The use of ultrastable Y zeolites in the Ferrier rearrangement of acetylated and benzylated glycals

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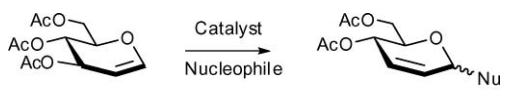
The Ferrier rearrangement of a selection of protected glycals was successfully performed using a commercially available H-USY zeolite CBV-720 as catalyst, selected after screening a range of similar catalysts. By incorporating either alcohols, thiophenol, trimethylsilyl azide or allyltrimethylsilane in the reaction it was shown that a range of *O*-, *S*-, *N*- and *C*-glycosides could be formed. With benzylated glucal and galactal in particular, use of the CBV-720 catalyst led to significantly higher yields of the 2,3-dehydroglycosides than previously reported.

Introduction

The Ferrier rearrangement[1] is well documented and provides easy access to 2,3-unsaturated glycals or pseudoglycals (Scheme 1). These are versatile intermediates in the total synthesis of several biologically active natural products, including antibiotics, antiviral and antitumor agents.[2] Following the early studies on the Ferrier rearrangement using simple Lewis acids such as BF_3, considerable attention has been given to investigating alternative catalysts for this reaction. These are mainly homogeneous catalysts and include $InCl_3$,[3] $ZrCl_4$,[4] $AuCl_3$,[5] $TiCl_4$,[6] $NbCl_5$,[7] $ZnCl_2$,[8] $FeCl_3$,[9] $CeCl_3{\cdot}7H_2O$,[10] $BiCl_3$,[11] $InBr_3$[12] and $LiBF_4$;[13] metal triflates like: $Dy(OTf)_3$,[14] $Er(OTf)_3$,[15] $In(OTf)_3$,[16] $Sc(OTf)_3$[17] and $Yb(OTf)_3$;[18] TMSOTf,[19] $BF_3{\cdot}Et_2O$,[20] ceric ammonium nitrate (CAN),[21] I_2 (NIS),[22] ZnR,[23] InR,[24] $B(C_6F_5)_3$,[25] $Pd(OAc)_2$,[26] POM (potassium dodecatungstocobaltate trihydrate, $K_5CoW_{12}O_{44}{\cdot}3H_2O$),[27] $FeSO_4.xH_2O$,[28] $Fe(NO_3)_3{\cdot}9H_2O$,[29] $Bi(NO_3)_3{\cdot}5H_2O$,[29,30] $La(NO_3)_2$,[31] reduced Ni with Grignard reagent[32] and DDQ.[33] A few effective heterogeneous catalysts have been developed, including Montmorillonite K-10,[34] silica gel,[35] $HClO_4$–SiO_2,[36] phosphomolybdic acid (PMA) on SiO_2,[37] Amberlyst-15,[38] and HY.[39] However, there are a number of general limitations associated with many of these catalysts. Firstly, the homogeneous catalysts have the problem of separation from the final products, an issue which has both environmental and economical consequences. In addition other limitations include the need for high temperatures, strong acidity (Mont. K-10, $TiCl_4$, $BF_3(OEt)_2$), strong oxidizing conditions (DDQ), incompatibility with acid-sensitive protecting groups, long reaction times, unsatisfactory yields, low stereoselectivity, the requirement for an excess of promoter ($BF_3(OEt)_2$), high cost (triflates), risk of explosion, requirements for large amounts of catalyst, limited reusability of the catalyst, and activity restricted to certain protecting groups on the substrates or certain types of nucleophile. There is therefore as yet no truly general methodology for the Ferrier rearrangement.



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Scheme 1 Ferrier rearrangement with acetylated glucal (**1**).

With the current movement towards more economically and environmentally sustainable processes the microporous and mesoporous materials like zeolites are emerging as promising catalysts in chemical processes relevant to the fine chemicals and pharmaceutical industry,[40] and their application as catalysts in reactions of carbohydrates has been recently reviewed.[41] Their low cost and easy removal from reaction mixtures present significant advantages. These considerations, and our own interest in developing alternative catalytic processes for classic reactions in carbohydrate chemistry,[42] have led to this investigation of a selection of commercially available zeolitic materials, including of the ultrastable Y zeolites (H-USY), as catalysts for the Ferrier rearrangement. A selection of acetylated or benzylated glycals were combined with a variety of nucleophiles in the presence of the catalyst, in order to evaluate the scope of this methodology for preparation of 2,3-unsaturated *C*-, *N*-, *O*- and *S*-glycosides. as summarized in Scheme 2.

R^1 = OAc or OBn
R^2 = H, OAc or OBn
R^3 = OAc or OBn, H
R^4 = H, OCH_2OAc or OCH_2OBn

Scheme 2 General scheme for the Ferrier rearrangement with zeolites.

Results and discussion

Screening of zeolites

A selection of acidic solids, ranging from more Brønsted-acidic to more Lewis-acidic materials was evaluated for catalytic

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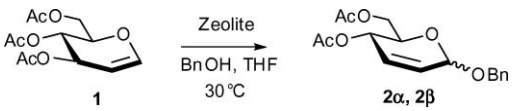
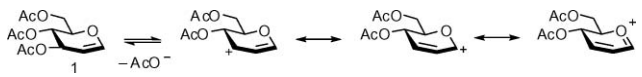
activity in the screening reaction of acetylated glucal with benzyl alcohol at 30 °C in THF (Scheme 3).



Scheme 3 Overview of the screening reaction.

