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Selective acetolysis of 6-deoxy-sugar oligosaccharide building blocks governed by the armed–disarmed effect

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Abstract

The effect of the arming–disarming protection in the acetolysis of 6-deoxy-sugar oligosaccharides has been for the first time systematically investigated. Starting from the newly synthesized methyl glycosides, the acetolysis conditions employed here afforded 1-*O*-Ac oligosaccharides selectively without cleavage of the interglycosidic bonds, if a suitable protecting group pattern was used. Actually, the behavior of armed–disarmed, armed-armed, and disarmed–disarmed 6-deoxy-sugar disaccharides in acetolysis reactions was investigated: the results fit well with the prediction made on the basis of the armed–disarmed effect.
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The armed–disarmed concept refers to the relative ease or difficulty of activating a sugar as a glycosyl donor in glycosylation reactions.[1] Disarmed glycosyl donors have highly electron withdrawing protecting groups (e.g., esters, amides) that destabilize the formation of the oxycarbenium ion/ion pair[2] during the course of the glycosylation, whereas less electron withdrawing protecting groups (e.g., ethers) are less destabilizing and therefore arm the glycosyl donor. The armed–disarmed concept had tremendous importance in the study and development of glycosylation reactions,[3] and its re-examinations and extensions to other reactions involving the anomeric position are still the object of several works of great importance in the field.[4]

Acetolysis of carbohydrates is a widely used reaction consisting in the cleavage of the glycosidic bond and the contemporary acetylation of hydroxyl groups thus formed and/or present before the solvolysis. Acetolysis finds extensive application as selective degradation method used for the structural elucidation of polysaccharides, especially when they contain (1→6) glycosidic linkages, which are extremely labile to acetolysis.[5] Similarly, the conversion of alkyl and aryl glycosides into 1-*O*-acetylated derivatives is commonly accomplished by acetolysis on monosaccharides[6] as well as oligosaccharides:[7] this reaction is often of key importance in an oligosaccharide synthesis, since 1-*O*-Ac derivatives could be easily converted into both glycosyl donors and glycosyl acceptors. Nevertheless, to the best of our knowledge, there is only one systematic report on the synthetic aspects of acetolysis of oligosaccharides; it concerns the comparison of reaction rate in peracetylated methyl glucobiosides.[8]

In this work, the effect of the arming–disarming protection in the acetolysis of 6-deoxy-sugar oligosaccharides is systematically investigated.[9] In principle, the armed–disarmed strategy could help to activate or stabilize the anomeric positions of an oligosaccharide and therefore to foresee its behavior during acetolysis, as already demonstrated in an analogue case regarding the solvolysis of caged 1,6-anhydro-pyranoses.[10] If the armed–disarmed concept would be joined with reaction conditions that are mild enough to discriminate between armed and disarmed

