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Highly chemo- and stereoselective glycosidation of permethacrylated *O*-glycosyl trichloroacetimidate reagents promoted by $TMSNTf_2$

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ABSTRACT

$TMSNTf_2$ has been used efficiently as a promoter in glycosidation reaction involving permethacrylated Schmidt reagents. While $TMSNTf_2$ is known to be a powerful activator for C=O double bonds, we have discovered that this reagent can activate C=N double bond selectively, even in the presence of excess C=O groups of permethacrylated *O*-glycosyl trichloroacetimidate substrates. Glycosides are synthesized in moderate to reasonable yields with an excellent overall β-stereoselectivity.

1. Introduction

The increased knowledge and understanding of the crucial roles of oligosaccharides in diverse biological processes, have stimulated tremendous synthetic efforts for the development of efficient and selective methods in glycoside synthesis.[1] Since the first glycoside preparation by Michael[2] and Fisher,[3] a great number of glycosidation strategies have been developed and constantly optimized. Among them, glycoside syntheses based on *O*-glycosyl trichloroacetimidates, discovered by Sinaÿ,[4] and known as 'Schmidt glycosidation' has emerged as the most popular approach, due to their remarkable donor properties, ease of formation, reactivity, and general applicability.[5] Nowadays a large number of catalysts for glycosidation reactions of trichloroacetimidates are known. Activation using $BF_3{\cdot}Et_2O$,[6] TMSOTf,[7] TBDMSOTf,[8] Tf_2O,[9] $ZnBr_2$,[10] AgOTf,[11] and several moisture-stable activating reagents such as I_2/Et_3SiH[12] or $HClO_4$/silica,[13] have been used successfully. Beside these promoters, it is also worthwhile to mention the use of 4 Å acid washed molecular sieves,[14] Amberlyst 15[15] and a cationic palladium[16] for the efficient activation of *O*-glycosyl trichloroacetimidates. More recently, the use of *N*-phenyl trifluoroacetimidate has contributed to expand considerably the imidate chemistry.[17] However, the majority of glycosidation reactions involving Schmidt reagents as glycosyl donor requires the use of robust compatible protecting groups such as ethers or esters, and little attention has been paid to the use of protected polymerizable Schmidt reagents bearing α,β-unsaturated esters. In continuation of our efforts to investigate the chemistry of permethacrylated carbohydrates,[18] we wish to report on the use of permethacrylated Schmidt reagents as useful glycosyl donors, upon activation with various Lewis acids, including $TMSNTf_2$. To date, $TMSNTf_2$ has exclusively been used as carbonyl activator, in different transformation such as Diels–Alder (DA) reactions,[19] Mukayaima–aldol condensations,[20] alkylations of α,β-unsaturated compounds,[21] and Friedel–Crafts alkylation. While $TMSNTf_2$ has been shown to activate efficiently α,β-unsaturated esters such as *trans*-methyl crotonate in DA reaction, this catalyst was also found to be chemically compatible with 2-azadiene.[22] This observation demonstrated the capabilities of $TMSNTf_2$ to activate selectively carbonyl group in the presence of C=N bond. During our investigations we have discovered that glycosidation reactions involving permethacrylated Schmidt glycosyl donors (Fig. 1) promoted by $TMSNTf_2$ afforded the expected glycosides, in good to moderate yields, with an excellent overall β-stereoselectivity. These unprecedented results demonstrate, for the first time that the

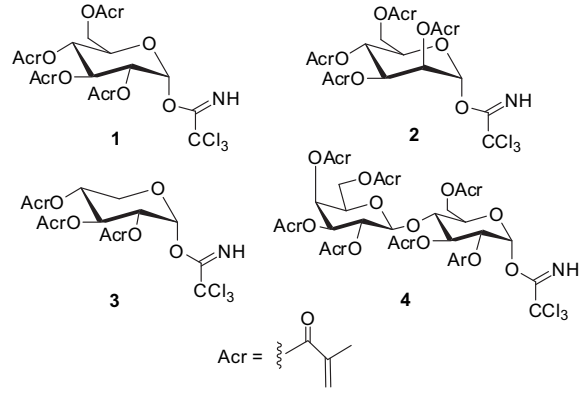

Figure 1. Activated permethacrylated *O*-glycosyl trichloroacetimidate reagents investigated.

