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Ferric sulfate hydrate-catalyzed O-glycosylation using glycals with or without microwave irradiation

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Abstract

We have developed a novel glycal-based O-glycosylation reaction, in which the substrates are not only peracetyl glycals but also perbenzyl glucals to afford the corresponding 2,3-unsaturated-*O*-glycosides via Ferrier rearrangement. The reaction of the perbenzyl glucal with various alcohols catalyzed by ferric sulfate hydrate ($Fe_2(SO_4)_3 \cdot xH_2O$) was successfully carried out to give 2,3-unsaturated D-*O*-glucosides with exclusive α-selectivity and no formation of addition products 2-deoxy hexopyranosides was observed. It is the first report on peralkyl glycal efficiently undergoing Ferrier rearrangement instead of addition of alcohols catalyzed by Lewis acids. $Fe_2(SO_4)_3 \cdot xH_2O$ is an effective, convenient, and environmentally benign heterogeneous catalyst. It has low catalytic loading and recyclable without significant loss of activity.

Keywords: O-Glycosylation; Ferrier rearrangement; Ferric sulfate hydrate; Peracetyl or perbenzyl glucal; 2,3-Unsaturated *O*-glycosides

1. Introduction

Ferrier rearrangement is an allylic rearrangement of glycal esters[1–3] in the presence of alcohols leading to 2,3-unsaturated glycosides. Since Ferrier rearrangement was discovered in 1969,[4] it has been routinely used in the area of carbohydrate chemistry. The unsaturated glycosides obtained through Ferrier rearrangement play an important role in the transformation of these compounds into other interesting carbohydrates.[5–7] 2,3-Unsaturated glycosides[8] have a unique place in carbohydrate chemistry, since they can be further functionalized and serve as chiral intermediate[8a,9] in the synthesis of biologically active compounds, such as glycopeptide blocks,[10] oligosaccharides,[11] and modified carbohydrates.[12] In addition, 2,3-unsaturated glycosides have also been employed in the synthesis of some important antibiotics,[13] nucleosides,[14] natural product-like compounds,[2b] and various natural products.[15]

The catalysts for the synthesis of 2,3-unsaturated glycosides via Ferrier rearrangement have continuously received extensive attention. A wide range of catalysts have been employed to form 2,3-unsaturated glycosides, such as $BF_3 \cdot OEt_2$,[16] $SnCl_4$,[17] $FeCl_3$,[18] $Sc(OTf)_3$,[19] $InCl_3$,[20] Montmorillonite K-10,[21] $BiCl_3$,[22] $Dy(OTf)_3$,[23] $CeCl_3 \cdot 7H_2O$,[24] $ZnCl_2$,[25] DDQ,[26] NIS,[27] $K_5CoW_{12}O_{40}$,[28] I_2,[29] CAN,[30] $HClO_4$–SiO_2,[31] $Bi(NO_3)_3 \cdot 5H_2O$,[32] $Fe(NO_3)_3 \cdot 9H_2O$,[32b] and $NbCl_5$.[33] These catalysts included Lewis acid catalysts and redox reagents. The acid catalysts, usually employed in sub-stoichiometric amount, generally provide good anomeric selectivity for the product under ambient conditions. However, they often suffer from the limited use of acid-labile glycal donors and acceptors. The oxidants are often required in stoichiometric amount, and long reaction time and/or high temperature are unavoidable. In addition, the reactions under these conditions usually give low anomeric selectivity for the product. Moreover, some of the catalysts are moisture sensitive and expensive. As a result, most of those methods do not satisfy the rule of green chemistry, and entail the problems of tedious work-up procedures and expensive reagents and equipment. Therefore, searching for environmentally benign and more economic synthetic methods with greater efficiency and more convenient procedures is still in strong demand.

In general, the substrates of Ferrier rearrangement are peracyl glycals or the glycals at least with 3-*O*-acyl group.