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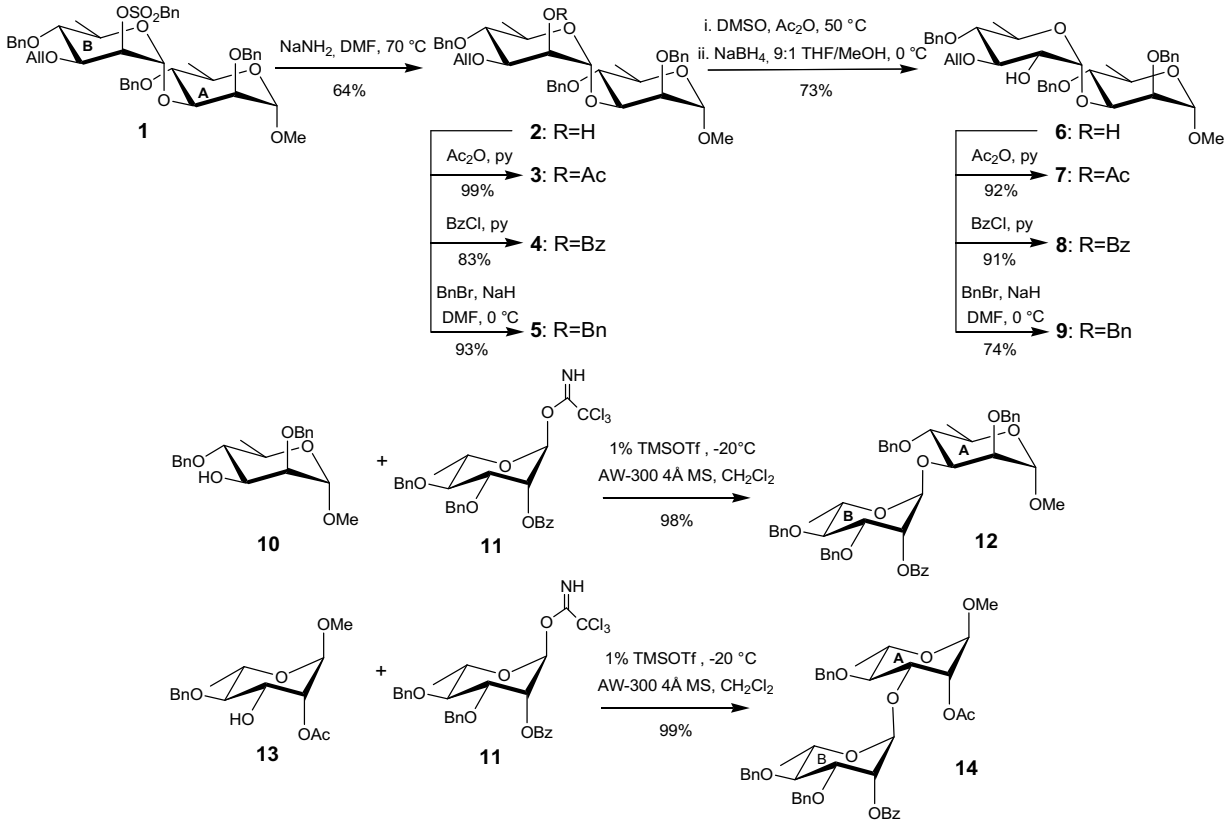
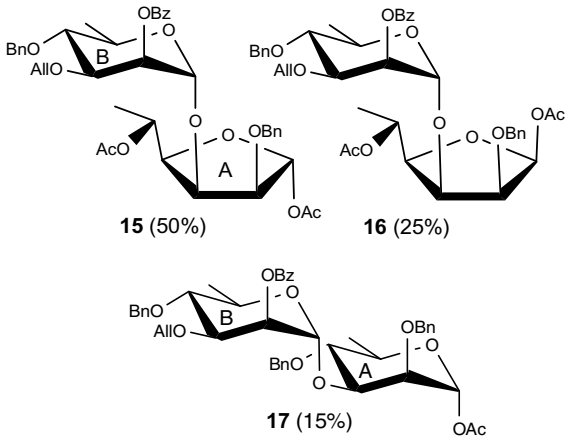
positions, the selective acetolysis of oligosaccharide building blocks could be accomplished in an easily foreseeable manner. For this purpose, a set of 6-deoxy-sugar disaccharide methyl glycosides with differently protected 2-*O*-positions was chosen as suitable model compounds. The synthesis of these disaccharides is presented in Scheme 1. Compounds **3**–**5** and **7**–**9** were obtained from the known disaccharide **1**.[11] De-*O*-benzensulfonylation with sodium



Scheme 1. Synthesis of a set of 6-deoxy-sugar disaccharide methyl glycosides.

Table 1
Screening of acetolysis conditions on model compound **4**

Entry	Protocol	Time	Products[a] (% Yield)
1	**A**	30 h	 **15** (50%) **16** (25%) **17** (15%)
2	**B**	48 h	No reaction
3	**C**	17 h	**17** (62%)
4	**D**	17 h	**17** (46%)

Reaction conditions: (A) $ZnCl_2$ (10 equiv). 2:1 v/v Ac_2O/AcOH, 0 °C; (B) NaI·BF_3·Et_2O, 9:2 v/v CH_3CN/AC_2O, rt; (C) 10:10:1 v/v/v Ac_2O/AcOH/TFA. 70 °C; (D) CSA, Ac_2O, 70 °C.

