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*Mendeleev Commun.*, 2008, **18**, 241–243
Mendeleev Communications

# Homogeneous azidophenylselenylation of glucals

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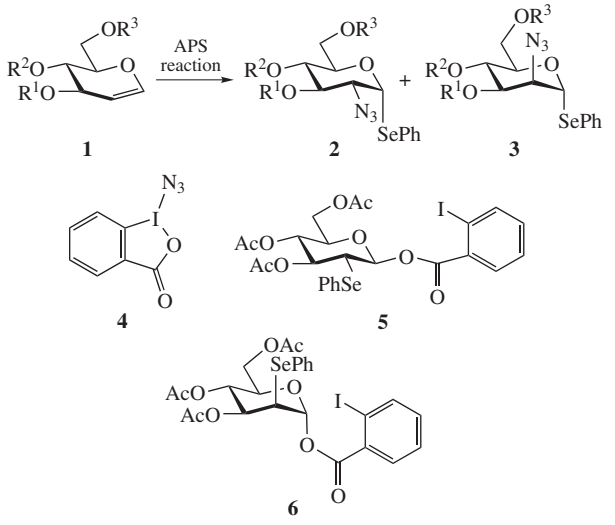
DOI: 10.1016/j.mencom.2008.09.003

The homogeneous azidophenylselenylation of diversely protected mono-, di- and trisaccharide glucals was studied to evaluate the influence of protective groups, $N_3$ and I donors, temperature and solvent on the stereoselectivity of the formation of corresponding phenyl 2-azido-2-deoxy-1-seleno-α-D-*gluco*- and -*manno*-adducts.

Glycosyl donors bearing an azido group at C-2 are important intermediates for oligosaccharide synthesis especially for the installation of α-galactosamine and α-glucosamine units.[1] Among the known methods[2] for introduction of the azido group into monosaccharide units, the azidophenylselenylation (APS reaction) of glycals[3] represents special interest as it allows the single-step straightforward preparation of phenyl glycosides of corresponding 2-azido-2-deoxy-1-seleno-adducts, which could be directly used as glycosyl donors.

Recently, we reported an efficient protocol[4] for the APS reaction in which a glycal is treated under homogenous conditions with $TMSN_3$ (instead of $NaN_3$ used in others procedures[3]) and $Ph_2Se_2$ in the presence of $PhI(OAc)_2$ in dichloromethane (DCM). This is an efficient stereoselective procedure for the transformation of D-galactals into phenyl 2-azido-2-deoxy-1-seleno-α-D-galactopyranosides, but in the case of triacetylglucal **1a** gave an inseparable mixture of *gluco*- and *manno*-isomers **2a** and **3a** in a ratio of 2.7:1 (Scheme 1). Here we describe the reaction conditions, *i.e.*, solvent, temperature and azide radical source, as well as the nature of blocking groups, as factors influencing stereoselectivity in the APS reaction of glucals. These characteristics are critical for the stereochemistry of the azidonitration of glucals.[2] In addition, we studied the applicability of APS reaction to the transformation of oligosaccharide glucals as such reactions open a direct way towards corresponding lactosaminyl and 3′-sialyllactosaminyl derivatives like compounds **2m–q**, which could be considered as convenient synthetic blocks for the assembling of complex oligosaccharide chains.




