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Functional Group Tolerance in Organocatalytic Regioselective Acylation of Carbohydrates

Yoshihiro Ueda, Wataru Muramatsu, Kenji Mishiro, Takumi Furuta, and Takeo Kawabata*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

kawabata@scl.kyoto-u.ac.jp

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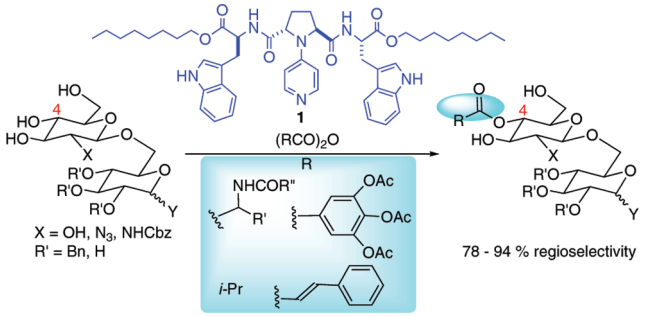
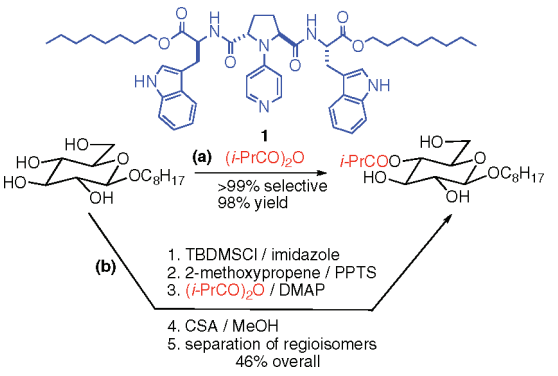


Organocatalytic regioselective acylation of mono- and disaccaharides with various functionalized acid anhydrides has been developed. Acylation of octyl β-D-glucopyranoside with acid anhydrides derived from α-amino acids, cinnamic acid, and gallic acid took place at C(4)-OH with 67−94% regioselectivity in the presence of catalyst **1**. Regioselective acylation of disaccharides with functionalized acid anhydrides was also achieved with 78−94% selectivity. Especially, a disaccharide with seven free hydroxy groups (X = OH, R′ = H) underwent acylation at C(4)-OH with 78% regioselectivity in the presence of **1**. Thus, functional group tolerance in the regioselective acylation catalyzed by **1** was found to be high.

Nonenzymatic regioselective functionalization of carbohydrates has been a fundamental challenge in current organic synthesis.[1] Kattnig and Albert reported a convenient method for the selective monoacylation of octyl β-D-glucopyranoside with a typical acylation catalyst, 4-dimethylaminopyridine (DMAP), and acetyl chloride to give the 6-*O*-acetate in 85% selectivity in 73% yield.[2] Since the primary hydroxy group at C-6 has the highest intrinsic reactivity, the selective introduction of an acyl group at C(6)−OH of carbohydrates is a reasonable consequence. Enzymatic acylation of carbohydrates has been know to often proceed on the primary hydroxy group at C-6.[3] On the other hand, chemoselective acylation of a secondary hydroxy group in the presence of a primary hydroxy group is much more difficult. Yoshida and co-workers reported the chemoselective acylation of a secondary hydroxy group at C(4) of octyl α-D-glucopyranoside in 61% selectivity with an acetic anhydride−DMAP system, where diacylation was minimized by the use of less (0.70 equiv) acetic anhydride.[4] Griswold and Miller reported an excellent approach to the selective introduction of an acetyl group at a secondary hydroxy group of octyl β-D-glucopyranoside by using peptide-based chiral catalysts.[5] Moderately selective 4-*O*-acylation has been achieved in a ratio of 22:58:11:9 for 6-*O*-, 4-*O*-, 3-*O*-, and 2-*O*-acylate, respectively, without the formation of diacylates. Recently, Onomura and co-workers reported Sn(IV)-catalyzed highly regioselective benzoylation of monosaccharides.[6] We also reported an organocatalytic one-step procedure for the chemo- and regioselective acylation of a secondary hydroxy group of monosaccharides.[7] With organocatalyst **1**,[8] acylation of the secondary hydroxy group at C(4) of octyl β-D-glucopyranoside proceeded in up to >99% selectivity in the presence of a primary hydroxy group at C(6) and two other secondary hydroxy groups at C(2) and C(3) (Scheme 1a). The same molecular transformation could be alternatively achieved by conventional protection/deprotection procedure via five steps in 46% overall yield (Scheme 1b). Thus, development of this process is expected to minimize the number of steps for functionalization of

