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ARTICLE

Diisopropylethylamine-Triggered, Highly Efficient, Self-Catalyzed Regioselective Acylation of Carbohydrates and Diols

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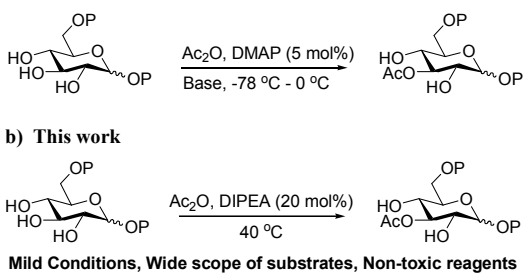
A diisopropylethylamine (DIPEA)-triggered, self-catalyzed, regioselective acylation of carbohydrates and diols is presented. The hydroxyl groups can be acylated by the corresponding anhydride in MeCN in the presence of a catalytic amount of DIPEA. This method is comparatively green and mild as it uses less organic base compared with other selective acylation methods. Mechanistic studies indicate that DIPEA reacts with the anhydride to form a carboxylate ion, and then the carboxylate ion could catalyze the selective acylation through a dual H-bonding interaction.

Introduction

Protection strategies are long-standing challenges in carbohydrate chemistry for the efficient preparation of high value-added carbohydrates and site-selective synthesis of building blocks for oligosaccharide synthesis.[1-8] Regioselective acylation is always very important in organic chemistry,[9-12] especially in the synthesis of oligosaccharide building blocks because it is convenient for the protection and deprotection of hydroxyl groups.[13-15] To date, many metal catalysts and organic small molecules have been employed in the regioselective acylation of diols and polyols, including tin (IV),[16-18] boron (IV),[19] copper (II),[20-22] and silver (I),[23] as well as a recently reported iron catalyst.[24] Organotin compounds were the most widely used reagents for the selective protection of carbohydrate for many years as they are easy to operate and always lead to high regioselectivity. However, organotin reagents can be inherently toxic, so this limits their range of applications.[25, 26] The Taylor's catalyst (diphenylboronic acid derivative, an effective nontoxic catalyst)-can catalyze regioselective acylation of carbohydrates and diols; however, it was not successfully applied for *trans*-diols.[19] Recently, an inexpensive catalyst, $Fe(acac)_3$, was developed for the regio/site-selective acylation of diols and carbohydrates containing a 1,2-*cis*-diol;[24] this is an efficient and green catalyst that could replace toxic organotin reagents, but it also faces challenges involving limited applicability.

In addition to metal catalyst, some enzymes[27, 28] and small organic molecules[15, 29-33] are often applied in the regioselective acylation of carbohydrates and diols. In 1988, Wong and coworkers developed lipase-catalyzed selective acylation of furanose and pyranose derivatives.[27] Then in 2005, Bornscheuer and coworkers developed lipase-catalyzed glucose fatty acid ester synthesis in ionic liquids, which means we can get high regioselectivity by enzyme catalyzed acylation.[28] In 2004, Kattnig and coworkers developed a dimethylaminopyridine (DMAP)-catalyzed method for the selective acetylation of octyl-β-D-glucopyranoside, which involved low temperature reaction conditions and low regioselectivities (Scheme 1a).[31] Then, in 2007, Kawabata and coworkers developed a DMAP-catalyzed method for the selective acylation of octyl-6-*O*-methyl-β-D-glucopyranoside, which leads to high regioselectivity for the 3-OH acylated products, but this method required 1.5 equiv. of collidine as a base, making it neither green nor atom economical (Scheme 1a).[32] In 2013, the Tan group developed *N*-methylimidazole-derived catalysts for the site-selective functionalization of complex carbohydrates,[15] which was a substantial step forward for the selective recognition of hydroxyl groups. Recently, Toda and coworkers developed a phosphonium ylide as an ionic nucleophilic catalyst for the selective acylation of primary hydroxyl groups of diols, and this method shows good regioselectivity for terminal hydroxyls, but it is not widely applicable.[33]

Scheme 1. Comparison of this method with previously reported methods.



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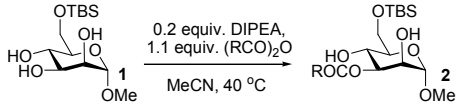
Here, we report an organic amine, diisopropylethylamine (DIPEA), which can be successfully used for the selective acylation of over 25 examples of carbohydrates and diols in the presence of an anhydride (Scheme 1b). In these reactions, the amount of DIPEA can be reduced to only 0.2 equiv., while stoichiometric or superstoichiometric organic amine is often used in other acylation reactions.[15, 21] It is clear that the use of a smaller amount of organic amine is more environmentally friendly and mild. In addition, based on our mechanism studies, we propose that the organic amine triggered the H-bonding-activated, self-catalyzed, selective acylation of the carbohydrates and diols.