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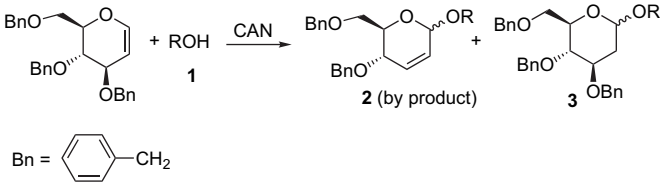
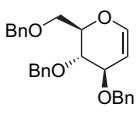
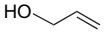
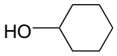
Perbenzyl glycals typically undergo addition reaction to form the corresponding addition products 2-deoxy *O*-glycosides instead of 2,3-unsaturated-*O*-glycosides. Benzyl is a very important protecting group in carbohydrate chemistry. To obtain benzyl-protected 2,3-unsaturated-*O*-glycosides via Ferrier reaction, 3-*O*-acyl-4,6-di-*O*-benzyl glycal was used as the Ferrier reaction substrate.[34] In this strategy, the hydroxy groups of the substrate should be protected selectively with benzyl and acyl groups. To date, convenient and effective approaches to benzyl-protected 2,3-unsaturated-*O*-glycosides directly from perbenzyl glycal have not been reported. CAN (ceric ammonium nitrate) was the only known reagent providing Ferrier rearrangement compounds as by-products from perbenzyl glycals. When CAN was applied, the reaction of perbenzyl glycal and alcohols led to the formation of 2-deoxy-glycoside (**3**) along with the Ferrier rearrangement product (**2**) due to the competition (Scheme 1).[30b] It was found that in the reaction of perbenzyl glucal with methanol, allyl alcohol, and cyclohexanol in the presence of 2 mol % of CAN, 2-deoxy products were formed as the major products along with the Ferrier products in the yields of 38%, 23%, and 18%, respectively (Table 1). Therefore, the development of a new glycal-based glycosylation method, in which the substrates include both peracyl and perbenzyl glucals, would represent an important advance.



Scheme 1. Reaction of perbenzyl glucal promoted by CAN.

In our efforts to develop highly efficient methods for functional group transformations, we found $Fe_2(SO_4)_3 \cdot xH_2O$ as an effective, reusable, operationally simple, and environmentally benign catalyst for tetrahydropyranylation[35] and preparation of acylals from aldehydes.[36] To further explore the potential of this reagent, we studied its behavior on both peracetyl glucal and perbenzyl glucal. The reaction of peracetyl glucal with alcohols catalyzed by $Fe_2(SO_4)_3 \cdot xH_2O$, as we anticipated, gave the Ferrier rearrangement products 2,3-unsaturated glucosides. However, this reaction was carried out with perbenzyl glucal, which, to our surprise, was also found to undergo Ferrier reaction instead of addition reaction. Both peracetyl and perbenzyl glucals reacted with alcohols catalyzed by $Fe_2(SO_4)_3 \cdot xH_2O$ to afford 2,3-unsaturated-*O*-glucosides in high yields with exclusive α-selectivity, no formation of 2-deoxy hexopyranosides (addition products) was observed. Encouraged by this result, we have explored $Fe_2(SO_4)_3 \cdot xH_2O$ as an efficient catalyst for Ferrier reaction of both peracetyl and perbenzyl glucals to synthesize the corresponding 2,3-unsaturated glucosides (Scheme 2).

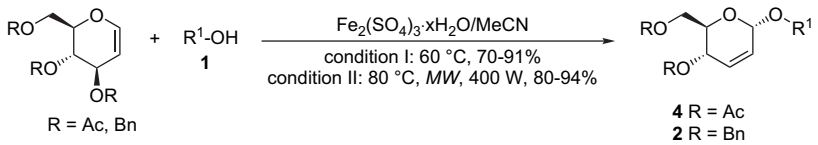
Table 1
Comparison of reaction results of $Fe_2(SO_4)_3 \cdot xH_2O$ with CAN

Glycal	Alcohol	Catalyst	Yields (%)	
			2 (α/β)	**3** (α/β)
	MeOH	$Fe_2(SO_4)_3 \cdot xH_2O$	81 (α only)	—
		CAN	38 (5:1)	56 (1.7:1)
		$Fe_2(SO_4)_3 \cdot xH_2O$	86 (α only)	—
		CAN	23 (4.7:1)	60 (1.1:1)
		$Fe_2(SO_4)_3 \cdot xH_2O$	82 (α only)	—
		CAN	18 (α only)	65 (11.5:1)