**Scheme 1** APS reaction of glucals **1**.

**Table 1** APS reactions of triacetylglucal **1a** ($R^1 = R^2 = R^3 = Ac$).[a]

| Entry | Solvent | *T*/°C | Azide donor | [I] donor | *t*/h | **2a**:**3a** ratio | Other products |
|---|---|---|---|---|---|---|---|
| 1 | $C_6F_6$ | 6 | $TMSN_3$ | $PhI(OAc)_2$ | 12 | 3.2:1 | |
| 2 | PhMe | –10 | $TMSN_3$ | $PhI(OAc)_2$ | 18 | 3.0:1 | |
| 3 | $CCl_4$ | –10 | $TMSN_3$ | $PhI(OAc)_2$ | 18 | 2.9:1 | |
| 4 | DCM | –10 | $TMSN_3$ | $PhI(OAc)_2$ | 4 | 2.7:1 | |
| 5 | EtOAc | –10 | $TMSN_3$ | $PhI(OAc)_2$ | 18 | 1.5:1 | |
| 6 | THF | –10 | $TMSN_3$ | $PhI(OAc)_2$ | 8 | 1.3:1 | |
| 7 | MeCN | –10 | $TMSN_3$ | $PhI(OAc)_2$ | 18 | 1:1 | |
| 8 | DMF | –10 | $TMSN_3$ | $PhI(OAc)_2$ | 18 | 1:1 | |
| 9 | $Et_2O$ | –10 | $TMSN_3$ | $PhI(OAc)_2$ | 48 | no reaction | |
| 10 | $Pr^iOH$ | –10 | $TMSN_3$ | $PhI(OAc)_2$ | 48 | no reaction | |
| 11 | DCM | –23 | $TMSN_3$ | $PhI(OAc)_2$ | 24 | 2.7:1 | |
| 12 | DCM | –40 | $TMSN_3$ | $PhI(OAc)_2$ | 144 | 2.7:1 | |
| 13 | EtOAc | –23 | $TMSN_3$ | $PhI(OAc)_2$ | 48 | 1.5:1 | |
| 14 | EtOAc | –40 | $TMSN_3$ | $PhI(OAc)_2$ | 144 | 1.5:1 | |
| 15 | MeCN | –23 | $TMSN_3$ | $PhI(OAc)_2$ | 48 | 1:1 | |
| 16 | MeCN | –40 | $TMSN_3$ | $PhI(OAc)_2$ | 144 | 1:1 | |
| 17 | DCM | –10 | $TMSN_3$ | PhI=O | 3 | 2.2:1 | |
| 18[b] | DCM | –10 | $TMSN_3$ | PhI=O | 24 | 2.2:1 | |
| 19 | DCM | –10 | $TBAN_3$ | $PhI(OAc)_2$ | 12 | 2.1:1 | |
| 20 | DMF | –10 | $NaN_3$ | $PhI(OAc)_2$ | 24 | 1.9:1 | |
| 21 | DCM | –10→ room temperature | **4** | **4** | 48 | no reaction | |
| 22 | $C_2H_4Cl_2$ | 78 | **4** | **4** | 3 | | **5**:**6**, 2:1 |
| 23 | $C_2H_4Cl_2$ | 78 | None | IBA | 3 | | **5**:**6**, 2:1 |

[a]In all entries the conversion was > 60% as determined by TLC and $^1$H NMR spectroscopy. [b]In entry 17 the reaction was performed according to standard procedure[4] while in entry 18 PhI=O was added after $TMSN_3$ that enlarged the reaction time.

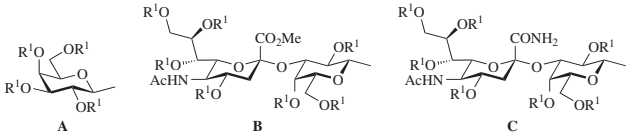
Commercially available triacetylglucal **1a** was chosen as a first model substrate in our study of APS reactions. The results of experiments under varied conditions are summarized in Table 1. The ratio of *gluco*- and *manno*-adducts **2a** and **3a** was determined by integration of corresponding H-1 signals [6.00 ppm (d, $J_{1,2}$ 3.6 Hz) for **2a**; 5.47 ppm (br. s, $J_{1,2} < 0.5$ Hz) for **3a**]. All APS reactions gave the adducts in a high yield of 75–90% except for several cases noted in Table 1.

The solvent effect was studied first. Thus, the replacement of DCM by a less polar solvent ($C_6F_6$, $CCl_4$ or PhMe) leads to an insignificant increase in the proportion of *gluco*-isomer **2a** (Table 1, entries 1–3), whereas the use of more polar solvents (EtOAc, MeCN and THF) decreased the yield of **2a** (entries 5–8) and increased the formation of **3a**. Solvents such as THF, DMF and $Pr^iOH$ were not inert in the APS reaction (entries 6, 8, 10). The insolubility of reagents in $Et_2O$ prevented the APS reaction

