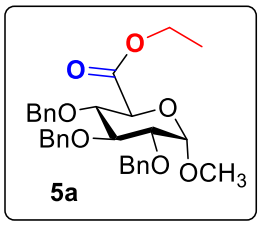
3.7 General procedure for preparation of uronic esters with various alcohols (6a-6l) using silica supported sulphuric acid

To a stirred solution of uronic acid (**1d)** (96 mg, 0.2 mmol, 1.0 equiv.) and alcohol (**6a-6l**) (2.0 equiv.), was added silica supported sulphuric acid (0.15 mmol) and stirred until the TLC showed complete conversion of starting material. The reaction mixture was filtered and rinsed properly using DCM. Further, the filtrate was neutralised using 0.5 mL of Et_3N and concentrated under reduced pressure. Column chromatography (SiO_2: 100-200 mesh) using EtOAc/petroleum ether afforded the pure uronic esters (**5a-5l**).

Note: In case of **5i** and **5l**, the reaction was carried out using DCM (1 mL) as solvent.

3.8 Analytical Data of uronic esters with different alcohols

3.8.1 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl, ethyl ester (5a)

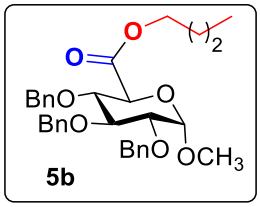


5a

Viscous liquid (97 mg, 95%), R_f value =0.5 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1742, 1241 cm^{-1} $[\alpha]_D^{20}$= +4.1 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.30 (m, 13H), 7.27–7.25 (m, 2H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.86–4.81 (m, 3H), 4.72–4.60 (m, 3H), 4.24–4.16 (m, 3H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.77 (dd, *J* = 9.9, 9.1 Hz, 1H), 3.61 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.43 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125

MHz, $CDCl_3$) δ 169.7, 138.6, 138.0, 137.9, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.7, 127.6, 98.7, 81.4, 79.7, 79.3, 75.8, 75.1, 73.6, 70.3, 61.6, 55.6, 14.0. HRMS: Calc. for $C_{30}H_{34}O_7$ $[M+Na]^+$: 529.2202, Obser. 529.2201.

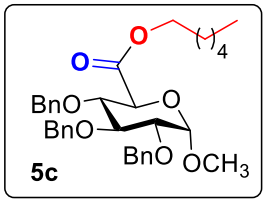
3.8.2 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl, n-butyl ester (5b)



5b

Viscous liquid (99 mg, 92%), R_f value =0.56 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1760, 1235 cm^{-1} $[\alpha]_D^{20}$= +12.4 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.29 (m, 13H), 7.27 (d, *J* = 7.6 Hz, 2H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.86–4.82 (m, 3H), 4.70–4.60 (m, 3H), 4.22–4.10 (m, 3H), 4.03 (t, *J* = 9.3 Hz, 1H), 3.78 (t, *J* = 9.5 Hz, 1H), 3.63–3.60 (m, 1H), 3.44 (s, 3H), 1.65–1.59 (m, 2H), 1.41–1.33 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 138.6, 138.0, 138.0, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.7, 127.6, 98.7, 81.4, 79.7, 79.4, 75.8, 75.1, 73.6, 70.3, 65.5, 55.6, 30.4, 19.0, 13.6. HRMS: Calc. for $C_{32}H_{38}O_7$ $[M+H]^+$: 535.2696, Obser. 535.2641.

3.8.3 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl, hexyl ester (5c)

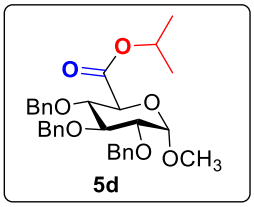


5c

Viscous liquid (103 mg, 91%), R_f value =0.6 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1728, 1232 cm^{-1} $[\alpha]_D^{20}$= +1.4 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.29 (m, 13H),

7.27–7.25 (m, 2H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.86–4.82 (m, 3H), 4.69–4.60 (m, 3H), 4.21 (d, *J* = 10.0 Hz, 1H), 4.18–4.08 (m, 2H), 4.03 (t, *J* = 9.3 Hz, 1H), 3.80–3.76 (m, 1H), 3.61 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.44 (s, 3H), 1.66–1.60 (m, 2H), 1.29–1.27 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 138.7, 138.1, 138.1, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.8, 127.7, 98.8, 81.5, 79.8, 79.5, 77.4, 77.1, 76.9, 76.0, 75.2, 73.7, 70.4, 65.9, 55.7, 31.4, 28.4, 25.5, 22.5, 14.0. HRMS: Calc. for $C_{34}H_{42}O_7$ $[M+Na]^+$: 585.2828, Obser. 585.2836.

3.8.4 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl isopropyl ester (5d)

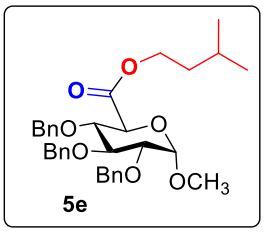


5d

Viscous liquid (98 mg, 94%), R_f value =0.5 in 15% EtOAc/ Hexane. IR υ_{max} (neat): 1755, 1220 cm^{-1} $[\alpha]_D^{20}$= -5.8 [c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.29 (m, 13H), 7.27–7.25 (m, 2H), 5.11–5.03 (m, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.87–4.80 (m, 3H), 4.69–4.59 (m, 3H), 4.16 (d, *J* = 10.0 Hz, 1H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.80–3.76 (m, 1H), 3.61 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.43 (s, 3H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.23 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 138.7, 138.2, 138.1, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 98.8, 81.5, 79.8, 79.5, 77.4, 77.1, 76.9, 75.9,

75.1, 73.7, 70.7, 69.5, 55.7, 21.8, 21.7. HRMS: Calc. for $C_{31}H_{36}O_7$ $[M+Na]^+$: 543.2359, Obser. 543.2366.

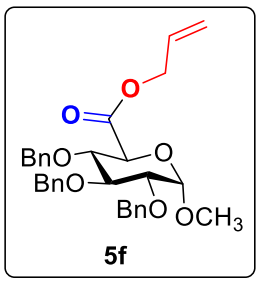
3.8.5 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl-(3-methyl-1-butyl) ester (5e)



5e

Viscous liquid (102 mg, 93%), R_f value =0.62 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1758, 1236 cm^{-1} $[\alpha]_D^{20}$= +2.5 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.31 (m, 13H), 7.27–7.25 (m, 2H), 5.32 (s, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.86–4.82 (m, 3H), 4.69–4.59 (m, 3H), 4.21–4.13 (m, 3H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.77 (dd, *J* = 9.9, 9.1 Hz, 1H), 3.61 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.43 (s, 3H), 1.70–1.65 (m, 1H), 1.52 (q, *J* = 7.0 Hz, 2H), 0.91 (d, *J* = 1.8 Hz, 3H), 0.89 (d, *J* = 1.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 138.5, 138.0, 137.9, 128.5, 128.4, 128.3, 128.2, 128.0, 128.0, 127.7, 127.7, 98.7, 81.4, 79.7, 79.3, 75.9, 75.1, 73.6, 70.3, 64.3, 55.6, 37.0, 25.0, 22.4, 22.3. HRMS: Calc. for $C_{33}H_{40}O_7$ $[M+Na]^+$: 571.2672, Obser. 571.2687.

3.8.6 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl, allyl ester (5f)

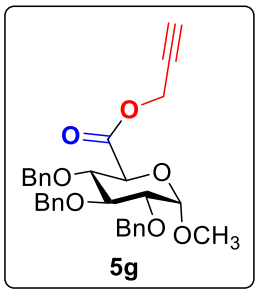


5f

Viscous liquid (89 mg, 86%), R_f value =0.45 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 3083, 1748, 1644, 1004, 917 cm^{-1} $[\alpha]_D^{20}$= +4.5 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.29 (m, 13H), 7.27–7.25 (m, 2H), 5.92–5.86 (m, 1H),

5.34 (ddd, *J* = 17.2, 2.8, 1.4 Hz, 1H), 5.25 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.87–4.80 (m, 3H), 4.70–4.58 (m, 5H), 4.24 (d, *J* = 10.0 Hz, 1H), 4.03 (t, *J* = 9.3 Hz, 1H), 3.78 (dd, *J* = 9.8, 9.2 Hz, 1H), 3.61 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 138.6, 138.0, 137.9, 131.3, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 119.1, 98.7, 81.4, 79.6, 79.3, 75.8, 75.1, 73.6, 70.3, 66.1, 55.6. HRMS: Calc. for $C_{31}H_{34}O_7$ $[M+Na]^+$: 541.2202, Obser. 541.2210.