2. Results and discussion

To obtain some preliminary information on this synthetically useful reaction, initial experiments were performed with peracetyl glucal as the donor and ethanol as the acceptor. We first examined the reaction between glucal and ethanol in various solvent systems. Tri-*O*-acetyl-D-glucal (0.1360 g, 0.5 mmol) was treated with ethanol (1.5 mmol) and $Fe_2(SO_4)_3 \cdot xH_2O$ (0.025 g, 0.005 mmol)[37] in CH_2Cl_2, MeCN, DMF, $(CH_3)_2CO$, or THF at 60 °C to give ethyl 2,3-unsaturated glycopyranoside. Anhydrous acetonitrile was shown to be superior to the other solvents in terms of yields and reaction time. To study the effect of the catalyst, the reactions were carried out in acetonitrile in the presence of 10, 5, 2, 1, and 0.5 mol % of $Fe_2(SO_4)_3 \cdot xH_2O$. The results showed that 1 mol % of $Fe_2(SO_4)_3 \cdot xH_2O$ was enough for a fairly high yield. With 0.5 mol % of $Fe_2(SO_4)_3 \cdot xH_2O$, a lower yield was observed under same reaction period. Meanwhile, we also tested the effect of reaction temperature on the catalyzed reaction. When the reaction was carried out at room temperature, the reaction was sluggish. When it was carried out at 60 °C, the maximum yield was obtained in a short reaction period. This success encouraged us to study the scope of the reaction under the optimized condition: in the presence of 1 mol % of catalyst, anhydrous acetonitrile as reaction solvent, and at 60 °C. The results of using $Fe_2(SO_4)_3 \cdot xH_2O$ as a catalyst in the glycosylation are summarized in Table 2 (condition I).

Treatment of 3,4,6-tri-*O*-acetyl-D-glucal with various alcohols under the optimized conditions led to the corresponding 2,3-unsaturated alkyl glycosides (condition I, entries 1–9). The ^1H NMR data of the glycosides confirmed the α-configuration of the glycosyl products formed in the above reactions by comparison with the literature data. According to the published results, most of the Ferrier reactions of 3,4,6-tri-*O*-acetyl-D-



Scheme 2. Reactions of glucals catalyzed by $Fe_2(SO_4)_3 \cdot xH_2O$.

glucal gave 2,3-unsaturated glycosides as a mixture of α- and β-anomers except Montmorillonite K-10[21b] and $NbCl_5$.[33] From the aspects of cost, efficiency, and stereoselectivity, $Fe_2(SO_4)_3 \cdot xH_2O$ is superior to the other catalysts used in most of the known methods.

In general, perbenzyl glycal catalyzed by Lewis acid undergoes addition of alcohols to form the corresponding addition products 2-deoxy *O*-glycosides instead of undergoing Ferrier rearrangement to afford 2,3-unsaturated-*O*-glycosides. To extend the scope of our catalyst, we also performed $Fe_2(SO_4)_3 \cdot xH_2O$-catalyzed reactions of perbenzyl glucal with various alcohols (condition I, entries 11–14). These reactions, to our surprise, also underwent Ferrier reaction instead of addition onto the glucal. 2,3-Unsaturated-*O*-glucosides were produced in high yields with exclusive α-selectivity and no formation of 2-deoxy hexopyranosides (addition products) was observed. It is noteworthy that $Fe_2(SO_4)_3 \cdot xH_2O$ was the first reagent to catalyze peralkyl glycal undergoing Ferrier rearrangement to produce 2,3-unsaturated glycoside as the exclusive product.

The scope of the new glycosylation was further examined in the context of disaccharide synthesis (entries 10 and 15). It has been found that many natural antibiotics possessing significant antitumor and antiviral activities contain *O*-glycosylated nucleoside substructure. 2,3-Unsaturated glycosides connected to nucleosides resulting from Ferrier rearrangements are the important intermediates for *O*-glycosylated nucleoside. We chose 2′,3′-di-*O*-acetyl-uridine (**1j**) as the glycosyl acceptor to react with both peracetyl and perbenzyl glucals. As shown in Table 2, these reactions also gave high yields and α-selectivity exclusively. It has been reported that the α-anomer of the 2,3-unsaturated glycosides adopted the $^0H_5$ conformation and the β-anomer the $^5H_0$ conformation.[38] Two anomers could be identified by the value of $J_{4'',5''}$ in ^1H NMR spectrum. The ^1H NMR of the products **4j** and **2j** showed that the $J_{4'',5''}$ values (**4j**: 10.0 Hz, **2j**: 10.0 Hz) were in accord with a favorable α-anomer, in which 4″-H and 5″-H were at *anti*-quasi-axial positions (Fig. 1).[5b]

Meanwhile, in our endeavor to develop a more efficient, rapid, and eco-friendly method for O-glycosylation, the microwave irradiation-assisted Ferrier rearrangement of peracetyl and perbenzyl glucals was explored (condition II, Scheme 2). It was found that the reaction of 3,4,6-tri-*O*-acetyl-D-glucal with alcohols (1.5 equiv) in the presence of $Fe_2(SO_4)_3 \cdot xH_2O$ (1 mol %) in acetonitrile under microwave irradiation afforded the Ferrier rearrangement products in good yields with very high α-selectivity. Therefore, further investigations were carried out to explore the optimized reaction conditions.

