$Dy(OTf)_3$-immobilized in ionic liquids: a novel and recyclable reaction media for the synthesis of 2,3-unsaturated glycopyranosides

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Received (in Cambridge, UK) 16th July 2002, Accepted 27th August 2002
First published as an Advance Article on the web 1st October 2002

D-Glycals react smoothly with a variety of alcohols, phenols and hydroxy α-amino acids in the presence of 5 mol% dysprosium triflate immobilized in 1-butyl-3-methylimidazolium hexafluorophosphate under mild reaction conditions to afford the corresponding 2,3-unsaturated glycopyranosides in excellent yields with high α-selectivity. The catalyst immobilized in ionic liquids was recycled in subsequent reactions without any apparent loss of activity.

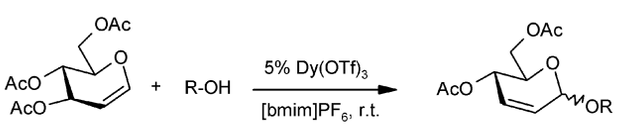
Introduction

Room temperature ionic liquids, especially those based on the 1-*N*-alkyl-3-methylimidazolium cation, have shown great promise as attractive alternatives to conventional solvents.[1] They are non-volatile, recyclable, easy to handle and thermally robust and in addition they are compatible with various organic and organometallic compounds. Indeed, ionic liquids are good solvents for transition-metal complexes in many homogeneously catalyzed reactions such as olefin hydrogenation, hydroformylation, epoxidation, allylation, Heck reaction, and Suzuki cross coupling reactions.[2] In many cases the products are weakly soluble in the ionic phase so that the catalyst can be easily separated by simple extraction. Because of the great potential of room temperature ionic liquids as environmentally benign media for catalytic processes, much attention is being currently focused on organic reactions catalyzed by ionic liquids. Several organic reactions catalyzed by ionic liquids have been reported with high performance.[3] This offered some clues that using ionic liquids as catalysts for those traditionally acid-base catalyzed synthetic reactions may not only be possible but also practical and even highly efficient. These ionic liquids showed enhancement in reaction rates and selectivity, compared to molecular organic solvents.

Aryl and alkyl 2,3-unsaturated glycosides are useful chiral intermediates in the synthesis of several biologically active natural products.[4] 2,3-Deoxy sugars, derived from 2,3-unsaturated glycosides are important building blocks in many bioactive molecules such as antibiotics.[5] The direct and straightforward method for the synthesis of 2,3-unsaturated glycosides is the acid-catalyzed allylic rearrangement of glycals in the presence of alcohols.[6] The reaction, as originally stated by Ferrier, involves intermediacy of a cyclic allylic oxocarbenium ion to which the nucleophile adds preferentially in a quasi-axial orientation. A variety of reagents are reported to promote this transformation, which include Lewis acids as well as oxidants.[7–10] Lanthanide triflates† are unique Lewis acids that are currently of great research interest. They are highly oxophilic and form strong but labile bonds with oxygen donor ligands. This feature has often allowed sub-stoichiometric amounts of the Lewis acids to be used to promote a variety of reactions.[11] Indeed, such Lewis acids are found to be effective in promoting many organic transformations. However, the use of dysprosium triflate as a catalyst in organic synthesis is rare.[12]

Results and discussion

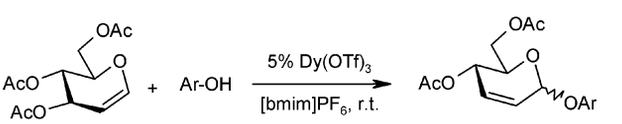
In view of the emerging importance of ionic liquids as novel reaction media and our interest on the catalytic applications of lanthanide triflates as water-tolerant and recyclable Lewis acids in carbon–carbon bond forming reactions,[13] we report herein our results on the $Dy(OTf)_3$ catalyzed glycosidation of glycals with alcohols in the hydrophobic 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. The treatment of 3,4,6-tri-*O*-acetyl-D-glucal with a range of alcohols using 5 mol% dysprosium triflate in 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid afforded the corresponding 2,3-unsaturated glycosides in excellent yields (Scheme 1).



