

194. Convenient Synthesis of 2-Azido-2-deoxy-aldoses by Diazo Transfer

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Dedicated to Prof. Dr. *Antonio Gómez-Sánchez* on the occasion of his 65th birthday.

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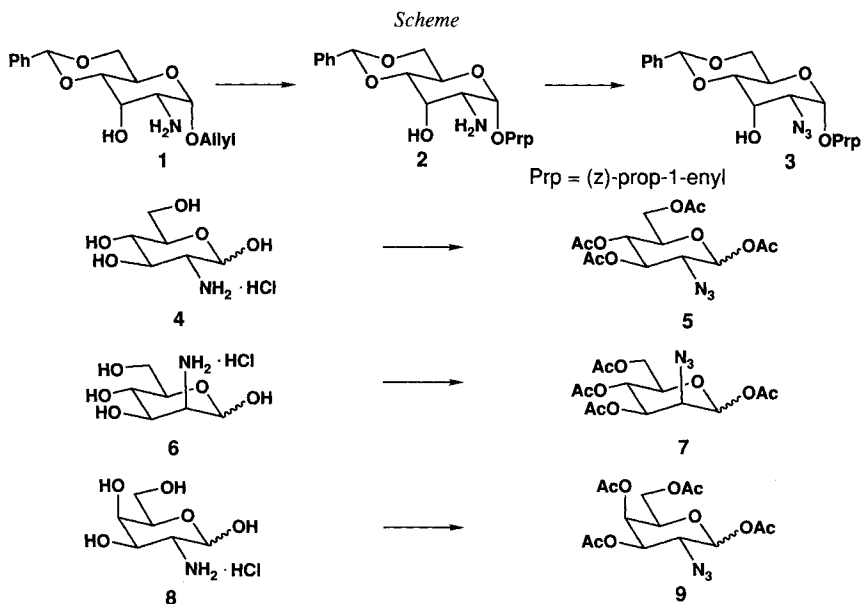
Diazo transfer from trifluoromethanesulfonyl azide (TfN_3) to 2-amino-2-deoxy-glycoses constitutes a high-yielding, simple procedure for the preparation of partially protected or unprotected 2-azido-2-deoxy-aldoses. Thus, the D-allosamine derivative **2** gave 93% of **3**, while diazo transfer to D-glucosamine, D-mannosamine, and D-galactosamine, followed by acetylation, yielded the azides **5**, **7**, and **9** in yields of 74–91, 65, and 70%, respectively.

Introduction. – The 2-Azido-2-deoxy derivatives of mono- and disaccharides are frequently used intermediates in the synthesis of amino-deoxy oligosaccharides (see [1] for leading ref.). These azides have been prepared by azidonitration of glycals [2], by addition of halogeno azides to glycals [3], and from 1,6-anhydroglycoses either by opening of epoxides [4] or by substitution of 2-*O*-triflates [5]. The diastereoselectivity of the azidonitration and halogeno-azide addition depends on the configuration of the glycal. It is high for the *lyxo*-glycals, leading to mixtures of 2-azido-2-deoxy-galactose nitrates [2], and lower for the *arabino*-glycals, leading to mixtures of 2-azido-2-deoxy-glucose and -mannose derivatives [6]. The preparation of 2-azido-2-deoxy-glycals from 1,6-anhydro sugars proceeds in a configurationally controlled way, but requires a relatively large number of steps.

The 6-Azido-6-deoxyhexoses have also been prepared from the corresponding acetamides by *N*-nitrosation, reduction, and *N*-acylation to *N,N'*-diacylhydrazines, and again *N*-nitrosation [7]; this method has been modified [8] for the transformation of 1,3,4,6-tetra-*O*-acetyl-2-*N*-benzyl-2-deoxy- β -D-glucopyranose (prepared from glucosamine) into the corresponding azide β -D-**5** [3] (*cf. Scheme*) in 49–55% overall yield. Finally, the synthesis of 5-azido-3,5-dideoxy-D-glycero-D-galacto-nonulosonic acid [9] involved the reaction of HN_3 with a diazo compound which was prepared by *N*-nitrosation of a derivative of *N*-acetylneuraminic acid.