**Table 2** APS reactions of diversely protected glucals.[a,†]

| Entry | Glucal | $R^1$ | $R^2$ | $R^3$ | Product(s) ratio and/or isolated yield |
|---|---|---|---|---|---|
| 1 | **1b** | Ac | –$CMe_2$– | | **2b**:**3b**, 1.7:1 |
| 2 | **1c** | Piv | –$CMe_2$– | | **2c**:**3c**, 1:1 |
| 3 | **1d** | TIPS | –$CMe_2$– | | **2d**, 85% |
| 4 | **1e** | Bz | Bz | Bz | **2e**:**3e**, 1:1 |
| 5 | **1f** | Piv | Piv | Piv | **2f**:**3f**, 1.6:1 |
| 6 | **1g** | MCA | MCA | MCA | **2g**:**3g**, 3.5:1 |
| 7 | **1h** | Bn | Bn | Bn | **2h**:**3h**, 1.3:1 |
| 8 | **1i** | TMS | TMS | TMS | **2i**:**3i**, 3:1 |
| 9 | **1j** | TES | TES | TES | **2j**:**3j**, 1.5:1 |
| 10 | **1k** | TIPS | TIPS | TIPS | **2k**, 81% |
| 11 | **1l** | TBS | TBS | TBS | **2l**, 75% |
| 12 | **1m** | Ac | **A** | Ac | **2m**:**3m**, 1:1, 89% |
| 13 | **1n** | TMS | **A** | TMS | **2n**, 78% |
| 14 | **1o** | TES | **A** | TES | **2o**, 87% |
| 15 | **1p** | Ac | **B** | Ac | **2p**:**3p**, 75% |
| 16 | **1q** | TES | **C** | TES | **2q**, 69% |

[a]The ratio of *gluco*- and *manno*-adducts were determined by integration of corresponding H-1 signals in $^1$H NMR spectra [5.8–6.1 ppm (d, $J_{1,2}$ 4.5–5.5 Hz) for *gluco*-adducts; 5.4–5.7 ppm (br. s, $J_{1,2} < 0.5$ Hz) for *manno*-adducts]. All APS reactions gave the products in total high yield (75–90%, as evaluated by TLC and $^1$H NMR spectroscopy) except the cases noted.




(entry 9). The temperature affected the reaction time rather than the ratio of *gluco*- and *manno*-adducts (entries 11–16) both in the nonpolar and polar solvents.

The formation of an azide radical was supposed to be the first step in azidonitration and APS reactions. Therefore, the stereoselectivity of the addition of the azide radical to the double bond controls the ratio of *gluco*- and *manno*-products. For the generation of the azide radical, different combinations of the donors of the azide anion and hypervalent iodine reagents could be used (entries 17–20).[5] Among them $PhI(OAc)_2$/$TMSN_3$ is the combination of choice.[4] Attempts to apply azidoiodinane **4**[6] as a possible source of azide radicals (entry 22) resulted in the formation of an unstable mixture of two adducts, presumably, compounds **5** and **6**. β-*Gluco*-configuration in dominating product and α-*manno*-configuration in minor one were deduced from the proton coupling constants in the $^1$H NMR spectrum.† Location of the PhSe group at C-2 of both compounds followed from the unusual high-field position of C-2 signals (46.3 and 46.4 ppm, respectively) in the $^{13}$C NMR spectrum.† Formation of compounds **5** and **6** could be connected with the oxidation of $Ph_2Se_2$ into $PhSe^+$ under the action of a hypervalent iodine reagent, as products **5** and **6** are formed in the presense of *o*-iodobenzoic acid (IBA) and the absense of an azide donor (entry 23).

Thus, the studied variations of reaction conditions did not reveal any protocol to run APS transformation with higher *gluco*-stereoselectivity than under initially proposed conditions [$TMSN_3$, $Ph_2Se_2$, $PhI(OAc)_2$, DCM, –10 °C]. Therefore, we investigated further the influence of blocking groups on the outcome of the APS reaction. Special attention was paid to glucals with non-acetyl protecting groups based on tendencies observed in azidonitration reactions.[2(*b*)]

The results of APS reaction of differently substituted glucals are given in Table 2. 4,6-O-Acetonated substrates with varied protecting groups at O(3) demonstrated the same tendencies in the formation of *gluco*- and *manno*-products **2** and **3**, which were observed in corresponding azidonitration reactions[2(*b*)] (entries 1–3). Thus, glucal **1d** with a bulky silyl group at O(3) gave *gluco*-product **2d** stereospecifically and in a high yield (entry 3). Unfortunately, the known methods for the introduction of other type of 4,6-O-acetal protections into carbohydrates[7] are not efficient in the case of glucals. Thus, we had to focus on the investigation of homo-3,4,6-tri-O-substituted glucal derivatives **1e**–**l**, which could be prepared from **1a** in a high yield.[8] The APS reaction proceeded non-selectively when an electron-donating substituent was present in the acyl O-protecting group (entry 4 in Table 1 *vs.* entries 4 and 5 in Table 2). The same results were obtained in the case of alkyl substitutents at O(3) (entry 7).