SCHEME 1. Organocatalytic One-Step Process (a) and Conventional Protection/Deprotection Procedure (b) for the Preparation of Octyl 4-*O*-Isobutyryl-β-D-glucopyranoside



† Dedicated to Prof. Kaoru Fuji on the occasion of his 70th birthday.

(1) For an example, see: Wang, C.-C.; Lee, J.-C.; Luo, S.-Y.; Kulkarni, S. S.; Huang, Y.-W.; Lee, C.-C.; Chang, K.-L.; Hung, S.-C. *Nature* **2007**, *446*, 896–899.

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(7) Kawabata, T.; Muramatsu, W.; Nishio, T.; Shibata, T.; Schedel, H. *J. Am. Chem. Soc.* **2007**, *129*, 12890–12895.

(8) Catalyst **1** is commercially available from Wako Pure Chemical Industries, Ltd.

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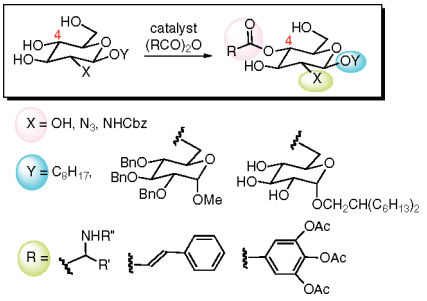

FIGURE 1. Catalytic regioselective introduction of functionalized acyl groups into carbohydrates.

carbohydrates. However, this protocol has been limited to the acylation of monosaccharides with nonfunctionalized acid anhydrides such as isobutyric anhydride and acetic anhydride. We therefore examined the functional group tolerance in the present process. Here, we describe the scope of the organocatalytic regioselective acylation of mono- and disaccaharides with various functionalized acid anhydrides (Figure 1).

Carbohydrates are involved in a wide range of intercellular processes including infection, metastasis, differentiation, and regulation of signaling, and so on.[9] To clarify the mechanisms of these events and to develop new therapeutics, chemical synthesis of carbohydrates is indispensable. However, multistep protection/deprotection procedures are usually required for their synthesis because of the lack of a direct method for the chemo- and regioselective manipulation of one of the multiple hydroxy groups of carbohydrates.[10]

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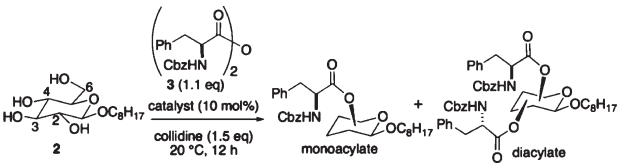
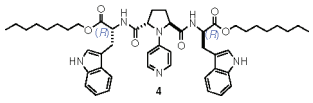
TABLE 1. Regioselectivity Profiles of Acylation of 2 with Anhydride 3[a]



entry	catalyst	solvent	mono-acylate (%)	regioselectivity[b] 6-*O*:4-*O*:3-*O*:2-*O*	diacylate (%)
1	DMAP	$CHCl_3$	38	43:19:37:1	23
2	**1**	$CHCl_3$	81	21:73:6:0	12
3	**4**	$CHCl_3$	68	29:58:13:0	15
4	**1**	toluene	70	20:73:5:1	13
5	**1**	THF	44	44:28:21:8	30
6	**1**	DMF	45	61:10:19:10	30

