Tetrahedron 72 (2016) 1005–1010

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A green and convenient method for regioselective mono and multiple benzoylation of diols and polyols

Xiaoling Zhang [a], Bo Ren [a], Jiantao Ge [a], Zhichao Pei [b,*], Hai Dong [a,*]

[a] Key laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry & Chemical Engineering, Huazhong University of Science & Technology, Luoyu Road 1037, Wuhan, 430074, PR China
[b] State Key Laboratory of Crop Stress Biology in Arid Areas and College of Science, Northwest A&F University, Yangling, Shaanxi, 712100, PR China

ARTICLE INFO

Article history:
Received 3 November 2015
Received in revised form 19 December 2015
Accepted 28 December 2015
Available online 30 December 2015

Keywords:
Regioselectivity
Benzoylation
H-bonding
Green chemistry
Carbohydrate

ABSTRACT

An efficient method for regioselective benzoylation of diols and polyols was developed. The benzoylation is catalyzed by only 0.2 equiv of benzoate anion in acetonitrile with the addition of a stoichiometric amount of benzoic anhydride under very mild condition, leading to high yields. Compared with all other methods, this method shows particular advantage in regioselective multiple benzoylation of polyols, and in avoiding the use of any metal-based catalysts and any amine bases, which is more environment-friendly.

1. Introduction

Studies on the roles of carbohydrates in life require various oligosaccharides. In order to synthesize the oligosaccharides, one of the most prominent challenges is to develop environment-friendly, convenient, efficient and high regioselective carbohydrate protection methods.[1–5] Selectively protected monosaccharides can be obtained through these methods and can act as either value-added intermediate products, or building blocks for the synthesis of oligosaccharides.[6–10] The most frequently used protection methods involve acetylation and benzoylation. Generally the benzoylated carbohydrates are more stable due to lower rates of both acyl group migration and neighboring group participation compared to acetylated carbohydrates. Accordingly, many regioselective benzoylation methods have been developed. The initial methods involve the use of stoichiometric amounts of organotins[11–16] and a large amount of heavy metal salts.[17–22] However, these methods have to be abandoned today due to the inherent potential toxicity of them. It seems that the methods using reduced amounts of organotins[23,24] or heavy metal-based complexes[25–31] as catalysis, or using certain nonmetallic catalysis,[32–34] are more environmental friendly. However, in all these methods, the uses of a large amount of organic amine bases are usually inevitable. In addition, most of the developed methods except for using organotin[35] are only appropriate to selective mono-benzoylation of polyols. For the organotin-mediated multiple carbohydrate esterification, more than two hydroxyl groups were regioselectively acylated by use of excess (2–3 equiv) organotin reagent in a one-pot process in light of description.[35] A regioselective acetylation method has been reported by us recently, where acetylation is enabled by only 0.3–0.6 equiv of acetate anion without the assistance of any other reagents (Fig. 1a).[36,37] The method is based on a H-bonding

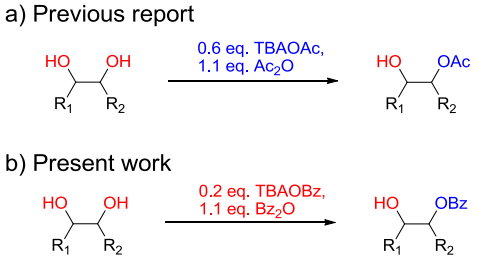


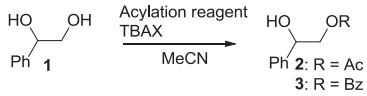
Fig. 1. a) Previous reported regioselective acetylation of diols catalyzed by acetate anion. b) Present developed regioselective benzoylation of diols catalyzed by benzoate anion.

* Corresponding authors. E-mail addresses: peizc@nwafu.edu.cn (Z. Pei), hdong@mail.hust.edu.cn (H. Dong).

http://dx.doi.org/10.1016/j.tet.2015.12.074
0040-4020/

activation mechanism where H-bonding between hydroxyl groups and anions can activate acetylation in the absence of a pyridine catalyst and lead to higher regioselectivities. We wondered if a green and regioselective benzoylation method by the application of this H-bonding activation principle could be developed. The initial attempts were failed in previous studies when we still used acetate anion as the catalyst. However, once we made clear the reaction mechanism, the new regioselective benzoylation method was developed by us when benzoate anion was used as the catalyst instead of acetate anion in present studies. Consequently, compared with all other methods, a more green method for regioselective mono and multiple benzoylation of diols and polyols was developed by us (Fig. 1b). The method avoids using any metal salts and any amine bases, and only uses 0.1–0.2 equiv of tetrabutylammonium benzoate (TBAOBz) as a catalyst in comparison with previous report[36,37] where 0.6 equiv acetate anion is necessary. High isolated yields were obtained, especially, in regioselective multiple benzoylation of polyols. The reason why benzoate shows higher catalytic reactivity is also discussed (Fig. 2).