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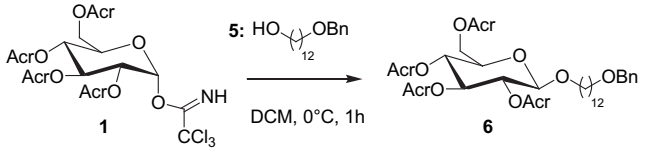
trichloroacetimidate function could be activated by $TMSNTf_2$ selectively to generate the oxocarbenium ion, even in the presence of excess methacrylate functions on the substrates. Since, all the common other Lewis acid tested behaved similarly to $TMSNTf_2$ in terms of efficiency, kinetics and stereoselectivity in the glycosidation, we decided to investigate the scope and the reactivity of $TMSNTf_2$, which has no literature precedent for this transformation, specially with substrates bearing compatible polyacrylate functions **1**–**4**.

2. Result and discussion

$TMSNTf_2$ was first prepared according to reported procedures that use the protodesylilation of allyltrimethylsilane with commercially available $HNTf_2$ at room temperature.[22,23] It is important to mention, that all the glycosidation reactions were carried out under an inert atmosphere and any other precautions were necessary for the handling of permethacrylated carbohydrates.[18b]

Permethacrylated *O*-glycosyl trichloroacetimidate reagent **1** was first used in glycosidation reaction with alcohol **5**[24] in the presence of the most commonly used activators such as TMSOTf and $BF_3{\cdot}Et_2O$ in standard conditions (DCM at 0 °C, for 1 h).[6] The reactions afforded stereoselectively the β-glycoside in reasonable yields, 44% and 51%, respectively (Table 1, entries 1, 2). We then experienced the reactivity of **1** in the presence of a catalytic amount of protic acids, such as TfOH and $HNTf_2$ (Table 1, entries 3 and 4). The reactions delivered cleanly and stereoselectively the expected β-glycoside **6** in comparable yields with the results obtained with TMSOTf and $BF_3{\cdot}Et_2O$. Triflic anhydride behaved similarly and afforded **6**, in moderate yield with a complete β stereoselectivity (Table 1, entry 5). It is important to point out that there was no literature precedent mentioning the use of these Lewis acids with permethacrylated *O*-glycosyl trichloroacetimidate reagents. However, only recently $HNTf_2$ has been reported for glycosidation reactions in ionic liquid for the activation of a glucopyranosyl diethyl phosphite[25] and glucopyranosyl fluoride.[26] With the goal of improving the overall efficiency of the reaction we envisioned to test other Lewis acid, that is, stronger than TMSOTf,[6] and that would still remain selective with methacrylate functions. To our delight, glycosidation of **1** with **5** performed with $TMSNTf_2$ yielded to β-glycoside **6** with 42% (Table 1, entry 6). Even though $TMSNTf_2$ is known to act as a strong C=O bond activator, the desired glycoside is obtained without alteration of the stereoselectivity and with comparable yield to the classical catalyst activators used previously. These results demonstrated the chemical compatibility of methacrylate groups with $TMSNTf_2$. Reactions carried out in the presence of 2,6-bis-*tert*-butyl-4-methylpyridine for neutralizing residual traces of TfOH in $TMSNTf_2$ gave also the expected product, however, with a decreased yield (36%) (Table 1, entry 7).[23] Attempts to reduce the amount of $TMSNTf_2$ to 10 mol % was detrimental to the conversion of **1** and only 23% of **6** was isolated (Table 1, entry 8). Identically, using 1 equiv or excess of $TMSNTf_2$ was unsatisfactory, due to partial polymerization of both the starting material **1** and the desired product **6**. In all cases, the product **6** of the reaction was easily detected by TLC monitoring, and full conversion of **1** was always observed. Traces of other more polar byproducts were observed, however, identification of their structures by NMR remained difficult. These side products might arise from the hydrolysis of the anomeric position of compound **1** or from the activation of the acrylate functions. Partial polymerization of **1** and **6** was only detected when 1 equiv of $TMSNTf_2$ was used.