In the case of tri-O-silylated glucals, the corresponding *gluco*-products were formed stereospecifically when the bulky TIPS

† For typical procedure of APS reaction see ref. 4.

**1p**: $^1$H NMR, δ: 6.26 (br. d, 1H, H-1, $J_{1,2}$ 6.0 Hz), 5.50 (m, 1H, H-8″), 5.38 (dd, 1H, H-7″, $J_{7'',6''}$ 2.2 Hz, $J_{7'',8''}$ 9.1 Hz), 5.36 (d, 1H, H-4′, $J_{4,3}$ 3.2 Hz), 5.11 (m, 2H, H-2′, NH), 4.92 (dd, 1H, H-3′, $J_{3,2}$ 9.1 Hz, $J_{3,4}$ 3.0 Hz), 4.80 (m, 1H, H-4″), 4.57 (dd, 1H, H-2, $J_{2,1}$ 6.0 Hz, $J_{2,3}$ 2.0 Hz), 4.44 (d, 1H, H-1′, $J_{1,2}$ 8.0 Hz), 4.40 (m, 1H, H-3), 4.37 (m, 1H, H-6A), 4.20 (m, 4H, H-6′A, H-6′B, H-9A″, H-9B″), 4.03 (m, 2H, H-6B, H-5″), 3.81 (m, 1H, H-5′), 3.71 (s, 3H, Me), 3.70 (m, 2H, H-4, H-5), 3.55 (d, 1H, H-6″, $J_{6,7}$ 2.1 Hz), 2.47 (dd, 1H, H-$3_{eq}$, $J_{3,3}$ 12.5 Hz, $J_{3,4}$ 4.3 Hz), 1.68 (t, 1H, H-$3_{eq}$, $J_{3,3} = J_{3,4} = 12.3$ Hz), 1.90–2.25 (m, 30H, Ac). $^{13}$C NMR, δ: 169.5–171.2 (C=O), 163.4 (C=O), 143.1 (C-1), 101.5 (C-2), 100.4 (C-1′), 97.3 (C-2″) 77.9, 75.3, 75.2, 74.0, 72.8, 71.9, 71.6, 71.5, 70.5, 68.9, 66.1, 64.4, 62.5, 61.8, 53.9 (C-5″), 39.2 (C-3″), 19.3–21.7 (Ac).

**1q**: $^1$H NMR, δ: 6.21 (br. d, 1H, H-1, $J_{1,2}$ 6.2 Hz), 4.41 (d, 1H, H-1′, $J_{1',2'}$ 7.9 Hz), 4.03 (m, 2H), 3.80–3.97 (m, 10H), 3.85 (m, 1H, H-2), 3.79 (m, 1H, H-3), 3.71–3.77 (m, 5H), 2.43 (dd, 1H, H-$3_{eq}$, $J_{3,3}$ 12.8 Hz, $J_{3,4}$ 4.1 Hz), 1.75 (t, 1H, H-$3_{eq}$, $J_{3,3} = J_{3,4} = 12.9$ Hz), 0.80–1.10 (m, 135H, Et). $^{13}$C NMR, δ: 142.3 (C-1), 100.4 (C-2), 100.0 (C-1′), 98.3 (C-2″), 74.0, 73.4, 71.6, 71.5, 71.2, 71.0, 70.5, 70.1, 69.8, 66.5, 63.1, 62.8, 60.1; 57.1, 53.0, 39.2 (C-3″).

