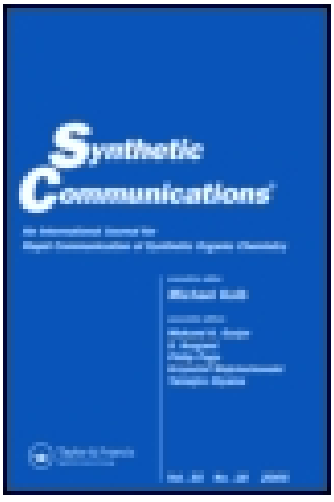

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Amberlyst 15-Catalyzed Efficient Synthesis of 2,3-Unsaturated Glycosides via Ferrier Rearrangement for Glycal

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Amberlyst 15–Catalyzed Efficient Synthesis of 2,3-Unsaturated Glycosides via Ferrier Rearrangement for Glycal

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Abstract: Amberlyst 15 serves as an inexpensive, effective, and environmentally friendly catalyst in converting 3,4,6-tri-*O*-acetyl-D-glucal (**1**) into 2,3-unsaturated *O*- and *S*-glycosides via Ferrier rearrangement in moderate to excellent yields with high α selectivity.

Keywords: Amberlyst 15, Ferrier rearrangement, glycal, glycosidation, 2,3-unsaturated glycoside

Preparation of 2,3-unsaturated glycosides has always received attention because of their synthetic versatility as potential precursors in the synthesis of complex carbohydrates, glycoconjugates, and many significant molecular, such as antibiotics and nucleosides, through subsequent elaboration of 2,3-alkene.[1,2] A conventional approach to 2,3-unsaturated glycosides involves treatment of glycals with *O*- or *S*-nucleophilic species in the presence of Lewis acids, which is popularly called the Ferrier rearrangement.[3] Numerous Lewis acids have been developed to drive the reaction, including $BF_3 \cdot Et_2O$,[4] $InCl_3$,[5] $SnCl_4$,[6] $Yb(OTf)_3$,[7] $Sc(OTf)_3$,[8] $FeCl_3$,[9] $BiCl_3$,[10] $ZnCl_2$,[11] $LiBF_4$,[12] clay montmorillionite K-10,[13] $Dy(OTf)_3$,[14] $ZrCl_4$,[15]

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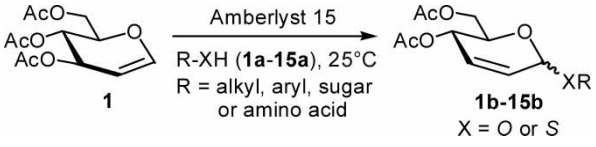
and $Pd(OAc)_2$.[16] In addition, electron-transfer catalyst $K_5CoW_{12}O_{40} \cdot 3H_2O$,[17] protic acid $HClO_4$ supported on silica gel,[18] and oxidants such as 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ)[19] and cerium(V) ammonium nitrate (CAN)[20] have also been used for the Ferrier reaction. Although some of these methods were successful for the production of 2,3-unsaturated glycosides, a number of them are practically inconvenient to use (most of Lewis acids are air sensitive); employ harsh reaction conditions (strong acidity or oxidation conditions, such as $BF_3 \cdot Et_2O$ and DDQ), and toxic or costly catalysts; and sometimes have low anomeric selectivity.

As part of our research concerning the development of a new promoter in glycosidation, we have investigated the synthesis of 2,3-unsaturated glycosides under a mild and environmentally benign process. Described herein is a heterogeneous solid acidic Amberlyst 15–catalyzed synthesis of 2,3-unsaturated *O*- and *S*-glycosides via Ferrier rearrangement starting from 3,4,6-tri-*O*-acetyl-D-glucal (**1**) in moderate to excellent yields with high selectivity possessing mild reaction conditions, an inexpensive and green catalyst (Scheme 1).

Initially, different media such as THF, CH_2Cl_2, MeCN, and PhMe were screened for the glycosidation of **1** with 1 equiv of isopropanol (**1a**) mediated by 20 wt% Amberlyst 15. The results are summarized as entries 1–4 in Table 1 and show that PhMe is the best choice of solvent with respect to the yield. Our attention was next focused on the effect of the quantity of Amberlyst 15 on this glycosidation in PhMe. It was demonstrated that the yield of product **1b** was greatly improved with a gradual enhancement of stereoselectivity through increasing the weight ratio of Amberlyst 15 to **1** (entries 4–6 in Table 1). The best result was achieved with the use of 80 wt% Amberlyst 15 affording **1b** in 95% yield and exclusively α-form.