Results and discussion

Organotin reagent-catalyzed reactions have been studied for a long time, and it was often proposed that complex stannylene dimer or polymer structures lead to good regioselectivities.[16] In 2012, Dong and coworkers predicted that any reagent that could form cyclic dioxolane-type intermediates with hydroxyl groups could achieve selectivities similar to those seen with organotin reagents.[34] Based on this, we developed the $Fe(dibm)_3$ (dibm, diisobutyrylmethane) catalyst, which showed excellent regioselectivities in the selective alkylation of carbohydrates and diols.[35, 36] As the selective protection pattern is similar, we decide to test the reactivity of this iron catalyst in the selective acylation of carbohydrates and diols.

Table 1. Comparison of results using variations of the "standard conditions".



Entry	$(RCO)_2O$	Various Conditions	Isolated Yield %
1	Ac_2O	Optimized conditions[a]	**92**
2	Bz_2O	Optimized conditions[a]	**93**
3	Ac_2O	0.1 equiv. $Fe(dibm)_3$, 1.2 equiv. DIPEA	92
4	Ac_2O	0.1 equiv. $Fe(acac)_3$, 1.2 equiv. DIPEA	92
5	Ac_2O	0.1 equiv. $Cu(acac)_2$, 1.2 equiv. DIPEA	93
6	Ac_2O	0.1 equiv. $Zn(acac)_2$, 1.2 equiv. DIPEA	88
7	Ac_2O	0.1 equiv. acetylacetone, 1.2 equiv. DIPEA	92
8	Ac_2O	1.2 equiv. DIPEA, rt.	91
9	AcCl	0.2 equiv. DIPEA	55[b]
10	Ac_2O	Without DIPEA	-[c]
11	Ac_2O	0.2 equiv. TEA	40[b]
12	Ac_2O	0.2 equiv. Pyridine	45[b]
13	Ac_2O	0.2 equiv. 2,4,6-collidine	40[b]
14	Ac_2O	0.2 equiv. K_2CO_3	82[d]
15	Ac_2O	0.1 equiv. DIPEA	83
16	Ac_2O	Reaction at rt.	82
17	Ac_2O	0.2 equiv. DMAP	65[e]

[a] Reactant (50 mg), $(RCO)_2O$ (1.1 equiv.), DIPEA (0.2 equiv.), MeCN (1 mL), 40 °C, 4-6 h. [b] Poor or no selectivity. [c] Low conversion (5-10% of **2**). [d] 10% of byproduct is also obtained. [e] 30% of byproduct is also obtained.

Initially, we expect to develop an iron catalyst that could selectively acylate diols and carbohydrates in the presence of an anhydride and DIPEA. Initially, we choose methyl 6-*O*-(*tert*-butyldimethylsilyloxy)-α-D-mannopyranoside, **1**, as the substrate to verify our hypothesis (Table 1). Thus, **1** is treated with 1.1 equiv. of acetic anhydride and 1.2 equiv. of DIPEA in the presence of a catalyst in acetonitrile at 40 °C for 4–6 h. To our surprise, when **1** is subjected to these reaction conditions, the iron catalyst, $Fe(dibm)_3$, affords the desired product in an isolated yield of approximately 92% (Table 1, Entry 3). Then, we change the catalyst to another common iron catalyst, $Fe(acac)_3$ (acac, acetylacetone), and we find a similarly good isolated yield (Table 1, Entry 4). We hypothesize that the iron was not involved in the reaction. Then, we change the catalyst to $Cu(acac)_2$ and $Zn(acac)_2$, and the same regioselectivities (near 90%) are obtained (Table 1, Entries 5-6). From these results, it appears that the ligand may be the key factor. Then, 0.1 equiv. of acetylacetone is used as the catalyst in the reaction, and the isolated yield is also 92% (Table 1, Entry 7). We immediately realize that the previously tested catalysts are not active in this reaction.