Acetylated glucal (**1**) has been recognized as one of the preferred starting materials for this reaction due to the acetate being a good leaving group, with the reaction understood to proceed *via* the formation of a cyclic allylic oxocarbenium ion intermediate (Scheme 4).[1,20c]



Scheme 4 Formation of allylic oxocarbenium ion from acetylated glucal in the Ferrier rearrangement.

In addition, it is known that *O*-glycosides are more readily formed in this reaction than other glycosides, and the adequate nucleophilicity of benzyl alcohol and the ease with which it can be subsequently removed if desired, suggested this as a good partner in the initial screening. The results of the screening of catalysts are summarized in Table 1.

Some zeolites with predominantly Brønsted acidity (H-Beta, H-BEA-30, Mordenites) and the SAPO-5 material show no or very low conversion for this reaction. New materials like the Metal Organic Frameworks (MOFs) with complex acidity characteristics[43] also showed no activity. In contrast, the range of H-USY zeolites (CBV-series) from CBV-712 to CBV-780 gave full conversion in acceptable reaction times, combined with high selectivities and stereoselectivities which are comparable to those reported for other catalysts. A clear exception was observed for the H-USY zeolite CBV-600 which only showed moderate conversion over a long reaction time.

The major difference between the H-USY zeolites and the proton-containing zeolites (BEA and Mordenites) is the presence of pores of mesoporous dimensions in the former as opposed to microporous dimensions in the latter. Zeolites in the CBV series arise from H-USY zeolites that have been treated with steam and leached with mineral acid. Starting from the mother Y zeolite (CBV-300), CBV-600 is obtained by steam treatment at 600 °C. Mild acid leaching of CBV-600 affords CBV-712. CBV-720, CBV-760 and CBV-780 are obtained by a second steam treatment at higher temperatures and leaching with mineral acids. The combination of leaching and steam treatment results in materials with disrupted crystal morphologies, with more cracks and voids (mesoporosity) and a progressively higher degree of dealumination with higher number in the series (Table 1).[44] This may account for the activity of these zeolites in the reaction in question, since the relatively large pores would allow for diffusion of the relatively large glycals and reaction products to and from active sites.

Table 1 Ferrier rearrangement of acetylated glucal with benzyl alcohol in the presence of different zeolites[a]

Catalyst	SiO_2/Al_2O_3	*t*/h	Conv. (%)	Sel. (%)	α : β
H-USY CBV-600	5.2	48	30	—	—
H-USY CBV-712	12	1	100	97	6 : 1
H-USY CBV-720	30	0.5	100	97	7 : 1
H-USY CBV-760	60	1	100	97	6 : 1
H-USY CBV-780	80	1	100	97	7 : 1
H-Beta (CP811 BC-25)	25	120	—	—	—
H-BEA 30	30	48	5	—	—
Mordenite 5.9	5.9	120	—	—	—
Mordenite 11	11	120	—	—	—
$Cu_3(BTC)_2$ (MOF)	—	150	—	—	—
SAPO-5	0.1	24	—	—	—

[a] Conditions: dry zeolite (90 wt%, 0.0612 g), THF (5 ml), acetylated glucal (0.25 mmol, 0.068 g) and BnOH (36.2 µl, 1.4 eq.). Reaction progress was monitored by TLC and reactions continued until starting glycal had been consumed, or no further change in reaction progress was evident. Conversions, selectivities and α : β ratios are determined by integration of selected signals in the ^{1}H NMR spectra of product mixtures.

Table 2 Evaluation of initial activity of CBV series zeolites for the Ferrier rearrangement

	Conv. (%)		
Zeolite	10 min[a]	10 min[b]	20 min[b]
CBV-600	—	—	<1
CBV-712	10	62	76
CBV-720	14	94	100
CBV-760	7	—	—
CBV-780	6	85	90

[a] Conditions: dry zeolite (22.5 wt%, 0.0612 g), THF (5 ml), acetylated glucal (1 mmol, 0.272 g) and BnOH (144.8 µl, 1.4 eq.). [b] Conditions: dry zeolite (90 wt%, 0.0612 g), THF (5 ml), acetylated glucal (0.25 mmol, 0.068 g) and BnOH (36.2 µl, 1.4 eq.). The zeolite was removed by filtration after the indicated time, and solvent and benzyl alcohol removed by distillation under vacuum. Conversions were determined by comparison of integrals of selected signals in the ^{1}H NMR spectra of the product mixtures.

The results shown in Table 1 compare reactions at full completion and hence only reflect the overall activity of the materials. Additional tests were therefore run with the H-USY CBV series in order to investigate the difference in initial activity (Table 2). In a first set of reactions, with a protocol similar to that of the screening reaction, the catalyst was removed by filtration after 20 min and conversions could be assessed from ^{1}H-NMR spectra of the recovered product mixtures. CBV-720 and CBV-780 showed the highest activity, as determined by % conversion, but since conversions were still well over 50%, tests were repeated with the catalyst being removed by filtration after just 10 min. CBV-720 and CBV-780 again emerged as the most active zeolites. In the last set of reactions the zeolite was again removed after 10 min but four times as much glucal was used (*i.e.* 22.5 wt% of catalyst) and CBV-720 showed the highest initial activity.

Zeolite CBV-720 with the highest initial activity and highest overall activity was selected for further investigation of optimum reaction parameters required for the Ferrier rearrangement.