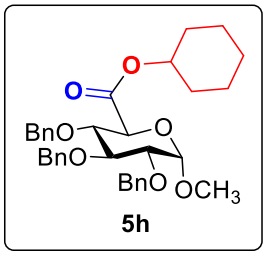
3.8.7 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl, propargyl ester (5g) [23]



5g

Viscous liquid (88 mg, 85%), R_f value =0.45 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 3324, 2126, 1750, 1226, 636 cm^{-1} $[\alpha]_D^{20}$= +1.9 [c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 18H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.85–4.80 (m, 3H), 4.70 (d, *J* = 2.5 Hz, 2H), 4.68–4.62 (m, 3H), 4.25 (d, *J* = 10.0 Hz, 1H), 4.01 (t, *J* = 9.3 Hz, 1H), 3.78–3.74 (m, 1H), 3.59 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.42 (s, 3H), 2.47 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 138.5, 137.9, 137.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 98.8, 81.3, 79.4, 79.2, 76.8, 75.9, 75.6, 75.1, 73.6, 70.1, 55.7, 52.9.

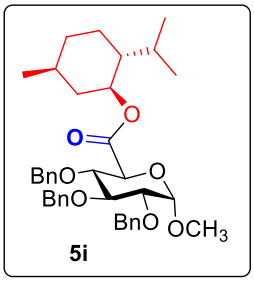
3.8.8 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl, cyclohexyl ester (5h)



5h

Viscous liquid (104 mg, 90%), R_f value =0.6 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1730, 2862, 1240 cm^{-1} $[\alpha]_D^{20}$= +3.9 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.41–7.24 (m, 15H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.83 (dd, *J* = 8.6, 4.1 Hz, 4H), 4.72–4.60 (m, 3H), 4.17 (d, *J* = 10.0 Hz, 1H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.78 (dd, *J* = 10.5, 8.5 Hz, 1H), 3.61 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.44 (s, 3H), 1.88–1.81 (m, 2H), 1.72 (s, 2H), 1.61–1.54 (m, 2H), 1.50–1.30 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 138.5, 138.1, 137.9, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 98.7, 81.4, 79.7, 79.3, 75.8, 75.1, 74.2, 73.6, 70.6, 55.5, 31.4, 31.3, 25.2, 23.7. HRMS: Calc. for $C_{34}H_{40}O_7$ $[M+Na]^+$: 583.2672, Obser. 583.2665.

3.8.9 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl-(L-menthyl) ester (5i)

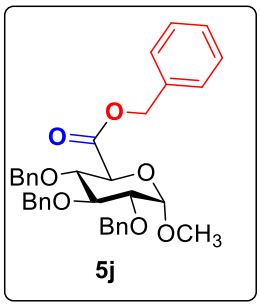


5i

Viscous liquid (101 mg, 82%), R_f value =0.65 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1746 cm^{-1} $[\alpha]_D^{20}$= -30.7 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.29–7.16 (m, 16H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.79–4.67 (m, 4H), 4.59–4.50 (m, 3H), 4.09 (d, *J* = 10.0 Hz, 1H), 3.92 (t, *J* = 9.3 Hz, 1H), 3.71–3.68 (m, 1H), 3.52 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.32 (s, 3H), 1.86 (dd, *J* = 8.8, 2.9 Hz, 1H), 1.78 (ddd, *J* = 13.9, 7.0, 2.6 Hz,

1H), 1.58 (d, *J* = 11.6 Hz, 2H), 1.36–1.31 (m, 2H), 0.97 (dd, *J* = 12.9, 2.6 Hz, 1H), 0.88–0.80 (m, 3H), 0.79–0.76 (m, 6H), 0.67 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 138.5, 138.0, 137.9, 128.5, 128.4, 128.2, 128.2, 128.0, 128.0, 127.7, 127.6, 127.5, 98.6, 81.5, 79.7, 79.3, 75.9, 75.7, 75.0, 73.6, 70.6, 55.4, 46.8, 40.5, 34.1, 31.3, 26.4, 23.6, 21.9, 20.5, 16.5. HRMS: Calc. for $C_{38}H_{48}O_7$ $[M+Na]^+$: 639.3298, Obser. 639.3298.

3.8.10 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl, benzyl ester (5j)

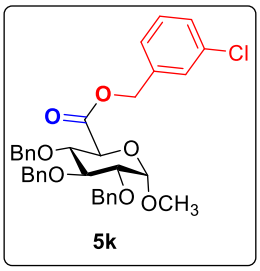


5j

Viscous liquid (103 mg, 90%), R_f value =0.56 in 15% EtOAc/ Hexane. IR υ_{max} (neat): 1745, 1235 cm^{-1} $[\alpha]_D^{20}$= -11.4 [c 0.1, $CHCl_3$]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.28 (m, 18H), 7.16 (dd, *J* = 6.5, 2.9 Hz, 2H), 5.22 (d, *J* = 12.3 Hz, 1H), 5.18 d, *J* = 12.3 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.85 (d, *J* = 1.6 Hz, 1H), 4.83 (d, *J* = 2.9 Hz, 1H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.70–4.66 (m, 2H), 4.49 (d, *J* = 10.8 Hz, 1H), 4.28 (d, *J* = 10.0 Hz, 1H), 4.03 (t, *J* = 9.3 Hz, 1H), 3.81–3.77 (m, 1H), 3.63 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 138.4, 137.9, 137.8, 135.0, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.6, 127.5, 98.7, 81.3, 79.6, 79.3, 75.8, 74.9, 73.5, 70.3, 67.2, 55.6.

HRMS: Calc. for $C_{35}H_{36}O_7$ $[M+Na]^+$: 591.2359, Obser. 591.2368.

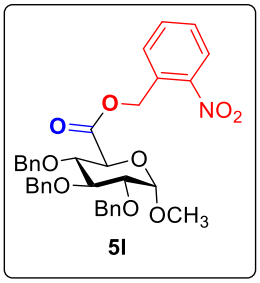
3.8.11 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl-(3-Chloro benzyl) ester (5k)



5k

Viscous liquid (102 mg, 84%), R_f value =0.55 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1752, 1240, 735, 702 cm^{-1} $[\alpha]_D^{20}$= +14.3 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.29 (m, 18H), 7.27 (s, 1H), 5.50 (s, 1H), 4.66–4.56 (m, 7H), 4.48(d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 12.1 Hz, 1H), 3.95 (d, *J* = 7.2, 1H), 3.72 (dd, *J* = 7.0, 6.1 Hz, 1H), 3.63 (s, 1H), 3.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 137.9, 137.8, 137.8, 128.5, 128.5, 128.0, 127.9, 127.8, 100.6, 76.7, 76.1, 76.0, 74.4, 72.0, 71.8, 71.2, 65.4. HRMS: Calc. for $C_{35}H_{35}ClO_7$ $[M+Na]^+$: 625.1969, Obser. 625.1988.

3.8.12 *α*-D-Glucopyranosiduronic acid, methyl 2, 3, 4-tris-*O*-benzyl-(2-nitrobenzyl) ester (5l) [12]



5l

Viscous liquid (105 mg, 85%), R_f value =0.56 in 15% EtOAc/ Hexane. IR: νmax(neat) 1742, 1425, 1120, 1090 cm^{-1} $[\alpha]_D^{20}$= -21.5 [c 0.1, $CHCl_3$]. ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 5.9, 3.6 Hz, 1H), 7.50 (dd, *J* = 5.7, 3.5 Hz, 1H), 7.44–7.41 (m, 2H), 7.39–7.30 (m, 11H), 7.25–7.24 (m, 2H), 7.20–7.15 (m, 2H), 5.59–5.50 (m, 2H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.88–

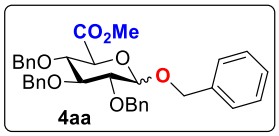
4.82 (m, 3H), 4.68 (d, *J* = 12.2 Hz, 2H), 4.57 (d, *J* = 11.0 Hz, 1H), 4.31 (d, *J* = 10.0 Hz, 1H), 4.05 (t, *J* = 9.3 Hz, 1H), 3.81 (t, *J* = 9.5 Hz, 1H), 3.62 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 147.2, 138.4, 137.9, 133.9, 131.6, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 125.1, 98.8, 81.5, 79.4, 79.3, 75.9, 75.0, 73.7, 70.3, 63.7, 55.7.