Effects of the reaction temperature and the power of microwave to the yield of Ferrier product were studied by using the reaction of 3,4,6-tri-*O*-acetyl-D-glucal with ethanol. At different temperatures and under different powers of microwave, the best yield (up to 89%) was obtained with the microwave irradiation power of 400 W at 80 °C for 6 min. A variety of alcohols then reacted with glucals in the presence of $Fe_2(SO_4)_3 \cdot xH_2O$ (1 mol %) following the same procedure and the results are summarized in Table 2 (condition II). Compared with the results obtained using condition I, condition II also demonstrated excellent stereoselectivity with even higher yields and significant shorter reaction time.

In view of green chemistry, recyclable catalysts are highly preferred. In our process, $Fe_2(SO_4)_3 \cdot xH_2O$ was easily recovered from the reaction mixture by filtration and subsequently used directly for the next reaction cycle. Using condition I for the glycosylation of alcohol with the recycled catalyst, this recycle protocol was repeated four times and the percentage of the catalyst recovery was always more than 90%, while the yields were always more than 84% (Table 3).

Mechanistically, it is proposed that $Fe_2(SO_4)_3 \cdot xH_2O$ as a weak Lewis acid could prompt the glycal to an allylic oxonium intermediate via cleavage of the C3 substituent, as shown in Scheme 3. The exclusive formation of the α-anomer may arise from the thermodynamic anomeric effect.

3. Conclusion

In conclusion, we have demonstrated a new glycal-based glycosylation method to produce 2,3-unsaturated-*O*-glycosides via Ferrier rearrangement, in which the substrates can be either peracetyl glucal or perbenzyl glucal. This is the first report on peralkyl glycals efficiently undergoing Ferrier rearrangement without formation of addition products 2-deoxy hexopyranosides. Both peracetyl and perbenzyl glucals underwent the Ferrier rearrangement in the presence of $Fe_2(SO_4)_3 \cdot xH_2O$ to afford the corresponding 2,3-unsaturated-*O*-glycosides in excellent yields and exclusive α-selectivity with or without microwave irradiation. $Fe_2(SO_4)_3 \cdot xH_2O$ is an efficient, convenient, and environmentally benign heterogeneous catalyst, used in very low percentage, and can be recovered and reused without significant loss of activity. The excellent α-selectivity, inexpensive, and reusable catalyst, and environmentally benign characters make this method an attractive way to prepare 2,3-unsaturated-*O*-glycosides from glycals.

4. Experimental section

4.1. General remarks

Acetonitrile was distilled from P_2O_5 followed by distillation from CaH_2 prior to use. All reagents were obtained from commercial sources and used without further purification. Preparation of 2′,3′-di-*O*-acetyl-uridine followed the known reaction in literature. The reactions under microwave irradiation were performed in a commercial microwave reactor (XH-100B, 100–1000 W, Beijing Xianghu Science and Technology Development Co. Ltd, Beijing, PR China). The temperature of the reaction mixture was measured by an immersed platinum resistance thermometer. The reactions were all carried out under a positive pressure of nitrogen and were monitored by TLC on silica gel 60 F_{254} (0.25 mm, E. Merck). Column chromatography was performed on silica gel 60 (230–400 mesh). The ratio between silica gel and crude product ranged from 100 to 50:1 (w/w). ^1H and ^{13}C NMR spectra were recorded on Bruker AC-400 NMR spectrometer in solutions of $CDCl_3$ or DMSO-d_6 using tetramethylsilane as the internal standard, δ values are

Table 2
$Fe_2(SO_4)_3 \cdot xH_2O$-catalyzed Ferrier rearrangement of glucals with alcohols in acetonitrile