Based on the optimal conditions, the glycosidations of **1** with other *O*-nucleophiles were systematically studied to extend the synthetic application of this reaction. Primary, secondary, allylic, propargyl alcohols, and cholesterol reacted with **1** with equal ease to produce the corresponding 2,3-unsaturated *O*-glycosides in excellent yields with high α-stereoselectivity (entries 1–7, Table 2). Glycosyl acceptors, such as methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**8a**, entry 8, Table 2), methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**9a**, entry 9, Table 2), 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**10a**, entry 10, Table 2), and allyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**11a**, entry 11, Table 2) were also employed to react with **1**



Scheme 1.

Table 1. Screening of solvent and quantity of Amberlyst 15 for the glycosidation of **1** with isopropanol (**1a**)[a]

Entry	Solvent	Wt% of Amberlyst 15 for **1**	Isolated yield of **1b** (%)	α/β[b]
1	THF	20	5	—
2	CH_2Cl_2	20	20	—
3	MeCN	20	40	α
4	PhMe	20	50	8/1
5	PhMe	50	75	10/1
6	PhMe	80	95	α

[a]Reactions were performed at 25 °C with 1 equiv of **1a** for 2h.
[b]Anomeric distributions were determined by ^{1}H NMR (400 MHz) spectroscopic analysis.

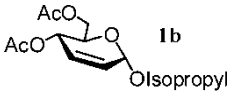
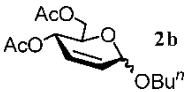
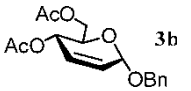
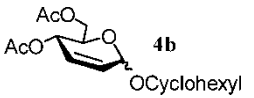
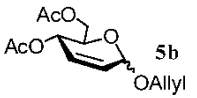
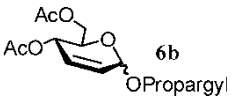
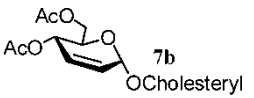
to furnish exclusively the corresponding $1 \rightarrow 3$, $1 \rightarrow 4$, and $1 \rightarrow 6$-linked α-disaccharides **8b**, **9b**, **10b**, and **11b** in 60%, 52%, 93%, and 89% yields, respectively, without cleavage of the acid-sensitive protecting groups, benzylidene and isopropylidene. The relative low yields of **8b** and **9b** were attributed reasonably to the steric hindrance of the secondary hydroxyls of **8a** and **9a**. Likewise, phenol (**12a**) was readily converted into the corresponding glycoside **12b** in 70% yield (entry 12, Table 2).

Amino acid alcohol **13a**[21] derived from threonine was also exposed to this procedure (entry 13, Table 2). The exclusive product was α-isomer **13b**, which can act as a useful glycosylated amino acid building block for the synthesis of glycopeptide. This procedure therefore provides a new access to the *O*-linked glycopeptide framework.

The versatility of the protocol was further evaluated through thioglycosidations of **1** with *p*-methylthiophenol **14a** and ethanethiol **15a**. Solvent was critical for the reactivity and stereoselectivity in these cases. For example, if run in PhMe, the glycosidation of **1** with **14a** gave 60% of **14b** as an α/β-anomeric mixture in a ratio of 1.2:1 (entry 14, Table 2). Fortunately, the stereochemical outcomes and the yields were considerably improved by the addition of 1,4-dioxane to the reaction system. As illustrated by entries 15 and 16 in Table 2, highly α-selective formations of the corresponding thioglycosides **14b** and **15b** were achieved in 89% and 90% yields, respectively, when the glycosidations were carried out in the mixed solvent of PhMe/1,4-dioxane (1/3, v/v).