Glucosamine is a cheap starting material and available in large amounts. It can easily be transformed into derivatives of 2-amino-2-deoxy allose which was required for the synthesis of allosamidin [10]. A method allowing the direct transformation of 2-amino-2-deoxyaldoses, and particularly glucosamine, into the corresponding azides would be welcome in the context of the synthesis of oligosaccharides [1]. Amines can be transformed into azides by diazo transfer from trifluoromethanesulfonyl azide (TfN_3) but, to the best of our knowledge, this method has not been applied to carbohydrates¹⁾. To check the scope of the reaction, we examined the transformation of the partially protected derivative **2** of D-allosamine, of D-glucosamine (**4**), D-mannosamine (**6**), and D-galactosamine (**8**) into the corresponding azides.

Results. – The allosamine derivative **2** [10] was prepared from the allyl glycoside **1** [10] (see the *Scheme*). D-Glucosamine (**4**), D-mannosamine (**6**), and D-galactosamine (**8**) were liberated *in situ* from their commercially available hydrochlorides. Considering its hazardous nature, TfN_3 was prepared *in situ* [12] and used in solution only. The concentration of the TfN_3 solution was determined by IR spectroscopy (intensity of the band at 2150 cm^{-1}) to be 0.26M, using the easily available TsN_3 and a microanalytically pure sample of **3** as independent standards. The result compares well with the one obtained by titration of liberated TfOH [12]. For the transformation of the amines **4**, **6**, and **8**, the preparation of the TfN_3 soln. was slightly modified. Its concentration was 0.40M. The transformation of the allosamine derivative **2** proceeded smoothly in $\text{MeCN}/\text{CH}_2\text{Cl}_2$ at room temperature over 2 h to give the crystalline and stable azide **3** in high yield.



¹⁾ Araki *et. al.* [11] have published the transformation of methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl- α -D-*altro*- and - α -D-*allo*-pyranoside into the corresponding azides in low yield using TsN_3/BuLi in benzene.

To overcome the problem of solubility of the amines **4**, **6**, and **8**, we chose a two-phase reaction in the presence of methyl(trioctyl)ammonium chloride as a phase-transfer agent, but the reaction was too slow to be of practical use. To ensure a homogeneous mixture, we added a solution of TiN_3 in CH_2Cl_2 to a solution of the amine in MeOH. In this manner, D-glucosamine (**4**) was transformed into the corresponding azide, which was isolated as a mixture of the anomeric acetates α - and β -D-**5** (74–91%). The synthesis of the *manno*- and *galacto*-azides **7** and **9**, respectively, proceeded similarly to the one of **5**, but yields were lower. Our procedure for the preparation of the 2-azido-2-deoxy derivatives **5**, **7**, and **9** of glucose, mannose, and galactose, respectively, compares favourably with the published ones.

The presence of a (Z)-propenyl substituent in **2** is evidenced in the ^1H -NMR spectrum by an apparent *quint*. at 4.66 ppm which is assigned to H-C(2'), the $^3J(1',2')$ value (6.2 Hz) being of the same magnitude as $^3J(2',\text{Me})$. H-C(3) appears as a *t* with a small coupling constant of 2.6 Hz, as it is typical for a 4C_1 conformation. The broad signal at 1.89 ppm, which disappears upon addition of D_2O , is assigned to NH_2 and OH. In the ^{13}C -NMR spectrum of **2**, the signals at 142.14 (*d*), 104.60 (*d*), and 9.42 (*q*) are evidencing the (Z)-propenyl substituent. The IR spectrum of **3** shows an absorption at 3570 cm^{-1} which is assigned to the OH valence vibration. The absence of other absorptions above 3000 cm^{-1} and the band at 2110 cm^{-1} indicate the transformation of the amino into the azido function. This transformation has little effect on the conformation of the pyranose ring as evidenced by the coupling constants in the ^1H -NMR spectrum. The signal of the C(3)–OH group appears between 2.75 and 2.50 ppm as a br. s.

We thank Dr. P. Dhar for her help in checking the procedures.