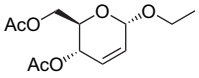
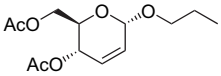
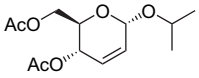
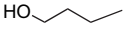
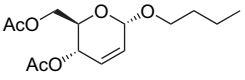
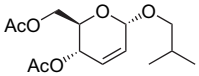
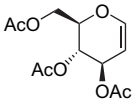
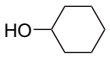
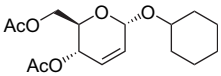
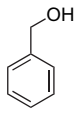
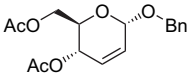
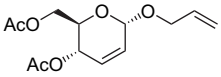
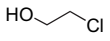
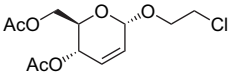
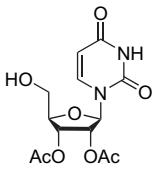
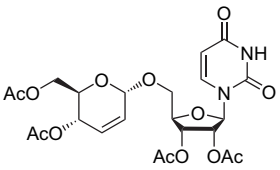
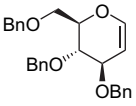
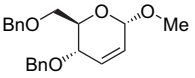
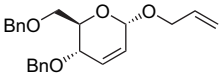
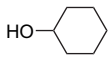
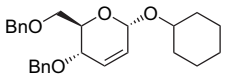
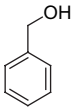
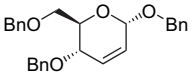
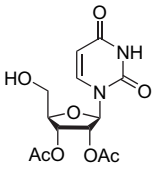
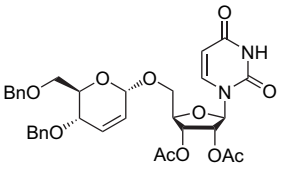
Entry	Substrate	Alcohol	Product	Condition I[a]		Condition II[b]	
				Time (h)	Yield[c] (%)	Time (min)	Yield[c] (%)
1		 **1a**	 **4a**	1	86	6	89
2		 **1b**	 **4b**	2	91	6	93
3		 **1c**	 **4c**	2	84	10	87
4		 **1d**	 **4d**	2.5	89	12	92
5		 **1e**	 **4e**	2.5	87	7	90
6		 **1f**	 **4f**	2	89	10	94
7		 **1g**	 **4g**	1.5	85	6	88
8		 **1h**	 **4h**	1.5	90	7	92
9		 **1i**	 **4i**	2	89	5	91
10		 **1j**	 **4j**	1.5	85[d]	6	88[e]
11		CH_3OH **1k**	 **2k**	1.5	81	4	87
12		 **1h**	 **2h**	2	86	10	90

Table 2 (*continued*)

Entry	Substrate	Alcohol	Product	Condition I[a] Time (h)	Yield[c] (%)	Condition II[b] Time (min)	Yield[c] (%)
13		 **1f**	 **2f**	2	82	7	84
14		 **1g**	 **2g**	2	84	6	86
15		 **1j**	 **2j**	1.5	70[f]	7	80[g]

[a] All the reactions were proceeded at 60 °C.
[b] All the reactions were irradiated at 80 °C, 400 W, 2450 MHz in a commercial microwave reactor (XH-100B, 100–1000 W, Beijing Xianghu Science and Technology Development Co. Ltd, Beijing, PR China). It takes about 5 min to achieve 80 °C under 400 W.
[c] Isolated yields.
[d] The yield was based on the 70% conversion rate of nucleoside.
[e] The yield was based on the 75% conversion rate of nucleoside.
[f] The yield was based on the 70% conversion rate of nucleoside.
[g] The yield was based on the 74% conversion rate of nucleoside.

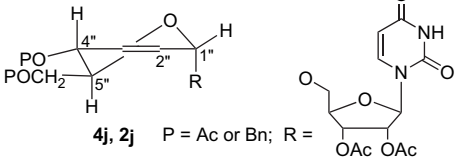


Figure 1. Preferred conformations of compounds **4j** and **2j**.

given in parts per million, and coupling constants (J) in hertz. The high-resolution mass spectra were collected at the Zhengzhou University Campus Instrumentation Center.

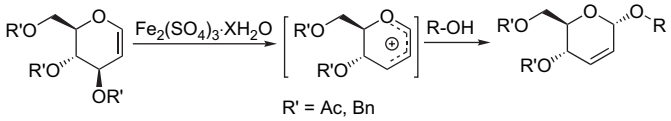
4.2. General procedure for the preparation of 2,3-unsaturated glycosides from glucals in anhydrous acetonitrile at 60 °C

To a stirred solution of 3,4,6-tri-*O*-acetyl-D-glucal (1 mmol) and alcohol (3 mmol) in anhydrous acetonitrile (5 mL) was added $Fe_2(SO_4)_3 \cdot xH_2O$ (0.01 mmol, 1 mol %). The mixture was stirred at 60 °C for appropriate time (condition I, Table 2). The reaction was monitored by TLC. After the completion, the reaction mixture was filtered and the filtrate was evaporated to recover the solvent. The residue was purified through silica-gel column chromatography. The pure product was characterized by GC–MS and ^{1}H NMR. The spectral data are comparable with literature data (**4a–4i**,[32b] **2k**,[16a] **2h**,[39] **2f**,[30b] and **2g**[40]).