Table 1
Glycosidation of **1** with different promoters



Entry	Promoters	Equiv	Isolated yield (%)	Ratio (β/α)
1	TMSOTf	0.5	44	1/0
2	$BF_3{\cdot}Et_2O$	0.5	51	1/0
3	TfOH	0.1	35	1/0
4	$HNTf_2$	0.1	48	1/0
5	Tf_2O	0.5	44	1/0
6	$TMSNTf_2$	0.5	42	1/0
7	$TMSNTf_2$	0.5[a]	36	1/0
8	$TMSNTf_2$	0.1[a]	23	1/0

[a] 0.1 Equiv of 2,6-bis-*tert*-butyl-4-methylpyridine was added in the reaction mixture.

The identification of the unknown reactivity and chemocompatibility of $TMSNTf_2$ with permethacrylated and peracetylated *O*-glycosyl trichloroacetimidate reagents prompted us to finally evaluate the substrate scope and the limitations of the reaction, as well as its influence on the stereoselectivity (Table 2).

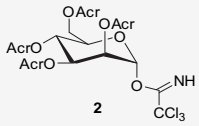
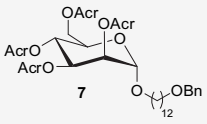
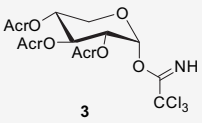
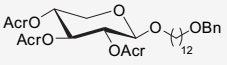
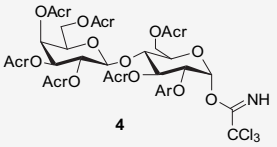
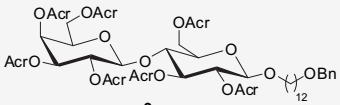
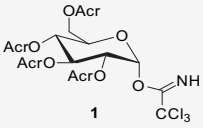
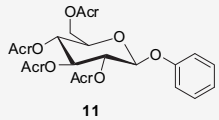
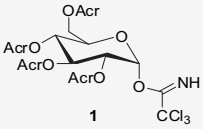
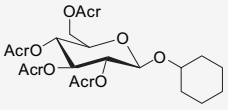
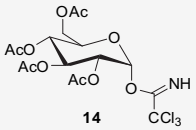
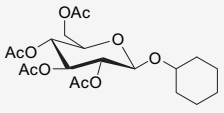
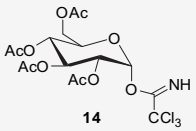
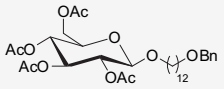
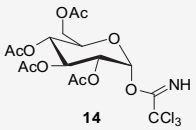
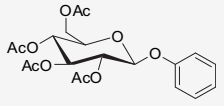
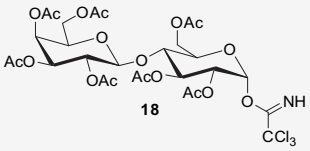
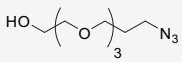
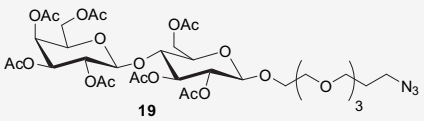
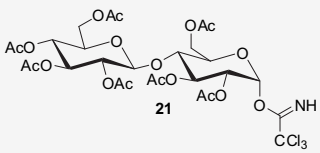
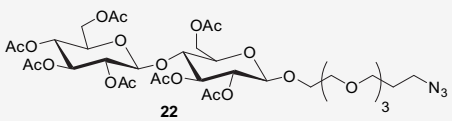
We have found that permethacrylated *O*-glycosyl trichloroacetimidate mannose **2** and xylose **3** derivatives behaved similarly to **1**, and provided **7** and **8** in good yield (Table 2, entries 1 and 2). While the reaction was highly stereoselective and delivered exclusively the α-glycoside for permethacrylated mannose **7**, a 5/2 ratio of the β/α anomers was obtained for permethacrylated xylose **8**. Permethacrylated Schmidt dissacharide such as the lactose derivative **4** gave satisfactorily the β-anomer **9**, although the yield was decreased to 23% (Table 2, entry 3). In this conditions, unactivated alcohol such as phenol **10** could also react with **1** in a stereoselective manner giving rise to **11** (41%) (Table 2, entry 4). While the reaction with primary alcohol **5** and phenol with **1** afforded the β-glycoside, we observed that the glycosidation with cyclohexanol **12** was not as selective and gave a 1/1 mixture of β/α glycoside **13** and in a less efficient manner (Table 2, entry 5). This lack of selectivity is not understood yet and might eventually, be ascribed to incomplete anchimeric assistance of the 2-methacrylate group of **1**. This result was partially corroborated when peracetylated Schmidt reagent **14** was submitted in strictly identical conditions. In this particular case the β-anomer was formed as the unique product **15** exclusively (Table 2, entry 6).