In the cases where inseparable α/β mixtures of 2,3-unsaturated glycosides were obtained, the ratios of two isomers could be determined by integration of the signals in NMR spectra of the products. The α-configuration of the major product was established by the chemical shifts of the anomeric protons and coupling constants for $J_{1,2}$ and $J_{4,5}$ in the ^{1}H NMR spectra.[22] nuclear Overhauser effect (NOE) experiments were carried out for further

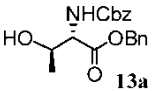
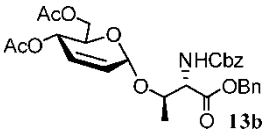
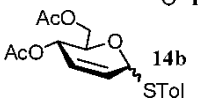
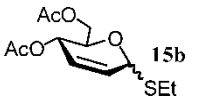
Table 2. 80 Wt% Amberlyst 15–catalyzed glycosidation of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) with alcohols and thiols[a]

Entry	Acceptor	Glycoside	Time (h)	Isolated yield (%)	α/β^b	Ref.
1	Isopropanol **1a**	 **1b**	2	95	α	[9]
2	*n*-Butanol **2a**	 **2b**	1	96	8/1	[9]
3	Benzyl alcohol **3a**	 **3b**	1.5	93	α	[9]
4	Cyclohexanol **4a**	 **4b**	1.8	95	10/1	[17]
5	Allyl alcohol **5a**	 **5b**	1.5	95	20/1	[8]
6	Propargyl alcohol **6a**	 **6b**	1.2	96	10/1	[8]
7	Cholesterol **7a**	 **7b**	2	95	α	[18]

8	**8a**	**8b**	2.6	60	α	—
9	**9a**	**9b**	2.8	52	α	[18]
10	**10a**	**10b**	3	93	α	[18]
11	**11a**	**11b**	3	89	α	—
12	Phenol **12a**	**12b**	3.5	70	α	[7]

(*continued*)

Table 2. Continued

Entry	Acceptor	Glycoside	Time (h)	Isolated yield (%)	α/β^b	Ref.
13	 **13a**	 **13b**	1	65	α	—
14	*p*-Methylthiophenol **14a**	 **14b**	1.5	60	1.2/1	[12]
15[c]	**14a**	**14b**	1.5	89	20/1	[12]
16[c]	Ethanethiol **15a**	 **15b**	1.5	90	8/1	[15]

[a]Reactions were performed at 25 °C with 1 equiv of the acceptors in PhMe, unless otherwise indicated.
[b]Anomeric distributions were determined by ^{1}H NMR (400 MHz) spectroscopic analysis.
[c]In PhMe/1,4-dioxane (1/3, v/v).

confirmation, in which considerable NOE enhancements were observed between H-1 and H-4 in all products. These data indicate that H-1 and H-4 are on the same side of the molecule and prove the α-stereochemistry.

It is noteworthy that the workup involves simple filtration, and the catalyst could be recycled after washing with acetone and air drying. The recovered Amberlyst 15 could be reused with a gradual loss of activity. For example, glycosidation of **1** with isopropanol mediated by 80 wt% recovered catalyst gave **1b** in the yields of 96% (2 h, only α-isomer) and 95% (overnight, only α-isomer) over two cycles.

In conclusion, a heterogeneous solid acid Amberlyst 15–catalyzed efficient and highly α-stereoselective Ferrier glycosidation has been developed to generate structurally diverse 2,3-unsaturated *O*- and *S*-glycosides. To the best of our knowledge, this is the first application of Amberlyst 15 to promote the Ferrier glycosidation of glycal.[23] In view of its high level of stereoselectivity combined with a simple operation, mild reaction conditions, and the utility of an inexpensive, recyclable resin, this method is convenient, economically viable, and green.

EXPERIMENTAL

Materials and Methods

3,4,6-Tri-*O*-acetyl-D-glucal (**1**) and Amberlyst 15 (dry) ion-exchange resin were purchased from Acros Chemical. All solvents used in the reactions were distilled from appropriate drying agents prior to use. Reactions were monitored by thin-layer chromatography (TLC) using silica-gel GF_{254} plates with detection by charring with 10% (v/v) H_2SO_4 in EtOH or by ultraviolet (UV) detection. Silica gel (100–200 mesh) was used for column chromatography. Optical rotations were measured with a PE-314 automatic polarimeter at $20 \pm 1^{\circ}C$ for solutions in a 1.0-dm cell. ESI-MS spectra were acquired on a BioTOF Q. Elemental analyses were obtained on a Carlo Erba 1106 instrument. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-E 200 or Varian Inova-400/54 spectrometers, with TMS as internal reference. Chemical shifts are expressed in parts per million (ppm) downfield from the internal Me_4Si absorption.