Table 3
The reusability of $Fe_2(SO_4)_3 \cdot xH_2O$ as catalyst for Ferrier reaction

Round	Alcohol	Catalyst recovered (mg)	Reaction time (min)	Yield[a,b] (%)
1	CH_3CH_2OH	328	60	86
2	CH_3CH_2OH	310	60	85
3	CH_3CH_2OH	280	70	85
4	CH_3CH_2OH	260	80	84

[a] The reactions were carried out at 60 °C.
[b] Isolated yield.



Scheme 3. Proposed mechanism of $Fe_2(SO_4)_3 \cdot xH_2O$-catalyzed Ferrier reaction.

4.3. General procedure for the preparation of 2,3-unsaturated glycosides from glucals under microwave irradiation

To a mixture of 3,4,6-tri-*O*-benzyl-D-glucal (1 mmol) and alcohol (3 mmol) was added $Fe_2(SO_4)_3 \cdot xH_2O$ (1 mol %) in anhydrous acetonitrile (2 mL) in a flask equipped with a condenser, and then irradiated in the XH-100B microwave oven at 80 °C and 400 W for several minutes (condition II, Table 2). After the completion of the reaction, monitored by TLC, the reaction mixture was treated following the procedure described above. The products were purified through silica-gel column chromatography. The pure product was characterized by GC–MS and ^{1}H NMR.

*4.4. Characterization of glucosides: 4″,6″-di-O-acetyl-2″,3″-dideoxy-α-D-erythro-hex-2″-enopyranosyl-(1→5)-2′,3′-di-O-acetyl-uridine (**4j**) and 4″,6″-di-O-benyl-2″,3″-dideoxy-α-D-erythro-hex-2″-enopyranosyl-(1→5)-2′,3′-di-O-acetyl-uridine (**2j**)*

Compound **4j**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.29 (s, 1H), 7.62 (d, J=8.0 Hz, 1H), 5.90−5.80 (m, 3H), 5.66−5.62 (m, 1H), 5.25−5.20 (m, 2H), 5.08 (d, J=10.0 Hz, 1H), 5.04 (s, 1H), 4.22 (d, J=2.8 Hz, 1H), 4.03−3.98 (m, 2H), 3.89−3.85 (m, 2H), 3.77−3.67 (m, 2H), 1.99 (s, 3H), 1.94 (s, 3H), 1.92 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.3, 170.1, 169.6, 169.5, 163.1, 150.6, 140.4, 129.8, 127.6, 102.8, 93.7, 86.4, 81.0, 72.5, 70.9, 67.2, 67.0, 63.8, 62.6, 20.9, 20.6, 20.5, 20.4, HRMS: $C_{23}H_{28}N_2O_{13}$+Na $(M+Na)^+$ calcd 563.1489, found 563.1488.

Compound **2j**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.28 (s, 1H), 7.64 (d, J=8.0 Hz, 1H), 7.24−7.13 (m, 10H), 6.07 (d, J=10.4 Hz, 1H), 5.88−5.86 (m, 1H), 5.75−5.71 (m, 1H), 5.63 (t, J=4.0 Hz, 1H), 5.26−5.22 (m, 2H), 4.97 (s, 1H), 4.43−4.33 (m, 4H), 4.21 (d, J=2.8 Hz, 1H), 3.89 (d, J=10.0 Hz, 1H), 3.79−3.66 (m, 3H), 3.54−3.46 (m, 2H), 1.93 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.5, 163.1, 150.6, 140.4, 138.5, 138.3, 131.4, 128.4, 128.0, 127.7, 127.6, 126.0, 102.8, 93.8, 86.4, 81.0, 72.4, 70.9, 70.2, 70.0, 69.5, 69.0, 66.9, 20.5, 20.4. HRMS: $C_{33}H_{36}N_2O_{11}$+H $(M+H)^+$ calcd 637.2397, found 637.2395.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.10.097.