**2d**: $^1$H NMR, δ: 7.20–7.70 (m, 5H, Ar), 5.96 (d, 1H, H-1, $J_{1,2}$ 5.2 Hz), 4.06 (dd, 1H, H-3, $J_{3,2}$ 9.2 Hz, $J_{3,4}$ 9.6 Hz), 4.17 (dd, 1H, H-6, $J_{6,5}$ 4.9 Hz, $J_{6,6}$ 11.7 Hz), 4.12 (t, 1H, H-3, $J_{3,2} = J_{3,4} = 9.3$ Hz), 3.84 (dd, 1H, H-2), 3.80 (br. d, 1H, H-6B, $J_{6A,6B}$ 11.5 Hz), 3.58 (t, 1H, H-4, $J_{4,3} = J_{4,5} = 9.2$ Hz), 1.05 (m, 21H, $Pr^i$). $^{13}$C NMR, δ: 137.6 (*ipso*-Ph), 126.7–131.0 (Ar), 101.6 ($Me_2CH$), 85.3 (C-1), 82.2 (C-4), 72.6 (C-3), 68.5 (C-6), 67.1 (C-2), 65.5 (C-5), 29.2, 19.0, 18.1, 12.8.

**2k**: $^1$H NMR, δ: 7.25–7.80 (m, 5H, Ar), 5.93 (d, 1H, H-1, $J_{1,2}$ 4.5 Hz), 4.19 (m, 1H, H-5), 4.07 (m, 1H, H-6A), 4.02 (br. d, 1H, H-2, $J_{2,1}$ 4.7 Hz), 4.00 (m, 1H, H-4), 3.95 (m, 1H, H-3), 3.77 (m, 1H, H-3), 0.90–1.10 (m, 63H, $Pr^i$). $^{13}$C NMR, δ: 127.0–132.2 (Ar), 85.2 (C-1), 80.5, 70.3, 64.9, 62.8, 59.9, 18.0 (Me), 12.6, 12.5, 12.2 ($Pr^i$).

**2l**: $^1$H NMR, δ: 7.20–7.70 (m, 35H, Ar), 5.89 (d, 1H, H-1, $J_{1,2}$ 4.7 Hz), 4.21 (m, 1H, H-5), 4.07 (m, 1H, H-6A), 3.99 (br. d, 1H, H-2, $J_{2,1}$ 4.7 Hz), 3.95 (m, 1H, H-4), 3.73 (2H, H-3, H-6B) 0.70–0.90 (3s, 27H, $Bu^t$). $^{13}$C NMR, δ: 127.0–135.2 (Ar), 85.7 (C-1), 79.3, 70.3, 64.5, 62.7, 60.1, 26.7–26.9 (Me), 19.1, 18.1, 15.2 ($Bu^t$).

**2m**: $^1$H NMR, δ: 7.25–7.75 (m, 5H, Ar), 6.01 (d, 1H, H-1, $J_{1,2}$ 5.1 Hz), 5.36 (d, 1H, H-4′, $J_{4,3}$ 3.2 Hz), 5.10 (m, 2H, H-2′, H-3), 4.90 (dd, 1H, H-3′, $J_{3,2}$ 9.2 Hz, $J_{3,4}$ 3.1 Hz), 4.48 (d, 1H, H-1′, $J_{1,2}$ 8.0 Hz), 4.40 (m, 1H, H-6A), 4.15 (m, 2H, H-6′A, H-6′B), 4.06 (m, 1H, H-6), 3.83 (m, 1H, H-5′), 3.72 (m, 2H, H-4, H-5), 3.55 (dd, 1H, H-2, $J_{2,1}$ 5.1 Hz, $J_{2,3}$ 9.1 Hz), 2.00–2.20 (6s, 18H, Ac). $^{13}$C NMR, δ: 169.3–170.9 (C=O), 137.6 (*ipso*-Ph), 126.6–129.8 (Ar), 101.0 (C-1′), 83.2 (C-1), 74.0, 71.5, 71.5, 70.8, 70.5, 67.4, 66.4, 63.1, 61.7, 60.7, 19.9–22.1 (Ac).