3.9 General procedure for glycosylation of uronic ester donors with various acceptors using silica supported sulphuric acid [24]:

A mixture of glycosyl donor (**4a**) (99 mg, 0.2 mmol, 1 equiv.), glycosyl acceptor (3 equiv. in case of non-sugar **a** and **b**, 1.2 equiv. in case of sugar **c**), and freshly activated molecular sieves (4Å, 300 mg) under argon in CH_2Cl_2 (5.0 mL) was stirred for 30 min at room temperature. The solution was cooled to -30 °C and NIS (1.1 equiv.) and TfOH (10 mol%) were added. The reaction was slowly allowed to reach 0 °C. The reaction was quenched by adding Et_3N on completion. The solid was filtered off and the filtrate was washed with 1 M HCl, sat. $NaHCO_3$ solution, 10% $Na_2S_2O_3$ and brine. The organic layer was separated, dried with anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (100-200 mesh) on silica gel to afford the corresponding glycoside.

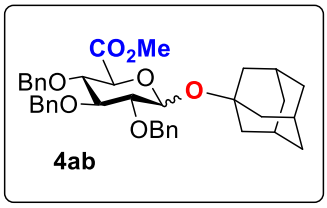
3.10 Analytical data of glycosylation products (4aa-4ac)

3.10.1 *β*-D-Glucopyranosiduronic acid-1, 2, 3, 4-*tetra*-*O*-benzyl-2-methyl ester (4aa)



White solid (102 mg, 89%), R_f value =0.7 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1775, 1230 cm^{-1} M.P. 111-113 °C. **α:β**= 1:1, ^1H NMR (500 MHz, $CDCl_3$) δ 7.43–7.25 (m, 21H), 5.02–4.55 (m, 9H), 4.33–4.07 (m, 1H), 3.97–3.87 (m, 1H), 3.78–3.74 (m, 3H), 3.70–3.58 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 169.1, 138.6, 138.3, 138.1, 137.9, 137.8, 137.0, 136.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.0, 128.01, 127.9, 127.9, 102.8, 95.9, 83.8, 81.8, 81.4, 79.6, 79.3, 79.3, 75.8, 75.7, 75.2, 75.1, 74.9, 74.5, 73.2, 71.4, 70.4, 69.4, 52.5, 52.4. HRMS: Calc. for $C_{35}H_{36}O_7$ $[M+Na]^+$: 591.2359, Obser. 591.2352.

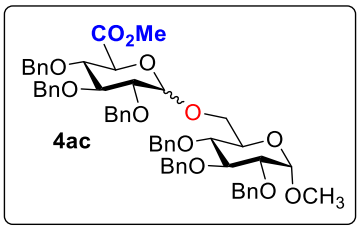
3.10.2 Methyl(2S,3S,4S,5R)-6-(((3S,5S,7S)-adamantan-1-yl) oxy)-3,4,5-tris(benzyloxy) tetra- hydro-2H-pyran-2-carboxylate (4ab)



Transparent viscous liquid (107 mg, 87%), R_f value =0.7 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1746, 1250 cm^{-1}. **α:β**= 3:1, ^1H NMR (500 MHz, $CDCl_3$) δ 7.40–7.28 (m, 16H), 5.32 (d, J = 3.0 Hz, 1H), 5.04–4.93 (m, 1H), 4.87–4.81 (m, 2H), 4.79–4.70 (m, 2H), 4.63 (t, J = 11.4 Hz, 1H), 4.50 (dd, J = 10.0, 2.0 Hz, 1H), 4.07 (t, J = 9.3 Hz, 1H), 3.93–3.83 (m, 1H), 3.79–3.70 (m, 3H), 3.61–3.59 (m, 1H), 2.19 (s, 3H), 1.96–1.83 (m, 6H), 1.70–1.63 (m,

6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 169.0, 138.8, 138.4, 138.3, 138.0, 138.0, 137.9, 128.4, 128.4, 128.4, 128.2, 128.2, 128.0, 128.0, 127.9, 127.8, 127.6, 96.6, 90.4, 84.3, 81.8, 81.4, 80.1, 79.5, 79.3, 75.8, 75.8, 75.7, 75.2, 75.2, 75.0, 74.2, 73.1, 70.1, 52.4, 52.4, 42.6, 42.3, 36.2, 30.6, 30.6. HRMS: Calc. for $C_{38}H_{44}O_7$ $[M+H]^+$: 613.3165, Obser. 613.3158.

3.10.3 *α*-D-Glucopyranoside, methyl-6-*O*-[6-methyl-2,3,4-*tris*-*O*-(phenylmethyl)-β-D-glucopyran- uronosyl]-2, 3, 4-*tris*-*O*-(phenylmethyl)-methyl ester (4ac) [25]



Transparent viscous liquid (158 mg, 85%), R_f value =0.7 in 20% EtOAc/ Hexane. IR υ_{max} (neat): 1754, 1218 cm^{-1} **α:β**= 1:1.5, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.09 (m, 30H), 4.90–4.43 (m, 14H), 4.40–3.85 (m, 3H), 3.78–3.53 (m, 8H), 3.48–3.22 (m, 5H).^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 168.9, 138.8, 138.8, 138.5, 138.3, 138.3, 138.2, 138.1, 138.1, 138.1, 137.8, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 104.1, 98.0, 97.8, 83.9, 82.1, 81.9, 81.6, 80.9, 80.1, 79.8, 79.6, 79.4, 79.2, 78.0, 77.6, 75.7, 75.7, 75.6, 75.0, 75.0, 74.9, 74.9, 74.5, 73.4, 73.4, 72.7, 70.4, 69.8, 68.9, 66.6, 55.2, 52.4, 52.4.