[a] Isolated yield.

Table 2
Acetolysis of 6-deoxy-sugar oligosaccharide methyl glycosides

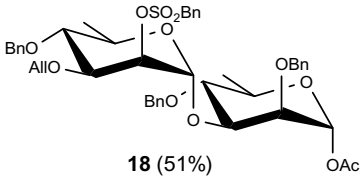
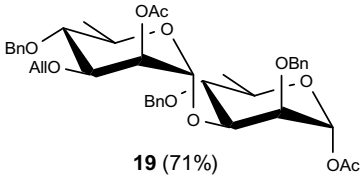
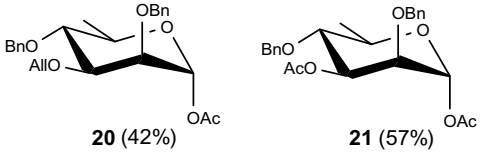
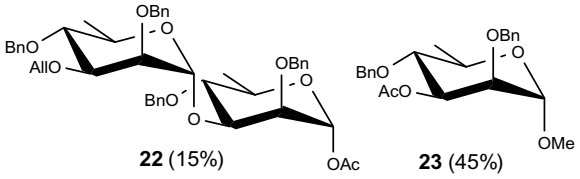
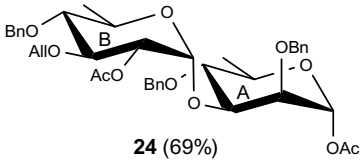
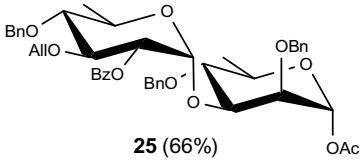
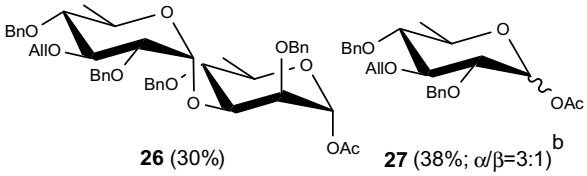
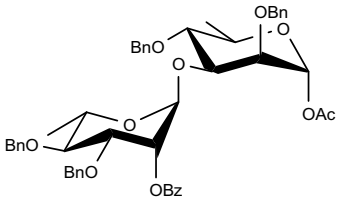
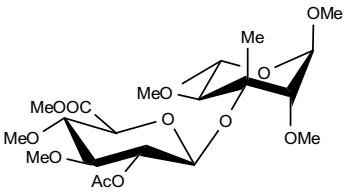
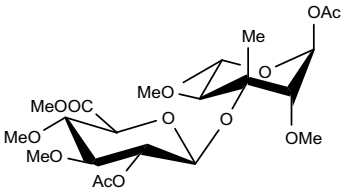
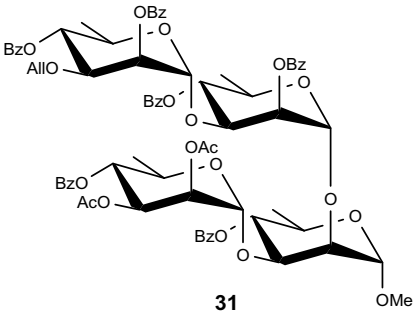
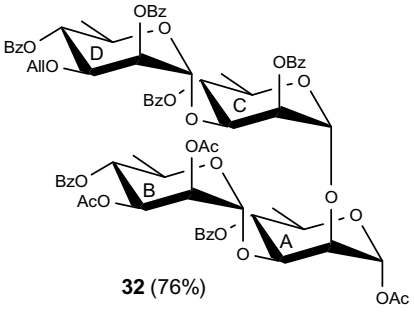
Entry	Oligosaccharide	Products[a] (% yields)	Reaction condition	Time
1	**1**	 **18** (51%)	A	19 h
2	**3**	 **19** (71%)	A	17 h
3	**5**	 **20** (42%) **21** (57%) **20** (60%) **21** (15%) **5** (13%)	A	30 h
4	**5**	 **22** (15%) **23** (45%)	A	11 h
5	**7**	 **24** (69%)	A	17 h
6	**8**	 **25** (66%) **21** (22%) **7** (9%)	A	16 h
7	**9**	 **26** (30%) **27** (38%; α/β=3:1)[b]	A	14 h
8	**12**	 **28** (54%)	A	20 h