Optimization of reaction conditions for CBV-720

In the first instance the effect of catalyst pre-treatment was examined. Samples of CBV-720 zeolite were heated to 400 °C and then either used directly in the reaction, without exposure to air, or allowed to cool down in ambient air. With the former,

Table 3 Results obtained for the CBV-720-catalysed Ferrier rearrangement of acetylated glucal with benzyl alcohol in different solvents[a]

Solvent	*t*/h	Conv. (%)	Sel. (%)	α : β	Colour of catalyst
CH_2Cl_2	2	100	99	7 : 1	Black
CH_3CN	1	100	99	5 : 1	Grey
THF	0.33	100	97	7 : 1	Light pink
DMF	48	—	—	—	White
EtOAc	0.33	100	99	7.5 : 1	Light grey
Et_2O	6[b]	100	99	7 : 1	White
Acetone	2.5	100	50	7 : 1	White
1,4-Dioxane	0.33	100	99	7 : 1	Orange
Nitromethane	72	80	60	5 : 1	Dark green

[a] Conditions: dry H-USY CBV-720 (90 wt%, 0.0612 g), solvent (5 ml), acetylated glucal (0.25 mmol, 0.068 g) and BnOH (36.2 μl, 1.4 eq.). Reaction progress was monitored by TLC. Conversions, selectivities and α : β ratios were determined by comparison of integrals of selected signals in the ^{1}H NMR spectra of the product mixtures. [b] TLC showed an estimated 30% conversion after 1.5 h; reaction was complete after 20 h, but all solvent had evaporated by then and reaction time was estimated at 6 h.

dry zeolite reaction was complete in only about 20 min, whereas with the latter the reaction required 36 h. It was thus clear that drying of the zeolite prior to reaction was essential.

The effect of substrate concentration and catalyst loading was then investigated. In the screening reactions described above, 90 wt% of zeolite to substrate was used. In a further experiment the concentration of glucal was doubled (0.1 M glucal) resulting in the load of CBV-720 halving to 45 wt%. In the second reaction the quantity of glycal was doubled again and the volume of solvent halved (0.4 M glucal) resulting in a catalyst load of 22.5 wt% zeolite. Full conversion was obtained after 1 h and 2.5 h respectively, as opposed to 20 min in the initial experiment. Selectivities and stereoselectivities were not affected. These results demonstrate that there is no significant deactivation of the catalyst upon increasing the concentration of the glycal, and that the zeolite can consequently be used in fairly small amounts, However, the rate of the reaction is significantly lowered by reducing the catalyst loading, and further reactions were therefore carried out at 90 wt% of catalyst to minimize reaction times.

Attention was then turned to the effect of solvent, bearing in mind the need to avoid limiting diffusion in zeolite-catalysed reactions, while also optimizing product selectivities. A range of solvents with different polarities was tested (Table 3), using the colour developed by the zeolite in the reaction as a qualitative measure of pore blocking or deactivation, a darker colour indicating a larger build-up of carbon deposits which could hamper recycling.

From the results shown in Table 3 it was evident that dichloromethane, acetonitrile, DMF, diethyl ether and nitromethane were unsuitable as solvents due to the long reaction times, deactivation of the zeolite or a combination of both. Acetone gave good conversions but poor selectivities towards the Ferrier rearrangement products, even if these were obtained with reasonable stereoselectivity, 1,4-dioxane, EtOAc and THF gave comparable reaction times, conversions and product selectivities, with THF showing the least tendency to cause discolouration and therefore deactivation of the zeolite. The effectiveness of zeolite CBV-720 in THF was further demonstrated by establishing that after 3 cycles of recovery and re-calcining of catalyst only minor lowering of the %yield of 2,3-unsaturated glycosides (to 93%) was observed. THF therefore appeared to be the optimal solvent for the reaction under the conditions applied.

Ferrier rearrangement with CBV-720 and various glycals

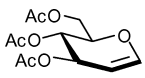
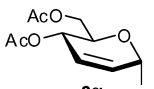
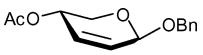
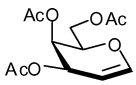
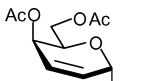
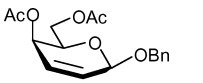
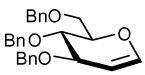
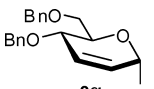
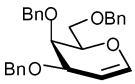
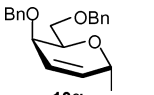
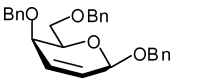
Using the optimum reaction conditions determined as described, the Ferrier rearrangement was then performed on a range of glycals varying in their relative stereochemistries (glucal, galactal, xylal) and protecting groups (acetyl, benzyl), in order to gain insight into stereochemical and stereo-electronic factors affecting reactivity in presence of the CBV-720 zeolite. An overview of the results is given in Table 4.

It is clear from our data that compounds carrying acetyl protecting groups (entries 1, 2 and 3) were much more reactive and gave significantly better yields than their benzyl-protected counterparts (entries 4 and 5). This is presumably due to the acetyl group being a better leaving group in the allylic rearrangement. With regard to the stereochemistry of the substrate, it is evident that glucal and xylal (entries 1 and 2) have similar reactivity which is significantly greater than that of galactal (entry 1 *vs.* entry 3 and entry 4 *vs.* entry 5). This observation is consistent with earlier findings.[19,34c]