1 2c-j 3c-j

Scheme 1

The glycosidation of tri-*O*-acetyl glucal with primary, secondary, benzylic, allylic and propargylic‡ alcohols proceeded smoothly at ambient temperature to afford the corresponding alkyl 2,3-unsaturated glycosides in high yields with the α-anomer as the major product. In a similar fashion, the tri-*O*-acetyl-D-glucal was rapidly glycosylated with phenols in the presence of $Dy(OTf)_3$ in $[bmim]PF_6$ ionic liquid to obtain aryl 2,3-unsaturated glycosides in excellent yields with high α-stereoselectivity (Scheme 2).



Ar = C_6H_5, 4-MeO-C_6H_4, 4-Br-C_6H_4, 4-NO_2-C_6H_4

1 2k-n 3k-n

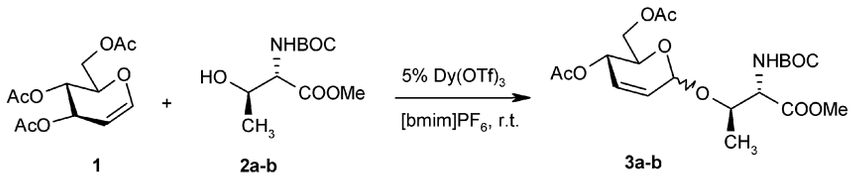
Scheme 2

In all cases, the products were obtained as a mixture of α- and β-anomers, with the α-anomer being favored. The α,β-ratio was determined on the basis of integrated ratios of

† The IUPAC name for triflate is trifluoromethanesulfonate.

‡ The IUPAC name for propargyl is prop-2-ynyl.

 DOI: 10.1039/b206957c



Scheme 3

the anomeric hydrogen in the ^{1}HMR spectrum of the crude product. These results encouraged us to extend this method for the glycosylation of tri-*O*-acetyl-D-glucal with other glycosyl acceptors such as *N*-BOC protected threonine and serine to produce the corresponding *O*-glycopyranosides, which are useful precursors in the synthesis of glycopeptide building blocks (Scheme 3).

In this reaction the catalytic activity of dysprosium triflate was strongly influenced by the nature of the anion. When a hydrophobic ionic liquid was used, the desired products were obtained in excellent yields, although dysprosium triflate is only slightly soluble and thus exists as a suspended form in these ionic liquids. In sharp contrast to these results, in a hydrophilic ionic liquid, such as [bmim]BF_4, the catalyst was highly soluble and thus totally immobilized in this ionic liquid but the products were obtained in good yields. Finally, the ionic liquid phase containing dysprosium triflate was recovered by simple extraction with ether after completion of the reaction. Second and third reactions using the recovered ionic liquid containing catalyst afforded similar yields to those obtained in the first run. No decrease in yield was observed in runs carried out using recycled ionic liquid and furthermore the products obtained were of the same purity as in the first run. However, in the absence of dysprosium triflate, the products were obtained in moderate yields (60–75%) under heating conditions at 80 °C after long reaction periods (5–8 h) in [bmim]BF_4 ionic liquid.[14] Because of the mild Lewis acidic nature of [bmim]BF_4, these glycosidation reactions proceeded even in the absence of catalyst and the results are presented in Table 1. There are no considerable differences in the α,β-ratios either in the presence or in the absence of catalyst in ionic liquid. Furthermore, there are no significant improvements in the reaction rates and yields when the reactions are carried out under strictly anhydrous conditions using either [bmim]BF_4 or [bmim]PF_6 ionic liquids. The presence of Cl^- ions in the ionic liquids was easily determined quantitatively by titration of the ionic liquids with silver nitrate solution. The purity of the ionic liquids was further compared with a commercial sample (Sigma-Aldrich Co.). Among other lanthanide triflates, scandium and ytterbium triflates were found to be equally effective for this transformation. Due to the presence of trace amount of ionic liquid in the ether layer, the product was purified by column chromatography on silica gel. Although, the glycosidation reactions proceeded smoothly in organic solvents such as dichloromethane and acetonitrile, these solvents could not be recycled in further runs. These simple experimental and product isolation procedures combined with the ease of recovery and reuse of this novel catalytic system are expected to contribute to the development of benign and waste-free chemical processes for the synthesis of *O*-glycopyranosides of synthetic importance. Thus, this method is an advancement on acid or oxidant promoted glycosidation processes. The scope and generality of this process is illustrated with respect to various alcohols, phenols and D-glucal and the results are presented in Table 1.