Table 1
Regioselective benzoylation of diols catalyzed by TBAOBz[a]



Entry	Acylation reagent	Catalysis	Yield[b]
1	AcCl	TBAOAc	—[c]
2	BzCl	TBAOAc	—[c]
3	Ac_2O	TBAOAc	**2** (90%)
4	Bz_2O	TBAOAc	A mixture (**2**, **3**)
5	Bz_2O	TBAOBz	**3** (87%)
6	Bz_2O	BzONa	—[c]
7	Bz_2O	0.2 equiv TBAOBz	**3** (89%)
8	Bz_2O	0.1 equiv TBAOBz	**3** (75%)
9[d]	Bz_2O	0.1 equiv TBAOBz	**3** (77%)
10	Bz_2O	Without catalyst	No reaction
11	Bz_2O	With 1 equiv TEA	No selectivity
12	Bz_2O	0.2 equiv BzONa, 0.2 equiv TBABr	**3** (73%)

[a] Reaction conditions: reactant (100 mg), acylation reagent (1.1 equiv), TBAX (0.3 equiv), 8–12 h.
[b] Isolated yield.
[c] Low conversion (<20%).
[d] Reaction time (24 h).

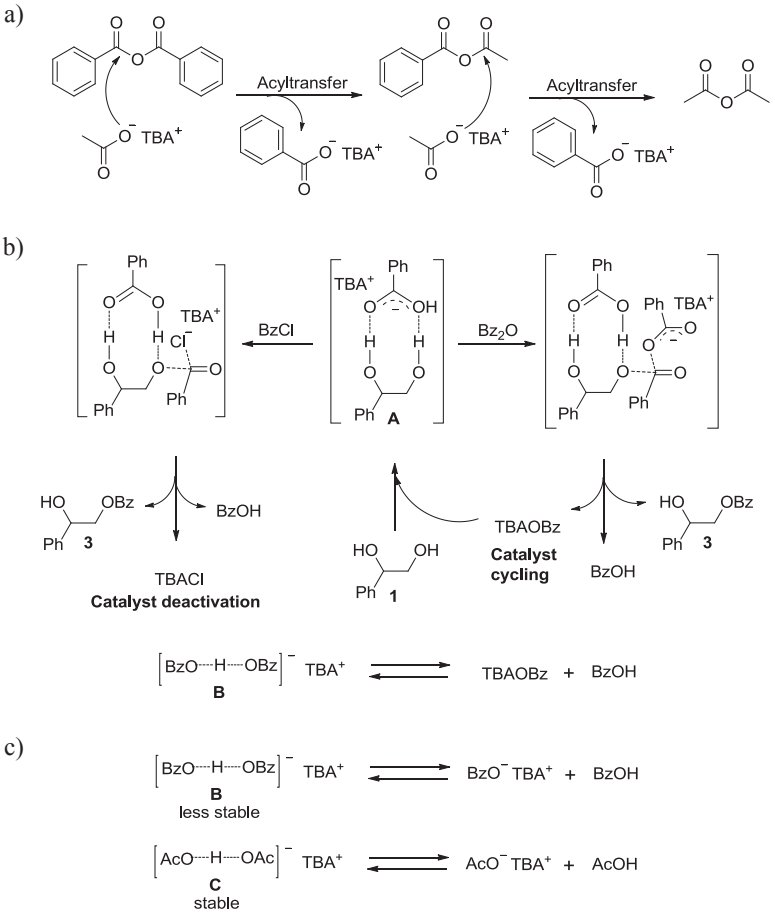


Fig. 2. a) Generation of acetic anhydride and benzoate anion through acyltransfer reaction. b) Proposed catalytic mechanism of regioselective benzoylation by BzO^-. c) The efficiency of the catalysis depending on the stability of the homo-conjugate H-bond complex.

2. Results and discussion

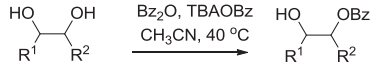
In light of the previous report,[36,37] it is easy to think that acetate anion as catalyst is used to fully explore the scope of electrophiles. Therefore, our initial try is to use acetate anion as catalyst and acetyl chloride or benzoyl chloride as acylation reagents in the regioselective acylation of 1-phenyl-1,2-ethanediol **1** (Table 1). However, very low conversions were obtained (Entries 1 and 2). The failed results could be explained by the formation of chlorine hydride when acyl chlorides as acylation reagents instead of the formation of acetic acid when acetic anhydride (Ac_2O) as the acylation reagent. Therefore, acetic anhydride (Ac_2O) and benzoic anhydride (Bz_2O) had to be as the acetylation reagents in the reaction. Indeed, the acylation proceed smoothly with anhydrides