**2n**: $^1$H NMR, δ: 7.25–7.75 (m, 5H, Ar), 6.01 (d, 1H, H-1, $J_{1,2}$ 5.1 Hz), 5.36 (d, 1H, H-4′, $J_{4,3}$ 3.2 Hz), 5.10 (m, 2H, H-2′, H-3), 4.90 (dd, 1H, H-3′, $J_{3,2}$ 9.2 Hz, $J_{3,4}$ 3.1 Hz), 4.48 (d, 1H, H-1′, $J_{1,2}$ 8.0 Hz), 4.40 (m, 1H, H-6A), 4.15 (m, 2H, H-6′A, H-6′B), 4.06 (m, 1H, H-6), 3.83 (m, 1H, H-5′), 3.72 (m, 2H, H-4, H-5), 3.55 (dd, 1H, H-2, $J_{2,1}$ 5.1 Hz, $J_{2,3}$ 9.1 Hz), 2.00–2.20 (6s, 18H, Ac). $^{13}$C NMR, δ: 169.3–170.9 (C=O), 137.6 (*ipso*-Ph), 126.6–129.8 (Ar), 101.0 (C-1′), 84.2 (C-1), 74.2, 71.5, 71.3, 70.1, 70.4, 67.7, 65.2, 63.1, 61.4, 60.8, 19.9–22.1 (Ac).

**2o**: $^1$H NMR, δ: 7.20–7.70 (m, 5H, Ar), 6.00 (d, 1H, H-1, $J_{1,2}$ 5.1 Hz), 4.41 (d, 1H, H-1′, $J_{1',2'}$ 7.8 Hz), 4.03 (dd, 1H, H-6A, $J_{6A,5}$ 4.0 Hz, $J_{6A,6B}$ 11.8 Hz), 3.81–3.92 (m, 7H, H-2′, H-3′, H-4′, H-5′, H-6B, H-6A′, H-6B′), 3.80 (m, 2H, H-2, H-3), 3.73–3.77 (m, 2H, H-4, H-5), 0.90–1.00 (m, 36H, $CH_2$), 0.50–0.70 (m, 54H, Me). $^{13}$C NMR, δ: 126.5–131.0 (Ar), 101.2 (C-1′), 82.2 (C-1), 74.0, 71.6, 71.5, 70.8, 70.5, 68.9, 66.5, 63.1, 62.0, 60.8.

and TBS substituents (entries 10, 11) were used. The smaller silyl protections (TMS and TES groups) provided remarkably lower stereoselectivity (entries 8, 9), but the portion of *gluco*-product was higher in the case of substrate **1i** with the TMS substituent.

Similarly to tri-O-acetylated **1a**, the APS transformations of peracetylated di- and trisaccharide derivatives **1m**[9] and **1p** were non-stereoselective (entries 12, 15), but the transformation of their per-O-silylated analogues **1n**,[10] **1o**[10] and **1q** gave only *gluco*-products **2n**,**o**,**q** contrary to the corresponding monosaccharide analogues **1i** and **1j** (entries 8, 9).

Synthesis of glucals **1p** and **1q** using known procedures[11–14] will be published elsewhere.

In conclusion, we have demonstrated that the stereoselectivity in the APS reaction of glucals depends on O-protecting groups in the glucal that gives the possibility to direct to a certain extent the stereochemical result of the reaction towards the formation of either *gluco*- or *manno*-products.

This work was supported by the Russian Foundation for Basic Research (grant no. 07-03-00225). A.A.S. acknowledges the support of INTAS (YS fellowship grant no. 03-55-1026). We are grateful to Yu. E. Tsvetkov, L. O. Kononov and A. I. Zinin for helpful discussions and to A. S. Shashkov and A. A. Grachev for recording the NMR spectra.