Finally we envisaged to extend the use of $TMSNTf_2$ as activator for peracetylated *O*-glycosyl trichloroacetimidate reagents. It appeared that the efficiency of the glycosidation was dependent on the structure of the nucleophilic alcohol acceptor. Indeed, while cyclohexanol **12** was successfully coupled with **14** (Table 2, entry 6), primary alcohol gave poor yield, 18% for the compound **16** (Table 2, entry 7) and the use of low nucleophilic phenol **10** afforded only traces amount of the expected product **17** (Table 2, entry 8). We have eventually found that more complex peracetylated *O*-glycosyl trichloroacetimidate disaccharides **18** and **21** reacted with functionalized alcohol **20** and yielded to **19** and **22** in acceptable yields for such complex functionalized sugars (Table 2, entries 9 and 10).

It is worthwhile to mention that pure β anomers were also formed exclusively when peracetylated substrates were used. However, as a general trend, peracetylated *O*-glycosyl trichloroacetimidate were less stable in the glycosidation conditions, since the hydrolyzed peracetylated carbohydrates were always formed as byproducts in large amounts. All together, these results demonstrate for the first time, the chemocompatibility of $TMSNTf_2$ in glycosidation reactions involving either permethacrylated *O*-glycosyl trichloroacetimidates, and to some extent with peracetylated *O*-glycosyl trichloroacetimidate.

In summary, we have reported the use of $TMSNTf_2$ for the selective activation of permethacrylated *O*-glycosyl trichloroacetimidates. The

Table 2
Glycosidation of permethacrylated *O*-glycosyl trichloroacetimidate carbohydrates with $TMSNTf_2$[a]

Entry	*O*-Glycosyl trichloroacetimidate	Alcohol	Product	Yield (%)	Ratio (β/α)
1	 **2**	**5**	 **7**	40	0/1
2	 **3**	**5**	 **8**	35	5/2
3	 **4**	**5**	 **9**	23	1/0
4	 **1**	 **10**	 **11**	41[b]	1/0
5	 **1**	 **12**	 **13**	23	1/1
6	 **14**	**12**	 **15**	37	1/0
7	 **14**	**5**	 **16**	18	1/0
8	 **14**	**10**	 **17**	Traces	/
9	 **18**	 **20**	 **19**	24	1/0
10	 **21**	**20**	 **22**	30	1/0

[a] 0.5 Equiv of $TMSNTf_2$ was used in DCM at 0 °C, for 1 h.
[b] The product **11** was contaminated with phenol **10** due to the same R_f of the compounds for purification carried out by column chromatography on silica.

reactions were highly stereoselective and favoured β-glycosides due to anchimeric assistance of the methacrylate group. The overall efficiency in terms of isolated yields, is comparable with other promoters, and the most important feature of these conditions still remain the chemocompatibility of the permethacrylated, as well as the acetate functions of the substrates with $TMSNTf_2$. Besides this we have also shown that protic acid such as $HNTf_2$ can also be used successfully to promote the glycosidation reactions for Schmidt reagents.