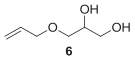
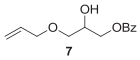
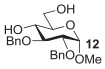
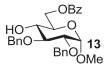
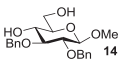
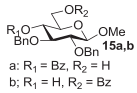
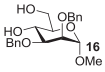
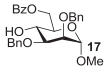
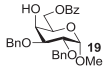
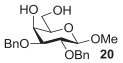
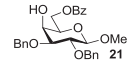
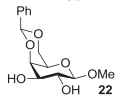
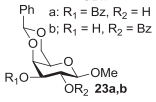
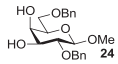
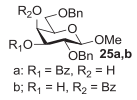
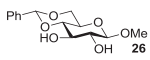
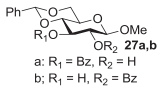
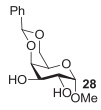
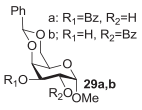
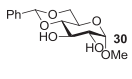
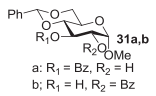
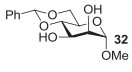
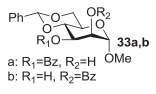
(Entry 3). However, a mixture of acetylation product **2** and benzoylation product **3** was obtained when Bz_2O was used as the acylation reagent (Entry 4). The reason might be explained by the transferring of acyl groups between Bz_2O and acetate anion (AcO^-) (Fig. 2a). Ac_2O and benzoate anion (BzO^-) might be generated through the acyltransfer process. Consequently, BzO^- had to be used as a catalyst in the regioselective benzoylation in order to avoid forming acetylated products. The benzoylation product **3** was obtained in 87% yield when compound **1** was allowed to react with 1.1 equiv of Bz_2O in the presence of 0.3 equiv of TBAOBz in acetonitrile at 40 °C for 8 h (Entry 5). However, 0.3 equiv of BzONa led to low conversion (Entry 6), likely due to its poor solubility in acetonitrile. Through optimization of the used amount of TBAOBz (Entries 7–9), it was found that 0.2 equiv of TBAOBz was the best for the reaction. 0.1 equiv of TBAOBz led to lower yields even when the reaction time was prolonged to 24 h. There was no reaction occurred without any catalyst (Entry 10). A mixture of 1-OBz, 2-OBz and 1,2-di-OBz products were obtained when 1 equiv of triethylamine was used instead of TBAOBz (Entry 11), indicating that there is no selectivity without the catalysis of benzoate anion. In order to verify the role of TBA cation, a combination of 0.2 equiv of BzONa and 0.2 equiv of TBABr was used to catalyze the reaction (Entry 12). It was found that the yield of **3** was increased by 73%. The reason must be the better solubility of benzoate anion in acetonitrile by the addition of TBA cation.

In light of the proposed mechanism showed in Fig. 2b, with Bz_2O as the acylation reagent, the catalysis BzO^- would form homo-conjugate H-bond complex with BzOH formed in the reaction. The formation and stability of homo-conjugate H-bond complexes $[BzOHOB_Z]^-$ (**B**) and $[AcOHOAc]^-$ (**C**) have been discussed in several papers.[38–41] Thus, with the reaction proceeding and BzOH generating, the homo-conjugate H-bond complex **B** was becoming increasingly and the dual H-bonding complex **A** were becoming decreasingly. Consequently, the efficiency of the catalysis depends on the relative stability of the homo-conjugate H-bond complex **B** and the dual H-bonding complex **A**. When the used amount of BzO^- was decreased by 0.1 equiv of compound **1**, the dual H-bonding complex **A** was difficult to form with the conversion rate reaching to approximate 80%. As a result, the yield could not be increased even if the reaction time was prolonged to 24 h. With BzCl as the acylation reagent, the catalysis BzO^- would be consumed by the formed HCl in the reaction since BzOH is much weaker acid, leading to low conversion (<20%). The homo-conjugate H-bond complex **B** may be less stable than the homo-conjugate H-bond complex **C** formed by AcO^- and AcOH likely due to the larger steric effect of benzoyl group than that of acetyl group (Fig. 2c).[40] The more stable complex **C** would decrease the efficiency of the catalysis acetate anion. It may be one of the reasons why 0.1–0.2 equiv of TBAOBz is used as catalysis in present reaction whereas 0.3–0.6 equiv of TBAOAc is necessary in previous report.

Based on these studies, 0.2 equiv of TBAOBz was further tested together with a range of diols (cf. Table 2): 1,2-diols **4** and **6**, with one primary hydroxyl group; 1,3-diols **8** and **10**, with one primary hydroxyl group; methyl glycoside 1,3-diols **12**, **14**, **16**, **18** and **20**, with one primary hydroxyl group; and methyl glycoside 1,2-diols **22**, **24**, **26**, **28**, **30** and **32**, without primary hydroxyl group. These compounds were allowed to react with 1.1 equiv of Bz_2O in the presence of 0.2 equiv of TBAOBz in acetonitrile at 40 °C for 8–12 h. The results (cf. Table 2) show high regioselectivities to primary hydroxyl group in most cases and excellent isolated yields (64–94%). The regioselectivities showed to methyl glycoside 1,2-diols **22**, **24**, **26**, **28**, **30** and **32**, which contain two secondary hydroxyl groups, are not very good. However, this method still takes advantageous since only very few over-benzoylated products were formed during all these reactions.