Table 2 (*continued*)

Entry	Oligosaccharide	Products[a] (% yields)	Reaction condition	Time
9	**14**	**14** (64%)	A	30 h
10[7j]	 **29**	 **30** (67%)	B	30 h
11	 **31**	**31** (95%)	A	25 h
12	**31**	 **32** (76%)	C	80 min

Reaction conditions: (A) 10:10:1 v/v/v/ Ac_2O/AcOH/TFA, 70 °C; (B) 10:10:0.5 v/v/v Ac_2O/AcOH/TFA, 60 °C; (C) 50:20:0.5 v/v/v Ac_2O/AcOH/H_2SO_4, 0 °C.

[a] Isolated yield.

[b] Anomeric ratio measured by ^1H NMR.

amide[12] gave alcohol **2** that was protected with an acetyl, benzoyl, or benzyl group to give compounds **3**, **4**, and **5**, respectively. In addition, alcohol **2** was epimerized via oxidation/reduction to give D-quinovose-D-rhamnose disaccharide **6**, which was acetylated, benzoylated, or benzylated to afford compounds **7**, **8**, and **9**, respectively. Disaccharides **12** and **14** were obtained by glycosylation of trichloroacetimidate donor **11**[13] with glycosyl acceptors **10**[14] and **13**,[15] respectively.

The next step of this work was the screening of acetolysis conditions that would be mild enough to point out the armed–disarmed effect.[16] A slight modification[17] of the known procedure using freshly fused $ZnCl_2$ in Ac_2O[18] (10 instead of 20 equiv of $ZnCl_2$; 0 °C instead of rt) was firstly tested on model compound **4** (Table 1, entry 1). MALDI-MS analysis of the crude reaction mixture revealed the absence of monosaccharide species obtained by the acetolytic cleavage of the interglycosidic bond, but the desired compound **17** was obtained in only 15% yield, whereas the furanose 1,5-di-*O*-Ac-derivatives **15**[19] and **16** were isolated as the main products (50% and 25% yields, respectively). The $BF_3{\cdot}OEt_2$/NaI/Ac_2O reagent system was recently reported to convert selectively primary benzyl and anomeric methyl groups into acetyls,[20] but **4** was recovered unaltered after 48 h. Finally, a slight modification of a recently reported selective acetolysis[7j] (10:10:1 v/v/v Ac_2O/AcOH/TFA at 70 °C; entry 3) was found to give the conversion of the methyl glycoside into the 1-*O*-acetyl derivative **17** in good yield (62%) with neither cleavage of the interglycosidic bond nor significant production of furanose species. Similar results were obtained with CSA/Ac_2O at 70 °C[21] but in slightly lower yield (entry 4).

