treatment) at an incident wavelength of 1.907 μm. Dipole moments μ were determined in anhydrous $CHCl_3$ by the Guggenheim method.[4] All solutions for EFISH, conductivity, and capacitance measurements were used immediately after preparation.

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Stereoselective Glycosylations

Dual Stereoselectivity of 1-(2′-Carboxy)benzyl 2-Deoxyglycosides as Glycosyl Donors in the Direct Construction of 2-Deoxyglycosyl Linkages**

Kwan Soo Kim, Jin Park, Yong Joo Lee, and Yong Sung Seo*

2-Deoxyglycosides are found as the integral part of many important natural products.[1] The stereocontrolled construction of 2-deoxyglycosyl linkages is more challenging than that of usual glycosyl linkages as the 2-deoxyglycosyl donors lack the stereodirecting substituent at C2 and the resulting glycosides are more acid-labile. Although the synthesis of 2-deoxy-α-glycopyranosides is relatively easier, the construction of 2-deoxy-β-glycopyranosyl linkages is a far more challenging problem[2] as the axial addition of a glycosyl acceptor to the oxocarbenium ion intermediate is a favorable process owing to the anomeric effect.[3] Therefore, the frequently used method for the synthesis of 2-deoxy-β-glycopyranosides employs the glycosyl donors with equatorial heteroatom substituents at C2 that can participate during glycosylation to direct the incoming acceptor to the β-face and are removed at a later stage.[4] Nevertheless, a direct and efficient method for the construction of the 2-deoxy-β-glycopyranosyl linkage by using a 2-deoxyglycopyranosyl donor would be more efficient and practical than the indirect methods. Although a few methods (e.g. glycosylation mediated by silver silicate[5] or silver zeolite,[6] the 2-deoxyglycosyl phosphite/TMSOTf (TMSOTf = trimethylsilyl trifluoromethanesulfonate) method,[7] and the glycosylation of 2-deoxyglycosyl fluoride with TiF_4[8] or $SnCl_2$,[9]) have been devised, the direct synthesis of 2-deoxy-β-glycopyranosides from 2-deoxyglycosyl donors still remains a difficult task. We have previously introduced (2′-carboxy)benzyl (CB) glycosides as glycosyl donors for the efficient β-mannopyranosylation.[10] We applied this CB glycoside methodology to the direct synthesis of 2-deoxyglycopyranosides and herein report the preparation of CB 2-deoxyglycosides from glycals and their α- or β-stereoselectivity (dual stereoselectivity) as glycosyl donors in the glycosylation reaction, depending on their protecting groups.

CB 2-deoxyglucoside **4** was readily obtained from the tribenzylglucal **1** as shown in Scheme 1. CB 4,6-*O*-benzylidene-2-deoxyglucoside **7**, on the other hand, was prepared from a 3,4,6-tri-*O*-acetyl-D-glucal via 2-deoxyglycosyl bromide **5**.[13] Glycosylations of the CB 2-deoxyglycosyl donors **4** and **7** were performed with primary alcohol acceptors **8**–**12** and with secondary alcohol acceptors **13**–**17**. Glycosylation of the benzyl-protected donor **4** with primary alcohol acceptors

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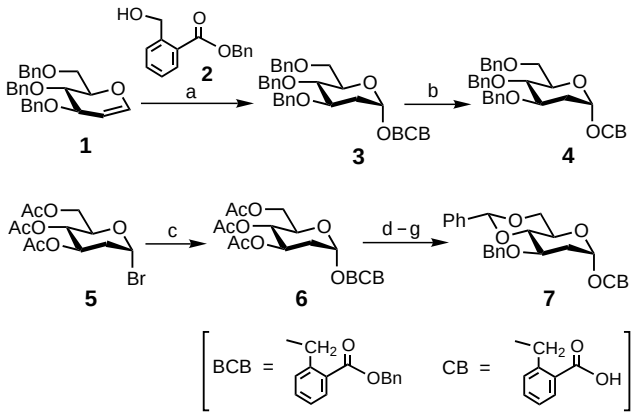
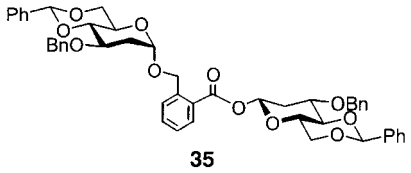