Experimental Part

General. Solvents were distilled before use. Normal workup means drying the org. phase (Na_2SO_4), filtration through a cotton plug, and evaporation of the solvent *i.v.* Solns. were evaporated at or below 40° in a Büchi rotary evaporator. Samples were dried in high vacuum (h.v.) at a pressure below 0.1 mbar. Qual. TLC: Merck precoated silica gel 60 F-254 plates; detection by spraying the plates with a soln. of 0.02M I_2 and 0.30M KI in 10% aq. H_2SO_4 soln., followed by heating at ca. 200° . Flash chromatography (FC): silica gel Merck 60 (40–63 μm). M.p.: uncorrected. Optical rotations: 1-dm cell; at 365, 436, 546, 578, and 589 nm; values at 589 nm were obtained from a regression curve. IR spectra: 3% soln. in CHCl_3 . ^1H - and ^{13}C -NMR spectra: at 300 MHz (^1H) and at 50 MHz (^{13}C); chemical shifts δ in ppm relative to TMS and coupling constants *J* in Hz. MS: by EI at 70 eV and by CI (isobutane).

(Z)-Prop-1-enyl 2-Amino-4,6-O-benzylidene-2-deoxy- α -D-allopyranoside (**2**). A soln. of **1** (3.97 g, 12.9 mmol) in DMSO (74 ml, dried over 4-Å molecular sieves) was added to a vigorously stirred suspension of *t*-BuOK (3.26 g, 29.1 mmol) in DMSO (74 ml). The slightly turbid brown mixture was heated to 50° under N_2 for 4 h 20 min, then poured onto 300 ml of ice-water, and extracted with Et_2O ($4 \times 250\text{ ml}$). The org. phase was washed with H_2O and brine. Normal workup yielded 3.77 g (95%) of **2** as slightly yellow, crystalline material. An anal. sample was obtained by recrystallization in AcOEt/hexane. R_f ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 95:5) 0.17. $[\alpha]_D^{25} = +58.3$ ($c = 1.1$, CHCl_3). IR: 3550w, 3390w, 3320w, 2980m, 2940m, 2860m, 1670s, 1580w, 1450w, 1380m, 1340m, 1125s, 1100s, 1050s, 1000s, 960s, 910m, 880m. ^1H -NMR (CDCl_3): 7.55–7.50 (*m*, 2 arom. H); 7.42–7.33 (*m*, 3 arom. H); 6.10 (*qd*, $J = 1.8, 6.2, 1$ olef. H); 5.61 (*s*, PhCH); 4.99 (*d*, $J = 3.9$, H-C(1)); 4.66 (*quint.*, $J = 6.7, 1$ olef. H); 4.36 (*dd*, $J = 5.2, 10.2$, H_{eq} -C(6)); 4.15 (*t*, $J = 2.6$, H-C(3)); 4.13 (*dt*, $J = 5.0, 10.0$, H-C(5)); 3.75 (*t*, $J = 10.3$, H_{ax} -C(6)); 3.60 (*dd*, $J = 2.8, 9.8$, H-C(4)); 3.05 (*t*, $J = 3.5$, H-C(2)); 1.66 (*dd*, $J = 1.7, 6.8$, Me); 1.89 (br. s, exchanged by D_2O , NH_2 , OH). ^{13}C -NMR (CDCl_3): 142.14 (*d*); 137.20 (*s*); 129.06 (*d*); 126.19 (*d*); 104.60 (*d*); 101.78 (*d*); 100.49 (*d*); 79.12 (*d*); 69.90 (*d*); 69.13 (*t*); 57.60 (*d*); 52.19 (*d*); 9.42 (*q*). CI-MS: 309 (11), 308 (56, $[M + 1]^+$), 251 (15), 250 (100). Anal. calc. for $\text{C}_{16}\text{H}_{21}\text{NO}_5$ (307.36): C 62.53, H 6.89, N 4.56; found: C 62.63, H 7.00, N 4.34.

(Z)-Prop-1-enyl 2-Azido-4,6-O-benzylidene-2-deoxy- α -D-allopyranoside (**3**). NaN_3 (8.00 g, 123.0 mmol) was dissolved at 23° in H_2O (20 ml) in a 50 ml flask, equipped with a septum and a N_2 balloon. CH_2Cl_2 (25 ml) was added to the vigorously stirred soln. at 0° . TiF_4 (freshly distilled over P_2O_5 under Ar; 4.1 ml, 25.0 mmol) was

added within 5 min by syringe. The mixture was stirred for 2 h at 0°, the org. layer was separated, and the aq. layer was extracted with CH_2Cl_2 (2×10 ml). The combined org. layers were extracted with sat. aq. NaHCO_3 soln. (20 ml) and H_2O (20 ml), dried (Na_2SO_4), filtered, and the TfN_3 soln. was stored at 4° over 4-Å molecular sieves, $c = 0.26\text{M}$.