3.11 Spectra of some compounds

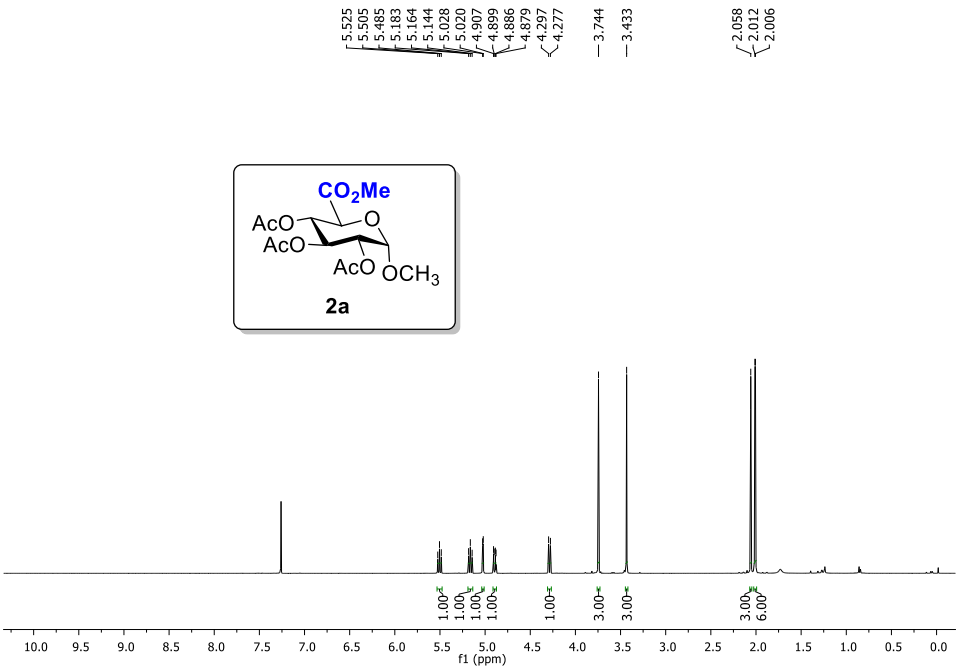


Figure 3.2 ^{1}H NMR spectrum of compound **2a** in $CDCl_3$

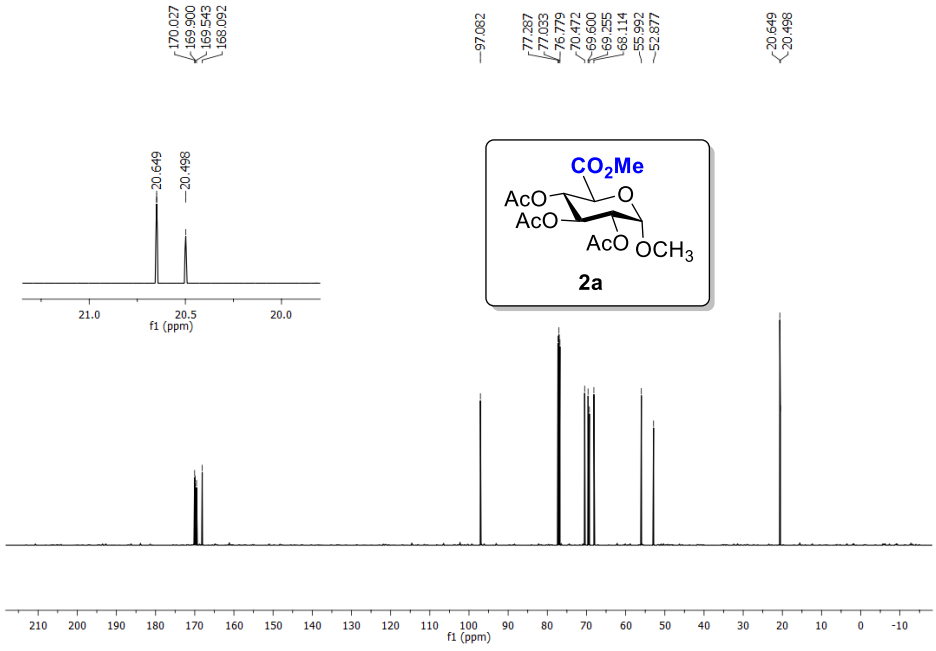


Figure 3.3 ^{13}C NMR spectrum of compound **2a** in $CDCl_3$

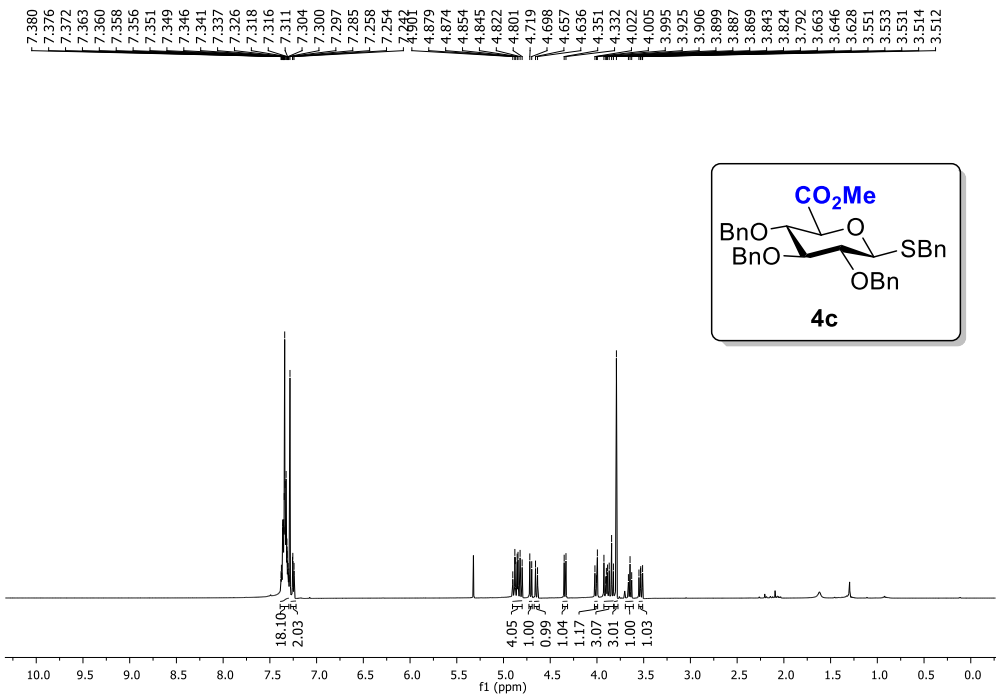


Figure 3.4 ^{1}H NMR spectrum of compound **4c** in $CDCl_3$

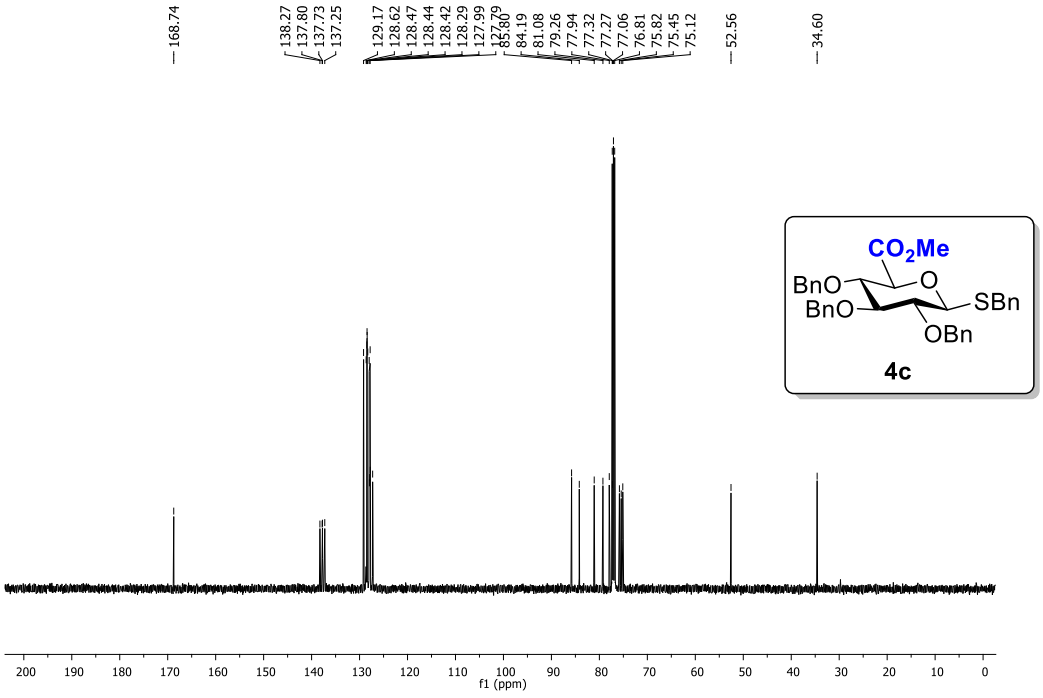


Figure 3.5 ^{13}C NMR spectrum of compound **4c** in $CDCl_3$

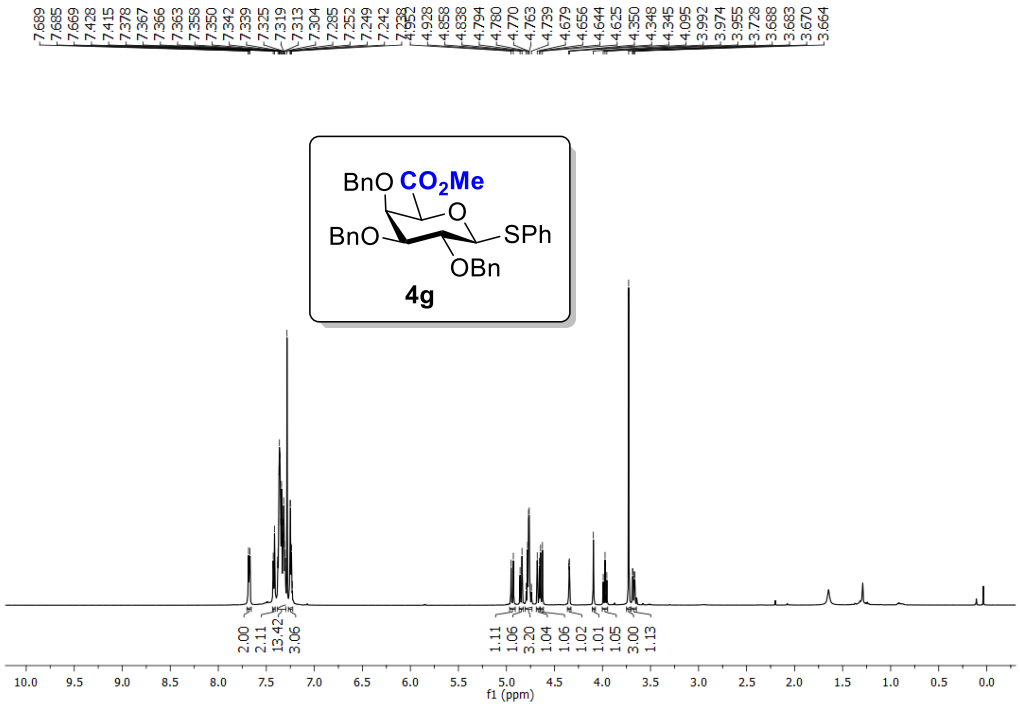


Figure 3.6 ^{1}H NMR spectrum of compound **4g** in $CDCl_3$

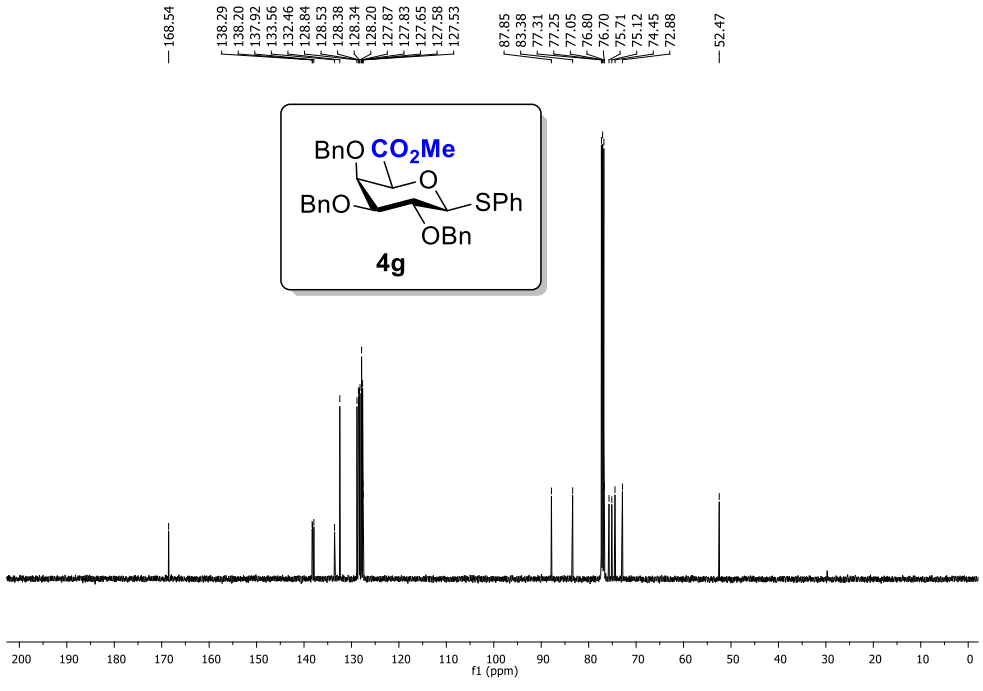