Scheme 1. Synthesis of CB 2-deoxyglycosides **4** and **7**: a) **2** (2.5 equiv), $Ph_3P{\cdot}HBr$[11] (0.05 equiv), 0→40 °C, 1 h, 89%; b) H_2, Pd/C (10%), NH_4OAc[12] (3.5 equiv), MeOH, 1 h, 90%; c) **2** (1.2 equiv), $Hg(CN)_2$, $HgBr_2$, CH_3CN, molecular sieves (4 Å), 0 °C, 20 min, 90%; d) NaOMe, MeOH, 20 min; e) $PhCH(OMe)_2$, CSA, DMF, 50 °C, 1 h, 90% over two steps; f) BnBr, NaH, DMF, 1 h, 84%; g) same as b), 92%. CSA = (±)-camphorsulfonic acid, DMF = *N*,*N*-dimethylformamide, Bn = benzyl.

8–**12** exhibited no significant stereoselectivity (Table 1, entries 1–5). For example, the dropwise addition of Tf_2O (1.2 equiv) to a stirred solution of **4** (1.0 equiv), the acceptor **8** (1.5 equiv), and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 2.4 equiv) in CH_2Cl_2 at −78 °C for 1 h led to the isolation of equal amounts of α- and β-disaccharides **18** in 98% yield (Table 1, entry 1). Some β-selectivity was observed when primary alcohols **10** (α/β 1:1.2), **11** (α/β 1:1.5), and **12** (α/β 1:1.7) were employed as the glycosyl acceptors (Table 1, entries 3–5). On the other hand, glycosylation of **4** with secondary alcohol donors **13**–**15** afforded the α-disaccharides exclusively (Table 1, entries 6–8) and with the secondary alcohol **16** afforded predominantly the α-disaccharide **26** (α/β 9.4:1; Table 1, entry 9).

Under the same reaction conditions, glycosylation of the benzylidene-protected donor **7** with primary alcohol acceptors **8** and **9** provided a mixture of almost equal amounts of α- and β-anomers of disaccharides **27** (α/β 1:1) and **28** (α/β 1:1.2), respectively, together with a minor amount of the self-condensed ester **35**, which must be derived from two



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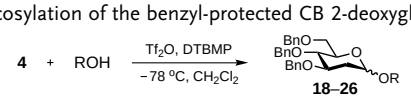
molecules of the glycosyl donor **7** (Table 2, entries 1 and 2). When primary alcohols **11** and **12** were used as glycosyl acceptors, the ratio of the resulting disaccharides increased substantially in favor of the β-anomer; α/β 1:2 for **29** and 1:5.1 for **30** (Table 2, entries 3 and 4). The highly β-selective glycosylation of **7** could be carried out with secondary alcohol acceptors. Thus, the β/α ratio in the reactions of **7** with acceptors **13** and **15** was 10:1 and that with **17** was 8:1

Table 1: Glycosylation of the benzyl-protected CB 2-deoxyglycoside **4**.



18–**26**

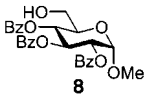
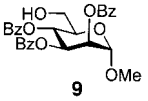
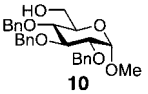
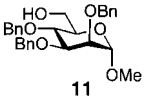
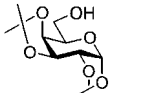
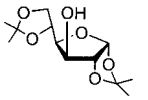
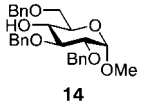
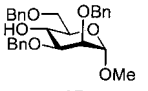
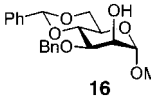
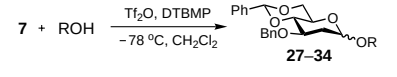
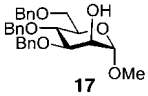
Entry	ROH	Product	Yield [%]	Ratio [α/β]
1	 **8**	**18**	98	1:1
2	 **9**	**19**	93	1:1
3	 **10**	**20**	94	1:1.2
4	 **11**	**21**	78	1:1.5
5	 **12**	**22**	93	1:1.7
6	 **13**	**23**	91	α only
7	 **14**	**24**	91	α only
8	 **15**	**25**	88	α only
9	 **16**	**26**	94	9.4:1

Table 2: Glycosylation of the benzylidene-protected CB 2-deoxyglycoside **7**.