Then, we only use 1.2 equiv. of DIPEA along with 1.1 equiv. of acetic anhydride in MeCN at room temperature, and the same excellent yield was obtained (Table 1, Entry 8). In contrast, when acetyl chloride is used instead of acetic anhydride in the reaction, only 55% of the desired product is obtained along with 40% byproduct (Table 1, Entry 9). A blank control experiment shows that without DIPEA, no substrate was acylated (Table 1, Entry 10). When other organic bases, like TEA (triethylamine), pyridine and 2,4,6-collidine, are used instead of DIPEA, all of them provide poor isolated yields of approximately 40%-45%, and some unreacted starting material is recovered (Table 1, Entries 11-13). When DMAP is used as base, we only get main product in isolated yield of 65% and some byproducts, as DMAP can form pyridinium acetate with acetic anhydride, which often strongly accelerates acylation reactions (Table 1, Entry 17). Then, when K_2CO_3 is used as the catalyst, the desired product is obtained in an isolated yield of 82% with 10% byproduct (Table 1, Entry 14). This appears to be an effective and green catalyst, but when it is extended to other substrates, we often observe over acylation products (Table 2, Entry 1), which means the alkalinity of K_2CO_3 is too strong for it to be used as a selective acylation catalyst. DIPEA is a comparatively mild organic base that has suitable steric hindrance and alkalinity to provide good regioselectivity in the acylation reactions. Therefore, the final optimized conditions are 0.2 equiv. of DIPEA and 1.1 equiv. of anhydride in MeCN at 40 °C, and both the acetylation and benzoylation products could be obtained in good isolated yields (Table 1, Entries 1-2) (NMR tracking in supporting information Figure S18).

To test the catalytic efficiency and substrate scope of this method, carbohydrates and diols are evaluated (Table 2). For substrates **3** and **6**, the acylated products are obtained with poor selctivities (Table 2, Entries 1-5). However, by comparison of the use of K_2CO_3 (Entry 1) with the use of DIPEA (Entry 2), it can be found that no diacylated products are obtained with the use of DIPEA, indicating the selectivity to mono-acylation. Thus, this method may be useful for preparing two building blocks simultaneously when these substrates are used. Next, substrates **9** and **12** are subjected to these conditions, and

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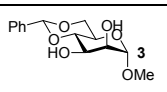
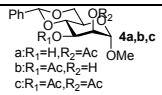
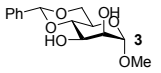
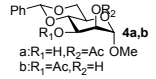
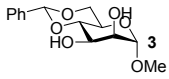
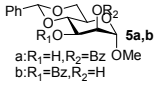
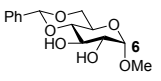
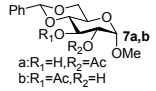
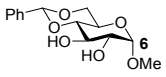
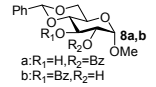
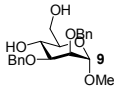
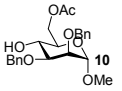
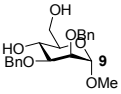
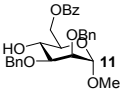
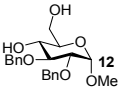
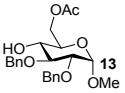
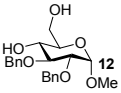
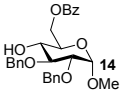
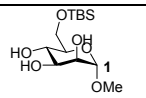
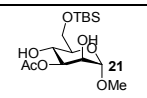
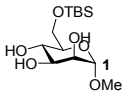
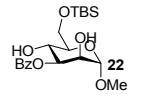
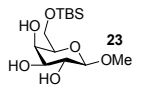
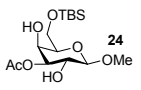
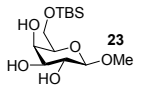
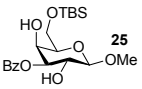
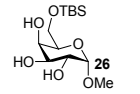
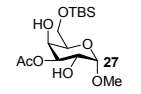
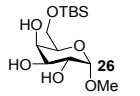
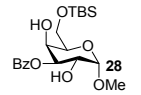
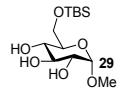
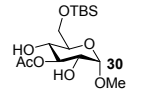
good isolated yields (82%-89%) are obtained (Table 2, Entries 6–9). To test the substrate scope, diols **15** and **18** are used as substrates, and high regioselectivities for the terminal hydroxyl acylated product are observed in both reactions, and the isolated yields are 85%-98% (Table 2, Entries 10–13). All the tests show that this method has good catalytic activity for the acylation of terminal hydroxyl groups.

Table 2. DIPEA-Catalyzed Regioselective Acetylation and Benzoylation of Diols.