Typical Experimental Protocol

To a stirred 0.2 M solution of 3,4,6-tri-*O*-acetyl-D-glucal **1** and the acceptor (1 equiv) in anhydrous solvent (as indicated in Table 2), Amberlyst 15 (80 wt% for **1**) was added in one portion at 25 °C. The mixture was stirred for the desired time (Table 2) until the complete disappearance of the starting materials as judged by TLC. The reaction mixture was filtered, and the

resin was washed with acetone. The combined filtrate and washings were concentrated under reduced pressure. The residue was subjected to column chromatography using petroleum ether–EtOAc as the eluant to afford the corresponding products. Following the same reaction conditions, *O*- and *S*-nucleophiles gave the corresponding 2,3-unsaturated glycosides as summarized in Table 2. Glycosides **1b**–**7b**, **9b**, **10b**, **12b**, **14b**, and **15b** are known compounds, and their ^{1}H and ^{13}C NMR data matched the reported data in the cited references (Table 2). Spectral data of new compounds that are not reported are listed next.

Data

Methyl *O*-(4′,6′-di-*O*-acetyl-2′,3′-dideoxy-α-D-*erythro*-hex-2′-enopyranosyl)-(1 → 3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (8b). From **1** (54.5 mg), colorless syrup, 71.8 mg (60%); R_f 0.3 (3:1, petroleum ether–EtOAc); $[\alpha]_D^{21}$C + 60.1 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.90 (s, 3H, COCH_3), 2.10 (s, 3H, COCH_3), 3.43 (s, 3H, OCH_3), 3.75–4.00 (m, 6H, H-6a, H-6b, H-5, H-6a′, H-6b′ and H-5′), 4.34 (dd, $J_{3,4}$ 10.0, $J_{4,5}$ 4.8 Hz, 1H, H-4), 4.59 (t, $J_{2,3}$, $J_{3,4}$ 9.6 Hz, 1H, H-3), 5.00 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.20 (dd, $J_{1,2}$ 3.6, $J_{2,3}$ 10.0 Hz, 1H, H-2), 5.24 (dd, $J_{3',4'}$ 1.6, $J_{4',5'}$ 9.6 Hz, 1H, H-4′), 5.54 (s, 1H, H-1′), 5.60 (s, 1H, PhC*H*), 5.78 (d, $J_{2',3'}$ 11.6 Hz, 1H, H-2′), 5.82 (dt, $J_{2',3'}$ 10.4, $J_{3',4'}$ 2.0 Hz, 1H, H-3′), 7.34–8.14 (m, 10H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.8, 170.0 (2 × *C*OCH$_3$), 165.8 (Ph*C*O), 137.0, 133.4, 129.8, 129.7, 129.1, 128.7, 128.5, 128.3, 128.2, 127.6, 126.3, 126.0 (aromatic, C-2′ and C-3′), 101.6 (Ph*C*H), 98.0 (C-1), 94.3 (C-1′), 82.7 (C-3), 72.4 (C-2), 71.9 (C-4), 69.0 (C-6), 66.4 (C-4′), 64.7 (C-5′), 62.4 (C-5), 62.1 (C-6′), 55.4 (O*C*H$_3$), 20.7, 20.6 (2 × CO*C*H$_3$); HR ESI-MS: calcd. for $C_{31}H_{34}O_{12}$ [M + Na]+: 621.1948; found: 621.1937. Anal. calcd for $C_{31}H_{34}O_{12}$: C, 62.20; H, 5.73+; found: C, 62.39; H, 5.79.

Allyl *O*-(4′,6′-di-*O*-acetyl-2′,3′-dideoxy-α-D-*erythro*-hex-2′-enopyranosyl)-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (11b). From **1** (54.5 mg), colorless syrup, 122.7 mg (89%); R_f 0.31 (3:1, petroleum ether–EtOAc); $[\alpha]_D^{21}$ + 34.4 (*c* 18.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.99 (s, 3H, COCH_3), 2.06 (s, 3H, COCH_3), 3.53 (dd, $J_{1,2}$ 3.6, $J_{2,3}$ 9.6 Hz, 1H, H-2), 3.59 (t, $J_{2,3}$, $J_{3,4}$ 9.2 Hz, 1H, H-3), 3.71 (d, $J_{4,5}$ 10.8 Hz, 1H, H-5), 3.83 (d, $J_{3,4}$ 9.6 Hz, 1H, H-4), 3.98–4.06 (m, 5H, OCH_{2a}CH=CH_2, H-6a, H-6b, H-5′, and H-6b′), 4.13–4.20 (m, 2H, OCH_{2b}CH=CH_2 and H-6a′), 4.64 (d, *J* 10.8 Hz, 1H, PhCH_2), 4.66 (d, *J* 12.4 Hz, 1H, PhCH_2), 4.77 (d, *J* 14.4 Hz, 1H, PhCH_2), 4.80 (d, $J_{1,2}$ 4.4 Hz, 1H, H-1), 4.81 (d, *J* 12.0 Hz, 1H, PhCH_2), 4.93 (d, *J* 10.8 Hz, 1H, PhCH_2), 5.00 (d, *J* 10.8 Hz, 1H, PhCH_2), 5.10 (s, 1H, H-1′), 5.22 (d, *J* 10.0 Hz, 1 H, OCH$_2$CH=CH_{2a}), 5.29 (s, 1H, H-4′), 5.33 (d, *J* 10.8 Hz, 1H, OCH$_2$CH=CH_{2b}), 5.85 (s, 2H,