3. Experimental

3.1. General

The general procedure for the preparation of *O*-glycosyl trichloroacetimidates **1**, **2**, **3** and **4** can be found in Ref. 18a. Compound **14** was prepared accordingly to the protocol described in the Ref. 27 and compounds **18** and **21** were synthesized following reported procedures.[28] Alcohol **20** was synthesized according to Ref. 29. The preparation of $TMSNTf_2$ has been performed following the Ghosez's protocol.[21]

3.2. General procedure for the glycosidation reactions of *O*-glycosyl trichloroacetimidates 1, 2, 3, 4, 14, 18 and 21 promoted by $TMSNTf_2$

The glycosyl donor (1 equiv) was dissolved in dichloromethane (concentration fixed at 50 mM) and alcohol **5**, **10**, **12** or **20** (1.2 equiv) was added. The reaction mixture was cooled down to 0 °C and $TMSNTf_2$ (0.5 equiv, freshly prepared DCM solution at 0.7 M) was slowly added. The mixture became brown after 10 min. After stirring for 1 h at 0 °C in DCM, the solvent was evaporated and the purification is performed by column chromatography with the indicated solvents.

*3.2.1. Synthesis of compound **6**.* From 600.0 mg of **1**, 411.4 mg of **6** was recovered as colourless oil (yield: 56%) (SiO_2, cyclohexane/EtOAc=8/2, R_f=0.46). For ^1H and ^{13}C NMR see Ref. 17b.

*3.2.2. Synthesis of compound **7**.* From 1.4 g of **2**, 1.1 g of **7** was recovered as yellow oil (yield: 40%) (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.75). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.27 (m, 5H), 6.15–5.93 (4s, 4H), 5.58–5.29 (m, 8H), 4.83 (s, 1H), 4.44 (s, 2H), 4.30–4.19 (m, 3H), 3.64 (m, 1H), 3.40 (m, 3H), 1.90–1.76 (m, 12H), 1.57 (m, 4H), 1.21 (m, 16H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.0, 166.3, 166.2, 166.1, 136.2, 135.8, 135.6, 135.5, 128.4, 127.6, 126.8, 126.7, 126.6, 126.0, 97.7, 73.0, 70.7, 70.5, 69.9, 68.8, 66.8, 62.9, 29.9–29.4, 26.3, 18.3–18.1; IR: ν (cm^{-1}) 2927, 2854, 1728, 1638, 1454, 1321, 1294, 1135, 1081; HRMS: (*m*/*z*): calcd for $C_{41}H_{58}O_{11}Li$: 733.4139 $[M+Li]^+$; found 733.4139.

*3.2.3. Synthesis of compound **8**.* From 334.4 mg of **3**, 296.0 mg of **8** was recovered as colourless oil (yield: 35%) (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.60). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.27 (m, 5H), 6.12–6.03 (m, 3H), 5.73 (t, 0.3H, *J*=9.0 Hz), 5.59–5.52 (m, 3H), 5.38 (t, 0.3H, *J*=7.8 Hz), 5.09–4.99 (m, 2H), 4.92 (m, 0.3H), 4.58 (d, 1H, *J*=6.7 Hz); 4.51 (s, 2H), 4.23 (m, 0.7H), 3.92–3.65 (m, 1.7H), 3.51–3.38 (m, 3.8H), 1.91–1.88 (m, 9.8H), 1.69–1.51 (m, 5H), 1.26 (m, 17H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 166.4, 165.9, 162.3, 138.9, 135.7, 135.5, 128.5, 127.7, 127.6, 126.9, 126.5, 100.8, 96.0, 73.0, 71.7, 71.3, 70.9, 70.7, 70.0, 69.8, 69.4, 68.7, 62.0, 58.6, 30.1–29.5, 27.0–26.0, 18.4; IR: ν (cm^{-1}) 2927, 2854, 1729, 1639, 1453, 1322, 1293, 1151, 1048; HRMS (*m*/*z*): calcd for $C_{36}H_{52}O_9Li$: 635.3771 $[M+Li]^+$; found 635.3770; mp: 82–85 °C.