27–**34**

Entry	ROH	Product	Yield [%]	Ratio [α/β]	Ester **35** [%]
1	**8**	**27**	92	1:1	8
2	**9**	**28**	80	1:1.2	16
3	**11**	**29**	83	1:2	14
4	**12**	**30**	85	1:5.1	12
5	**13**	**31**	76	1:10	14
6	**14**	**32**	72	β only	16
7	**15**	**33**	78	1:10	16
8	 **17**	**34**	71	1:8	17

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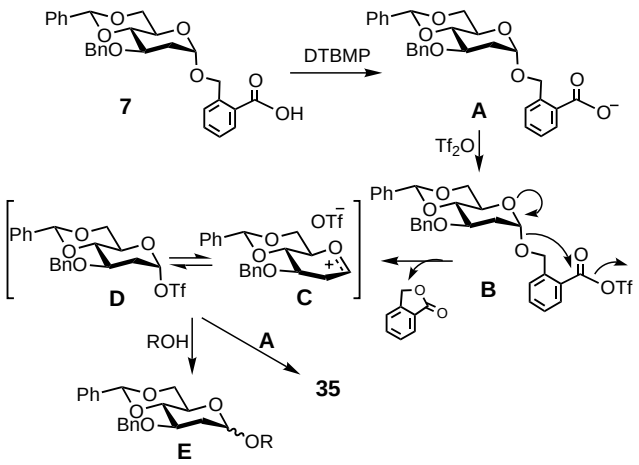

Scheme 2. Plausible mechanism for the formation of disaccharides and the self-condensed ester **35**.

(Table 2, entries 5, 7, and 8). Glycosylation of **7** with **14**, on the other hand, afforded the β-anomer of disaccharide **32** exclusively (Table 2, entry 6) in 72% yield along with the self-condensed ester **35** in 16% yield.

Formation of the self-condensed ester **35** probably resulted from the coupling between the carboxylate anion **A**, which was generated by deprotonation of **7** by DTBMP, and the oxocarbenium ion **C** or the C-1 triflate intermediate **D** as shown in Scheme 2. Generation of a substantial amount of ester **35** led us to postulate that the conversion of the carboxylate **A** into the triflate **B** was slower than the formation of **C** or **D** by the lactonization of the mixed anhydride **B**. We envisaged that if the conversion rate of **A** into **B** was enhanced or the concentration of **A** was kept at a minimum during the glycosylation, the formation of the ester **35** would be suppressed. We therefore ran several glycosylation reactions under modified conditions. Other bases such as triethylamine, pyridine, and 4-dimethylaminopyridine were rather detrimental to the glycosylation reaction, whereas a three- to fivefold excess of the glycosyl acceptor did not decrease the amount of the ester **35**. On the other hand, slow addition of either the glycosyl donor **7** or DTBMP to the mixture of all other reactants greatly affected the course of the reaction to give only the disaccharide without the formation of the ester **35**, although the α/β selectivity was lost. For example, slow addition of the donor **7** to a solution of the acceptor **13**, DTBMP, and Tf_2O in CH_2Cl_2 at −78 °C afforded only the disaccharide **31** (α/β 1:1.5) in 92% yield, whereas slow addition of DTBMP to a solution of **7**, **13**, and Tf_2O in CH_2Cl_2 at −78 °C gave exclusively **31** (α/β 1:1) in 90% yield.

Complete reversal of the stereoselectivity from α to β simply by changing the protecting group of the 2-deoxyglycosyl donor from a benzyl to a benzylidene in the present glycosylation reaction is unprecedented. The precise mechanistic details underlying this reversal of selectivity and the lack of selectivity with primary alcohol acceptors are not yet clear. Nevertheless, it is quite reasonable to assume that in the glycosylation of the benzylidene-protected CB 2-deoxyglycoside **7** with secondary alcohols, the β-disaccharides were formed by S_N2-like displacement of the α-triflate **D** (or a tight ion pair) by the acceptor alcohol ROH (Scheme 2). In this case, the equilibrium might highly favor the α-triflate **D** over the oxocarbenium ion **E** owing to the 4,6-*O*-benzylidene protective group. Previously, highly β-selective mannopyranosylations with 4,6-*O*-benzylidene-protected mannosyl donors have been reported[10,14] and the S_N2-like displacement of the α-triflate by the acceptor has been suggested for the β-selectivity by Crich and Sun.[15] No or poor β-selectivity in the reaction of **7** with primary alcohols might be interpreted by assuming that more reactive primary alcohols reacted with both the α-triflate **D** and the oxocarbenium ion **C** (Scheme 2) before the equilibrium was established. In this respect, it is also noteworthy that the more hindered primary alcohol donor **13** showed a substantial β-selectivity (α/β 1:5.1). The α-selectivity in the glycosylation of the benzyl-protected CB 2-deoxyglycoside **4** with secondary alcohols might be explained if the β-triflate exists in equilibrium. It has been suggested that the α-glucoside was formed by the S_N2-like displacement of the β-halide[16] found in equilibrium and was less stable but more reactive than the corresponding α-anomer.