The stereochemistry of the products of the Ferrier rearrangement is generally dominated by the anomeric effect resulting in the preferred formation of α-products. The results in Table 4 show however that the orientation of ring substituents and the nature of the protecting groups play important roles as well. For example, acetylated glucal (entry 1) yields predominantly the α-glycoside while acetylated xylal (entry 2) gives the β-glycoside as the major product. This suggests an important role for the substituent at C-5, possibly by restricting the conformational flexibility of the ring. The role of the protecting group on the hydroxymethyl group attached to C-5 can be illustrated by comparing results for the acetylated glucal (entry 1) with the benzylated glucal (entry 4), with the former giving a poorer selectivity towards α-glycoside than the latter (6 : 1 *vs.* 10 : 1). This could be attributed to the greater steric influence of the bulky benzyl group in shielding the β-face of the substrate. The influence of the C-4 substituent is seen when glucal derivatives (entries 1 and 4) are compared with galactal derivatives (entries 3 and 5). For both acetyl- and benzyl-protected substrates the stereoselectivity of the reaction is lower for the galactals. These results are consistent with previous observations, and the unpredictability of galactal reactivity in the Ferrier reaction has been noted.[19,36b] An exceptionally high stereoselectivity (19 : 1) using phosphomolybdic acid supported on silica gel as catalytic system[37] has been reported, but in our hands afforded an α : β ratio of only 10 : 1.

A significant advantage of zeolite CBV-720 is in the superior reactivity of benzylated glycals (entries 4 and 5). Relatively few reports have appeared with data on Ferrier rearrangements of benzylated glycals,[3a,21a,21c,39] most of them recording disappointing yields, whereas the use of H-USY CBV-720 zeolite affords yields of up to 80% in reasonable reaction times and with good stereoselectivities.

Table 4 Results of Ferrier rearrangement of various glycals in the presence of H-USY zeolite CBV-720[a]

Entry	Substrate	Nucleophile	*t*/h	Products	Yield (%)	α : β
1	 **1**	BnOH	0.33	 **2α**  **2β**	97	7 : 1
2	 **3**	BnOH	0.33	 **4α**  **4β**	90	1 : 2
3	 **5**	BnOH	1	 **6α**  **6β**	90	3 : 1
4	 **7**	BnOH	6	 **8α**  **8β**	80	10 : 1
5	 **9**	BnOH	12	 **10α**  **10β**	80	7 : 1

[a] Conditions: dry H-USY CBV-720 (90 wt%), glycal (0.25 mmol), BnOH (36.2 μl, 1.4 eq.), THF (5 ml), 30 °C. Reaction progress was monitored by TLC. Yield and α : β ratios were determined by comparison of integrals of selected signals in the ^{1}H NMR spectra of the product mixtures

Ferrier rearrangement with different nucleophiles

The Ferrier rearrangement was also tested with a range of nucleophiles other than benzyl alcohol in order to evaluate the scope for formation of other glycosides. Tri-*O*-acetyl-D-glucal (**1**) was therefore treated with 4-penten-1-ol, thiophenol, allylamine, benzylamine, trimethylsilyl azide and allyltrimethylsilane in the presence of CBV-720 under the standard conditions (Table 5, entries 6–11). Furthermore tri-*O*-benzyl-D-glucal (**7**) was tested with tetradecanol and thiophenol under similar conditions (Table 5, entries 12 and 13). The results for **1** show the successful formation of an additional *O*-glycoside as well as examples of *S*-, and *C*-glycosides, with the attempted preparation of *N*-glycosides being unsuccessful. The reaction times and yields were favourable, and stereoselectivities modest in the *S*-, and *C*-glycosides. The reaction with TMS-azide gave satisfactory conversion and yield but produced an approximately 1 : 1 mixture of the C-3 and the C-1 adducts (**13α,β** and **14α,β**). This result is analogous to that reported by Kawabata *et al.*[18b] who could only overcome this by adding a substituent on the C-2 position, and has been explained as being a consequence of preference of the soft azide nucleophile for attack at the softer C-3 electrophilic centre.[45] As found with benzyl alcohol as nucleophile, good results were obtained with alternative nucleophiles reacting with tri-*O*-benzyl-D-glucal. While the less the sterically demanding tetradecanol gives a lower stereoselectivity (compare entries 4 and 12), the use of thiophenol as a nucleophile afforded phenylthioglucosides **17α,β** in an excellent α : β ratio of 10 : 1.

Conclusions

The Ferrier rearrangement has been successfully performed with a H-USY zeolite CBV-720 as catalyst with a selection of glycals, and nucleophiles to provide efficient access to a range of 2,3-unsaturated glycosides. The best results were achieved with acetylated and benzylated glucals with alcoholic nucleophiles, where conversions and selectivities were similar to the best reported in the literature. The most notable results are those with benzylated glucal and galactal, for which significantly higher yields were achieved than previously described. These results show the potential for the use of H-USY as a general catalyst for the Ferrier rearrangement, and extend the scope of these solid catalysts in organic chemistry in general. The results of this study indicate that the ideal catalyst for the Ferrier rearrangement requires an optimal balance of the number and strength of Brønsted acid sites combined with good accessibility of these sites, as reflected by their micro- and mesoporosity. Techniques such as solid state ^{29}Si and ^{27}Al NMR and XPS are being employed in an ongoing attempt to rationalize these findings.[44b]

Experimental

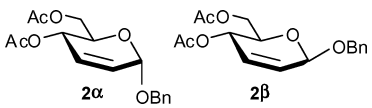
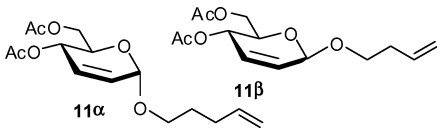
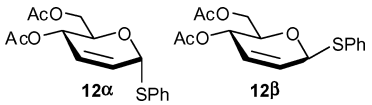
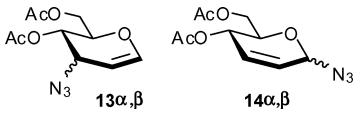
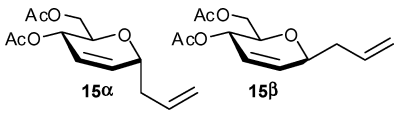
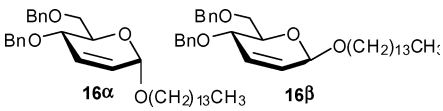
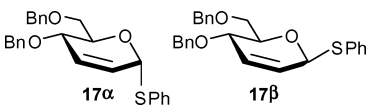
General