To a soln. of **2** (2.50 g, 8.10 mmol) and 4-(dimethylamino)pyridine (4.35 g, 35.6 mmol; recrystallized in toluene) in MeCN (50 ml, distilled from CaH_2), TfN_3 soln. (39 ml, 10.9 mmol, as prepared above) was added at 23° within 10 min by syringe. After 2 h, the mixture was concentrated at 30° to ca. 3 ml. FC (125 g of SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 99:1) gave 2.42 g (93%) of **3**. R_f (hexane/AcOEt 8:2) 0.43. An anal. sample was crystallized from MeCN/AcOEt. $[\alpha]_D^{25} = 142.3$ ($c = 0.65$, CHCl_3). M.p. 157–159° (dec.). IR: 3570m, 2980w, 2920m, 2860m, 2200w, 2110s, 1670m, 1450w, 1340w, 1170s, 1100s, 1060s, 1030s, 1010s, 960m, 910m. $^1\text{H-NMR}$ (CDCl_3): 7.54–7.48 (m, 2 arom. H); 7.44–7.36 (m, 3 arom. H); 6.14 (qd, $J = 1.7, 6.2$, 1 olef. H); 5.61 (s, PhCH); 5.18 (d, $J = 3.9$, H-C(1)); 4.73 (quint., $J = 6.7$, 1 olef. H); 4.56 (t, $J = 2.8$, H-C(3)); 4.38 (dd, $J = 5.2, 10.0$, H_{eq} -C(6)); 4.28 (dt, $J = 5.1, 9.9$, H-C(5)); 3.75 (t, $J = 10.1$, H_{ax} -C(6)); 3.58 (dd, $J = 2.7, 9.6$, H-C(4)); 3.20 (t, $J = 3.5$, H-C(2)); 2.75–2.50 (br. s, exchanged with D_2O , OH); 1.70 (dd, $J = 1.6, 6.9$, Me). $^{13}\text{C-NMR}$: 144.18 (d); 136.84 (s); 129.21 (d); 128.25 (d); 126.16 (d); 105.50 (d); 101.81 (d); 98.60 (d); 78.27 (d); 69.34 (d); 68.81 (t); 57.96 (d); 9.51 (q). CI-MS: 334 (25, $[M + 1]^+$), 306 (100), 248 (20). Anal. calc. for $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_5$ (333.35): C 57.65, H 5.75, N 12.61; found: C 57.52, H 5.78, N 12.55.