In conclusion, we have developed a highly α- and β-stereoselective (dual stereoselective) method for the synthesis of 2-deoxyglycosides by employing CB 2-deoxyglycosides as glycosyl donors. Glycosylation of the 4,6-*O*-benzylidene-protected glycosyl donor **7** with secondary alcohols afforded predominantly β-glycosides whereas glycosylation of the benzyl-protected glycosyl donor **4** with secondary alcohols afforded α-glycosides.

Experimental Section

Typical procedure (**34**): A mixture of **7** (40 mg, 0.084 mmol, 1 equiv), **17** (59 mg, 0.127 mmol, 1.5 equiv), DTBMP (41 mg, 0.202 mmol, 2.4 equiv), and activated molecular sieves (4 Å) in dichloromethane (8 mL) was stirred at room temperature for 30 min. Tf_2O (17.0 μL, 0.101 mmol, 1.2 equiv) was added to this mixture at −78 °C. The resulting mixture was stirred at −78 °C for 1 h before the addition of saturated aqueous $NaHCO_3$ (10 mL). The reaction mixture was filtered and the organic layer was separated, washed with saturated aqueous sodium chloride solution (10 mL), dried, filtered, and concentrated. The residue was purified by means of silica-gel flash-column chromatography to afford the separable disaccharides β-**34** (42 mg, 63%), α-**34** (5 mg, 8%), and the self-condensed ester **35** (6 mg, 17%). β-**34**: $R_f = 0.70$ (hexane/ethyl acetate 2:1); $[\alpha]_D = +0.74$ ($c = 0.20$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.68$–1.81 (m, 1H), 2.25 (ddd, $J = 2.1$, 4.5, 13.6 Hz, 1H), 3.24–3.33 (m, 1H), 3.30 (s, 3H), 3.58–3.90 (m, 8H), 4.12 (d, $J = 9.8$ Hz, 1H), 4.29 (dd, $J = 4.9$, 10.4 Hz, 1H), 4.66 (dd, $J = 2.0$, 9.8 Hz, 1H), 4.56 and 4.81 (q, $J = 12.1$ Hz, 2H), 4.59 (s, 2H), 4.69 and 4.93 (q, $J = 11.3$ Hz, 2H), 4.71 (s, 2H), 4.74 (d, $J = 1.6$ Hz, 1H), 5.58 (s, 1H), 7.21–7.57 ppm (m, 25H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 37.7$, 54.8, 66.7, 68.9, 69.1, 71.5, 72.2, 72.6, 72.7, 74,6, 75.1, 77.4, 80.4, 83.2, 99.0, 101.0, 101.4, 126.2, 127.8, 128.0, 128.4, 128.5, 129.0, 137.7, 138.4, 138.6, 138.7 ppm; elemental analysis (%): calcd for $C_{48}H_{52}O_{10}$ (788.9): C 73.08, H 6.64; found: C 73.10, H 6.70. α-**34**: $R_f = 0.60$ (hexane/ethyl acetate 2:1); $[\alpha]_D = +0.94$ ($c = 0.20$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.76$ (ddd, $J = 3.6$, 11.3, 13.2 Hz, 1H), 2.33 (dd, $J = 5.1$, 13.2 Hz, 1H), 3.27 (s, 3H), 3.64–3.93 (m, 10H), 4.21 (dd, $J = 4.5$, 9.8 Hz, 1H), 4.57 (d, $J = 10.9$ Hz, 1H), 4.62 (s, 2H), 4.63 (d, $J = 11.6$ Hz, 1H), 4.67 and 4.77 (q, $J = 11.9$ Hz, 2H), 4.72–4.76 (m, 2H), 4.94 (d, $J = 11.0$ Hz, 1H), 5.06 (d, $J =$