Commercially obtained compounds were used as received. Solvents used were AR grade or dried according to common procedures. Reaction progress was monitored by TLC. Conversion, selectivities and α : β ratios were determined by integration of selected signals from the ^{1}H spectra. NMR spectra were recorded on a Bruker AMX 300 or a Varian Mercury 300 (300 MHz) and a Varian Unity 400 (400 MHz).

Substrates

Acetylated glucal was commercially obtained. Benzylated glucal, acetylated and benzylated galactal and acetylated xylal were synthesized according to literature procedures.

Table 5 Results of the Ferrier rearrangement of acetylated glucal (**1**) and benzylated glucal (**7**) with various nucleophiles in the presence of H-USY zeolite CBV-720[a]

Entry	Glucal	Nucleophile	*t*/h	Products	Yield (%)	α : β
1	**1**	Benzyl alcohol	0.33	 **2α** **2β**	97	7 : 1
6	**1**	4-Penten-1-ol	0.5	 **11α** **11β**	95	10 : 1
7	**1**	Thiophenol	0.75	 **12α** **12β**	90	5 : 3
8	**1**	AzidoTMS	3	 **13α,β** **14α,β**	80 (**13** + **14**)	**13** : **14** = 1 : 1 **13α** : **13β** = 3 : 2 **14α** : **14β** = 7 : 2
9	**1**	Allyl TMS	1	 **15α** **15β**	70	2 : 1
10	**1**	Benzylamine	48	—[b]	—	—
11	**1**	Allylamine	24	—[b]	—	—
12	**7**	$CH_3(CH_2)_{13}OH$	7	 **16α** **16β**	75	5 : 1
13	**7**	Thiophenol	6	 **17α** **17β**	72	10 : 1

[a] Conditions: dry H-USY CBV-720 (90 wt%, 0.0612 g), **1** (0.25 mmol, 0.068 g), nucleophile (1.4 eq.), THF (5 ml), 30 °C. Reaction progress was monitored by TLC. Yield and α : β ratios were determined by comparison of integrals of selected signals in the ^{1}H NMR spectra of the product mixtures. [b] No products detected.

Catalysts

The CBV zeolites (Zeolyst), H-beta CP811-BC25 (Zeolyst), H-Beta BEA-30 zeolite (SüdChemie) and Mordenites were commercially obtained. SAPO-5[46] and $Cu(BTC)_3$[43] were prepared according to previously reported methods. All materials except $Cu_2(BTC)_3$ were dried for 6 h at 400 °C (heating rate 1 °C min^{-1}) prior to reaction. $Cu_2(BTC)_3$ was dried at 110 °C. None of the materials were allowed to fully cool down before use.

Reaction protocols

Standard reactions. Tri-*O*-acetyl-D-glucal with benzyl alcohol: dry catalyst (61.2 mg) was weighed into a reaction vessel and solvent (5 ml) was immediately added. Tri-*O*-acetyl-D-glucal (68 mg, 0.25 mmol) was added, followed by benzyl alcohol (36.2 μl, 1.4 eq.). The reaction vessel was closed and stirred at 30 °C. On completion of the reaction, as judged by TLC, the reaction mixture was filtered to remove zeolite and the filtrate was taken up in DCM, then washed with 1 M NaOH (2 ×) and H_2O (1 ×). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The identity of products and the ratio of stereoisomers was determined from key signals in the ^{1}H and ^{13}C NMR spectra, with the aid of COSY, HSQC and DEPT analysis.

Reactions with recycled catalyst

Reactions were performed with acetylated glucal (**1**), BnOH and CBV-720 in THF following the same protocol as described above. Reaction mixtures were stirred for 2.5 h, then filtered to recover the zeolite, which was then heated at 10 °C min^{-1} to

400 °C in an oven and left overnight at this temperature prior to use in the next experiment. A sequence of 3 experiments was performed in this way, giving products **2α,β** in yields of 95%, 93% and 93%, respectively.

Other glycals and nucleophiles

An analogous protocol to that described above was applied, using glycal (0.25 mmol), catalyst (90% of mass of glycal) and nucleophile (0.35 mmol, 1.4 equivalents). For benzylated glucal the workup consist of washing with H_2O (3 ×), but not with NaOH.

Reactions with higher concentration of glycal

45 wt%: analogous protocol as above with dry zeolite CBV-720 (61.2 mg), THF (5 ml), tri-*O*-acetyl-D-glucal (136 mg, 0.5 mmol) and benzyl alcohol (72.4 µl).
22.5 wt%: analogous protocol as above with: dry zeolite CBV-720 (61.2 mg), THF (2.5 ml), tri-*O*-acetyl-D-glucal (272 mg, 1 mmol) and benzyl alcohol (144.8 µl).

NMR data

Product numbering refers to entries in Table 4 and 5; only detected signals are reported.