**2p**: $^1$H NMR, $\delta$: 7.20–7.70 (m, 5H, Ar), 5.99 (d, 1H, H-1, $J_{1,2}$ 5.2 Hz), 5.50 (m, 1H, H-8″), 5.38 (dd, 1H, H-7″, $J_{7'',6''}$ 2.2 Hz, $J_{7'',8''}$ 9.1 Hz), 5.36 (d, 1H, H-4′, $J_{4,3}$ 3.2 Hz), 5.11 (m, 2H, H-2′, NH), 4.92 (dd, 1H, H-3′, $J_{3,2}$ 9.1 Hz, $J_{3,4}$ 3.0 Hz), 4.80 (m, 1H, H-4″), 4.57 (dd, 1H, H-2, $J_{2,1}$ 6.0 Hz, $J_{2,3}$ 2.0 Hz), 4.44 (d, 1H, H-1′, $J_{1,2}$ 8.0 Hz), 4.40 (m, 1H, H-3), 4.37 (m, 1H, H-6A), 4.20 (m, 4H, H-6′A, H-6′B, H-9A″, H-9B″), 4.03 (m, 2H, H-6B, H-5″), 3.81 (m, 1H, H-5′), 3.72 (s, 3H, OMe), 3.70 (m, 2H, H-4, H-5), 3.55 (d, 1H, H-6″, $J_{6,7}$ 2.1 Hz), 2.47 (dd, 1H, H-3$_{eq}$, $J_{3,3}$ 12.5 Hz, $J_{3,4}$ 4.3 Hz), 1.68 (t, 1H, H-3$_{eq}$, $J_{3,3} = J_{3,4}$ = 12.3 Hz), 1.90–2.25 (m, 30H, Ac). $^{13}$C NMR, $\delta$: 126.5–131.0 (Ar), 126.5–131.0 (Ar), 100.4 (C-1′), 97.3 (C-2″) 83.2 (C-1), 77.9, 75.3, 75.2, 74.0, 72.8, 71.9, 71.6, 71.5, 70.5, 68.6, 65.7, 63.2, 62.7, 62.3, 61.2 (C-2), 54.9 (C-5″), 39.9 (C-3″), 19.3–21.6 (Ac).

**2q**: $^1$H NMR, $\delta$: 7.20–7.70 (m, 5H, Ar), 5.95 (d, 1H, H-1, $J_{1,2}$ 5.0 Hz), 4.02 (m, 2H), 3.94 (m, 1H, H-2), 3.81–3.96 (m, 10H), 3.79 (m, 1H, H-3), 3.72–3.78 (m, 5H), 2.42 (dd, 1H, H-3$_{eq}$, $J_{3,3}$ 12.8 Hz, $J_{3,4}$ 4.1 Hz), 1.75 (t, 1H, H-3$_{eq}$, $J_{3,3} = J_{3,4}$ = 12.9 Hz), 0.80–1.10 (m, 135H, Et). $^{13}$C NMR, $\delta$: 133.1–127.4 (Ar), 100.4 (C-2″), 100.3 (C-1′), 98.1 (C-2″), 84.1 (C-1), 74.0, 73.2, 71.5, 71.0, 70.5, 70.1, 69.1, 66.3, 63.1, 62.4, 60.1, 56.2, 53.0, 39.2 (C-3″), 10.4–12.7 (Et), 0.4–2.9 (Et).

**3m**: $^1$H NMR, $\delta$: 7.20–7.70 (m, 5H, Ar), 5.72 (d, 1H, H-1, $J_{1,2}$ 1.4 Hz), 5.37 (d, 1H, H-4′, $J_{4',3'}$ 3.5 Hz), 5.32 (dd, 1H, H-3, $J_{3,2}$ 9.0 Hz, $J_{3,4}$ 3.2 Hz), 5.15 (dd, 1H, H-2′, $J_{2',1'}$ 8.0 Hz, $J_{2',3'}$ 10.0 Hz), 4.97 (dd, 1H, H-3′, $J_{3',2'}$ 10.0 Hz, $J_{3',4'}$ 3.4 Hz), 4.55 (d, 1H, H-1′, $J_{1',2'}$ 8.0 Hz), 4.36 (m, 3H, H-6A, H-6′A, H-6′B), 4.30 (m, 1H, H-2), 4.05 (m, 2H, H-5′, H-6B), 3.93 (m, 2H, H-4, H-5), 2.00–2.20 (6s, 18H, Ac). $^{13}$C NMR, $\delta$: 169.6–170.9 (C=O), 137.5 (*ipso*-Ph), 126.5–131.0 (Ar), 101.2 (C-1′), 82.2 (C-1), 74.0, 71.6, 71.5, 70.8, 70.5, 68.9, 66.5, 63.1, 62.0, 60.8, 19.6–22.0 (Ac).