In summary, this paper describes a novel and highly efficient method for the synthesis of *O*-glycopyranosides from tri-*O*-acetyl derivatives of D-glucal and alcohols, phenols and hydroxy α-amino acids using a novel and recyclable catalytic system; dysprosium triflate immobilized in air and moisture-stable room temperature ionic liquids. The notable features of this procedure are mild reaction conditions, simplicity in operation, improved yields, enhanced reaction rates and selectivity, cleaner reaction profiles and reusability of the catalytic system which make it a convenient, economic and eco-friendly chemical process for the synthesis of glycopyranosides of synthetic importance.

Experimental

1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) ionic liquids were prepared according to the procedures reported in the literature.[15]

Melting points were recorded on a Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. ^{1}H-NMR spectra were recorded on a Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. CHN analyses were recorded on a Vario EL analyzer. The optical rotations were measured on a Jasco Dip 360 Digital polarimeter in units of 10^{-1} deg cm^2 g^{-1}.

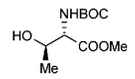
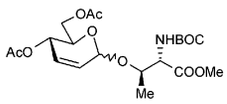
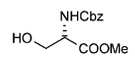
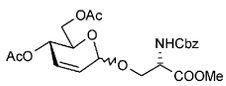
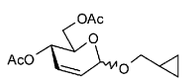
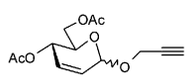
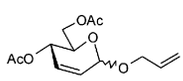
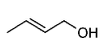
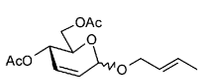
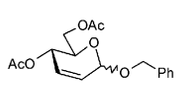
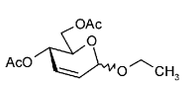
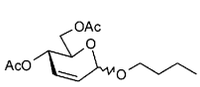
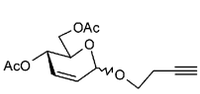
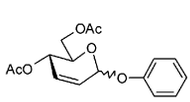
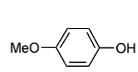
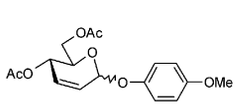
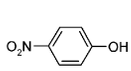
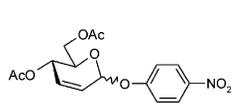
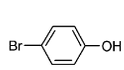
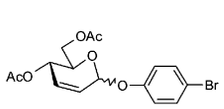
General procedure

A mixture of D-glucal (2 mmol), alcohol or phenol (4 mmol) and dysprosium triflate (5 mol%) in 1-butyl-3-methylimidazolium hexafluorophosphate (2 mL) was stirred at ambient temperature under an N_2 atmosphere for an appropriate time (Table 1). After completion of the reaction as indicated by TLC, the reaction mixture was extracted with diethyl ether (4 × 10 mL). The combined ether layers were dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography on silica gel (Merck, 100–200 mesh, ethyl acetate–hexane, 1 : 9) to afford pure glycoside. The rest of the viscous ionic liquid was further washed with ether and dried at 80 °C under reduced pressure to retain its activity in subsequent runs.

2-(*N*-*tert*-Butoxycarbonylamino)-1-methyl-3-methoxycarbonylethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3a). $[\alpha]_D^{25}$ 42.4 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.30 (d, 3H, J = 6.3 Hz, CH_3), 1.43 (s, 9H, $C(CH_3)_3$), 2.08 (s, 6H, –$COCH_3$), 3.80 (s, 3H, $COOCH_3$), 4.08 (m, 1H, H-5), 4.17 (dd, 1H, J = 1.8, 9.7 Hz, α-CH), 4.18–4.23 (m, 2H, H_a-6 and H_b-6), 4.38 (dq, 1H, J = 1.8, 6.3 Hz, β-CH), 5.0 (d, 1H, J = 1.2 Hz, H-1), 5.15 (d, 1H, J = 9.7 Hz, NH), 5.26 (dd, 1H, $J_{3,4}$ = 1.2 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 5.68 (d, 1H, $J_{2,3}$ = 10.3 Hz, H-2), 5.84 (dd, 1H, $J_{3,4}$ =1.2 Hz, $J_{3,2}$ = 10.3 Hz, H-3). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 18.7, 20.7, 20.7, 20.9, 28.2, 52.3, 52.4, 58.1, 63.0, 65.1, 66.9, 68.1, 76.2, 80.0, 95.4, 107.9, 109.8, 127.4, 129.0, 134.9, 155.9, 170.2, 170.7, 171.4. Anal. calcd for $C_{20}H_{31}NO_{10}$(445.46): C, 53.93; H, 7.01; N, 3.14. Found: C, 53.96; H, 7.05; N, 3.17%.