Table 2
Regioselective benzoylation of diols catalyzed by TBAOBz[a]

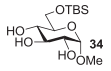
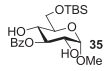
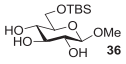
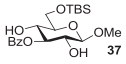
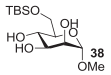
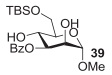
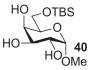
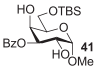
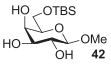
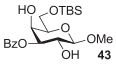
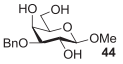
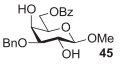
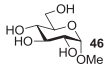
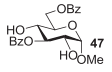
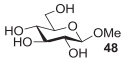
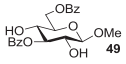
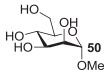
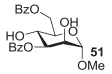
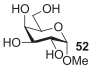
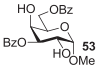
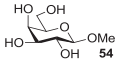
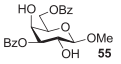
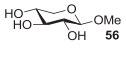
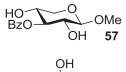
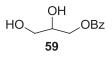
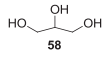
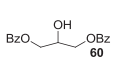


Entry	Reactant	Product	Yield (%)[b]
1			91
2			81
3			88
4			82
5			76
6			a/b (9/64)
7			88
8			90
9			94
10			a/b (70/14)
11			a/b (65/19)
12			a/b (48/30)
13			a/b (31/50)
14			a/b (30/52)
15			a/b (36/40)

[a] Reaction conditions: reactant (100 mg), Bz_2O (1.1 equiv), TBAOBz (0.2 equiv), MeCN (1 mL), 40 °C, 8–12 h.
[b] Isolated yield.

In the further experiments, 0.2–0.4 equiv of TBAOBz was tested together with a range of polyols (cf. Table 3): methyl glycosides **34**, **36**, **38**, **40** and **42**, in which the 6-OH groups were silylated; methyl β-D-galactoside **44**, in which the 3-OH group were benzylated; free methyl glycosides **46**, **48**, **50**, **52**, **54** and **56**; and glycerol **58**. When compounds **34**, **36**, **38**, **40**, **42**, **44**, **56** and **58** were allowed to react with 1.1 equiv of Bz_2O in the presence of 0.2 equiv of TBAOBz in

Table 3
Regioselective benzoylation of polyols catalyzed by TBAOBz[a]

Entry	Reactant	Product	Condition	Yield(%)[b]
1	 **34**	 **35**	A	83
2	 **36**	 **37**	A	78
3	 **38**	 **39**	A	84
4	 **40**	 **41**	A	85
5	 **42**	 **43**	A	84
6	 **44**	 **45**	A	85
7	 **46**	 **47**	B	70[c]
8	 **48**	 **49**	B	72
9	 **50**	 **51**	B	79
10	 **52**	 **53**	B	83
11	 **54**	 **55**	B	91
12	 **56**	 **57**	A	84
		 **59**	A	67[d]
13	 **58**	 **60**	B	70

[a] Reaction conditions: reactant (100 mg), A) Bz_2O (1.1 equiv), TBAOBz (0.2 equiv), CH_3CN (1 mL), 40 °C, 8–12 h; B) Bz_2O (2.1 equiv), TBAOBz (0.4 equiv), CH_3CN/DMF (5:1), 40 °C, 8–12 h.
[b] Isolated yield.
[c] Mixed with 13% methyl 4,6-OBz α-D-glucoside.
[d] Mixed with 6% 2-OBz glycerol.

acetonitrile, 3-OH groups were selectively benzoylated for compounds **34**, **36**, **38**, **40**, **42** and **56** to obtain high isolation yields of compounds **35**, **37**, **39**, **41**, **43** and **57** (78–85%), and primary hydroxyl groups were selectively benzoylated for compounds **44** and **58** to obtain high isolation yields of compounds **45** (85%) and **59** (73%). When compounds **46**, **48**, **50**, **52** and **54** were allowed to react with 2.1 equiv of Bz_2O in the presence of 0.4 equiv of TBAOBz in acetonitrile, 3, 6-*di*-OBz products **47**, **49**, **51**, **53** and **55** were obtained in high isolated yields (72–91%). Benzoylation of glycerol **58** led to selective benzoylation of two primary hydroxyl groups under this condition.

The isolated yields of the major product in most examples (Tables 2 and 3) are quite good (>80% yield), indicating high regioselectivities of these reactions (>80%). For some examples with yields lower than 70%, the product distribution is given as isolation ratios (9/64, 70/14, 65/19, 48/30, 31/50, 30/52 and 36/40 for entry **6**, entries **10**–**15** in Table 2, respectively). As the benzoylation is catalyzed by benzoate anion through a dual H-bonding complex, once one of hydroxyl groups is benzoylated, the left neighbor hydroxyl group will be difficult to be benzoylated due to the lack of the dual H-bonding complex. We proposed the regioselectivities should be mainly controlled by steric effect of substrates. Thus, for diols or polyols with a primary hydroxyl, the primary hydroxyl groups were selective benzoylated due to their minimum steric effect. For glycoside polyols in which the 6-OH groups have been protected, 3-OH groups have the minimum steric effects since they neighbored two hydroxyl groups whereas 2- and 4-OH groups neighbored a bulky group separately except for 3-OH, leading to good selectivities to 3-OH. The acidity of hydroxyl group for substrates should also play an important role on the regioselectivity. It might be the reason why the 3-position of compound **56** is highly selective benzoylated though 4-OH groups of **56** have the minimum steric effect.