Benzyl-4,6-di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (1)[14,29,36c]

α: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, aromatic), 5.81 (dd, J = 10.38 and 0.95 Hz, 1H, H-3), 5.77 (ddd, J = 10.22, 2.48 and 1.76 Hz, 1H, H-2), 5.25 (ddd, J = 9.33, 2.90 and 1.45 Hz, 1H, H-4), 5.05 (d, J = 1.77 Hz, 1H, H-1), 4.72 (d, J = 11.71 Hz, 1H, OCH_2Ph), 4.52 (d, J = 11.71 Hz, 1H, OCH_2Ph), 4.19–4.13 (m, 1H, H-6), 4.10–4.01 (m, 2H, H-5 and H-6′), 2.01 and 1.99 (s, 2×3H, CH_3-acetyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.2 (3 × C=O), 137.6 (aromatic), 129.2 (C-3), 128.4, 128.0, 127.8, 127.7 (aromatic), 126.9 (C-2), 93.6 (C-1), 70.2 (*C*H_2Ph), 67.1 (C-5), 65.3 (C-4), 62.9 (C-6), 20.9 and 20.7 (2 × OCO*C*H_3).

β: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92–5.89 (m, 2H, H-2 and H-3), 5.14–5.11 (m, 2H, H-1 and H-4), 4.80 (d, J = 11.79 Hz, 1H, OCH_2Ph), 4.54 (d, J = 11.85 Hz, 1H, OCH_2Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.4 (C-3), 126.0 (C-2), 93.8 (C-1), 72.8 (C-5), 69.4 (*C*H_2Ph), 64.3 (C-4), 63.4 (C-6).

Benzyl-D-4-*O*-acetyl-2,3-dideoxypent-2-eno*glycero*pyranoside (xylal) (2)[47]

α: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4–7.25 (m, 5H, aromatic), 6.12–5.85 (m, 2H, H-2 and H-3), 5.35–5.25 (m, 1H, H-4), 5.04 (br s, 1H, H-1), 4.82 (d, J = 11.71 Hz, 1H, OCH_2Ph), 4.58 d, J = 11.71 Hz, 1H, OCH_2Ph), 4.00–3.80 (m, 2H, H-5 and H-5′), 2.07 (s, 3H, CH_3-acetyl); ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.0 (C-3), 126.9 (C-2), 93.3 (C-1), 69.6 (*C*H_2Ph), 65.0 (C-4), 60.0 (C-5), 21.0 (OCO*C*H_3).

β: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4–7.25 (m, 5H, aromatic), 6.12–5.85 (m, 2H, H-2 and H-3), 5.10 (d, J = 2.33 Hz, 1H, H-1), 4.98–4.92 (m, 1H, H-4), 4.79 (d, J = 11.83 Hz, 1H, OCH_2Ph), 4.59 d, J = 11.67 Hz, 1H, OCH_2Ph), 4.21 (dd, J = 12.98 and 2.78 Hz, 1H, H-5′), 3.86 (d, J = 13.12 Hz, 1H, H-5′), 2.09 (s, 3H, CH_3-acetyl); ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.8 (C-3), 125.1 (C-2), 92.0 (C-1), 70.6 (*C*H_2Ph), 63.3 (C-4), 61.3 (C-5), 21.1 (OCO*C*H_3).

Benzyl-4,6-di-*O*-acetyl-2,3-dideoxy-D-*threo*-hex-2-enopyranoside (galacatal) (3)

α: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4–7.28 (m, 5H, aromatic), 6.3–5.6 (m, 2H, H-2 and H-3), 5.39–5.29 (m, 1H, H-4), 5.10 (d, J = 2.7 Hz, 1H, H-1), 4.69 (d, J = 11.8 Hz, 1H, OCH_2Ph), 4.50 (d, J = 11.8 Hz, 1H, OCH_2Ph), 4.30–3.90 (m, 3H, H-5, H-6 and H-6′), 2.14 and 2.06 (s, 2 × 3H, CH_3-acetyl).

β: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4–7.28 (m, 5H, aromatic), 6.3–5.6 (m, 2H, H-2 and H-3), 5.39–5.29 (m, 1H, H-4), 5.17 (d, J = 2.6 Hz, 1H, H-1), 4.82 (d, J = 11.52 Hz, 1H, OCH_2Ph), 4.59 (d, J = 11.56 Hz, 1H, OCH_2Ph), 4.30–3.90 (m, 3H, H-5, H-6 and H-6′), 2.09 and 2.08 (s, 2 × 3H, CH_3-acetyl).

1,4,6-Tri-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (4)[20b,26a]

α: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4–7.2 (m, 15H, aromatic), 6.09 (d, J = 10.28 Hz, 1H, H-2), 5.79 (dt, J = 10.16 Hz, 2.25 Hz, 2.5 Hz and 2.16 Hz, 1H, H-3), 5.13 (br s, 1H, H-1), 4.82–4.40 (m, 6H, 3 × OCH_2Ph), 4.19 (d, J = 9.41 Hz, 1H), 4.00 (d, J = 10.04 Hz, 1H), 3.73 (dd, J = 10.66 and 3.84 Hz, 1H), 3.63 (dd, J = 10.56 and 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2–137.9 and 128.5–127.5 (aromatic), 130.8, 126.5 (C-2 and C-3), 93.9 (C-1), 73.4, 71.0, 70.0 (3 × O*C*H_2Ph), 70.4, 69.3 (C-4 and C-5), 68.8 (C-6).

β: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.07 (d, 1H, H-2), 5.88 (dt, J = 10.03 and 0.86 Hz, 1H, H-3), 5.21 (br s, 1H, H-1).