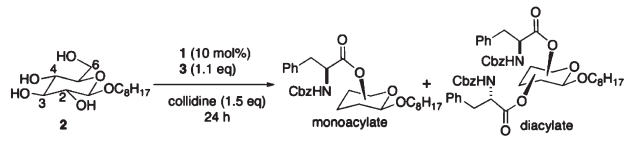
[a]The reactions were carried out with a substrate concentration of 0.1 M. [b]Percent regioselectivity among four monoacylates.



However, we have developed an organocatalytic one-step procedure for the chemo- and regioselective acylation of glucose derivatives.[7] We further examined regioselective introduction of functionalized acyl groups into various carbohydrates. At first, acylation of octyl β-D-glucopyranoside (**2**) with acid anhydride **3** derived from phenylalanine was examined (Table 1). The expected products, sugar-amino acid hybrids, have been known to show ACE inhibitory activity and also to be candidates for an artificial sweetner.[11] Acid anhydride **3** was prepared from *N*-Cbz-phenylalanine and triphosgene. Regioselectivity profiles of acylation of **2** with DMAP and catalysts **1** and **4** were investigated.[12,13] Treatment of **2** with 10 mol % of DMAP in $CHCl_3$ at 20 °C for 24 h gave four monoacylates, the 6-*O*-, 4-*O*-, 3-*O*-, and 2-*O*-acylates, in a ratio of 43:19:37:1 in a combined yield of 38% together with 23% of diacylates (entry 1). Thus, totally random acylation took place by DMAP catalysis. In contrast, glucose derivative **2** underwent acylation preferentially on the secondary hydroxy group at C(4) (58−73% regioselectivity among monoacylates) even in the presence of a free primary hydroxy group at C(6) by treatment with C_2-symmetric chiral PPYs **1** and **4** (entries 2 and 3). As previously observed in the acylation of **2** with isobutyric anhydride,[7] catalyst **1** with an L-tryptophan substructure showed better selectivity than catalyst **4** with a D-tryptophan substructure. Analysis of the products was unambiguously performed by careful investigation of ^{1}H NMR and COSY spectrum of the mixture of four monoacylates with an authentic sample of the pure 4-*O*-acylate of **2**, which was obtained via conventional protection/deprotection sequences (see Supporting Information).

We then investigated the solvent effects on the regioselectivity of acylation with catalyst **1** (Table 1, entries 4−6). Toluene, THF, and DMF were investigated in addition to $CHCl_3$. The polarity of the solvents roughly correlated with the chemo- and regioselectivity of acylation. The highest selectivity (73%) for 4-*O*-acylation was observed in the less polar solvents toluene and $CHCl_3$ (entries 2 and 4), whereas

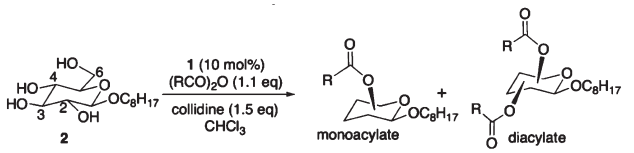
TABLE 2. Effects of Temperature and Concentration on Regioselectivity of 1-Catalyzed Acylation of 2



entry	*T* (°C)	concn (M)	mono-acylate (%)	regioselectivity[a] 6-*O*:4-*O*: 3-*O*:2-*O*	diacylate (%)
1	20	0.1	81	21:73:6:0	12
2	0	0.1	89	8:91:2:0	8
3	−20	0.1	88	6:93:1:0	10
4	−20	0.02	93	5:94:1:0	2
5	−20	0.07	90	6:93:1:0	7
6[b]	−20	0.07	88	6:93:1:0	
7	−20	0.2	89	7:91:2:0	8
8	−30	0.1	86	5:94:1:0	9
9	−40	0.1	85	5:94:1:0	10
10	−50	0.1	89	9:89:2:0	8

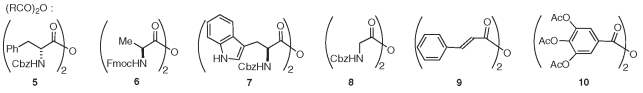
[a]Percent regioselectivity among four monoacylates. [b]1 mol % of catalyst **1** was used.