Entry	Conditions	Reactant	Product	Isolated yield (%)
1	C		 a:R_1=H,R_2=Ac b:R_1=Ac,R_2=H c:R_1=Ac,R_2=Ac	a/b/c (45/35/15)
2	A		 a:R_1=H,R_2=Ac b:R_1=Ac,R_2=H	a/b (60/35)
3	B		 a:R_1=H,R_2=Bz b:R_1=Bz,R_2=H	a/b (48/45)
4	A		 a:R_1=H,R_2=Ac b:R_1=Ac,R_2=H	a/b (47/46)
5	B		 a:R_1=H,R_2=Bz b:R_1=Bz,R_2=H	a/b (45/45)
6	A			85
7	B			82
8	A			89
9	B			86
10	A			90
11	B			98
12	A			85
13	B			85

Reaction conditions: A. 50 mg Substrate, 1 mL MeCN, 0.2 equiv. DIPEA, 1.1equiv. Ac_2O, 40 °C, 8-12 h. B. 50 mg Substrate, 1 mL MeCN, 0.2 equiv. DIPEA, 1.1equiv. Bz_2O, 40 °C, 8-12 h. C. 50 mg Substrate, 1 mL MeCN, 0.2 equiv. K_2CO_3, 1.1 equiv. Ac_2O, 40 °C, 8-12 h.

Table 3. DIPEA-Catalyzed Regioselective Acylation of Polyols.

Entry	Conditions	Reactant	Product	Isolated yield (%)
1	A			92
2	B			93
3	A			93
4	B			96
5	A			85
6	B			86
7	A			99
8	B			98
9	A			82
10	B			88
11	A			85
12	B			81

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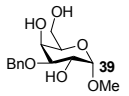
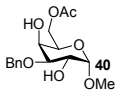
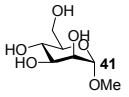
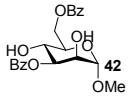
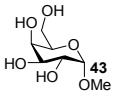
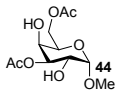
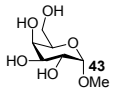
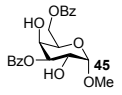
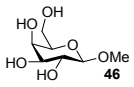
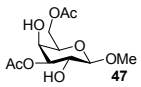
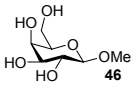
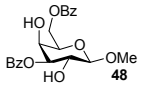
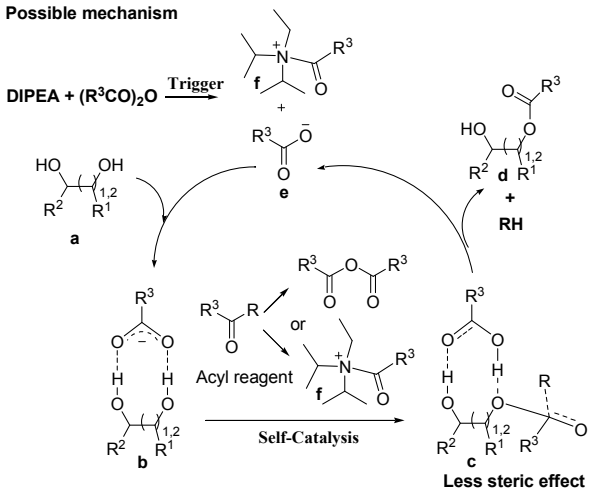
13	A	 **39**	 **40**	89
14	D	 **41**	 **42**	88
15	C	 **43**	 **44**	85
16	D	 **43**	 **45**	84
17	C	 **46**	 **47**	90
18	D	 **46**	 **48**	87

Reaction conditions: A. 50 mg Substrate, 1 mL MeCN, 0.2 equiv. DIPEA, 1.1equiv. Ac_2O, 40 °C, 8-12 h. B. 50 mg Substrate, 1 mL MeCN, 0.2 equiv. DIPEA, 1.1 equiv. Bz_2O, 40 °C, 8-12 h. C. 50 mg Substrate, 1 mL MeCN, 0.1 mL DMF, 0.4 equiv. DIPEA, 2.2 equiv. Ac_2O, 40 °C, 8-12 h. D. 50 mg Substrate, 1 mL MeCN, 0.1 mL DMF, 0.4 equiv. DIPEA, 2.2 equiv. Bz_2O, 40 °C, 8-12 h.