3.0 Hz, 1H), 5.61 (s, 1H), 7.21–7.51 ppm (m, 25H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 36.5$, 54.8, 63.2, 69.3, 71.5, 72.2, 72.8, 74.8, 74.9, 75.2, 77.2, 80.4, 84.1, 98.2, 98.9, 101.5, 124.3, 126.3, 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 129.0, 138.4, 138.6, 138.8 ppm; elemental analysis (%): calcd for $C_{48}H_{52}O_{10}$ (788.9): C 73.08, H 6.64; found: C 73.06, H 6.69. **35**: $R_f = 0.55$ (hexane/ethyl acetate 2:1); $[\alpha]_D = +0.15$ ($c = 0.20$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 1.86 (ddd, $J = 3.8$, 11.3, 13.2 Hz, 1H), 1.99 (m, 1H), 2.36 (dd, $J = 5.3$, 13.2 Hz, 1H), 2.45 (ddd, $J = 2.4$, 4.8, 13.2 Hz, 1H), 3.50–3.60 (m, 1H), 3.69–3.94 (m, 6H), 4.04–4.16 (m, 1H), 4.25 (dd, $J = 4.2$, 9.5 Hz, 1H), 4.37 (dd, $J = 4.8$, 9.8 Hz, 1H), 4.70 and 4.87 (q, $J = 11.8$ Hz, 2H), 4.72 and 4.85 (q, $J = 12.1$ Hz, 2H), 4.91 and 5.03 (q, $J = 14.5$ Hz, 2H), 5.05 (d, $J = 2.7$ Hz, 1H), 5.61 (s, 1H), 5.63 (s, 1H), 6.00 (dd, $J = 2.2$, 9.9 Hz, 1H), 7.24–7.64 (m, 23H), 8.03 ppm (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 36.4$, 36.7, 63.5, 67.3, 67.5, 68.8, 69.3, 72.9, 73.2(2), 74.3, 82.8, 84.1, 92.6, 98.0, 101.5, 101.6, 126.2, 127.1, 127.5, 127.7, 127.8, 127.9, 128.0, 128.4(2), 128.5, 128.6, 129.0, 129.1, 131.2, 133,3, 137.5, 137.7, 138.3, 138.9, 140.8, 164.8 ppm; calcd for $C_{48}H_{48}O_{11}$ (800.9): C 71.98, H 6.04; found: C 71.78, H 6.10.

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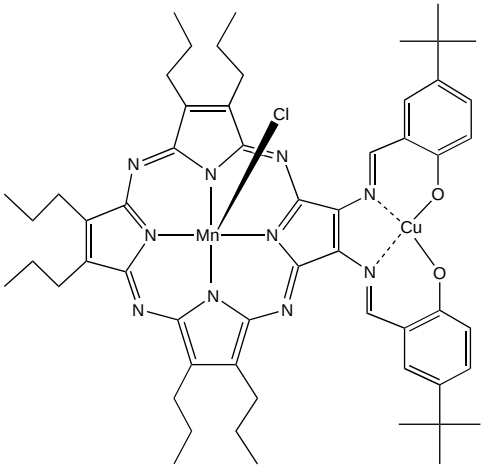
Spin Coupling between Metal Ions

Porphyrazines as Molecular Scaffolds: Periphery–Core Spin Coupling between Metal Ions of a Schiff Base Porphyrazine**

Min Zhao, Charlotte Stern, Anthony G. M. Barrett, and Brian M. Hoffman**

The periphery of a metalloporphyrazine (pz) can be readily functionalized with heteroatoms that coordinate additional metal ions, and this opens the way to high-spin molecules and molecular arrays based on exchange coupling between the metal ions.[1] We previously reported evidence for core–periphery spin coupling when a metal ion is bound to a peripheral dithiolene.[1–3] We show here that the pz molecule can be used as a scaffold on which to build complex peripheral chelating ligands, and that the resulting dimetallic complex shows some remarkable core–periphery spin coupling. We have synthesized the Schiff base appended porphyrazine (**1**) where the core metal ion is Mn^{III} with spin $S = 2$, and the peripheral ion is Cu^{II} with $S = 1/2$; have obtained its crystal structure, and characterized the $S = 3/2$ and 5/2 total-spin manifolds created by strong core–periphery M_1–M_2 spin coupling; and have



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