TABLE 3. Catalytic Regioselective Acylation of 2 with Functionalized Acid Anhydrides



entry	$(RCO)_2O$	*T* (°C)	concn (M)	*t* (h)	mono-acylate (%)	regioselectivity[a] 6-*O*:4-*O*: 3-*O*:2-*O*	diacylate (%)
1	**3**	−20	0.02	24	93	5:94:1:0	2
2	**5**	−20	0.07	24	82	8:88:4:0	10
3	**6**	−50	0.07	24	75	1:86:13:0	17
4	**7**	−20	0.07	24	76	27:70:3:6	10
5	**8**	−50	0.07	24	76	23:67:10:0	15
6	**9**	−30	0.1	96	88	3:94:3:0	6
7	**10**	−50	0.05	165	78	11:87:2:0	

[a]Percent regioselectivity among four monoacylates.



acylation of the primary hydroxy group was predominant (61%) in a polar solvent, DMF (entry 6). The observed solvent effects indicate that the driving force for selective 4-*O*-acylation may involve H-bonding between the substrate and the catalyst. Another interesting phenomenon is that a higher ratio of 4-*O*-acylation is associated with a higher yield for monoacylation (entries 1−6). This implies that acylation of the secondary hydroxy group at C-4 would proceed in an accelerative manner. The tendency is consistent with our previous observation that competitive acylation of a 1:1 mixture of **2** and 2-phenylethanol in the presence of **1** afforded the 4-*O*-isobutyrate of **2** exclusively.[7] This tendency indicate that catalyst **1** promotes accelerated acylation of the secondary hydroxy group at C(4) of **2**.

Temperature effects were next investigated (Table 2). A decrease in the reaction temperature to 0 °C increased the regioselectivity for 4-*O*-acylation to 91% (entry 2). Further decrease in the temperature at −40 °C increased the regioselectivity up to 94% (entry 9). However, acylation at −50 °C resulted in a small decrease in the regioselectivity to 89%, probably due to the poor solubility of the substrate and catalyst at the low temperature (entry 10). Effects of the concentration were next investigated in the acylation at −20 °C (entries 3−5 and 7). Decrease in the concentration increased the regioselectivity and the yield for monoacylation. Treatment of **2** with 10 mol % of catalyst **1** and 1.1 equiv of **3** in $CHCl_3$ at −20 °C at the concentration of 0.02 M gave the 4-*O*-acylate in 94% regioselectivity and 91% yield for monoacylation together with 2% formation of the diacylates (entry 4). With only 1 mol % of catalyst **1**, regioselective acylation at C(4)−OH proceeded with 93% selectivity and 88% yield for monoacylation (entry 6).

The optimized reaction conditions were applied to the regioselective acylation of **2** with acid anhydrides derived from various amino acids (Table 3, entries 1−5). Acylation of **2** with acid anhydrides derived from L-phenylalanine, D-phenyalanine, L-tryptophan, L-alanine, and glycine proceeded in the presence of 10 mol % of catalyst **1** to give the 4-*O*-acylates with 67−94% regioselectivity and 76−93% yields for monoacylation (entries 1−5). This protocol was applied to regioselective introduction of cinnamoyl and galloyl groups into carbohydrates because carbohydrates with cinnamoyl and/or galloyl substructures have been frequently found in biologically active glycosides.[14,15] Treatment of **2** with cinnamic anhydride (**9**) in the presence of 10 mol % of **1** gave the 4-*O*-acylate with 94% regioselectivity and 88% yield for monoacylation (entry 6). Similary, regioselective galloylation was achieved by the use of catalyst **1** to give the 4-*O*-acylate with 87% regioselectivity and 78% yield for monoacylation (entry 7). In these acylation reactions, analysis of regioselectivity was unambiguously performed by careful investigation of ^1H NMR of the mixture of monoacylates by comparison with an authentic sample of the major acylate, which was obtained in a pure form by HPLC separation of the mixture of the monoacylates or obtained independently by conventional protection/deprotection sequences (see Supporting Information).