The DIPEA catalyst is further used in the acylation of polyols and carbohydrates with polyol structures (Table 3). For glycosides in which the 6-OH is silylated (**1, 23, 26, 29** and **32**), the 3-OH moiety is acylated in 82–99% isolated yields (Table 3, Entries 1-10). For 3-OBn-protected compounds (**35**, **37** and **39**), the 6-OH moiety is acylated or benzoylated in isolated yields of 81%-89% (Table 3, Entries 11-13). Then, free glycosides **41**, **43** and **46** are treated with 2.2 equiv. of anhydride and 0.4 equiv. of DIPEA, and in all cases, 3,6-diacylated products are generated with good isolated yields (84%-90%, Table 3, Entries 14-18). Good regioselectivities are observed for the acylations of all the polyols.

Based on the extended substrate scope experiments, this is a very efficient and green method for the regioselective acylation of diols and carbohydrates, but the catalytic mechanism remains unclear. Compared with our previously reported TBAOAc- and TBAOBz-activated acylation reactions,[37-39] it appears they all have similar selectivities and patterns in the protection of specific substrates. Therefore, we want to clarify the mechanism by NMR tests. By variable-temperature NMR experiments, we can determine whether the substrate forms H-bonds with the catalysts.[40] The catalyst (0.2 equiv of TBAOAc or 0.2 equiv of DIPEA or without catalyst) is added to a solution of 1-phenyl-1,2-ethanediol (10 mg) in dry CD_3CN (0.5 mL), and then a series of variable-temperature ^1H NMR tests are performed from 20 °C to 60 °C (Figure S4 to Figure S15 in Supporting Information). When no catalyst is added to the solution, the transformation constant of the OH chemical shift with temperature is $3.4*10^{-3}$ K^{-1}, when 0.2 equiv. of DIPEA is added, the transformation constant of the OH chemical shift with temperature is $3.7*10^{-3}$ K^{-1}, and when 0.2 equiv of TBAOAc is added to the solution, the transformation constant of the OH chemical shift with temperature is $4.8*10^{-3}$ K^{-1} (Figure S1 to Figure S3 in Supporting Information). These results prove that the DIPEA did not form intermolecular H-bonds with the substrate, and TBAOAc indeed form intermolecular H-bonds with the substrate as predicted in the previous work. This also means that DIPEA is only serving as a base in the reaction for the formation of the carboxylate ion, and it is the formation of the H-bonds between the carboxylate ion and the substrate that activates the reaction. Further experiments are conducted to compare the H-bond effects with the addition of 1.0 equiv. of Ac_2O, the addition of 0.2 equiv. of DIPEA and the addition of both 1.0 equiv. of Ac_2O and 0.2 equiv. of DIPEA (Figure S16 in the Supporting Information). The results indicate that when TBAOAc formed H-bonds with the substrates at 20 °C, the chemical shift of the hydroxyl group moves downfield, from 3.500 to 3.810. When DIPEA is added, the chemical shift of the hydroxyl group only moves from 3.500 to 3.509. Finally, when DIPEA react with Ac_2O in CD_3CN, ^1H NMR tracking of the reaction shows the chemical shift of the hydroxyl group moved from 3.295 to 3.507 in 20 minutes (Figure S17 in the Supporting Information). This result also supports the proposed H-bonding-activated mechanism, which means that when DIPEA reacts with Ac_2O, an increasing amount of carboxylate ion is formed and more H-bonds are formed, so the chemical shift of the hydroxyl group moves downfield as the reaction progresses.

Scheme 2. Proposed DIPEA-triggered, self-catalyzed acylation mechanism.



Therefore, we propose a DIPEA-triggered, self-catalyzed, regioselective acylation mechanism, as shown in Scheme 2. In the proposed approach, the anhydride reacts with DIPEA to form carboxylate ion **e** and acylammonium intermediate **f**. Then, carboxylate ion **e** forms dual H-bonds with substrate **a**, and the acyl reagent (anhydride or **f**) selectively attacks the less hindered hydroxyl group to generate acylated product **d** and regenerate carboxylate ion **e**. It is possible that anhydride or **f** attacks the dual H-bonds of intermediate **b**, and which acyl

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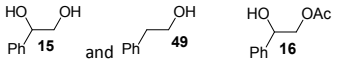
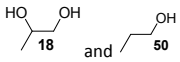
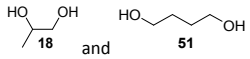
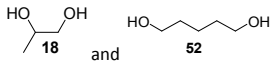
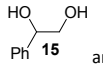
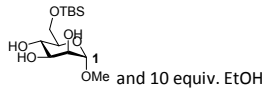
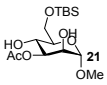
reagent is active remains unclear. Therefore, a catalytic amount of base could effectively activate the regioselective acylation. In addition, in the base-triggered processes, suitable steric hindrance and alkalinity of the base can lead to good regioselectivity, which is why only DIPEA is selected as an appropriate base. The catalytic process cannot be initiated with acyl chloride (Entry 9 in Table 1) due to the lack of carboxylate ion.