The previously synthesized disaccharides were therefore subjected to acetolysis with 10:10:1 v/v/v Ac_2O/AcOH/TFA at 70 °C.[22] The results are summarized in Table 2. They demonstrate that the acetolysis was strictly dependent on the arming–disarming protection of the 2-*O*-positions. Actually, when the monose unit A was protected with an arming benzyl group at position *O*-2 and the B one carried a 2-*O*-disarming ester or sulfonate protecting group (compounds **1**, **3**, **7**, **8**, **12**, entries 1, 2, 5, 6, 8), the acetolysis proceeded selectively at the armed anomeric position,

whatever the configuration of the C-2_B was.[19] Indeed, TLC and MALDI-MS analysis of the crude reaction mixtures demonstrated in all cases that only traces of the monosaccharide compounds as well as disaccharide furanose species could be detected. A very similar literature case[7j] is also reported (entry 10): still in accordance with the armed–disarmed concept, the 1-*O*-Ac disaccharide **30** was obtained. On the contrary, the acetolysis of the disarmed–disarmed disaccharide **14** was expected to proceed noticeably more slowly. Indeed, after 30 h at 70 °C the desired 1-*O*-Ac disaccharide was detected in very low quantities (⩽5%) whereas the starting compound was recovered in 64% yield (entry 9). Finally, the acetolysis of the armed-armed disaccharides **5** and **9** gave contemporary cleavage of both glycosidic linkages as expected, affording 1-*O*-acetylated monosaccharide derivatives as main products (entries 3, 4, 7). The hypothesis that the cleavage of the interglycosidic bond started only after the complete acetolysis of the methyl aglycone was ruled out by quenching the acetolysis before the complete disappearance of the starting material: a high amount of monosaccharide compounds was obtained anyway (entry 4). It is also worth noting that D-quinovose-D-rhamnose 1-*O*-Ac disaccharide **26** was recovered in double yield with respect to the D-rhamnose-D-rhamnose analogue **22** (entries 4 and 7), as expected from the greater acetolysis rate of *manno*-configured sugars with respect to the *gluco*-configured ones.[23]

The last two entries regard the acetolysis of the tetrasaccharide methyl glycoside **31**,[24] which carries disarming acyl groups at positions O-2_B, O-2_C, and O-2_D and is glycosylated at position O-2_A. Acetolysis with 10:10:1 v/v/v Ac_2O/AcOH/TFA at 70 °C did not affect **31** (entry 11), as expected because of the less arming effect of the carbohydrate moiety on O-2_A with respect to a benzyl group.[25] Nevertheless, stronger conditions (50:20:0.5 v/v/v Ac_2O/AcOH/H_2SO_4 at 0 °C) were proven to be effective for the conversion of **31** into **32**[19] in good yield (76%) without affecting the interglycosidic bonds, still in agreement with the armed–disarmed concept (entry 12).

In our opinion, this selective acetolysis reaction based on the armed–disarmed strategy could arise as a useful tool for 6-deoxy-sugar chemistry. Actually, it was demonstrated that the behavior of 6-deoxy-sugar oligosaccharide building blocks in this reaction can be easily predicted on the basis of the arming–disarming protecting group pattern. Moreover, the already scatterly reported examples of methyl oligosaccharide acetolysis on 6-deoxy-sugar containing compounds[7a–d,l] fit well with the behavior systematically reported here. Therefore, this study provides a new valuable tool for protecting group manipulation strategies in oligosaccharide total synthesis.

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19. *Analytical and spectral data of selected compounds:* Compound **15**: $[\alpha]_D$ +5.9 (*c* 0.8, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07–7.26 (m, 15H, H-Ar), 6.22 (d, 1H, $J_{1,2} = 3.0$ Hz, H-1_A), 5.87 (m, 1H, $OCH_2CH{=}CH_2$), 5.38 (dd, 1H, $J_{2,3} = 3.4$ Hz, $J_{2,1} = 2.0$ Hz, H-2_B), 5.28 (dd, 1H, $J_{vic} = 18.0$ Hz, $J_{gem} = 1.5$ Hz, *trans* $OCH_2CH{=}CHH$), 5.18 (q, 1H, $J_{5,6} = J_{5,4} = 6.0$ Hz, H-5_A), 5.12 (dd, 1H, $J_{vic} = 10.0$ Hz, $J_{gem} = 1.5$ Hz, *cis* $OCH_2CH{=}CHH$), 4.94 (d, 1H, $J_{gem} = 11.0$ Hz, $OCHHPh$), 4.91 (d, 1H, $J_{1,2} = 2.0$ Hz, H-1_B), 4.64 (m, 3H,