The protocol was applied to the regioselective acylation of disaccharides. Acylation of Glc-Glc disaccharide **11** with isobutyric anhydride proceeded to give the 4-*O*-isobutyrate **12** with 94% regioselectivity and 94% yield for monoacylation (Scheme 2a). Similarly, *N*-Cbz-protected phenyalanine ester **13** and cinnamoyl ester **14** were directly prepared from **11** with 83% and 85% regioselectivity, respectively (Scheme 2, b and c). Azide-substituted disaccharide **15** and GlcNCbz-Glc derivative **17** underwent acylation on treatment with isobutyric anhydride in the presence of 10 mol % of **1** to give **16** with 93% regioselectivity and 92% yield for monoacylation and **18**

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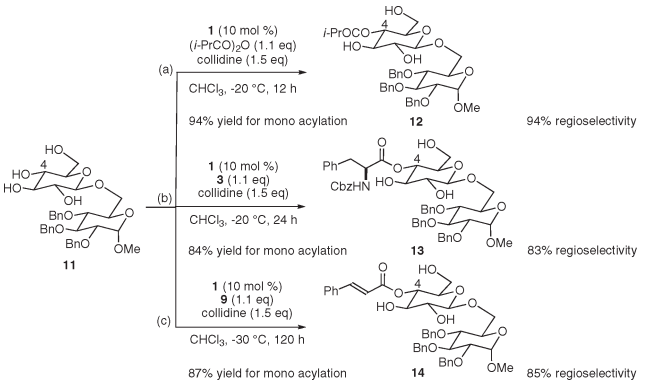
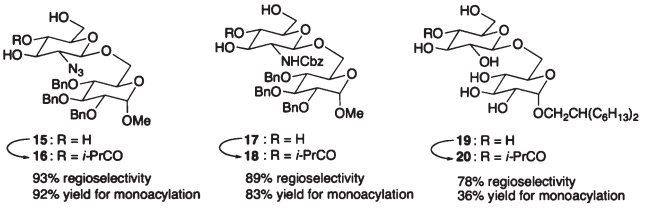
(15) Acylates of carbohydrates have been found to show different biological activities depending on the position and structure of the acyl groups; see: (a) Guiard, J.; Collmann, A.; Gilleron, M.; Mori, L.; De Libero, G.; Prandi, J.; Puzo, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 9734–9738. (b) Aich, U.; Campbell, C. T.; Elmouelhi, N.; Weier, C. A.; Sampathkumar, S.-G.; Choi, S. S.; Yarema, K. J. *ACS Chem. Biol.* **2008**, *3*, 230–240.

SCHEME 2. Catalytic Regioselective Acylation of Disaccharide 11



SCHEME 3. Catalytic Regioselective Acylation of Disaccharides 15, 17, and 19



with 89% regioselectivity and 83% yield for monoacylation, respectively (Scheme 3). We finally examined regioselective acylation of disaccharide **19** with seven free hydroxy groups. Acylation of **19** was sluggish even in the presence of catalyst **1** probably due to the poor solubility of **19** in $CHCl_3$. Treatment of **19** with 1.1 equivalents of isobutyric anhydride in the presence of 30 mol % of catalyst **1** in $CHCl_3$ at −20 °C gave **20** with 78% regioselectivity and 36% yield for monoacylation together with diacylates (27%) and 40% recovery of starting material. Although the chemical yield was far from satisfactory, regioselective acylation of a particular secondary hydroxy group out of seven hydroxy groups in different microenvironments appears surprisingly refined.

