



Highly chemo- and stereoselective glycosidation of permethacrylated O-glycosyl trichloroacetimidate reagents promoted by TMSNTf₂

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ABSTRACT

TMSNTf₂ has been used efficiently as a promoter in glycosidation reaction involving permethacrylated Schmidt reagents. While TMSNTf₂ 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.

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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 Michael² 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 Sinaï,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 BF₃·Et₂O,⁶ TMSOTf,⁷ TBDMSOTf,⁸ Tf₂O,⁹ ZnBr₂,¹⁰ AgOTf,¹¹ and several moisture-stable activating reagents such as I₂/Et₃SiH¹² or HClO₄/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 15¹⁵ and a cationic palladium¹⁶ 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 TMSNTf₂. To date, TMSNTf₂ has exclusively been used as carbonyl activator, in different transformation such as Diels–Alder (DA) reactions,¹⁹ Mukayama–aldol condensations,²⁰ alkylations of α,β-unsaturated compounds,²¹ and Friedel–Crafts alkylation. While TMSNTf₂ 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 TMSNTf₂ 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 TMSNTf₂ 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

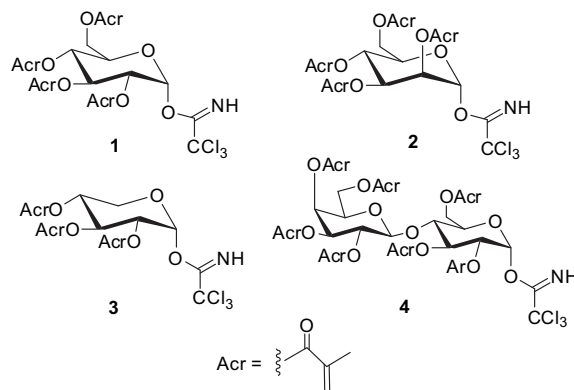


Figure 1. Activated permethacrylated O-glycosyl trichloroacetimidate reagents investigated.

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trichloroacetimidate function could be activated by TMSNTf₂ 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 TMSNTf₂ in terms of efficiency, kinetics and stereoselectivity in the glycosidation, we decided to investigate the scope and the reactivity of TMSNTf₂, which has no literature precedent for this transformation, specially with substrates bearing compatible polyacrylate functions **1–4**.

2. Result and discussion

TMSNTf₂ was first prepared according to reported procedures that use the protodesilylation of allyltrimethylsilane with commercially available HNTf₂ 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 BF₃·Et₂O 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 HNTf₂ (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 BF₃·Et₂O. 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 HNTf₂ has been reported for glycosidation reactions in ionic liquid for the activation of a glucopyranosyl diethyl phosphite²⁵ 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 TMSNTf₂ yielded to β-glycoside **6** with 42% (Table 1, entry 6). Even though TMSNTf₂ 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 TMSNTf₂. Reactions carried out in the presence of 2,6-bis-*tert*-butyl-4-methylpyridine for neutralizing residual traces of TfOH in TMSNTf₂ gave also the expected product, however, with a decreased yield (36%) (Table 1, entry 7).²³ Attempts to reduce the amount of TMSNTf₂ 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 TMSNTf₂ 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 TMSNTf₂ was used.

The identification of the unknown reactivity and chemocompatibility of TMSNTf₂ 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).

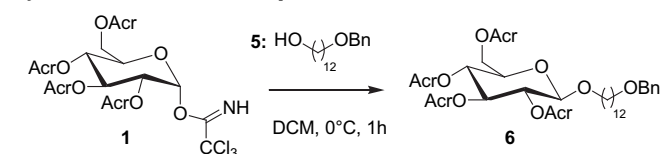
We have found that permethacrylated *O*-glycosyl trichloroacetimidate mannose **2** and xylose **3** derivatives behaved similarly to **1**, and provided **7** and **8** in good yield (Table 2, entries 1 and 2). While the reaction was highly stereoselective and delivered exclusively the α-glycoside for permethacrylated mannose **7**, a 5/2 ratio of the β/α anomers was obtained for permethacrylated xylose **8**. Permethacrylated Schmidt disaccharide 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 TMSNTf₂ 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 TMSNTf₂ 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 TMSNTf₂ for the selective activation of permethacrylated *O*-glycosyl trichloroacetimidates. The

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 ·Et ₂ O	0.5	51	1/0
3	TfOH	0.1	35	1/0
4	HNTf ₂	0.1	48	1/0
5	Tf ₂ O	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.

Table 2Glycosidation of permethacrylated *O*-glycosyl trichloroacetimidate carbohydrates with TMSNTf₂^a

Entry	<i>O</i> -Glycosyl trichloroacetimidate	Alcohol	Product	Yield (%)	Ratio (β/α)
1		5		40	0/1
2		5		35	5/2
3		5		23	1/0
4				41 ^b	1/0
5				23	1/1
6		12		37	1/0
7		5		18	1/0
8		10		Traces	/
9				24	1/0
10		20		30	1/0

^a 0.5 Equiv of TMSNTf₂ 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 TMSNTf₂. Besides this we have also shown that protic acid such as HNTf₂ 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 TMSNTf₂ 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 TMSNTf₂

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 TMSNTf₂ (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%) (SiO₂, cyclohexane/EtOAc=8/2, *R*_f=0.46). For ¹H and ¹³C 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%) (SiO₂, cyclohexane/EtOAc=7/3, *R*_f=0.75). ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₄₁H₅₈O₁₁Li: 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%) (SiO₂, cyclohexane/EtOAc=7/3, *R*_f=0.60). ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₃₆H₅₂O₉Li: 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%) (SiO₂, cyclohexane/EtOAc=7/3, *R*_f=0.53). ¹H NMR (CDCl₃, 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); ¹³C NMR-APT (CDCl₃, 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 C₅₉H₈₀O₁₉Li: 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%) (SiO₂, cyclohexane/EtOAc=7/3, *R*_f=0.60). ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₈H₃₆O₁N: 546.2339 [M+NH₄]⁺; 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%) (SiO₂, cyclohexane/EtOAc=7/3, *R*_f=0.55). ¹H NMR (CDCl₃, 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); ¹³C NMR-APT (CDCl₃, 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%) (SiO₂, cyclohexane/EtOAc=7/3, *R*_f=0.50). ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₀H₃₀O₁₀Na⁺: 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%) (SiO₂, cyclohexane/EtOAc=7/3, *R*_f=0.32). For ¹H and ¹³C 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%) (SiO₂, cyclohexane/EtOAc=3/7, *R*_f=0.3). ¹H NMR (CDCl₃, 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); ¹³C NMR-APT (CDCl₃, 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+NH₃]⁺.

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%) (SiO₂, cyclohexane/EtOAc=2/8, *R*_f=0.3). ¹H NMR (CDCl₃, 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); ¹³C NMR-APT (CDCl₃, 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

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tet.2010.02.068](https://doi.org/10.1016/j.tet.2010.02.068).

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