1,4,6-Tri-*O*-benzyl-2,3-dideoxy-D-*threo*-hex-2-enopyranoside (galacatal) (5)[21a]

α: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4–7.2 (m, 15H, aromatic), 6.12 (dd, J = 10.14 and 5.11 Hz, 1H, H-3), 5.99 (dd, J = 10.09 and 2.93 Hz, 1H, H-2), 5.16 (d, J = 2.77 Hz, 1H, H-1), 4.70–4.40 (m, 6H, OCH_2Ph), 4.00–3.60 (m, 4H, H-4, H-5, H-6 and H-6′).

β: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.20 (dd, 1H, H-3), 6.00 (dd, 1H, H-2), 5.21 (dd, 1H, H-1).

Pent-4-enyl-4,6-di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (6)[20c,22]

α: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.90–5.76 (m, 3H, H-2, H-3 and O$(CH_2)_3$C*H*=CH_2), 5.31 (ddd, J = 9.63, 3.01 and 1.56 Hz, 1H, H-4), 5.03 (ddd, 1H, OC$H_2(CH_2)_2$CH=CH_2), 5.03–5.00 (m, 1H, H-1), 5.00–4.95 (dtd, 1H, OC$H_2(CH_2)_2$CH=CH_2), 4.24 (dd, J = 12.16 and 5.38 Hz, 1H, H-6), 4.21–4.14 (dd, J = 12.06 and 2.45 Hz, 1H, H-6′), 4.10 (ddd, J = 9.49, 5.43 and 2.46 Hz, 1H, H-5), 3.79 (td, J = 9.63, 6.67 and 6.67 Hz, 1H, OC$H_2(CH_2)_2$CH=CH_2), 3.52 (td, J = 9.65, 6.45 and 6.45 Hz, 1H, OC$H_2(CH_2)_2$CH=CH_2), 2.19–2.11 (m, 2H, OCH_2(CH_2)$_2$CH=CH_2), 2.09 and 2.08 (s, 2 × 3H, CH_3-acetyl), 1.76–1.67 (m, 2H, OCH_2(CH_2)$_2$CH=CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7 and 170.2 (2 × C=O),

137.9 ($O(CH_2)_3CH{=}CH_2$), 129.0 (C-2), 127.8 (C-3), 114.9 ($O(CH_2)_3CH{=}CH_2$), 94.4 (C-1), 68.2 ($OCH_2(CH_2)_2CH{=}CH_2$), 66.9 (C-5), 65.2 (C-4), 63.0 (C-6), 30.3 and 28.9 ($OCH_2(CH_2)_2CH{=}CH_2$), 20.9 and 20.8 ($OCOCH_3$).

β: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.21–5.18 (m, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6 and 170.2 (2 × C=O), 137.9 ($O(CH_2)_3CH{=}CH_2$), 130.5 (C-2), 126.0 (C-3), 114.8 (($O(CH_2)_3CH{=}CH_2$), 95.1 (C-1), 70.6 ($OCH_2(CH_2)_2CH{=}CH_2$), 67.7 (C-5), 64.3 (C-4), 63.4 (C-6), 30.2 and 28.8 ($OCH_2(CH_2)_2CH{=}CH_2$), 20.9, and 20.7 ($OCOCH_3$).

Thiophenyl-4,6-di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (7)[48]

α: ^{1}H NMR (300 MHz, $CDCl_3$); δ 7.34–7.26 (m, 5H, aromatic), 6.06 (ddd, J = 10.11, 3.18 and 1.95 Hz, 1H, H-2), 5.86 (td, J = 10.13, 1.73 and 1.73 Hz, 1H, H-3), 5.76 (td, J = 3.56, 1.89 and 1.89 Hz, 1H, H-1), 5.38 (qd, J = 9.54, 2.03, 2.00 and 2.00 Hz, 1H, H-4), 4.47 (ddd, J = 9.01, 5.87 and 2.55 Hz, 1H, H-5), 4.35–4.19 (m, 2H, H-6 and H-6′), 2.11 and 2.06 (s, 2 × 3H, CH_3-acetyl); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7 and 170.3 (2 × C=O), 132.7 (C-2), 131.8 (C-3), 130-127 (5C, aromatic), 83.7 (C-1), 67.3 (C-4), 65.2 (C-5), 63.1 (C-6), 21.0 and 20.7 ($OCOCH_3$).

β: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57–7.52, 5.96 (td, J = 10.22, 1.78 and 1.78 Hz, 1H, H-2), 5.81 (td, J = 10.19, 2.43 and 2.43 Hz, 1H, H-3), 5.63 (dd, J = 4.53 and 2.20 Hz, 1H, H-1), 5.25–5.10 (m, 1H, H-4), 4.35–4.19 (m, 2H, H-6 and H-6′), 3.91 (ddd, J = 7.51, 5.47 and 4.24 Hz, 1H, H-5), 2.09 and 2.06 (s, 2 × 3H, CH_3-acetyl); ^{13}C NMR (75 MHz, $CDCl_3$): δ 81.4 (C-1), 74.9 (C-4), 64.5 (C-5), 63.3 (C-6), 20.9 and 20.8 ($OCOCH_3$).

3-Azido-4,6-di-*O*-acetyl-1,2-dideoxy-D-*erythro*-hex-2-enopyranoside (8A)[49]

α: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.53 (d, J = 5.96 Hz, 1H, H-1), 5.10 (dd, J = 10.51 and 4.33 Hz, 1H), 4.90 (t, J = 5.86 Hz, 1H), 2.09 and 2.15 (s, 2 × 3H, CH_3-acetyl); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5 and 169.6 (2 × C=O), 146.9 (C-1), 96.4 (C-2), 68.0 (C-4 or C-5), 61.8 (C-6), 53.3 (C-3).