3. Conclusion

Based on dual H-bonding principle, we developed an efficient method for regioselective benzoylation of diols and polyols. The benzoylation is catalyzed by 0.2 equiv of benzoate anion for benzoylation of one hydroxyl group in acetonitrile with the addition of a stoichiometric amount of benzoic anhydride under very mild condition, leading to high selectivities and isolation yields. Compared with other methods, this method shows particular advantage in regioselective multiple benzoylation of polyols, and in avoiding the use of any metal-based catalysts and any amine bases. Therefore, although the method requires more catalysis (0.2 equiv), it is still advantageous compared to methods using less catalysis (<0.1 equiv) but much more amine bases (>1 equiv).

4. Experimental section

4.1. General

All commercially available starting materials and solvents were of reagent grade and dried prior to use. Chemical reactions were monitored with thin-layer chromatography using precoated silica gel 60 (0.25 mm thickness) plates. High-resolution mass spectra HRMS where obtained by electrospray ionization (ESI) and Q-TOF detection. Flash column chromatography was performed on silica gel 60 (0.040–0.063 mm). 1H and 13C spectra were recorded with a 400 MHz and 100 MHz instrument at 298 K in $CDCl_3$, using the residual signals from *d*-chloroform (^1H: δ=7.25 ppm; ^{13}C: δ=77.2 ppm), as internal standard. Assignments were made by first order analysis of the spectra, supported by standard ^1H–^1H correlation spectroscopy (COSY).

4.2. General procedure for regioselective mono benzoylation

Diols and polyol reactants (100 mg) were allowed to react with benzoic anhydride (1.1 equiv) in acetonitrile (1 mL) at 40 °C for 8–12 h in the presence of TBAOBz (0.2 equiv). The reaction mixture was directly purified by flash column chromatography (hexanes/EtOAc=2:1 to 1:1), affording the pure selectively protected derivatives.

4.3. General procedure for regioselective multiple benzoylation

Polyol reactants (100 mg) were allowed to react with benzoic anhydride (2.1 equiv) in a mixture of 2 mL MeCN and 0.2 mL DMF at 40 °C for 8–12 h in the presence of TBAOBz (0.4 equiv). The reaction

mixture was directly purified by flash column chromatography (hexanes/EtOAc=2:1 to 1:1), affording the pure selectively protected derivatives.

4.4. 2-Hydroxy-3-Allyloxypropyl benzoate 7

Colorless oil, ^{1}H NMR (400 MHz, CDCl3) δ=8.05 (d, 2H, J=7.2 Hz, Ph), 7.57 (t, 1H, J=7.6 Hz, Ph), 7.45 (t, 2H, J=7.6 Hz, Ph), 5.96–5.86 (m, 1H, $CH_2C\mathbf{H}=CH_2$), 5.32–5.27 (m, 1H, $CH_2CH=C\mathbf{H}_2$), 5.21 (dd, 1H, J=1.2 Hz, 10.4 Hz, $CH_2CH=C\mathbf{H}_2$), 4.46–4.38 (m, 2H, CH_2OBz), 4.20–4.15 (m, 1H, C**H**OH), 4.05 (d, 2H, J=5.6 Hz, $C\mathbf{H}_2CH=CH_2$), 3.62 (dd, 1H, J=4 Hz, 10 Hz, $CH_2OAllyl$), 3.56 (dd, 1H, J=6.4 Hz, 9.6 Hz, $CH_2OAllyl$). ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.7, 134.2, 133.2, 129.7, 128.4, 117.5, 77.4, 77.0, 76.7, 72.4, 70.9, 69.0, 66.0 ppm. ESI-HRMS m/z calcd for $C_{13}H_{16}O_4[M+Na]^+$: 259.0946. Found 259.0966.

4.5. Methyl 2,3-di-*O*-benzyl-6-*O*-benzoyl-α-D-glucopyranoside 13

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.03 (d, 2H, J=7.6 Hz, Ph), 7.62–7.28 (m, 13H, Ph), 5.01 (d, 1H, J=11.2 Hz, $PhCH_2$), 4.80–4.75 (m, 2H, H-1, $PhCH_2$), 4.68–4.60 (m, 3H, $PhCH_2$, H-6a), 4.51 (dd, 1H, J=2.0 Hz, 12 Hz, H-6b), 3.90–3.87 (m, 1H, H-5), 3.84 (t, 1H, J=9.2 Hz, H-4), 3.56–3.51 (m, 2H, H-2, H-3), 3.40 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.8, 138.6, 138.0, 133.2, 129.8, 128.7, 128.5, 128.4, 128.1, 128.1, 128.0, 127.8, 98.2, 81.3, 79.7, 75.7, 73.2, 70.1, 69.5, 63.8, 55.3 ppm. ESI-HRMS m/z calcd for $C_{28}H_{30}O_7[M+Na]^+$: 501.1890. Found 501.1895.