1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-D-glucopyranose (5). NaN_3 (8.00 g, 123.0 mmol) was dissolved at 23° in H_2O (20 ml) in a 100-ml three-neck round-bottom flask, equipped with a dropping funnel, a septum, and a N_2 balloon. CH_2Cl_2 (25 ml) was added to the vigorously stirred soln. at 0°. Tf_2O (freshly dist. over P_2O_5 under Ar, 4.1 ml, 25.0 mmol) was added within 30 min. The mixture was stirred for 2 h at 0°, the org. layer separated, and the aq. layer extracted with CH_2Cl_2 (2×10 ml). The combined org. layers were washed with sat. aq. NaHCO_3 soln. (20 ml) and H_2O (20 ml), dried (MgSO_4), filtered, and the TfN_3 soln. was stored at 4° over 4-Å mol. sieves, $c = 0.40\text{M}$. A suspension of D-glucosamine hydrochloride (100 mg, 0.46 mmol) in MeOH (distilled over $\text{Mg}(\text{OMe})_2$, 2 ml) was treated with a 0.5M soln. of NaOMe in MeOH (1.1 ml, 0.55 mmol) and stirred for 10 min at 26°. Dilution with MeOH (4.9 ml) and treatment with 4-(dimethylamino)pyridine (60 mg, 0.49 mmol) furnished a clear, colorless soln., to which the 0.40M TfN_3 soln. (3 ml, 1.2 mmol) was added at 26° within 10 min by syringe. After stirring for 18 h at 26° under N_2 , the solvent was evaporated at 30° i.v. The oily, white suspension of the residue in anh. pyridine (3 ml) was treated at 0° with Ac_2O (2 ml) and stirred under N_2 for 4 h at this temp. It was diluted with CH_2Cl_2 (25 ml) and washed with 1M aq. HCl (2×25 ml). The combined aq. layers were extracted with CH_2Cl_2 (3×10 ml). The combined org. layers were washed with sat. aq. NaHCO_3 soln. (40 ml) and brine (40 ml), dried (Na_2SO_4) and concentrated i.v. FC (hexane/AcOEt 3:1) of the residue afforded 160 mg (91% from **4**) of **5**. Colorless oil. R_f (hexane/AcOEt 2:1) 0.33. $[\alpha]_D^{25} = +51.6$ ($c = 0.8$, CDCl_3) ($[\alpha]_D^{20}$ of $\alpha\text{-D-5} = +130$, $\beta\text{-D-5} = +8$, $c = 1.0$, CHCl_3 [3]). IR (film): 2118s, 1755s, 1432w, 1370m, 1220s, 1143w, 1110w, 1075m, 1050m. $^1\text{H-NMR}$ (CDCl_3): ($\alpha\text{-D}/\beta\text{-D} = 45:55$); 6.25 (d, $J = 3.7$, 0.45 H, H-C(1)); 5.51 (d, $J = 8.6$, 0.55 H, H-C(1)); 5.41 (dd, $J = 9.4, 10.4$, 0.45 H, H-C(3)); 5.1–4.9 (m, 1.55 H, H-C(3), 2 H-C(4)); 4.24 (dd, $J = 4.5, 12.4$, 0.55 H, H-C(6)); 4.25 (dd, $J = 4.1, 12.5$, 0.45 H, H-C(6)); 4.04 (dd, $J = 2.2, 12.4$, 0.55 H, H-C(6)); 4.12–3.98 (m, 0.9 H, H-C(5), H-C(6)); 3.76 (ddd, $J = 2.2, 4.5, 9.7$, 0.55 H, H-C(5)); 3.62 (dd, $J = 3.7, 10.5$, 0.45 H, H-C(2)); 3.62 (dd, $J = 8.6, 9.8$, 0.55 H, H-C(2)); 2.15 (s, 1.35 H, AcO); 2.14 (s, 1.65 H, AcO); 2.06 (s, 1.35 H, AcO); 2.04 (s, 1.65 H, AcO); 2.03 (s, 3 H, 2 AcO); 2.00 (s, 1.35 H, AcO); 1.98 (s, 1.65 H, AcO). $^{13}\text{C-NMR}$ (CDCl_3): 170.35 (s); 169.67 (s); 169.60 (s); 169.46 (s); 169.38 (s); 168.38 (s); 168.34 (s); 92.4 (d); 89.84 (d); 72.57 (d); 70.63 (d); 69.63 (d); 67.83 (d); 67.74 (d); 62.48 (d); 61.32 (t); 60.18 (d); 20.70 (q); 20.68 (q); 20.46 (q); 20.35 (q).