Figure 3.7 ^{13}C NMR spectrum of compound **4g** in $CDCl_3$

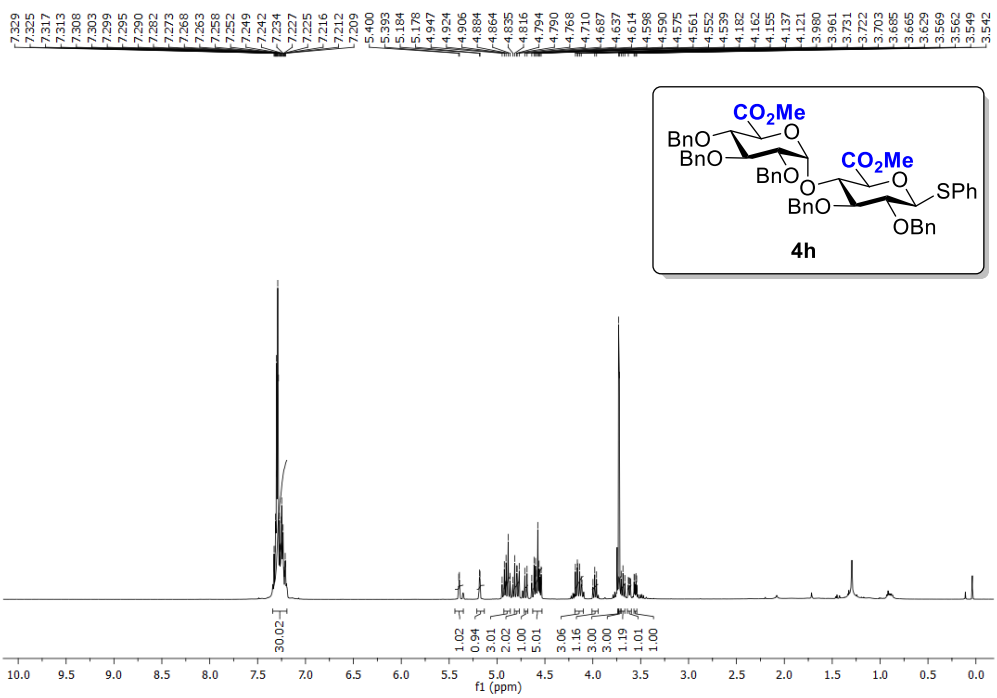


Figure 3.8 ^{1}H NMR spectrum of compound **4h** in $CDCl_3$

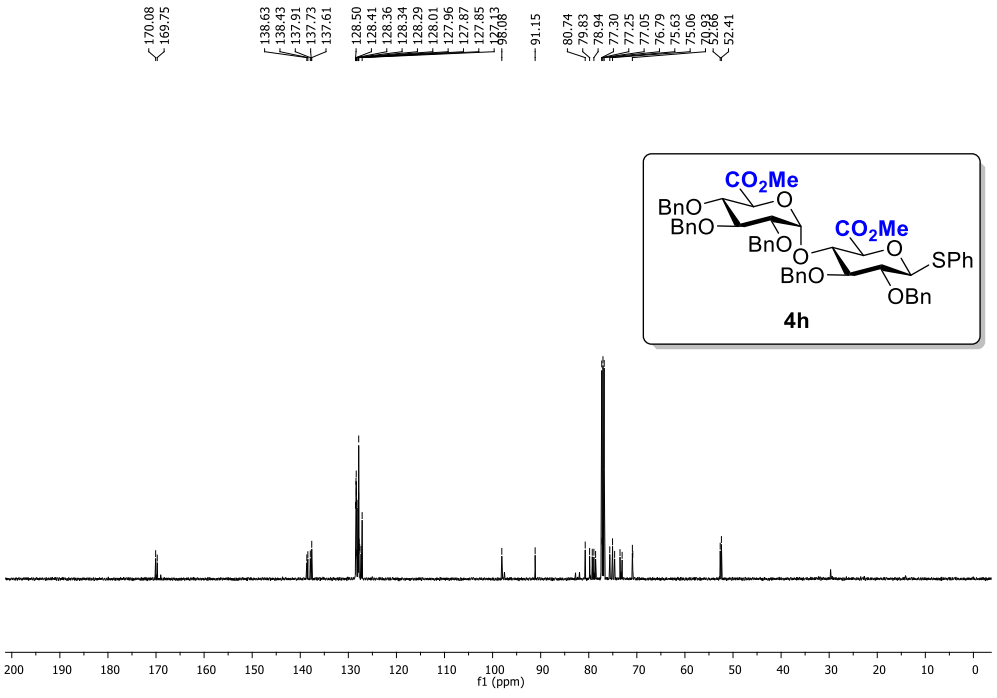


Figure 3.9 ^{13}C NMR spectrum of compound **4h** in $CDCl_3$

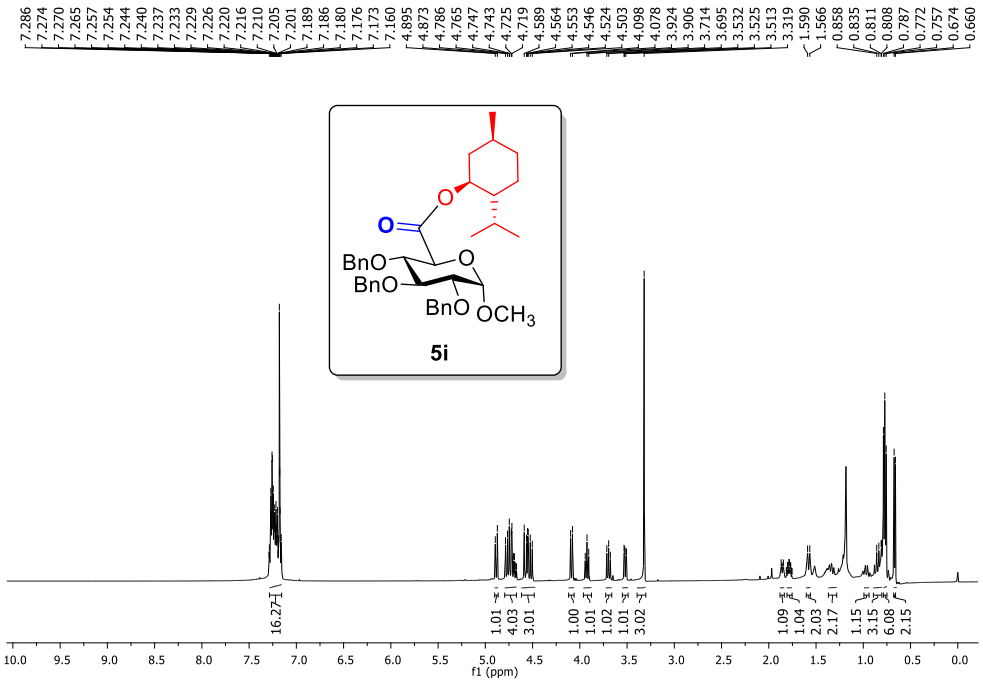


Figure 3.10 ^{1}H NMR spectrum of compound **5i** in $CDCl_3$

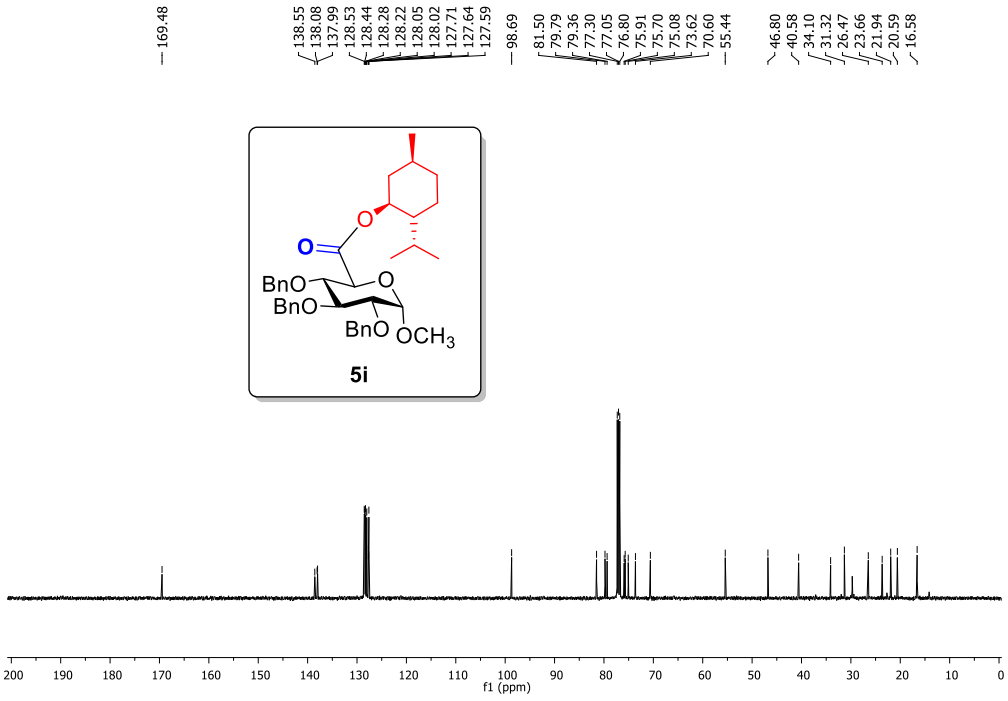


Figure 3.11 ^{13}C NMR spectrum of compound **5i** in $CDCl_3$

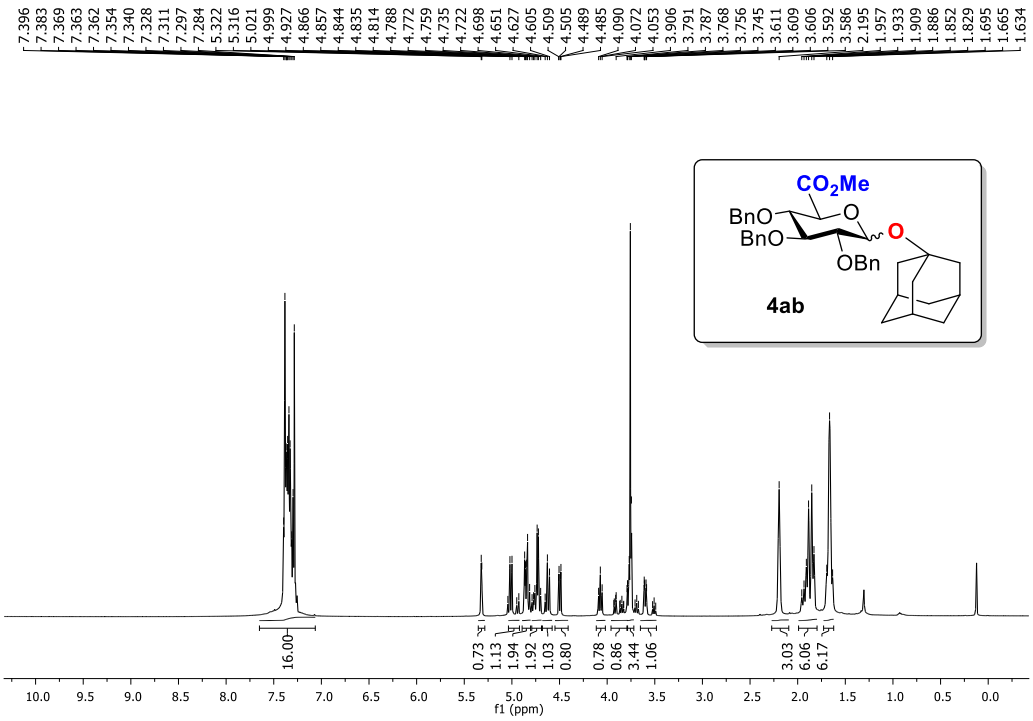


Figure 3.12 ^{1}H NMR spectrum of compound **4ab** in $CDCl_3$

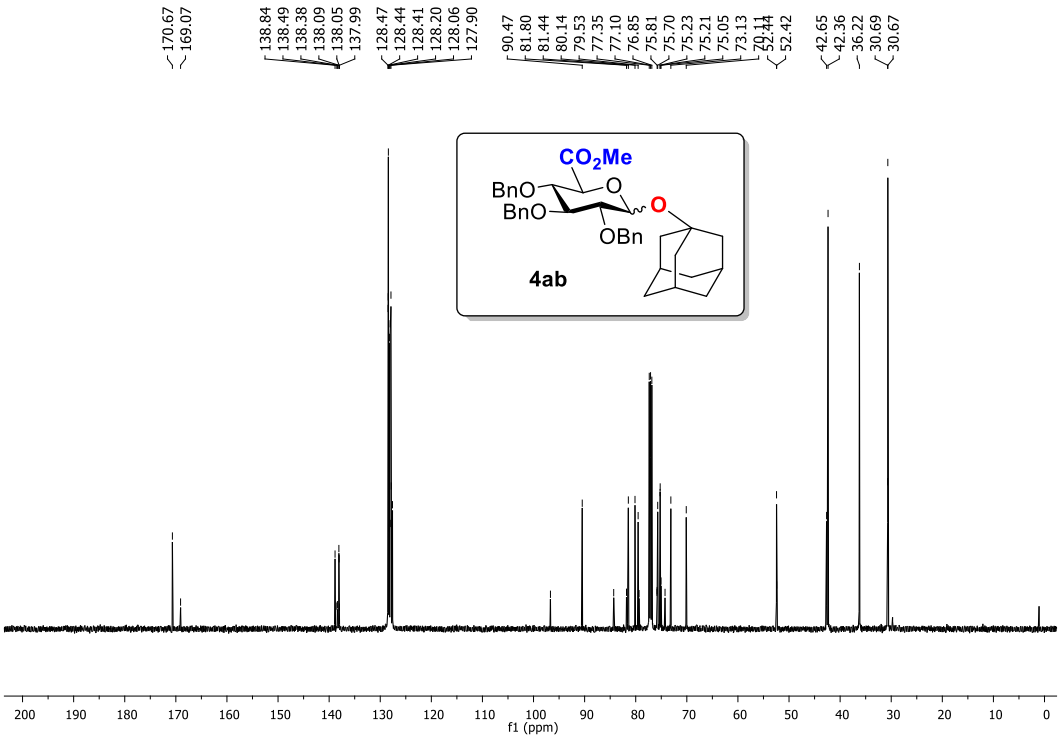