3OC*H*HPh), 4.43 (t, 1H, $J_{3,4} = J_{3,2} = 5.4$ Hz, H-3_A), 4.20 (m, 2H, H-4_A, OC*H*HCH=CH_2), 4.09 (m, 2H, H-5_B, OC*H*HCH=CH_2), 3.96 (m, 2H, H-2_A, H-3_B), 3.49 (t, 1H, $J_{4,5} = J_{4,3} = 9.0$ Hz, H-4_B), 2.08 (s, 3H, CH_3CO), 2.06 (s, 3H, CH_3CO), 1.31 (d, 3H, $J_{6,5} = 6.0$ Hz, H-6_A), 1.21 (d, 3H, $J_{6,5} = 6.0$ Hz, H-6_B); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 169.9, 169.8, 165.5 (3CO), 138.6, 137.1 (2C_{ipso}-Bn), 134.6 (OCH$_2$*C*H=CH_2), 133.1 (C_{ipso}-Bz), 129.9–127.6 (C-Ar), 117.3 (OCH$_2$CH=*C*H$_2$), 99.5, 98.3 (C-1_A, C-1_B), 81.4, 80.8, 79.7, 77.4, 76.6, 75.0, 72.5, 70.6, 69.7, 68.6, 68.5 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 2O*C*H$_2$Ph, O*C*H$_2$CH=CH_2), 21.4, 21.2 (2*C*H$_3$CO), 18.2, 16.4 (C-6_A, C-6_B). MALDI-MS for $C_{40}H_{46}O_{12}$ (*m*/*z*): M_r (calcd) 718.30, M_r (found) 741.03 $(M+Na)^+$. Anal. Calcd: C, 66.84; H, 6.45. Found: C, 66.68; H, 6.32.

Compound **17**: $[\alpha]_D$ −2.5 (*c* 1.2, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.07–7.16 (m, 20H, H-Ar), 6.14 (d, 1H, $J_{1,2} = 2.0$ Hz, H-1_A), 5.84 (m, 1H, OCH$_2$C*H*=CH$_2$), 5.68 (dd, 1H, $J_{2,1} = 1.6$ Hz, $J_{2,3} = 3.4$ Hz, H-2_B), 5.25–5.21 (m, 2H, H-1_B, *trans* OCH$_2$CH=C*H*H), 5.08 (dd, 1H, $J_{vic} = 10.2$ Hz, $J_{gem} = 1.8$ Hz, *cis* OCH$_2$CH=C*H*H), 4.95 (d, 1H, $J_{gem} = 11.0$ Hz, OC*H*HPh), 4.90 (d, 1H, $J_{gem} = 11.0$ Hz, OC*H*HPh), 4.79 (d, 1H, $J_{gem} = 12.0$ Hz, OC*H*HPh), 4.72–4.62 (m, 3H, 3OC*H*HPh), 4.19 (dd, 1H, $J_{gem} = 12.0$ Hz, $J_{vic} = 5.0$ Hz, OC*H*HCH=CH_2), 4.12–4.05 (m, 2H, H-3_A, OC*H*HCH=CH_2), 3.98 (dd, 1H, $J_{3,2} = 3.2$ Hz, $J_{3,4} = 9.2$ Hz, H-3_B), 3.91–3.65 (m, 4H, H-2_A, H-4_A, H-5_A, H-5_B), 3.51 (t, 1H, $J_{4,5} = J_{4,3} = 9.6$ Hz, H-4_B), 2.06 (s, 3H, CH_3CO), 1.32 (d, 3H, $J_{6,5} = 6.2$ Hz, H-6_B), 1.29 (d, 3H, $J_{6,5} = 6.2$ Hz, H-6_A); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 169.2, 165.5 (2CO), 138.6, 137.8, 137.5 (3C_{ipso}-Bn), 134.6 (OCH$_2$*C*H=CH_2), 133.1 (C_{ipso}-Bz), 129.8–125.3 (C-Ar), 117.1 (OCH$_2$CH=*C*H$_2$), 99.5 (C-1_B), 91.2 (C-1_A), 80.1, 79.9, 77.6, 77.4, 76.7, 75.5, 75.2, 72.6, 72.5, 70.6, 69.6, 68.4 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 3 O*C*H$_2$Ph, O*C*H$_2$CH=CH_2), 21.0 (*C*H$_3$CO), 18.2, 18.1 (C-6_A, C-6_B). MALDI-MS for $C_{45}H_{50}O_{11}$ (*m*/*z*): M_r (calcd) 766.34, M_r (found) 789.42 $(M+Na)^+$. Anal. Calcd: C, 70.48; H, 6.57. Found: C, 70.28; H, 6.34.