2-(*N*-Benzyloxycarbonylamino)-3-methoxycarbonylethyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3b). $[\alpha]_D^{25}$ 36.3 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.0 (s, 3H, –$COCH_3$), 2.05 (s, 3H, –$COCH_3$), 3.78 (s, 3H, COOMe), 3.95–4.0 (m, 2H, β-CH_2), 4.05–4.10 (m, 1H, H-5), 4.12–4.18 (m, 2H, H_a-6 and H_b-6), 4.45–4.55 (m, 1H, α-CH), 4.90 (s, 1H, H-1), 5.08 (s, 2H, CH_2–Ph), 5.03 (br s, 1H, NH), 5.23 (dd, 1H, $J_{3,4}$

Table 1 Synthesis of *O*-glycopyranosides from D-glucal and alcohols in ionic liquids

Entry	Alcohol/Phenol	Product[a]	5% $Dy(OTf)_3$[bmim]PF_6^-		[bmim]BF_4		Ratio[d] α : β
			Time/h	Yield (%)[b]	Time/h[c]	Yield (%)[b]	
a			3.0	85	7.0	62	9 : 1
b			4.0	80	8.0	65	9 : 1
c			1.5	95	3.5	75	7 : 1
d			1.5	93	4.0	70	10 : 1
e			1.5	91	3.0	75	7 : 1
f			2.0	87	3.5	72	6 : 1
g			3.5	85	5.0	70	6 : 1
h			2.5	88	3.5	75	7 : 1
i			2.0	86	5.0	71	8 : 1
j			2.0	90	4.0	75	10 : 1
k			1.5	89	6.5	68	10 : 1
l			0.5	95	5.5	70	15 : 1
m			2.0	85	7.0	60	10 : 1
n			1.0	92	6.0	65	12 : 1

[a] All products were characterized by ^{1}HNMR, IR and mass spectra. [b] Isolated and unoptimized yields. [c] Reactions were carried out at 80 °C. [d] The ratio was determined on the basis of integration ratios of anomeric hydrogen

=1.3 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 5.68 (d, $J_{2,3}$ = 10.3 Hz, 1H, H-2), 5.80 (dd, 1H, $J_{3,4}$ = 1.3 Hz, $J_{3,2}$ = 10.3 Hz, H-3). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 20.7, 52.4, 54.4, 62.7, 63.0, 65.0, 66.9, 67.3, 69.2, 95.0, 126.9, 127.9, 128.0, 128.4, 129.5, 136.1, 170.0, 170.3, 170.5. Anal. calcd for $C_{22}H_{27}NO_{10}$(465.45): C, 56.77; H, 5.85; N, 3.01. Found: C, 56.80; H, 5.87; N, 3.05%.

Cyclopropyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3c). $[\alpha]_D^{25}$ 105.6 (*c* = 1.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.15–0.25 (m, 2H, $-CH_2-$), 0.50–0.60 (m, 2H, $-CH_2-$), 1.05–1.15 (m, 1H, –CH–), 2.08 (s, 6H, $-COCH_3$), 3.38–3.50 (m, 2H, $-OCH_2-$), 4.05–4.12 (m, 1H, H-5), 4.15–4.20 (m, 2H, H_a-6, H_b-6), 5.02 (s, 1H, H-1), 5.30 (dd, 1H, *J* = 1.2, 9.5 Hz, H-4), 5.80–5.85 (m, 2H, H-2, H-3).^{13}C NMR ($CDCl_3$, 50 MHz) δ: 2.9, 3.1, 10.4, 20.5, 20.7, 62.8, 65.1, 66.7, 72.5, 73.1, 93.6, 127.8, 128.8, 169.8, 170.2. IR (KBr) *v*: 3379, 3007, 1744, 1374 cm.$^{-1}$. Anal. calcd for $C_{14}H_{20}O_6$(284.30): C, 59.15; H, 7.09. Found: C, 59.23; H, 7.15%.