*3.2.4. Synthesis of compound **9**.* From 380.0 mg of **4**, 100.0 mg of **9** was recovered as a white solid (yield: 23%) (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.53). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.27 (m, 5H), 6.12–5.89 (6s, 7H), 5.58–5.42 (m, 7H), 5.31 (t, 1H, *J*=8.5 Hz), 5.21 (m, 1H), 5.05–4.95 (m, 2H), 4.54 (d, 1H, *J*=8.5 Hz), 4.47–4.42 (m, 3H), 4.17–3.95 (m, 3H), 3.95 (m, 2H), 3.75 (m, 1H), 3.63 (m, 1H), 3.39 (m, 3H), 1.98–1.72 (m, 21H), 1.55 (m, 4H), 1.15 (m, 16H),; ^{13}C NMR-APT ($CDCl_3$, 75 MHz) δ (ppm): 166.6–165.7, 136.0–135.1, 128.4, 127.6, 127.5, 127.2, 127.1, 126.9, 126.7, 126.2, 100.9, 100.6, 75.8, 72.8, 71.7, 71.4, 71.1, 70.6, 70.2, 69.6, 67.3, 62.3, 61.4, 29.8–29.4, 26.2, 25.8, 18.3; IR: ν (cm^{-1}) 2929, 2856, 1750, 1639, 1452, 1322, 1294, 1155, 1076; HRMS (*m*/*z*): calcd for $C_{59}H_{80}O_{19}Li$: 1099.5454 $[M+Li]^+$; found 1099.5407; mp: 82–85 °C.

*3.2.5. Synthesis of compound **11**.* From 100 mg of **1**, 36.1 mg of **11** was recovered as a white solid (yield: 41%) (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.60). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.27–6.81(m, 7H), 6.15–6.04 (m, 4H), 5.60–5.50 (m, 5H), 5.44–5.40 (m, 1H), 5.31 (t, *J*=9.1 Hz, 1H), 5.17 (d, *J*=8.0 Hz, 1H), 4.35–4.15 (m, 2H), 3.99–3.94 (m, 1H), 1.89–1.75 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 167.0, 166.5, 165.9, 165.8, 157.1, 135.9, 135.5, 135.2, 135.1, 129.7, 127.3, 127.2, 126.8, 126.5, 120.7, 117.3, 99.6, 72.8, 72.5, 71.5, 69.2, 63.0, 18.4; IR: ν (cm^{-1}) 2959, 2929, 1726, 1637, 1591, 1495, 1453, 1404, 1379, 1319, 1295, 1231, 1144, 1075, 1045, 1016; HRMS (*m*/*z*): calcd for $C_{28}H_{36}O_1N$: 546.2339 $[M+NH_4]^+$; found 546.2338; mp: 104–106 °C.

*3.2.6. Synthesis of compound **13**.* From 110.0 mg of **1**, 22.0 mg of **13** was recovered as a white solid (yield: 23%) (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.55). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.14–6.11 (3s, 4H), 5.60–5.51 (m, 4H), 5.42 (t, *J*=9.6 Hz, 1H), 5.21 (t, *J*=10.0 Hz, 1H), 5.12 (t, *J*=7.6 Hz, 1H), 4.70 (d, *J*=8.0 Hz, 1H), 4.37–4.20 (m, 2H), 3.88–3.82 (m, 1H), 3.62–3.59 (m, 1H), 1.94–1.72 (m, 12H), 1.75–1.62 (m, 4H), 1.47–1.20 (m, 7H); ^{13}C NMR-APT ($CDCl_3$, 100 MHz) δ (ppm): 166.6, 166.1, 165.9, 165.8, 136.0–135.2, 127.0–126.2, 99.8, 94.6, 77.5, 76.8, 73.1, 72.1, 71.9, 71.8, 70.6, 69.6, 69.4, 67.8, 63.1, 63.0, 33.4, 31.6, 25.5, 24.0, 23.7, 18.5–18.3; IR: ν (cm^{-1}) 2933, 2856, 1731, 1638, 1453, 1320, 1295, 1150, 1018; MM-ES (*m*/*z*): 435.1 [M-cyclohexanol]$^+$; mp: 92–93 °C.