**3p**: $^1$H NMR, $\delta$: 7.20–7.70 (m, 5H, Ar), 5.99 (d, 1H, H-1, $J_{1,2}$ 5.2 Hz), 5.50 (m, 1H, H-8″), 5.38 (dd, 1H, H-7″, $J_{7'',6''}$ 2.2 Hz, $J_{7'',8''}$ 9.1 Hz), 5.36 (d, 1H, H-4′, $J_{4,3}$ 3.2 Hz), 5.11 (m, 2H, H-2′, NH), 4.92 (dd, 1H, H-3′, $J_{3,2}$ 9.1 Hz, $J_{3,4}$ 3.0 Hz), 4.80 (m, 1H, H-4″), 4.57 (dd, 1H, H-2, $J_{2,1}$ 6.0 Hz, $J_{2,3}$ 2.0 Hz), 4.44 (d, 1H, H-1′, $J_{1,2}$ 8.0 Hz), 4.40 (m, 1H, H-3), 4.37 (m, 1H, H-6A), 4.20 (m, 4H, H-6′A, H-6′B, H-9A″, H-9B″), 4.03 (m, 2H, H-6B, H-5″), 3.81 (m, 1H, H-5′), 3.72 (s, 3H, OMe), 3.70 (m, 2H, H-4, H-5), 3.55 (d, 1H, H-6″, $J_{6,7}$ 2.1 Hz), 2.47 (dd, 1H, H-3$_{eq}$, $J_{3,3}$ 12.5 Hz, $J_{3,4}$ 4.3 Hz), 1.68 (t, 1H, H-3$_{eq}$, $J_{3,3} = J_{3,4}$ = 12.3 Hz), 1.90–2.25 (m, 30H, Ac). $^{13}$C NMR, $\delta$: 169.6–171.4 (C=O), 126.5–131.0 (Ar), 101.5 (C-2), 100.4 (C-1′), 97.3 (C-2″), 75.3, 75.2, 74.0, 72.8, 71.9, 71.6, 71.5, 70.8, 70.5, 68.9, 66.1, 64.4, 62.5, 62.8, 60.0 (C-2), 53.9 (C-5″), 39.1 (C-3″), 19.3–21.7 (Ac).

**5** (in the mixture with **6**, see entries 22 and 23, Table 1): $^1$H NMR, $\delta$: 7.10–8.10 (m, 4H, Ar), 5.81 (d, 1H, H-1, $J_{1,2}$ 9.4 Hz), 5.17 (t, 1H, H-3, $J_{3,2} = J_{3,4}$ = 9.1 Hz), 5.08 (t, 1H, H-4, $J_{4,3} = J_{4,5}$ = 9.1 Hz), 4.30 (m, 1H, H-6), 4.06 (dd, 1H, H-6′, $J_{5,6'}$ 2.2 Hz, $J_{6',6}$ 12.5 Hz), 3.74 (ddd, 1H, H-5, $J_{5,4}$ 8.9 Hz, $J_{5,6}$ 2.3 Hz, $J_{5,6'}$ 4.6 Hz), 3.41 (t, 1H, H-2, $J_{2,1} = J_{2,3}$ = 9.2 Hz), 1.95–2.20 (3s, 9H, Ac). $^{13}$C NMR, $\delta$: 170.0–174.2 (C=O), 127.8–141.8 (Ar), 94.4 (C-1), 93.4 (C-I), 72.4 (C-5), 72.2 (C-3), 69.2 (C-4), 61.7 (C-6), 46.3 (C-2), 20.7 (Ac).

**6** (in the mixture with **5**, see entries 22 and 23, Table 1): $^1$H NMR, $\delta$: 7.10–8.10 (m, 4H, Ar), 6.68 (d, 1H, H-1, $J_{1,2}$ 1.5 Hz) 5.55 (m, 2H, H-3, H-4), 4.45 (m, 1H, H-6), 4.20 (m, 2H, H-5, H-6′), 4.08 (dd, 1H, H-2, $J_{2,1}$ = 1.8 Hz, $J_{2,3}$ 3.8 Hz), 1.95–2.20 (3s, 9H, Ac). $^{13}$C NMR, $\delta$: 170.0–174.2 (C=O), 127.8–141.8 (Ar), 95.6 (C-1), 94.6 (C-I), 71.6 (C-5), 70.7 (C-4), 66.6 (C-3), 46.4 (C-2), 20.7 (Ac).

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*Received: 16th July 2008; Com. 08/3182*