Compound **24**: $[\alpha]_D$ +60.6 (*c* 1.4, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.41–7.26 (m, 15H, H-Ar), 6.16 (m, 1H, H-1_A), 5.89 (m, 1H, OCH$_2$C*H*=CH$_2$), 5.23 (dd, 1H, $J_{vic} = 17.4$ Hz, $J_{gem} = 1.6$ Hz, *trans* OCH$_2$CH=C*H*H), 5.21 (br s, 1H, H-1_B), 5.12 (dd, 1H, $J_{vic} = 10.2$ Hz, $J_{gem} = 1.6$ Hz, *cis* OCH$_2$CH=C*H*H), 4.99 (d, 1H, $J_{gem} = 11.6$ Hz, OC*H*HPh), 4.87 (m, 2H, H-2_B, OC*H*HPh), 4.77 (d, 1H, $J_{gem} = 11.6$ Hz, OC*H*HPh), 4.70–4.57 (m, 3H, 3OC*H*HPh), 4.24 (m, 2H, OC*H*$_2$CH=CH_2), 4.02–3.86 (m, 3H, H-3_A, H-3_B, H-5_B), 3.78 (m, 2H, H-2_A, H-5_A), 3.63 (t, 1H, $J_{4,3} = J_{4,5} = 9.4$ Hz, H-4_A), 3.17 (t, 1H, $J_{4,3} = J_{4,5} = 10.0$ Hz, H-4_B), 2.10 (s, 3H, $COCH_3$), 1.79 (s, 3H, $COCH_3$), 1.26 (d, 3H, $J_{6,5} = 5.6$ Hz, H-6_A), 1.18 (d, 3H, $J_{6,5} = 6.2$ Hz, H-6_B); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.5, 169.3 (2CO), 138.3, 138.2, 137.7 (3C_{ipso}-Bn), 134.9 (OCH$_2$*C*H=CH_2), 128.4–127.3 (C-Ar), 116.6 (OCH$_2$CH=*C*H$_2$), 98.0 (C-1_B), 90.8 (C-1_A), 83.7, 79.3, 79.1, 77.6, 77.1, 75.1, 74.8, 74.1, 73.3, 72.3, 70.5, 67.7 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 3O*C*H$_2$Ph, O*C*H$_2$CH=CH_2), 21.1, 20.7 (2*C*H$_3$CO), 18.0, 17.9 (C-6_A, C-6_B). MALDI-MS for $C_{40}H_{48}O_{11}$ (*m*/*z*): M_r (calcd) 704.32, M_r (found) 727.03 $(M+Na)^+$. Anal. Calcd: C, 68.16; H, 6.86. Found: C, 68.30; H, 7.00.