References and notes

1. (a) Schreiber, S. L. *Science* **2000**, *287*, 1964; (b) Spring, D. R. *Org. Biomol. Chem.* **2003**, *1*, 3867; (c) Shang, S.; Tan, D. S. *Curr. Opin. Chem. Biol.* **2005**, *9*, 1; (d) Arya, P.; Quevillon, S.; Joseph, R.; Wei, C.-Q.; Gan, Z.; Parisien, M.; Sesmilo, B.; Reddy, P. T.; Chen, Z.-X.; Durieux, P.; Laforce, D.; Campeau, L. C.; Khadem, S.; Daroszewska, M.; Barnes, M. L. *Pure Appl. Chem.* **2005**, *77*, 163.
2. (a) Kubota, H.; Lim, J.; Depew, K. M.; Schreiber, S. L. *Chem. Biol.* **2002**, *9*, 265; (b) Hotha, S.; Tripathi, A. *J. Comb. Chem.* **2005**, *7*, 968.
3. Collins, P.; Ferrier, R. *Monosaccharides: their Chemistry and their Roles in Natural Products*; Wiley: Chichester, UK, 1995.
4. Ferrier, R. J.; Prasad, N. *J. Chem. Soc. C* **1969**, 570.
5. (a) Holder, N. *Chem. Rev.* **1982**, *82*, 287; (b) Liu, Z. J.; Zhou, M.; Min, J. M.; Zhang, L. H. *Tetrahedron: Asymmetry* **1999**, *10*, 2119; (c) Brito, T. M.; Silva, L. P.; Siqueira, V. L.; Srivastava, R. M. *J. Carbohydr. Chem.* **1999**, *18*, 609.
6. Srivastava, R. M.; Oliveira, F. J. S.; Silva, L. P.; Filho, J. R. F.; Oliveira, S. P.; Lima, V. L. M. *Carbohydr. Res.* **2001**, *332*, 335.
7. Danishefsky, S. J.; Bilodeau, M. T. *Angew. Chem., Int. Ed.* **1996**, *35*, 1380.
8. (a) Fraser-Reid, B. *Acc. Chem. Res.* **1985**, *18*, 347; (b) Ferrier, R. J. *Adv. Carbohydr. Chem. Biochem.* **1969**, 199; (c) Ramnauth, J.; Poulin, O.; Rakhit, S. P.; Maddaford, S. P. *Org. Lett.* **2001**, *3*, 2013.
9. Tolstikov, A. G.; Tolstikov, G. A. *Russ. Chem. Rev.* **1993**, *62*, 579.
10. (a) Dorgan, B. J.; Jackson, R. F. W. *Synlett* **1996**, 859; (b) Chambers, D. J.; Evans, G. R.; Fairbanks, A. J. *Tetrahedron: Asymmetry* **2005**, *16*, 45.
11. (a) Seeberger, P. H.; Bilodeau, M. T.; Danishefsky, S. J. *Aldrichimica Acta* **1997**, *30*, 75; (b) Danishefsky, S. J.; Bilodeau, M. T. *Angew. Chem., Int. Ed.* **1996**, *120*, 13515.
12. Schmidt, R. R.; Angerbauer, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 783.
13. Williams, N. R.; Wander, J. D. *The Carbohydrates in Chemistry and Biochemistry*; Academic: New York, NY, 1980; p 761.
14. (a) Bracherro, M. P.; Cabrera, E. F.; Gomez, G. M.; Peredes, L. M. R. *Carbohydr. Res.* **1998**, *308*, 181; (b) Schmidt, R. R.; Angerbauer, R. *Carbohydr. Res.* **1979**, *72*, 272.
15. (a) Domon, D.; Fujiwara, K.; Ohtaniuchi, Y.; Takezawa, A.; Takeda, S.; Kawaski, H.; Murai, A.; Kawai, H.; Suzuki, T. *Tetrahedron Lett.* **2005**, *46*, 8279; (b) Reddy, B. G.; Vankar, Y. D. *Tetrahedron Lett.* **2003**, *44*, 4765; (c) Lewis, A.; Stefanuti, I.; Swain, S. A.; Smith, S. A.; Taylor, R. J. K. *Tetrahedron Lett.* **2001**, *42*, 5549; (d) Patterson, I.; Keown, L. E. *Tetrahedron Lett.* **1997**, *38*, 5727.