H-2′ and H-3′), 5.93 (m, 1H, $OCH_2CH{=}CH_2$), 7.26–7.36 (m, 15H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.6, 170.2 (2 × $COCH_3$), 138.7, 138.3, 138.1, 128.9, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4 (aromatic, C-2′ and C-3′), 133.7 ($OCH_2CH{=}CH_2$), 118.2 ($OCH_2CH{=}CH_2$), 95.5 (C-1′), 94.7 (C-1), 82.0, 80.0, 77.9 (3 × $PhCH_2$), 75.7 (C-3), 74.9 (C-2), 73.1 ($OCH_2CH{=}CH_2$), 70.2 (C-5), 68.2 (C-4), 67.0 (C-6), 66.9 (C-5′), 65.1 (C-4′), 62.7 (C-6′), 20.9, 20.7 (2 × $COCH_3$); HR ESI-MS: calcd. for $C_{37}H_{41}O_{10}$ $[M + Na]^+$: 668.2597; found: 668.2590. Anal. calcd. for $C_{37}H_{41}O_{10}$: C, 68.82; H, 6.40; found: C, 69.02; H, 6.51.

Benzyl *N*-(benzyloxycarbonyl)threonine 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (13b). From **1** (54.5 mg), colorless syrup, 72.2 mg (65%); R_f 0.25 (3:1, petroleum ether–EtOAc); $[\alpha]_D^{21}$ − 1.7 (*c* 12.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.33 (d, $J_{\beta,\gamma}$ 6.4 Hz, 3H, CH_3-γ), 2.04 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 3.98 (m, 1H, H-5), 4.13 (d, $J_{5,6}$ 4.0 Hz, 2H, H-6a, H-6b), 4.35 (m, 1H, H-β), 4.41 (dd, $J_{\alpha,\beta}$ 9.6, $J_{\alpha,NH}$ 2.0 Hz, 1H, H-α), 4.69 (s, 1H, N*H*), 5.12 (d, *J* 12.0 Hz, 1H, $PhCH_2$), 5.13 (s, 2H, $PhCH_2$), 5.18 (dd, $J_{3,4}$ 1.2, $J_{4,5}$ 9.2 Hz, 1H, H-4), 5.22 (d, $J_{1,2}$ 2.8 Hz, 1H, H-1), 5.24 (d, *J* 12.0 Hz, 1H, $PhCH_2$), 5.47 (d, $J_{2,3}$ 10.0 Hz, 1H, H-3), 5.72 (d, $J_{2,3}$ 10.4 Hz, 1H, H-2), 7.30–7.37 (m, 15H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.6, 170.2 (2 × $COCH_3$), 170.3 (*C*OOBn), 156.6 (NH*C*OOBn), 136.1, 135.1, 128.8, 128.6, 128.5, 128.1, 128.0, 127.2 (aromatic, C-2 and C-3), 95.6 (C-1), 76.3, 67.3 (2 × $PhCH_2$), 67.2 (C-β), 66.9 (C-5), 65.1 (C-4), 63.0 (C-6), 56.9 (C-α), 20.9, 20.7 (2 × $COCH_3$), 18.8 (CH_3-γ); HR ESI-MS: calcd. for $C_{29}H_{33}NO_{10}$ $[M + Na]^+$: 578.2002; found, 578.1988. Anal. calcd. for $C_{29}H_{33}NO_{10}$: C, 62.69; H, 5.99; N, 2.52; found: C, 62.88; H, 6.07; N, 2.65.

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