Table 4. Competitive acylation of hydroxyl groups.

Entry	Reactant	Product	Isolated yield (%)
1			84
2			82
3			80
4			81
5	 and 10 equiv. EtOH		90
6	 and 10 equiv. EtOH		86

Reaction condition: 50 mg Substrate, 1 mL MeCN, 0.2 equiv. of DIPEA, 1.0 equiv. of Ac_2O, 40 °C, 8-12h.

Support for the dual H-bond-activated mechanism is also found when diols **15** and **18** and 1.0 equiv. of their corresponding monohydric alcohol (**49** and **50**) are co-reacted with 1.0 equiv. of acetic anhydride in a competition reaction (Table 4, Entries 1-2). Mono-acylated products **16** and **19** are obtained from **15** and **18** in 84% and 82% isolated yields, respectively, whereas no acylated product is obtained from **49** and **50**. As proposed, only 1,2- and 1,3-diols can form stable double H-bonded intermediates that could undergo acylation. To test this, we compare the acylation of 1,2-propanediol (**18**, a 1,2-diol) with the acylations of 1.0 equiv. of 1,4-butanediol (**51**, a 1,4-diol) and 1,5-heptanediol (**52**, a 1,5-diol) using catalytic DIPEA as the base (Table 4, Entries 3–4). Mono-acylated product **19** (obtained from **18**) is isolated in 80% and 81% isolated yields, respectively. In fact, when 10 equiv. of EtOH is reacted with **15** (diol) or **1** (glycoside), we also obtain only the acylated products of the diol, and no EtOAc is found (Table 4, Entries 5-6). All of these results support the proposed mechanism in which the carboxylate ion activated the regioselective acylation by dual H-bonds.

Conclusions

In conclusion, a simple, efficient, green and widely applicable organic amine-triggered self-catalyzed method for the regioselective acylation of diols and carbohydrates has been developed. Compared with other acylation methods, this method is more environmentally friendly because it requires less organic amine. This reaction avoids the use of environmentally unfriendly metal ions, and it is operationally simple, which may improve its applicability. In addition, based on our mechanism studies, we proposed that the simple base triggered the reaction, and the reaction was then activated by the H-bonding between the generated carboxylate ion and the diols.

Experimental section

General: All commercially available starting materials and solvents were of reagent grade and were used without further purification. Chemical reactions were monitored with thin-layer chromatography using precoated silica gel 60 (0.25 mm thickness) plates. High-resolution mass spectra (HRMS) were obtained by electrospray ionization (ESI) and Q-TOF detection. Flash column chromatography was performed on silica gel 60 (SDS 0.040-0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded with a JNM-ECZ600R/S3 instrument at 298K in $CDCl_3$ using the residual signals from $CHCl_3$ (^{1}H: δ = 7.26 ppm; ^{13}C: δ = 77.2 ppm) as the internal standard. ^{1}H NMR peak assignments were made by first-order analysis of the spectra and were supported by standard ^{1}H-^{1}H correlation spectroscopy (COSY).

General Method for Testing the H-bonds between the Diols and Catalysts by Variable-Temperature NMR Experiments: The catalyst (0.2 equiv. of TBAOAc, 0.2 equiv. of DIPEA or without catalyst) was added to a solution of 1-phenyl-1,2-ethanediol (10 mg) in dry CD_3CN (0.5 mL), and then a series of variable-temperature ^{1}H NMR tests were performed from 20 °C to 50 °C.

General Method for the Regioselective Acylation of Diols and Polyols: Diol and polyol reactants (50 mg) were allowed to react with anhydride (1.1-2.2 equiv.) in 1 mL of dry acetonitrile or a mixed solvent (MeCN–DMF, 10:1) at 40 °C for 8 h to 12 h in the presence of DIPEA (0.1–0.2 equiv.). After cooling and evaporation of the solvent, the reaction mixture was directly purified by flash column chromatography (hexanes–EtOAc 3:1 to 1:1) and afforded the pure selectively protected derivatives. Spectroscopic data of all known products were in accordance with those reported in the literature.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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