β: ^{13}C NMR (75 MHz, $CDCl_3$): δ 98.1 (C-2), 53.4 (C-3).

1-Azido-4,6-di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (8B)[49]

α: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.96 (dt, J = 10.19 Hz, 1H, H-2 or H-3), 5.78 (dt, 1H, H-2 or H-3), 5.57 (br s, 1H, H-1), 5.36–5.33 (m, 1H, H-4), 4.43-4.05 (m, 3H, H-5, H-6 and H-6′), 2.11 and 2.12 (s, 2 × 3H, CH_3-acetyl); ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.6 (C-2 or C-3), 126.3 (C-2 or C-3), 68.8 (C-4 or C-5), 64.5 (C-4 or C-5), 62.5 (C-6), 57.6 (C-1).

β: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.05 (ddd, 1H, H-2 or H-3), 5.86 (dt, 1H, H-2 or H-3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.5 (C-2 or C-3), 128.0 (C-2 or C-3).

Allyl-4,6-di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (9)[4,12,18c]

α: ^{1}H NMR (300 MHz, $CDCl_3$); δ 6.06–5.60 (m, 3H, H-2, H-3 and $-CH_2CH{=}CH_2$), 5.35–5.20 (m, 1H, H-4), 5.18–5.05 (m, 2H, $-CH_2CH{=}CH_2$), 4.35–4.05 (m, 3H, H-1, H-6 and H-6′), 4.01–3.92 (m, 1H, H-5), 2.54–2.25 (m, 2H, $-CH_2CH{=}CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1 and 170.3 (2 × C=O), 133.9, 132.7 and 123.6 (C-2, C-3 and $-CH_2CH{=}CH_2$), 117.5 ($-CH_2CH{=}CH_2$), 71.3 (C-1), 69.7 (C-4), 64.9 (C-5), 62.8 (C-6), 37.8 ($-CH_2CH{=}CH_2$), 20.6 and 20.8 (2 × $OCOCH_3$).

β: ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1 and 170.2 (2 × C=O), 133.3, 132.2 and 125.0 (C-2, C-3 and $-CH_2CH{=}CH_2$), 117.6 ($-CH_2CH{=}CH_2$), 74.2 (C-1), 74.15 (C-4), 65.5 (C-5), 63.6 (C-6), 39.3 ($-CH_2CH{=}CH_2$), 20.6 and 20.8 (2 × $OCOCH_3$).

Tetradecanyl-4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (12)[39a]

α: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.22 (m, 10 H, aromatic), 6.06 (d, J = 10.29 Hz, 1H), 5.77 (dt, J = 10.38, 2.43 and 1.99 Hz, 1H, H-2), 5.01 (m, 4H, 2 × OCH_2Ph), 4.17 (dd, J = 9.34, 1.00 Hz, 1H, H-4), 3.96 (q, 1H, H-5), 3.81–3.58 (m, 3H, H-6, H-6′ and $-OCH_2-$), 3.48 (td, J = 9.53, 6.55 and 6.55 Hz, 1H, $-OCH_2-$), 1.9–0.5 (m, 27H, aliphatic); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2 (aromatic) 130.5 (C-3), 128.3, 128.3, 127.8, 127.7 and 127.6 (aromatic), 126.8 (C-2), 94.6 (C-1), 73.3 and 71.0 (OCH_2Ph), 70.4 (C-4), 69.1 (C-5), 68.9 (C-6), 68.7 ($-OCH_2-$), 31.9, 29.8, 29.7, 29.4, 29.3 and 22.7 (aliphatic), 14.1 ($-CH_3$).

β: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.03 (d, J = 10.34 Hz, 1H, H-3), 5.83 (dt, 1H, H-2), 5.10 (d, J = 1.28 Hz, 1H).

Thiophenyl-4,6-di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (13)

Yellowish oil, R_f: 0.8 (1 : 9 EtOAc : petroleum ether), HRMS (EI+): 418.8 m/z.

α: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57–7.52 (m, 2H, S*Ph*), 7.34–7.22 (m, 13H, aromatic), 6.04 (td, J = 10.21, 1.29 and 1.29 Hz, 1H, H-2), 5.98 (ddd, J = 10.19, 2.67 and 1.53 Hz, 1H, H-3), 5.77 (br s, 1H, H-1), 4.63 (dd, J = 11.82 and 2.51 Hz, 2H, OCH_2Ph), 4.49 (dd, J = 11.81, 5.54 Hz, 2H, OCH_2Ph), 4.33 (ddd, J = 9.28, 3.91 and 2.55 Hz, 1H, H-5), 4.24 (ddd, J = 9.27, 3.30 and 1.56 Hz, 1H, H-4), 3.79–3.76 (m, 2H, H-6 and H-6′); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.6 (1C, S*Ph*), 129.1 (C-2), 127.2 (C-3), 129.0-127.3 (17C, aromatic), 84.1 (C-1), 73.3 (CH_2Ph), 71.2 (CH_2Ph), 70.3 (C-4), 69.7 (C-5), 69.0 (C-6).

β: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.87 (td, J = 2.68, 1.66 and 1.66 Hz, 1H, H-2), 5.81-5.77 (m, 1H, H-3), 5.64 (q, J = 2.15, 2.13 and 2.13 Hz, 1H, H-1); ^{13}C NMR (75 MHz, $CDCl_3$): δ 81.1 (C-1), 71.8 (CH_2Ph), 71.0 (CH_2Ph).

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