1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-D-mannopyranose (7). As described for **5**, **6** (100 mg, 0.46 mmol) was treated with a 0.5M soln. of NaOMe in MeOH (1.1 ml; 0.55 mmol), 4-(dimethylamino)pyridine (60 mg, 0.49 mmol), and a 0.40M TfN_3 soln. (3 ml, 1.2 mmol), followed by acetylation of the crude product, to give, after FC (hexane/AcOEt 3:1), 112 mg (65 %) of **7**. Colorless oil. R_f (hexane/AcOEt 2:1) 0.31. $[\alpha]_D^{25} = +40.8$ ($c = 1.5$, CDCl_3) ($[\alpha]_D^{20}$ of $\alpha\text{-D-7} = +81.4$, $c = 1.0$, CHCl_3 [5]). IR (film): 2117s, 1750s, 1430w, 1370m, 1220s, 1150m, 1090m(sh), 1050m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): ($\alpha\text{-D}/\beta\text{-D} = 76:24$); 6.09 (d, $J = 1.9, 0.76$ H, H-C(1)); 5.81 (d, $J = 1.4, 0.24$ H, H-C(1)); 5.48–5.31 (m, 1.52 H, H-C(3), H-C(4)); 5.27 (t, $J = 9.8, 0.24$ H, H-C(4)); 5.04 (dd, $J = 3.7, 9.8$, 0.24 H, H-C(3)); 4.23 (dd, $J = 4.9, 12.4$, 0.24 H, H-C(6)); 4.21 (dd, $J = 4.6, 12.4$, 0.76 H, H-C(6)); 4.08 (dd, $J = 2.2, 12.4$, 0.76 H, H-C(6)); 4.06 (dd, $J = 2.4, 12.4$, 0.24 H, H-C(6)); 4.03–3.95 (m, 1 H, H-C(2), H-C(5)); 3.99 (dd, $J = 1.9, 3.3$, 0.76 H, H-C(2)); 3.70 (ddd, $J = 2.4, 4.9, 9.9$, 0.24 H, H-C(5)); 2.16 (s, 0.72 H, AcO); 2.13 (s, 2.28 H, AcO); 2.09 (s, 3 H, AcO); 2.07 (s, 2.28 H, AcO); 2.06 (s, 0.72 H, AcO); 2.03 (s, 2.28 H, AcO); 2.02 (s, 0.72 H, AcO). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 170.58 (s); 169.93 (s); 169.26 (s); 168.07 (s); 91.33 (d); 91.17 (d); 73.25 (d); 71.60 (d); 70.72 (d); 70.50 (d); 65.32 (d); 64.94 (d); 61.75 (t); 61.01 (d); 60.48 (d); 20.75 (q); 20.59 (q); 20.49 (q).

1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-D-galactopyranose (**9**). As described for **5**, **8** (100 mg, 0.46 mmol) was treated with a 0.5M soln. of NaOMe in MeOH (1.1 ml, 0.55 mmol), 4-(dimethylamino)pyridine (60 mg, 0.49 mmol), and a 0.40M TfN₃ soln. (3 ml, 1.2 mmol), followed by acetylation of the crude product, to give, after FC (hexane/AcOEt 3:1), 122 mg (70%) of **9**. Colorless oil. *R_f* (hexane/AcOEt 2:1) 0.34. $[\alpha]_D^{25} = +36.7$ (*c* = 1.6, CDCl₃) ($[\alpha]_D^{20}$ of α -D-**9** = +91.7, *c* = 1.05, CHCl₃ [2]). IR (film): 2120 s. ¹H-NMR (CDCl₃): (α -D/ β -D = 40:60); 6.29 (*d*, *J* = 3.7, 0.4 H, H-C(1)); 5.51 (*d*, *J* = 8.5, 0.6 H, H-C(1)); 5.44 (*dd*, *J* = 1.3, 3.2, 0.4 H, H-C(4)); 5.34 (*dd*, *J* = 1.0, 3.4, 0.6 H, H-C(4)); 5.28 (*dd*, *J* = 3.2, 11.1, 0.4 H, H-C(3)); 4.86 (*dd*, *J* = 3.3, 10.8, 0.6 H, H-C(3)); 4.25 (*ddd*, *J* = 1.3, 6.6, 6.8, 0.4 H, H-C(5)); 4.15–4.02 (*m*, 2 H, 2 H-C(6), 2 H'-C(6)); 3.97 (*ddd*, *J* = 1.1, 6.1, 7.2, 0.6 H, H-C(5)); 3.90 (*dd*, *J* = 3.7, 11.1, 0.4 H, H-C(2)); 3.80 (*dd*, *J* = 8.5, 10.8, 0.6 H, H-C(2)); 2.16 (*s*, 1.8 H, AcO); 2.14 (*s*, 1.2 H, AcO); 2.13 (*s*, 3 H, AcO); 2.04 (*s*, 1.2 H, AcO); 2.03 (*s*, 1.8 H, AcO); 2.00 (*s*, 1.2 H, AcO); 1.99 (*s*, 1.8 H, AcO). ¹³C-NMR (50 MHz, CDCl₃): 170.12 (*s*); 169.76 (*s*); 169.65 (*s*); 169.41 (*s*); 168.38 (*s*); 92.71 (*d*); 90.30 (*d*); 71.58 (*d*); 71.14 (*d*); 68.58 (*d*); 66.76 (*d*); 66.11 (*d*); 60.96 (*t*); 60.84 (*t*); 59.60 (*d*); 56.73 (*d*); 20.68 (*q*); 20.41 (*q*).

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