Figure 3.13 ^{13}C NMR spectrum of compound **4ab** in $CDCl_3$

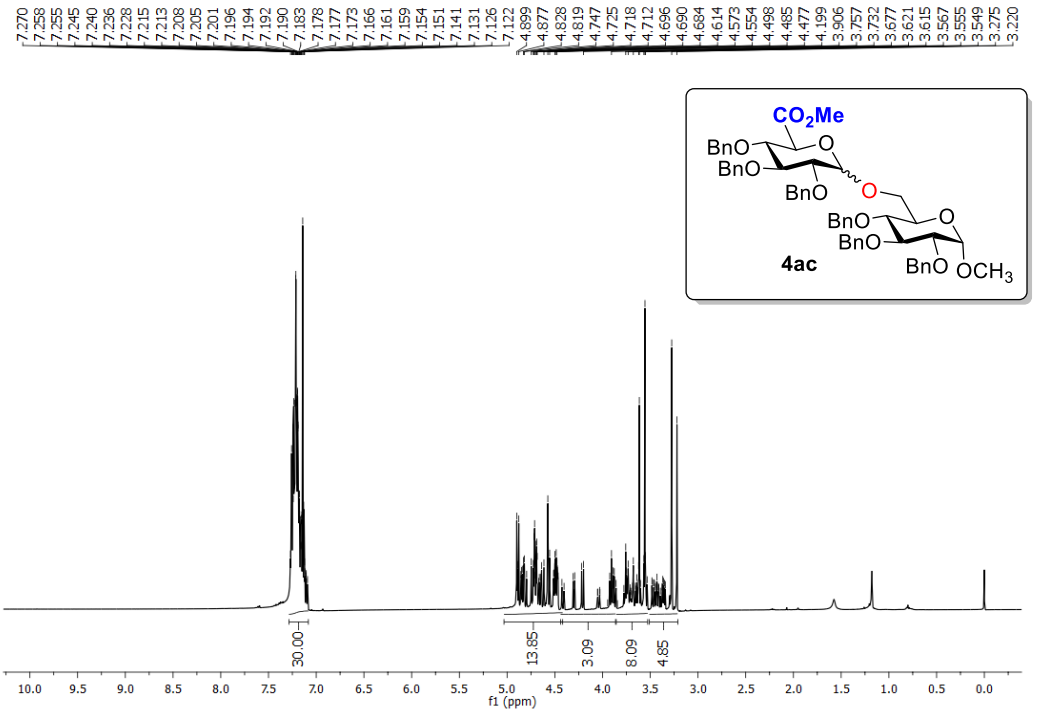


Figure 3.14 ^{1}H NMR spectrum of compound **4ac** in $CDCl_3$

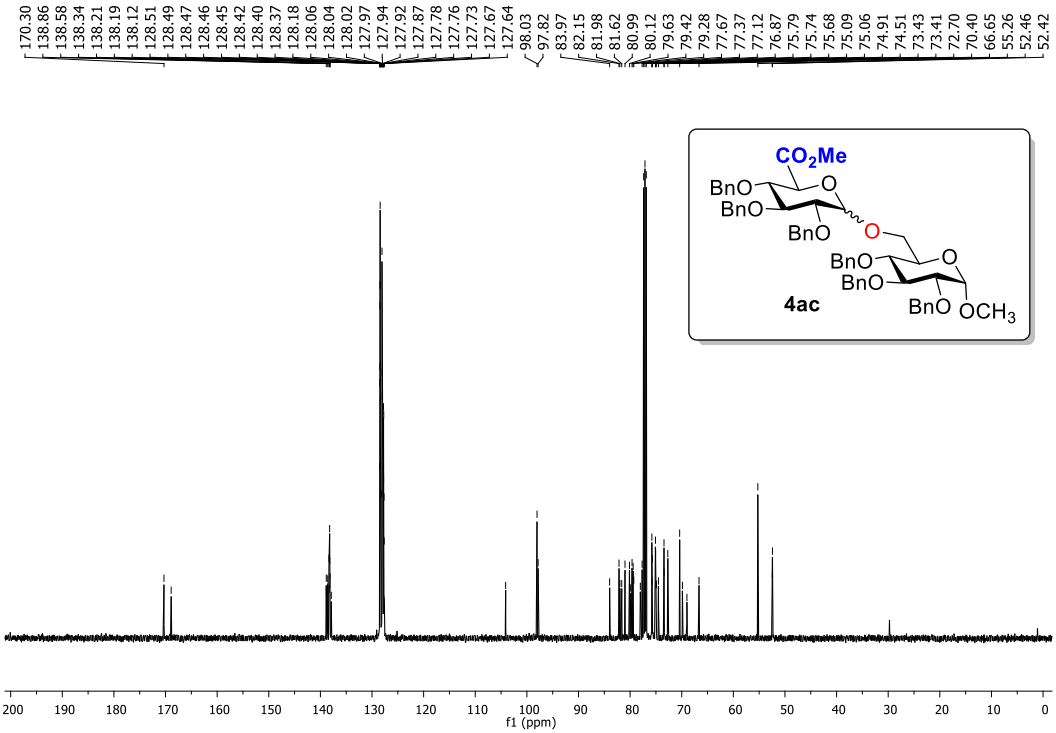


Figure 3.15 ^{13}C NMR spectrum of compound **4ac** in $CDCl_3$

2.12 References

[1] Varki, *Essentials of Glycobiology*, Cold Spring Harbor Laboratory Press, New York (USA) (1999). (b) P. H. Seeberger, D. B. Werz, *Nat. Rev. Drug Discov. 4* (2005) 751-763. (c) P. H. Seeberger, D. B. Werz, *Nature 446* (2007) 1046-1051. (d) T. K. Lindhorst, *Essentials of Carbohydrate Chemistry and Biochemistry*, Wiley-Vch Verlag GmbH & Co. Weinheim (2008). (e) B. Ernst, J. L. Magnani, *Nat. Rev. Drug Discov. 8* (2009) 661–677. (f) T. J. Boltje, T. Buskas, G. J. Boons, *Nature Chem. 1* (2009) 611–622. (g) M. C. Galan, D. Benito-Alifonso, G. M. Watt, *Org. Biomol. Chem. 9* (2011) 3598-3610.

[2] G. O. Aspinall, *The polysaccharides*; Academic Press: New York (1985). (b) L. J. Van den Bos, J. D. C. Codée, R. E. J. N. Litjens, J. Dinkelaar, H. S. Overkleeft, G. A. van der Marel, *Eur. J. Org. Chem.* (2007) 3963-3976. (c) J. D. C. Codée, A. E. Christina, M. T. C. Walvoort, H. S. Overkleeft, G. A. van der Marel, *Top. Curr. Chem. 301* (2011) 253-289.