4.6. Methyl 2,3-di-*O*-benzyl-6-*O*-benzoyl-β-D-glucopyranoside 15b

Colorless oil, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, 2H, J=7.6 Hz, Ph), 7.63–7.30 (m, 13H, Ph), 4.90 (d, 1H, J=11.2 Hz, $PhCH_2$), 4.78–4.69 (m, 3H, $PhCH_2$), 4.62 (dd, 1H, J=6 Hz, 11.2 Hz, H-6a), 4.58 (dd, 1H, J=6.8 Hz, 11.2 Hz, H-6a), 4.30 (d, 1H, J=8 Hz, H-1), 3.99 (d, 1H, J=2.8 Hz, H-4), 3.74 (t, 1H, J=6.4 Hz, H-5), 3.65 (dd, 1H, J=8 Hz, 9.6 Hz, H-2), 3.57 (s, 3H, OMe), 3.54 (dd, J=3.2 Hz, 9.2 Hz, H-3), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 138.6, 137.8, 133.2, 129.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 104.7, 80.4, 78.9, 75.1, 72.8, 71.9, 66.7, 63.4, 57.0 ppm. ESI-HRMS m/z calcd for $C_{28}H_{30}O_7[M+Na]^+$: 501.1890. Found 501.1893.

4.7. Methyl 2,3-di-*O*-benzyl-6-*O*-benzoyl-α-D-mannopyranoside 17

Colorless oil, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, 2H, J=7.6 Hz, Ph), 7.62–7.28 (m, 13H, Ph), 4.82 (s, 1H, H-1), 4.70–4.62 (m, 5H, $PhCH_2$, H-6a, H-6b), 4.53 (d, J=12 Hz, 1H, $PhCH_2$), 4.13 (t, 1H, J=9.6 Hz, H-5), 3.90–3.83 (m, 2H, H-3, H-4), 3.77 (dd, 1H, J=2.8, 9.2 Hz H-2), 3.39 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 138.1, 138.0, 132.9, 130.1, 129.8, 128.6, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 99.1, 79.5, 74.0, 72.6, 71.8, 70.8, 66.6, 64.0, 54.9. ESI-HRMS m/z calcd for $C_{28}H_{30}O_7[M+Na]^+$: 501.1890. Found 501.1898.

4.8. Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside 35

Colorless oil, ^{1}H NMR (CDCl3, 400 MHz): 1H NMR (CDCl3, 400 MHz) δ=8.09 (d, 2H, J=7.2 Hz, Ph), 7.56 (t, 1H, J=7.4 Hz, Ph), 7.44 (t, 2H, J=7.7 Hz, Ph), 5.35 (t, 1H, J=9.6 Hz, H-3), 4.81 (d, 1H, J=3.6 Hz, H-1), 3.92 (dd, 1H, J=10.6 Hz, 4.9 Hz, H-6a), 3.88 (dd, 1H, J=10.6 Hz, 5.6 Hz, H-6b), 3.80–3.69 (m, 3H, H-2, H-4, H-5), 3.46 (s, 3H, OMe), 0.91 (s, 9H, $SiC(Me)_3$, 0.11 (s, 6H, $Si(Me)_2$). ^{13}C NMR (CDCl3, 100 MHz) δ 167.9, 133.3, 130.0, 129.8, 128.4, 99.3, 71.1, 71.0, 70.7, 63.9, 55.3, 25.9, 18.4, −5.4. ESI-HRMS m/z calcd for $C_{20}H_{32}O_7Si$ $[M+Na]^+$: 435.1815. Found 435.1809.

4.9. Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-β−D-glucopyranoside 37

Colorless oil, ^{1}H NMR (CDCl3, 400 MHz): δ 8.10 (d, 2H, J=7.2 Hz, Ph), 7.57 (t, 1H, J=7.6 Hz, Ph), 7.45 (t, 2H, J=7.6 Hz, Ph), 5.22 (t, 1H, J=9.2 Hz, H-3), 4.34 (d, 1H, J=8 Hz, H-1), 3.98 (dd, 1H, J=10.4 Hz, 4.8 Hz, H-6a), 3.91 (dd, 1H, J=10.4 Hz, 5.6 Hz, H-6b), 3.83 (t, 1H, J=9.2 Hz, H-4), 3.61 (m, 4H, H-2, OMe), 3.51–3.46 (m, 1H, H-5), 0.90 (s, 9H, $SiC(Me)_3$, 0.11 (s, 6H, $Si(Me)_2$). ^{13}C NMR (CDCl3, 100 MHz) δ 167.6, 133.4, 130.0, 129.6, 128.4, 103.7, 78.5, 74.7, 72.4, 71.6, 64.5, 57.2, 25.9, 18.3, −5.4; ESI-HRMS m/z calcd for $C_{20}H_{32}O_7Si[M+Na]^+$: 435.1815. Found: 435.1826.