16. (a) Descotes, G.; Martin, J. C. *Carbohydr. Res.* **1977**, *56*, 168; (b) Klaffke, W.; Pudlo, P.; Springer, D.; Thieme, J. *Liebigs Ann. Chem.* **1991**, 509.
17. Grynkiewicz, G.; Priebe, W.; Zamojski, A. *Carbohydr. Res.* **1979**, *68*, 33.
18. (a) Masson, C.; Soto, J.; Bessodes, M. *Synlett* **2000**, 1281; (b) Tilve, R. D.; Alexander, M. V.; Khandekar, A. C.; Samant, S. D.; Kanetkar, V. R. *J. Mol. Catal. A: Chem.* **2004**, *223*, 237.
19. Yadav, J. S.; Reddy, B. V. S.; Murthy, C. V. S. R.; Kumar, G. M. *Synlett* **2000**, 1450.
20. Babu, B. S.; Balasubramanian, K. K. *Tetrahedron Lett.* **2000**, *41*, 1271.
21. (a) Shanmugasundaram, B.; Bose, A. K.; Balasubramanian, K. K. *Tetrahedron Lett.* **2002**, *43*, 6795; (b) Ronaldo, N. O.; Filho, J. R. F.; Srivastava, R. M. *Tetrahedron Lett.* **2002**, *43*, 2141.
22. Swamy, N. R.; Venkateswarlu, Y. *Synthesis* **2002**, 598.
23. Yadav, J. S.; Reddy, B. V. S.; Reddy, J. S. S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2390.
24. Yadav, J. S.; Reddy, B. V. S.; Reddy, K. B.; Satyanarayana, M. *Tetrahedron Lett.* **2002**, *43*, 7009.
25. Bettadaiah, B. K.; Srinivas, P. *Tetrahedron Lett.* **2003**, *44*, 7257.
26. Toshima, K.; Ishizuka, T.; Matsuo, G.; Nakata, M.; Konoshita, M. *J. Chem. Soc., Chem. Commun.* **1993**, 704.
27. Lopez, J. C.; Gomez, A. M.; Valverde, S.; Fraser-Reid, B. *J. Org. Chem.* **1995**, *60*, 3851.
28. Rafiee, E.; Tangestaninejad, S.; Habibi, M. H.; Mirkhani, V. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3611.
29. Koreeda, M.; Houston, T. A.; Shull, B. K.; Klemke, E.; Tuinman, R. J. *Synlett* **1995**, 90.
30. (a) Yadav, J. S.; Reddy, B. V. S.; Pandey, S. K. *New J. Chem.* **2001**, *25*, 538; (b) Pachamuthu, K.; Vankar, Y. D. *J. Org. Chem.* **2001**, *66*, 7511.
31. Agarwal, A.; Rani, S.; Vankar, Y. D. *J. Org. Chem.* **2004**, *69*, 6137.
32. (a) Banik, B. K.; Adler, D.; Nguyen, P.; Srivastava, N. *Heterocycles* **2003**, *61*, 101; (b) Naik, P. U.; Nara, S. J.; Harjani, J. R.; Salunkhe, M. M. *J. Mol. Catal. A: Chem.* **2005**, *234*, 35.
33. Hotha, S.; Tripathi, A. *Tetrahedron Lett.* **2005**, *46*, 4555.
34. Kim, H.; Men, H.; Lee, C. *J. Am. Chem. Soc.* **2004**, *126*, 1336.
35. Li, L.; Zhu, L.; Zhang, X.; Zhang, G.; Qu, G. *Can. J. Chem.* **2005**, *83*, 1120.
36. Zhang, X.; Li, L.; Zhang, G. *Green Chem.* **2003**, *5*, 646.
37. $Fe_2(SO_4)_3 \cdot xH_2O$ used in the experiments was purchased from the Beijing Chemical Factory (A.R. grade). The mole of $Fe_2(SO_4)_3 \cdot xH_2O$ is calculated based on the formula: $M_{Fe_2(SO_4)_3 \cdot xH_2O} = 0.5(W_{Fe_2(SO_4)_3 \cdot xH_2O}\mathrm{Fe(III)}\% \div 55.8)$.
38. Herscovici, J.; Montserret, R.; Antonakis, K. *Carbohydr. Res.* **1998**, *176*, 219.
39. Lesueur, C.; Nouguier, R.; Bertrand, M. P.; Hoffmann, P.; De Mesmaeker, A. *Tetrahedron* **1994**, *50*, 5369.
40. Kashyap, S.; Hotha, S. *Tetrahedron Lett.* **2006**, *47*, 2021.