[3] M. Petitou, J. C. Lormeau, J. Choay, *Nature 350* (1991) 30-33. (b) D. M. Weinberger, K. Trzcinski, Y. J. Lu, D. Bogaert, A. Brandes, J. Galagan, P. W. Anderson, R. Malley and M. Lipsitch, *Plos Pathog. 5* (2009) e1000476. (c) M. T. C. Walvoort, W. de Witte, J. van Dijk, J. Dinkelaar, G. Lodder, H. S. Overkleeft, J. D. C. Codée, G. A. van der Marel, *Org. Lett. 13* (2011) 4360-4363. (d) M. T. C. Walvoort, H. van den Elst, O. J. Plante, L. Kröck, P. H. Seeberger, H. S. Overkleeft, G. A. van der Marel, J. D. C. Codée, *Angew. Chem. Int. Ed. 51* (2012) 4393-4396. (e) M. Mende, C. Bednarek, M. Wawryszyn, P. Sauter, M. B. Biskup, U. Schepers, S. Brase, *Chem. Rev. 116* (2016) 8193-8255. (f) S. K. Kim, *Marine Glycobiology: Principles and Applications*; CRC Press, Taylor & Francis Group: New York (2017). (g) S. Li, Z. Wang, G. A. van der Marel, J. D. C. Codée, *Synthesis of Uronic Acid Containing Oligosaccharides, in Comprehensive Glycoscience* (Second Edition), Editor(s): Joseph J. Barchi, Elsevier (2021) 200-227.

[4] S. H. Khan, *Modern Methods in Carbohydrate Synthesis*, CRC Press, Taylor & Francis Group (1996). (b) D. B. Werz, S. Vidal, *Modern Synthetic Methods in Carbohydrate Chemistry: From Monosaccharides to Complex Glycoconjugates*, Wiley-VCH Verlag GmbH & Co. KGaA (2014).

[5] N. Chida, E. Yamada, S. Ogawa, *J. Carbohydr. Chem. 7* (1988) 555-570. (b) L. D. Proctor, A. J. Warr, *Org. Proc. Res. Dev. 6* (2002) 884–892. (c) P. Siengalewicz, J. Mulzer, U. Rinner, *Synthesis of Esters and Lactones. In Comprehensive Organic Synthesis* (Second Edition), P. Knochel, Ed. Elsevier: Amsterdam (2014) 355-410. (d) M. C. Pirrung, *9-Conducting the Reaction Itself. In Handbook of Synthetic Organic Chemistry* (Second Edition), M. C. Pirrung, Ed. Academic Press (2017) 83-109.

[6] W. Pilgrim, P. V. Murphy, *J. Org. Chem. 75* (2010) 6747-6755. (b) S. L. Tang, N. L. B. Pohl, *Org. Lett. 17* (2015) 2642-2645. (c) L. Beswick, S. Ahmadipour, J.

P. Dolan, M. Rejzek, R. A. Field, G. J. Miller, *Carbohydr. Res. 485* (2019) 107819.

[7] A. K. Singh, V. K. Kanaujiya, V. Tiwari, S. Sabiah, J. Kandasamy, *Org. Lett. 22* (2020) 7650–7655. (b) V. Tiwari, V. N. Badavath, A. K. Singh, J. Kandasamy, *J. Indian Chem. Soc. 97* (2020) 227-236. (c) V. Tiwari, A. K. Singh, P. Chaudhary, P. H. Seeberger, J. Kandasamy, *Org. Chem. Front. 6* (2019) 3859-3863. (d) K. B. Mishra, J. Kandasamy, *Asian J. Org. Chem. 8* (2019) 549–554. (e) A. K. Singh, R. Venkatesh, J. Kandasamy, *Synthesis 51* (2019) 4215-4230. (f) K.B. Mishra, A. K. Singh, J. Kandasamy, *J. Org. Chem. 83* (2018) 4204-4212. (g) A. K. Singh, J. Kandasamy, *Org. Biomol. Chem. 16* (2018) 5107-5112. (h) V. Tiwari, V. N. Badavath, A. K. Singh, J. Kandasamy, *Tetrahedron Lett. 59* (2018) 2511-2514. (i) A. K. Singh, V. Tiwari, K. B. Mishra, S. Gupta, J. Kandasamy, *Beilstein J. Org. Chem. 13* (2017) 1139–1144.

[8] R. S. Varma, *Green Chem. 1* (1999) 43-55. (b) N. E. Leadbeater, M. Marco, *Chem. Rev. 102* (2002) 3217-3274. (c) P. Munnik, P. E. de Jongh, K. P. de Jong, *Chem. Rev. 115* (2015) 6687–6718. (d) S. Bhattacharyya, B. Basu, *Green Techniques for Organic Synthesis and Medicinal Chemistry*, John Wiley & Sons (2018) 269–289. (e) A. Corma, H. Garcia, *Adv. Synth. Catal. 348* (2006) 1391-1412.

[9] M. Kaur, S. Sharma, P. M. Bedi, *Chinese J. Catal. 36* (2015) 520-549. (b) A. Pramanik, S. Bhar, *New J. Chem. 45* (2021) 16355-16388.

[10] V. K. Rajput, B. Mukhopadhyay, *Tetrahedron Lett. 47* (2006) 5939-5941. (b) B. Mukhopadhyay, *Tetrahedron Lett. 47* (2006) 4337-4341. (c) V. K. Rajput, B. Roy, B. Mukhopadhyay, *Tetrahedron Lett. 47* (2006) 6987-6991. (d) B. Roy, B. Mukhopadhyay, *Tetrahedron Lett. 48* (2007) 3783-3787. (e) J. F. Zhou, X. Chen, Q. B. Wang, B. Zhang, L. Y. Zhang, A. Yusulf, Z. F. Wang, J. B. Zhang, J. Tang, *Chin. Chem. Lett. 21* (2010) 922-926. (f) J. Zhang, B. Zhang, J. Zhou, J. Li, C. Shi, T. Huang, Z. Wang, J. Tang, *J. Carbohydr. Chem. 30* (2011) 165–177. (g) B. Liu, Z. Zhang, *RSC Adv. 3* (2013) 12313-12319.

[11] X. Chen, J. She, Z. C. Shang, J. Wu, P. Zhang, *Synth. Commun.* **2009**, *39*, 947-957.

[12] V. Tiwari, A. K. Singh, P. Chaudhary, P. H. Seeberger, J. Kandasamy, *Org. Chem. Front.* **2019**, *6*, 3859-3863.

[13] T. Rosenau, A. Potthast, N. S. Zwirchmayr et al. *Cellulose* **2017**, *24*, 3703–3723.

[14] (a) P. Kováč, J. Alföldi, M. Košík, *Chem. Pap.* **1974**, *28*, 820-832. (b) A. M. Esmurziev, A. Reimers, T. Andreassen, N. Simic, E. Sundby, B. H. Hoff, *Molecules* **2012**, *17*, 820-835.

[15] (a) G. Witkowski, A. Zawisza, M. Malik, S. Jarosz, In *Carbohydr. Chem.* **2015**, 52-59, CRC Press. (b) A. De Raadt, A. E. Stütz, *Carbohydr. Res.* **1991**, *220*, 101-115.

[16] A. K. C. Schmidt, C. B. Stark, *Org. Lett.* **2011**, *13*, 4164-4167.

[17] S. Van der Vorm, T. Hansen, H. S. Overkleeft, G. A. Van der Marel, J. D. C. Codée, *Chem. Sci.* **2017**, *8*, 1867-1875.

[18] S. van der Vorm, J. M. van Hengst, M. Bakker, H. S. Overkleeft, G. A. van der Marel, J. D. Codée, *Angew. Chem.* **2018**, *130*, 8372-8376.

[19] J. Dinkelaar, A. R. de Jong, R. van Meer, M. Somers, G. Lodder, H. S. Overkleeft, J. D. Codee, G. A. van der Marel, *J. Org. Chem*. **2009**, *74*, 4982-4991.

[20] S. Bera, R. J. Linhardt, *J. Org. Chem.* **2011**, *76*, 3181-3193.

[21] L. J. van den Bos, J. D. Codée, J. C. van der Toorn, T. J. Boltje, J. H. van Boom, H. S. Overkleeft, G. A. van der Marel, *Org. Lett.* **2004**, *6*, 2165-2168.

[22] L. J. van den Bos, J. Dinkelaar, H. S. Overkleeft, G. A. van der Marel, *J. Am. Chem. Soc.* **2006**, 128, 13066.

[23] K. Cheng, J. Liu, X. Liu, H. Li, H. Sun, J. Xie, *Carbohydr. Res.* **2009**, *344*, 841-850.

[24] C. Alex, S. Visansirikul, A. V. Demchenko, *Org. & Biomol. Chem. 19* (2021) 2731-2743.

[25] J. Dinkelaar, A. R. de Jong, R. van Meer, M. Somers, G. Lodder, H. S. Overkleeft, J. D. Codee, G. A. van der Marel, *J. Org. Chem*. *74* (2009) 4982-4991.