4.10. Methyl 3-*O*-benzyl-6-*O*-benzoyl-β-D-galactopyranoside 45

Colorless oil, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, 2H, J=7.2 Hz, Ph), 7.58 (t, 1H, J=7.6 Hz, Ph), 7.45 (t, 2H, J=7.6 Hz, Ph), 7.40–7.30 (m, 5H, Ph), 4.75 (t, 2H, J=12 Hz, $PhCH_2$), 4.63 (dd, 1H, J=11.6, 6 Hz, H-6a), 4.57 (dd, 1H, J=11.6 Hz, 7.2 Hz, H-6b), 4.19 (d, 1H, J=7.6 Hz, H-1), 4.00 (d, 1H, J=2.8 Hz, H-4), 3.83–3.77 (m, 2H, H-2, H-5), 3.55 (s, 3H, OMe), 3.48 (dd, 1H, J=9.6 Hz, 3.2 Hz, H-3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ=166.4, 137.6, 133.2, 129.7, 128.7, 128.5, 128.2, 128.0, 103.8, 80.4, 72.4, 72.3, 71.0, 66.4, 63.3, 57.0; ESI-HRMS m/z calcd for $C_{21}H_{24}O_7[M+Na]^+$: 411.1420. Found: 411.1429.

4.11. Methyl 3,6-di-*O*-benzoyl-β-D-glucopyranoside 49

Colorless oil, ^{1}H NMR (CDCl3, 400 MHz): δ 8.09–8.06 (m, 4H, Ph), 7.60–7.55 (m, 2H, Ph), 7.47–7.42 (m, 4H, Ph), 5.24 (t, 1H, J=9.2 Hz, H-3), 4.71 (dd, 1H, J=4 Hz, 12 Hz, H-6a), 4.64 (dd, 1H, J=2 Hz, 12 Hz, H-6b), 4.38 (d, 1H, J=8 Hz, H-1), 3.79–3.73 (m, 2H, H-4, H-5),3.67 (dd, 1H, J=8 Hz, 9.6 Hz, H-2), 3.58 (s, 3H, OMe). ^{13}C NMR (CDCl3, 100 MHz) δ=167.8, 167.0, 133.6, 133.3, 130.1, 129.8, 129.7, 129.3, 128.5, 128.4, 103.9, 78.4, 74.5, 72.3, 69.4, 63.7, 57.4; ESI-HRMS m/z calcd for $C_{21}H_{22}O_8[M+Na]^+$: 425.1213. Found: 425.1224.

4.12. Methyl 3,6-di-*O*-benzoyl-α-D-galactopyranoside 53

Colorless oil, ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.06 (d, 2H, J=7.2 Hz, Ph), 7.97 (d, 2H, J=7.2 Hz, Ph), 7.53 (t, 1H, J=7.2 Hz, Ph), 7.49 (t, 1H, J=7.2 Hz, Ph), 7.40 (t, 2H, J=7.8 Hz, Ph), 7.36 (t, 2H, J=7.8 Hz, Ph), 5.31 (dd, 1H, J=3 Hz, 10.2 Hz, H-3), 4.88 (d, 1H, J=3.6 Hz, H-1), 4.54 (dd, 1H, J=5.4 Hz, 11.4 Hz, H-6a), 4.50 (dd, 1H, J=7.2 Hz, 11.4 Hz, H-6b), 4.24 (m, 2H, H-2, H-4), 4.16 (t, 1H, J=6 Hz, H-5), 3.42 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 166.4, 133.6, 133.4, 133.3, 129.9, 129.7, 129.6, 128.5, 99.7, 73.8, 68.17, 68.0, 67.3, 63.3, 55.6; ESI-HRMS m/z calcd for $C_{21}H_{22}O_8[M+Na]^+$: 425.1213. Found: 425.1220.

4.13. Glycerol 1,3-dibenzoate 60

Colorless oil, ^{1}H NMR (CDCl3, 400 MHz) δ 8.07–8.05 (m, 4H, Ph), 7.58 (t, 1H, J=7.2 Hz, Ph), 7.46–7.43 (m, 7H, Ph), 4.78–4.57 (m, 4H, $CH_2\times2$), 4.42–4.37 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 100 MHz) δ=166.7, 133.4, 129.8, 129.6, 128.5, 68.6, 65.9; ESI-HRMS m/z calcd for $C_{17}H_{16}O_5[M+Na]^+$: 323.0895. Found: 323.0878.

Acknowledgements

This study was supported by the National Nature Science Foundation of China (No. 21272083), and the Chutian Project-Sponsored by Hubei Province. The authors are also grateful to the

staffs in the Analytical and Test Center of HUST for support with the NMR instruments.

Supplementary data

Supplementary data (Synthesis method of substrates, Characterization of known compounds, ^{1}H NMR and ^{13}C NMR-spectra of known and new compounds) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.12.074.