*3.2.7. Synthesis of compound **15**.* From 100 mg of **14**, 32.0 mg of **15** was recovered as a white solid (yield: 37%) (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.50). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.19 (t, *J*=9.6 Hz, 1H), 5.08 (t, *J*=9.6 Hz, 1H), 4.98–4.93 (m, 1H), 4.58 (d, *J*=8.0 Hz, 1H), 4.28–4.21 (m, 1H), 4.13–4.07 (m, 1H), 3.70–3.59 (m, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.91–1.65 (m, 5H), 1.53–1.40 (m, 2H), 1.35–1.18 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 170.9, 170.5, 169.6, 169.4, 99.5, 78.2, 73.1, 71.8, 68.8, 62.3, 33.3, 31.6, 25.6, 23.7, 20.9–20.7; IR: ν (cm^{-1}) 2935, 1732, 1558, 1541, 1456, 1230,1037; HRMS (*m*/*z*): calcd for $C_{20}H_{30}O_{10}Na^+$: 453.1737 $[M+Na]^+$; found 453.1735; mp: 80–81 °C.

*3.2.8. Synthesis of compound **16**.* From 105.0 mg of **14**, 24.0 mg of **16** was recovered as colourless oil (yield: 18%) (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.32). For ^1H and ^{13}C NMR, see Ref. 17b.

*3.2.9. Synthesis of compound **19**.* From 574.0 mg of **18**, 148.0 mg of **19** was recovered as colourless oil (yield: 24%) (SiO_2, cyclohexane/EtOAc=3/7, R_f=0.3). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 5.32 (d, *J*=3.0 Hz, 1H), 5.18 (t, *J*=9.3 Hz, 1H), 5.07 (t, *J*=7.8 Hz, 1H), 4.96–4.87 (m, 2H), 4.50 (t, *J*=8.4 Hz, 3H), 4.13–4.06 (m, 6H), 3.89–3.61 (m, 14H), 3.42 (t, *J*=6.0 Hz, 2H), 2.12–1.94 (m, 21H); ^{13}C NMR-APT ($CDCl_3$, 75 MHz) δ (ppm): 171.0–169.5, 101.5, 101.2, 76.4, 73.3, 72.7, 72.2, 71.4, 71.1, 70.7–70.2, 69.5, 69.2, 67.0, 62.2, 61.1, 51.0, 21.2–20.9; MM-ES (*m*/*z*): 855.2 $[M+NH_3]^+$.

*3.2.10. Synthesis of compound **22**.* From 159 mg of **21**, 52.4 mg of **22** was recovered as a colourless oil (yield: 30%) (SiO_2, cyclohexane/EtOAc=2/8, R_f=0.3). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 5.21–5.06 (m, 3H), 4.94–4.87 (m, 2H), 4.57–4.48 (m, 3H), 4.40 (dd, *J*=4.5 Hz, 16.2 Hz, 1H), 4.25 (t, *J*=4.5 Hz, 1H), 4.15–4.13 (m, 1H), 4.03 (dd, *J*=1.8 Hz, 12.3 Hz, 1H), 3.95–3.82 (m, 2H), 3.74–3.59 (m, 14H), 3.44 (t, *J*=6.0 Hz, 2H), 2.12–1.97 (m, 21H); ^{13}C NMR-APT ($CDCl_3$, 75 MHz) δ (ppm): 171.2–169.5, 101.3, 101.2, 76.5, 73.4, 72.3–71.9, 70.4–70.1,

69.0, 68.0, 62.0, 61.8, 50.9, 21.1–20.9; MM-ES (m/z): 855.2 $[M+NH_3]^+$.

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Supplementary data

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