The 4-*O*-acylates of the glucose moiety were universally obtained as the major acylate in the acylation of various carbohydrates with various functionalized acid anhydrides. Thus, functional group tolerance in the present process was found to be high. This seems surprising to us because the hydrogen-bonding interactions between C(6)- and C(3)-OH of the glucose moiety and the catalyst (Figure 2, yellow rectangles), which was proposed to be responsible for the selective 4-*O*-acylation,[7] are supposed to be specifically operative even in the presence of many other hydrogen bond donors and acceptors (blue circles).

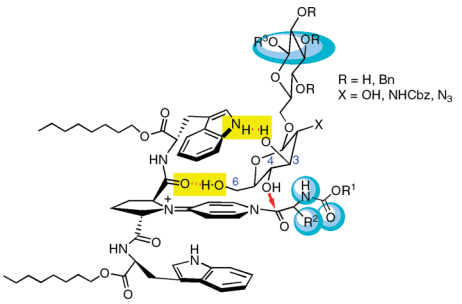


FIGURE 2. Functional group (blue circles) tolerance in molecular recognition via hydrogen bonding (yellow rectangles).

Experimental Section

General Procedure for Catalytic Regioselective Acylation. A sugar substrate (1.0 equiv), catalyst (10 mol %), and 2,4,6-collidine (1.5 equiv) were dissolved in $CHCl_3$ at 20 °C. After the mixture was cooled to the temperature specified in Tables 1−3 and Schemes 2 and 3, an acid anhydride (1.1 equiv) was added to the mixture. The resulting mixture was stirred at the temperature for the period indicated in Tables 1−3 and Schemes 2 and 3. The reaction was quenched with saturated aq NH_4Cl and extracted with AcOEt. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by SiO_2 column chromatography or preparative SiO_2 TLC to give the acylated products.

Octyl 4-*O*-((*S*)-2-Benzyloxycarbonylamino-3-phenylpropanoyl)-β-D-glucopyranoside (Table 1). Colorless crystals (AcOEt/hexane); mp140−142 °C; $[\alpha]^{20}_D$ −41 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.13 (m, 10H), 5.30 (d, J = 6.8 Hz, 1H), 5.06 (ABq, J_{AB} = 12.0 Hz, $\Delta\nu_{AB}$ = 16.5 Hz, 2H), 4.86 (t, J = 9.2 Hz, 1H), 4.46 (q, J = 6.8 Hz, 1H), 4.28 (d, J = 7.6 Hz, 1H), 3.87 (dt, J = 9.2, 7.2 Hz, 1H), 3.68 (br s, 1H), 3.65 (t, J = 9.6 Hz, 1H), 3.51 (dt, J = 9.2, 7.2 Hz, 1H), 3.45 (t, J = 8.4 Hz, 1H), 3.42−3.32 (m, 1H), 3.30−3.20 (m, 2H), 3.15−3.00 (m, 2H), 2.10 (br s, 1H), 1.68−1.56 (m, 2H), 1.40−1.18 (m, 10H), 0.88 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.74, 156.24, 135.72, 135.22, 129.21, 128.85, 128.58, 128.39, 128.30, 127.45, 102.50, 74.25, 73.56, 73.45, 72.35, 70.38, 67.48, 61.19, 55.76, 37.35, 31.78, 29.56, 29.36, 29.18, 25.89, 22.62, 14.08; IR (KBr) 3573, 3487, 3340, 1730, 1706, 1536 cm^{-1}; MS (EI) m/z (rel intensity) 573 (M^+, 0.1), 443 (2), 300 (10), 120 (15), 91 (100); HRMS calcd for $C_{31}H_{43}O_9N$ 573.2955, found 573.2938.

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Supporting Information Available: Experimental methods, characterization data for all new compounds, and copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.