References and notes

1. 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.
2. Witschi, M. A.; Gervay-Hague, J. *Org. Lett.* **2010**, *12*, 4312–4315.
3. Bourdreux, Y.; Lemetais, A.; Urban, D.; Beau, J. M. *Chem. Commun.* **2011**, 2146–2148.
4. Zhou, Y. X.; Ramstrom, O.; Dong, H. *Chem. Commun.* **2012**, 5370–5373.
5. Ren, B.; Wang, M. Y.; Liu, J. Y.; Ge, J. T.; Dong, H. *ChemCatChem* **2015**, *7*, 761–765.
6. Zhang, Q.; van Rijssel, E. R.; Walvoort, M. T. C.; Overkleeft, H. S.; van der Marel, G. A.; Codee, J. D. C. *Angew. Chem., Int. Ed.* **2015**, *54*, 7670–7673.
7. Tang, S.-L.; Pohl, N. L. B. *Org. Lett.* **2015**, *17*, 2642–2645.
8. Wu, B.; Ge, J.; Ren, B.; Pei, Z.; Dong, H. *Tetrahedron* **2015**, *71*, 4023–4030.
9. Schmidt, D.; Schuhmacher, F.; Geissner, A.; Seeberger, P. H.; Pfrengle, F. *Chem.—Eur. J.* **2015**, *21*, 5709–5713.
10. Danishefsky, S. J.; Shue, Y. K.; Chang, M. N.; Wong, C. H. *Acc. Chem. Res.* **2015**, *48*, 643–652.
11. Thieffry, S. A. *J. Chem. Soc. Perkin Trans. 1* **1979**, 1568–1573.
12. Ogawa, T.; Matsui, M. *Tetrahedron* **1981**, *37*, 2363–2369.
13. Holzapfel, C. W.; Koekemoer, J. M.; Matais, C. F. *S. Afr. J. Chem.* **1984**, *37*, 19–26.
14. Helm, R. F.; Ralph, J.; Anderson, L. *J. Org. Chem.* **1991**, *56*, 7015–7021.
15. Jenkins, D. J.; Potter, B. V. L. *Carbohydr. Res.* **1994**, *265*, 145–149.
16. Peri, F.; Cipolla, L.; Nicotra, F. *Tetrahedron Lett.* **2000**, *41*, 8587–8590.
17. Gridley, J. J.; Osborn, H. M. I.; Suthers, W. G. *Tetrahedron Lett.* **1999**, *40*, 6991–6994.
18. Osborn, H. M. I.; Brome, V. A.; Harwood, L. M.; Suthers, W. G. *Carbohydr. Res.* **2001**, *332*, 157–166.
19. Gangadharmath, U. B.; Demchenko, A. V. *Synlett* **2004**, 2191–2193.
20. Gray, I. J.; Kluger, R. *Carbohydr. Res.* **2007**, *342*, 1998–2002.
21. Dhiman, R. S.; Kluger, R. *Org. Biomol. Chem.* **2010**, *8*, 2006–2008.
22. Evtushenko, E. V. *Carbohydr. Res.* **2012**, *359*, 111–119.
23. Demizu, Y.; Kubo, Y.; Miyoshi, H.; Maki, T.; Matsumura, Y.; Moriyama, N.; Onomura, O. *Org. Lett.* **2008**, *10*, 5075–5077.
24. Muramatsu, W.; William, J. M.; Onomura, O. *J. Org. Chem.* **2012**, *77*, 754–759.
25. Matsumura, Y.; Maki, T.; Murakami, S.; Onomura, O. *J. Am. Chem. Soc.* **2003**, *125*, 2052–2053.
26. Mazet, C.; Roseblade, S.; Kohler, V.; Pfaltz, A. *Org. Lett.* **2006**, *8*, 1879–1882.
27. Evtushenko, E. V. *J. Carbohydr. Chem.* **2010**, *29*, 369–378.
28. Lauber, M. B.; Daniliuc, C.-G.; Paradies, J. *Chem. Commun.* **2013**, 7409–7411.
29. Allen, C. L.; Miller, S. J. *Org. Lett.* **2013**, *15*, 6178–6181.
30. Chen, I. H.; Kou, K. G. M.; Le, D. N.; Rathbun, C. M.; Dong, V. M. *Chem.—Eur. J.* **2014**, *20*, 5013–5018.
31. Evtushenko, E. V. *J. Carbohydr. Chem.* **2015**, *34*, 41–54.
32. Muramatsu, W.; Kawabata, T. *Tetrahedron Lett.* **2007**, *48*, 5031–5033.
33. Lee, D.; Taylor, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 3724–3727.
34. Lee, D.; Williamson, C. L.; Chan, L.; Taylor, M. S. *J. Am. Chem. Soc.* **2012**, *134*, 8260–8267.
35. Zhang, Z. Y.; Wong, C. H. *Tetrahedron* **2002**, *58*, 6513–6519.
36. Zhou, Y. X.; Rahm, M.; Wu, B.; Zhang, X. L.; Ren, B.; Dong, H. *J. Org. Chem.* **2013**, *78*, 11618–11622.
37. Ren, B.; Rahm, M.; Zhang, X. L.; Zhou, Y. X.; Dong, H. *J. Org. Chem.* **2014**, *79*, 8134–8142.
38. Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48–76.
39. Amendola, V.; Boiocchi, M.; Fabbrizzi, L.; Palchetti, A. *Chem.—Eur. J.* **2005**, *11*, 5648–5660.
40. Kutt, A.; Leito, I.; Kaljurand, I.; Soovali, L.; Vlasov, V. M.; Yagupolskii, L. M.; Koppel, I. A. *J. Org. Chem.* **2006**, *71*, 2829–2838.
41. Amendola, V.; Esteban-Gomez, D.; Fabbrizzi, L.; Palchetti, A. *Acc. Chem. Res.* **2006**, *39*, 343–353.