Prop-2-ynyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3d). Solid, mp 72–74 °C; $[\alpha]_D^{25}$ 145 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz): *δ* 2.08 (s, 6H, $COCH_3$), 2.40–2.45 (m, 1H, H-3^1), 4.05–4.15 (m, 1H, H-5), 4.18 (dd, 2H, *J* = 4.9, 11.5 Hz, H_a-6, H_b-6), 4.25–4.30 (m, 2H, H-1^1), 5.20 (d, 1H, *J* = 1.2 Hz, H-1), 5.35 (dd, 1H, *J* = 1.2, 9.8 Hz, H-4), 5.85 (dd, 1H, $J_{2,3}$ = 10.3 Hz, H-2), 5.87 (dd, 1H, $J_{3,4}$ = 1.2 and 10.3 Hz, H-3). IR (KBr) *ν*: 3300, 2120, 1745, 1605 cm.$^{-1}$. Anal. calcd for $C_{13}H_{16}O_6$ (268.26): C, 58.20; H, 6.01. Found: C, 58.18; H, 6.05%.

Allyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3e). Solid, mp 42–43 °C; $[\alpha]_D^{25}$ 80.4 (*c* = 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 2.08 (s, 6H, –$COCH_3$), 4.03–4.30 (m, 5H, H-5, H_a-6, H_b-6, H_a-1^1, H_b-1^1), 5.08 (br s, 1H, H-1), 5.22 (dq, 1H, *J* = 10.4, H_a-3^1), 5.28–5.38 (m, 2H, H-4, H_b-3^1), 5.83–6.0 (m, 3H, H-2, H-3, H-2^1). ^{13}C NMR ($CDCl_3$, 50 MHz) *δ*: 20.75, 20.93, 62.91, 65.23, 66.91, 69.25, 93.66, 117.51, 127.71, 129.21, 134.04, 170.26, 170.75. IR (KBr) *ν*: 3375, 2926, 1733, 1535, 1441 cm.$^{-1}$. Anal. calcd for $C_{13}H_{18}O_6$(270.28): C, 57.78; H, 6.71. Found: C, 57.80; H, 6.74%.

But-2-enyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3 f). $[\alpha]_D^{25}$ 83.4 (*c* = 2.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 1.75 (d, 3H, *J* = 6.5 H z, CH_3–), 2.08 (s, 6H, –$COCH_3$), 4.03–4.30 (m, 5H, H-5, H_a-6, H_b-6, H_a-1^1, H_b-1^1), 5.03 (s, 1H, H-1), 5.30 (dd, 1H, *J* = 1.1, 9.5 Hz, H-4), 5.58–5.70 (m, 2H, H_a-2^1, H_b-2^1), 5.78–5.90 (m, 2H, H-2, H-3). ^{13}C NMR ($CDCl_3$, 50 MHz) *δ*: 17.5, 20.5, 20.7, 62.8, 63.3, 65.2, 66.7, 68.7, 93.1, 126.7, 127.7, 128.9, 130.0, 130.4, 169.9, 170.4. IR (KBr) *ν*: 3378, 2920, 1745, 1546, 1451 cm.$^{-1}$ Anal. calcd for $C_{14}H_{20}O_6$ (284.30): C, 59.15; H, 7.09. Found: C, 59.20; H, 7.13%.

Benzyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3g). $[\alpha]_D^{25}$ 125 (*c* = 1.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 2.10 (s, 6H, –$COCH_3$), 4.11–4.16 (m, 2H, H-5, H_a-6), 4.24 (dd, 1H, *J* = 5.0, 11.5 Hz, H_b-6), 4.60 (d, 1H, *J* = 11.7 Hz, CH_2–Ph), 4.80 (d, 1H, *J* = 11.7 Hz, CH_2–Ph), 5.13 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-1), 5.35 (dd, 1H, $J_{3,4}$ = 1.2 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 5.82–5.92 (m, 2H, H-2, H-3), 7.30–7.40 (m, 5H, aromatic). Anal. calcd for $C_{17}H_{20}O_6$ (320.33): C, 63.74; H, 6.29. Found: C, 63.8; H, 6.31%.

Ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3h). $[\alpha]_D^{25}$ 111 (*c* = 1.0, $CHCl_3$), ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 1.25 (t, 3H, *J* = 6.5 Hz, CH_3), 2.10 (s, 6H, –$COCH_3$), 3.50–3.60 (m, 1H, –OCH_2–), 3.75–3.85 (m, 1H, –OCH_2–), 4.05–4.10 (m, 1H, H-5), 4.15 (dd, 1H, *J* = 4.8, 11.6 Hz, H_a-6), 4.25 (dd, 1H, *J* = 4.8, 11.5 Hz, H_b-6), 5.0 (s, 1H, H-1), 5.30 (dd, 1H, $J_{3,4}$ = 1.1 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 5.80–5.90 (m, 2H, H-2 and H-3). ^{13}C NMR ($CDCl_3$, 50 MHz) *δ*: 15.2, 20.7, 20.9, 63.3, 64.2, 65.2, 66.7, 94.1, 127.9, 128.9, 170.2, 170.7. Anal. calcd for $C_{12}H_{18}O_6$ (258.27): C, 55.81; H, 7.02. Found: C, 55.83; H, 7.07%.

Butyl 4,6-di-*O*-acetyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3i). $[\alpha]_D^{25}$ 61.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 0.92 (t, 3H, *J* = 6.7 Hz, CH_3), 1.30–1.49 (m, 2H, CH_3–*C*H_2–),1.58–1.63 (m, 1H, CH_3–CH_2–*C*H_2–), 2.06 (s, 6H, $COCH_3$), 3.43–3.52 (m, 1H, –OCH_2–), 3.70–3.81 (m, 1H, –OCH_2–), 4.0–4.10 (m, 1H, H-5), 4.18–4.23 (m, 2H, H_a-6,H_b-6), 4.98 (s, 1H, H-1), 5.35 (dd, 1H, $J_{3,4}$ = 1.2 Hz, $J_{4,5}$ = 9.3 Hz, H-4), 5.80–5.85 (m, 2H, H-2, H-3). Anal. calcd for $C_{14}H_{22}O_6$ (286.32): C, 58.73; H, 7.74. Found: C, 58.75; H, 7.75%.

But-3-ynyl 4,6-di-*O*-acetyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3j). $[\alpha]_D^{25}$ 45.4 (*c* = 2.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 1.98 (m, 1H, H-4^1), 2.07 (s, 6H), 2.55–2.60 (m, 2H, H_a-2^1, H_b-2^1), 3.65–3.73 (m, 1H, H_a-1^1), 3.85–3.95 (m, 1H, H_b-1^1), 4.10–4.15 (m, 1H, H-5), 4.20 (dd, 2H, *J* = 4.5 and 11.5 Hz, H_a-6, H_b-6), 5.12 (s, 1H, H-1), 5.35 (dd, 1H, *J* = 1.1 and 9.3 Hz), 5.85 (d, 1H, $J_{2,3}$ = 10.3 Hz, H-2), 5.87 (dd, 1H, $J_{3,4}$ = 1.2 and $J_{2,3}$ = 10.3 Hz, H-3). ^{13}CNMR ($CDCl_3$, 50 MHz) *δ*: 19.9, 20.6, 20.8, 62.7, 65.0, 66.7, 66.9, 69.3, 80.8, 94.4, 127.3, 129.2, 170.1, 170.6. IR (KBr) *ν*: 3285, 2926, 2121, 1739, 1373 cm.$^{-1}$ Anal. calcd for $C_{14}H_{18}O_6$ (282.29): C, 59.57; H, 6.43. Found: C, 59.60; H, 6.45%.

Phenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3k). Solid, mp 47–48 °C, $[\alpha]_D^{25}$ 165.5 (*c* = 1.45, C_2H_5OH); ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 1.98 (s, 3H, –$COCH_3$), 2.09 (s, 3H, –$COCH_3$), 4.13 (dd, 1H, *J* = 1.8 and 11.6 Hz, H_a-6), 4.20–4.25 (ddd, 1H, *J* = 1.8 and 5.0, 9.5 Hz, H-5), 4.28 (dd, 1H, *J* = 5.0, 11.6 Hz, H_b-6), 5.39 (dd, 1H, *J* = 1.0 and 9.5 Hz, H-4), 5.69 (d, 1H, *J* = 1.0 Hz, H-1), 5.98–6.03 (m, 2H, H-2, H-3), 7.0–7.30 (m, 5H, Ar-H). ^{13}C NMR ($CDCl_3$, 50 MHz) *δ*: 20.4, 20.7, 29.6, 62.4, 64.9, 67.7, 92.6, 126.9, 129.8, 169.6, 170.0. Anal. calcd for $C_{16}H_{18}O_6$ (306.31): C, 62.74; H, 5.92. Found: C, 62.80; H, 5.95%.

***p*-Methoxyphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3l).** Solid, mp 69–70 °C; $[\alpha]_D^{25}$ 123 (*c* = 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 2.05 (s, 3H, $COCH_3$), 2.15 (s, 3H, $COCH_3$), 3.80 (s, 3H, –OCH_3), 4.18 (dd, 2H, *J* = 5.0, 11.5 Hz, H_a-6, H_b-6), 4.25 (m, 1H, H-5), 5.35 (dd, 1H, *J* = 1.0 and 9.5 Hz, H-4), 5.51 (d, 1H, *J* = 1.1 Hz, H-1), 6.0 (br s, 2H, H-2, H-3), 6.80 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.05 (d, 2H, *J* = 8.0 Hz, Ar-H).

***p*-Nitrophenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3m).** Solid, m.p 94–95 °C; $[\alpha]_D^{25}$ 174 (*c* = 1.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 1.97 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 4.11–4.19 (m, 2H, H-5, H_a-6), 4.27 (dd, 1H, *J* = 5.1 and 11.6 Hz, H_b-6), 5.41 (dd,1H, *J* = 1.2 and 9.5 Hz, H-4), 5.81 (br s, 1H, H-1), 6.01 (dd, 1H, *J* = 1.2 and 10.2 Hz, H-3), 6.11 (d, 1H, *J* = 10.2, H-2), 7.19 (d, 2H, *J* = 9.0 Hz, Ar-H), 8.20 (d, 2H, *J* = 9.0 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 50 MHz) *δ*: 20.6, 20.9, 29.6, 62.4, 64.7, 68.4, 92.7, 116.7, 125.9, 131.2, 142.6, 161.9, 170.1, 170.5. Anal. calcd for $C_{16}H_{17}NO_8$ (351.31): C, 54.71; H, 4.88; N, 3.99. Found: C, 54.73; H, 4.90; N, 4.01%.

***p*-Bromophenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3n).** $[\alpha]_D^{25}$ 117 (*c* = 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 2.0 (s, 3H, $COCH_3$), 2.15 (s, 3H, $COCH_3$), 4.12–4.32 (m, 3H, H-5, H_a-6, H_b-6), 5.40 (dd, 1H, *J* = 1.2 and 9.5 Hz, H-4), 5.68 (s, 1H, H-1), 5.98–6.02 (m, 2H, H-2, H-3), 7.02 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.42 (d, 2H, *J* = 8.0 Hz, Ar-H).^{13}C NMR ($CDCl_3$, 50 MHz) *δ*: 20.6. 20.8, 29.6, 62.5, 64.9, 67.9, 93.0, 114.8, 118.8, 123.4, 126.6, 129.7, 130.4, 132.3, 156.1, 170.1, 170.5. Anal. calcd for $C_{16}H_{17}BrO_6$ (385.20): C, 49.89; H, 4.45; Br, 20.74. Found: C, 49.90; H, 4.48; Br, 20.76%.

Acknowledgements

BVS and JSS thank CSIR, New Delhi, for the award of fellowships.

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