Compound **32**: $[\alpha]_D$ −65.9 (*c* 1.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13–7.24 (m, 30H, H-Ar), 6.26 (d, 1H, $J_{1,2} = 1.8$ Hz, H-1_A), 5.68 (dd, 1H, $J_{2,3} = 3.4$ Hz, $J_{2,1} = 1.6$ Hz, H-2_C), 5.65 (t, 1H, $J_{4,5} = J_{4,3} = 9.8$ Hz, H-4_C), 5.51–5.38 (m, 3H, H-3_B, H-4_A, OCH$_2$C*H*=CH$_2$), 5.33 (br s, 1H, H-1_C), 5.30–5.22 (m, 4H, H-1_D, H-2_D, H-4_B, H-4_D), 5.08 (dd, 1H, $J_{2,3} = 3.3$ Hz, $J_{2,1} = 2.0$ Hz, H-2_B), 5.00 (d, 1H, $J_{1,2} = 1.6$ Hz, H-1_B), 4.87 (dd, 1H, $J_{vic} = 17.4$ Hz, $J_{gem} = 1.6$ Hz, *trans* OCH$_2$CH=C*H*H), 4.77 (dd, 1H, $J_{vic} = 10.2$ Hz, $J_{gem} = 1.6$ Hz, *cis* OCH$_2$CH=C*H*H), 4.59 (dd, 1H, $J_{3,4} = 9.8$ Hz, $J_{3,2} = 3.2$ Hz, H-3_C), 4.31–4.20 (m, 3H, H-3_A, H-5_B, H-5_C), 4.08 (dd, 1H, $J_{2,3} = 3.3$ Hz, $J_{2,1} = 1.8$ Hz, H-2_A), 4.03 (dq, 2H, $J_{5,4} = 9.7$ Hz, $J_{5,6} = 6.2$ Hz, H-5_A, H-5_D), 3.82 (dd, 1H, $J_{3,4} = 9.8$ Hz, $J_{3,2} = 3.2$ Hz, H-3_D), 3.75 (dd, 1H, $J_{gem} = 12.0$ Hz, $J_{vic} = 5.4$ Hz, OC*H*HCH=CH_2), 3.57 (dd, 1H, $J_{gem} = 12.0$ Hz, $J_{vic} = 5.4$ Hz, OC*H*HCH=CH_2), 2.18 (s, 3H, $COCH_3$), 1.93 (s, 3H, $COCH_3$), 1.60 (s, 3H, $COCH_3$), 1.38 (d, 3H, $J_{6,5} = 6.2$ Hz, H-6_A), 1.34 (d, 3H, $J_{6,5} = 6.2$ Hz, H-6_C), 1.26 (d, 3H, $J_{6,5} = 6.2$ Hz, H-6_D), 1.14 (d, 3H, $J_{6,5} = 6.2$ Hz, H-6_B). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 168.7, 168.6 (3C=O Ac), 166.1, 165.9, 165.5, 165.4, 165.2, 165.1 (6C=O Bz), 134.0 (OCH$_2$*C*H=CH_2), 133.5–132.8 (6C_{ipso}), 130.0–128.2 (C-Ar), 117.2 (OCH$_2$CH=*C*H$_2$), 100.3, 99.8, 99.3 (C-1_B, C-1_C, C-1_D), 92.1 (C-1_A), 77.7, 75.2, 73.9, 73.1, 73.0, 72.5, 72.2, 71.5, 70.2, 70.0, 69.6, 69.2, 68.4, 67.9, 67.8, 67.7,60.4 (C-2_A, C-2_B, C-2_C, C-2_D, C-3_A, C-3_B, C-3_C, C-3_D, C-4_A, C-4_B, C-4_C, C-4_D, C-5_A, C-5_B, C-5_C, C-5_D, O*C*H$_2$CH=CH_2), 21.0, 20.5, 20.2 (3 *C*H$_3$C=O), 17.8, 17.7, 17.5, 17.4 (C-6_A, C-6_B, C-6_C, C-6_D). MALDI-MS for $C_{75}H_{76}O_{26}$ (*m*/*z*): M_r (calcd) 1392.46, M_r (found) 1415.06 $(M+Na)^+$. Anal. Calcd: C, 64.65; H, 5.50. Found: C, 64.41; H, 5.29.

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