

The influence of electronic factors on palladium-mediated cycloisomerization: a systematic investigation of competitive 5-*exo-dig* versus 6-*endo-dig* cyclizations of sugar alkynols

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Abstract

Pd-mediated cycloisomerization of 3-*C*-alkynyl-*allo*- and ribofuranose derivatives was investigated in detail to understand the influence of electronic factors on the regioselectivity in ring closure reaction. The reactions in general are influenced by the electronic nature of the substituent on the alkyne unit. A preference for *endo-dig* cyclization over *exo-dig* is noted, if the alkynyl substituent is not sufficiently electron withdrawing.

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1. Introduction

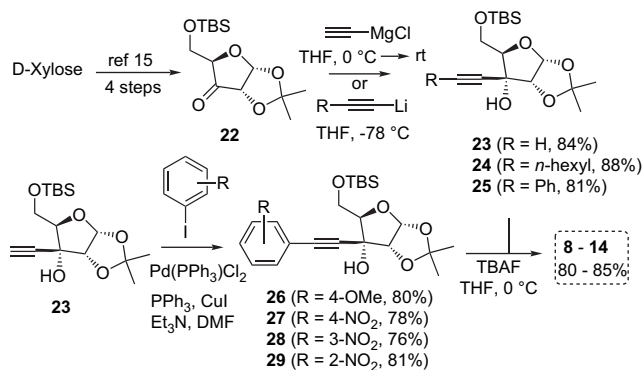
Transition metal-mediated addition of *C*- and heteroatom nucleophiles across a carbon–carbon double and/or triple bonds is one of the most interesting and important reactions in organic chemistry.¹ The intramolecular version of this reaction falls under the broad category of cycloisomerization reactions. Cycloisomerization reactions are characterized by their complete atom economy and has been recognized as an attractive tool for delivering complex molecular diversity.² Cycloisomerization of alkynols is projected as a tool to synthesize oxygen-containing heterocycles encompassing functionalized furan, pyran, benzopyran, and spiroketal skeletons.³ Various transition metals like palladium, platinum, tungsten, molybdenum, ruthenium, rhodium, gold, and iridium have been explored as catalysts for cycloisomerization reactions.⁴ The key issue is the mode of cyclization, i.e., *exo-dig* versus *endo-dig*.⁵ There are several instances in the literature which indicate that the obtuse angle of 120°–127° for the approach of a nucleophile to a triple

bond triggers the dominance of 5-*exo-dig* over 6-*endo-dig* for electronically unbiased acetylenes.⁶ The majority of theoretical and experimental studies to understand 5-*exo-dig* versus 6-*endo-dig* cyclizations consider mainly the base-mediated cyclization with hard nucleophiles,⁷ however, investigations dealing with metal-catalyzed cyclizations^{8,10} are rare.

The pioneering work by Utimoto on the Pd-mediated cycloisomerization of alkynyl diols leading to the formation of bicyclic and spiroacetal natural products has indeed disclosed some of the aspects related to the regiochemistry of these cyclizations.^{3g} In one example it has been found that the mode of cyclization depends upon the relative orientation of both reacting groups (Scheme 1) as noticed with the mercury(II)-mediated cyclization reported by Schwartz and Reideker earlier.⁹ The participation of enolic –OH of 1,3-diketones in metal dependent *endoexo* selective cycloisomerization was reported by Gulias et al.¹⁰ In this context, recently we reported a preliminary investigation dealing with the influence of electronic factors on the Pd-mediated cycloisomerization reaction.¹¹

Herein we describe a complete compilation of our investigations dealing with electronic control over the cycloisomerization of 3-*C*-alkynylfuranosyl derivatives (Fig. 1) using a set of two different alkynol models (8–14 and 15–21) for

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Scheme 1. Synthesis of 3-C-alkynyl-ribofuranose derivatives **8–14**.

5-*exo-dig* versus 6-*endo-dig* mode of competitive cyclizations. In the case of the first set of compounds **8–14**, the cycloisomerization is expected to lead to [3.3.0] or [3.4.0]dioxabicyclic enol ether derivatives, whereas the formation of fused [2.2.1] or [3.2.1]bicyclic acetal derivatives is possible from the second set of compounds **15–21** (Fig. 1). Because these bicyclic acetals exist in many biologically active and structurally diverse natural products,¹² the results from the present investigation will be important for the strategic construction of these molecular skeletons.¹³ It is pertinent to mention that the metal-mediated cycloisomerization reactions of carbohydrate precursors have been less explored and mainly confined to glycals, *exo*-glycals, and related derivatives.¹⁴

2. Results and discussion

2.1. Synthesis of cycloisomerization substrates **8–21**

Two different approaches have been adopted for the synthesis of the substrates **8–21**. The first approach involves the addition of $\text{HC}\equiv\text{C}-\text{MgCl}$ or a suitable $\text{R}-\text{C}\equiv\text{C}-\text{Li}$ (R : $-n\text{-C}_6\text{H}_{13}$ or $-\text{Ph}$) and the second one utilizes the Sonogashira coupling of the ethynyl Grignard product with the respective substituted iodoarenes.

The synthesis of the requisite model 3-C-alkynyl-ribofuranose derivatives **8–14** was started from the known 3-ulose

derivative **22**.¹⁵ According to known procedure D-xylose was converted to **22** in four steps with an overall yield of 42%. Addition of ethynylmagnesium chloride, prepared by exchange with *n*-butylmagnesium chloride, gave **23**, and of the lithiated salts of 1-octyne and phenylacetylene (Scheme 1) gave **24** and **25**, respectively. To prepare the other substrates, the Sonogashira coupling¹⁶ reaction of **23** with different aryl iodides was carried out to give compounds **26–29**. The TBS group present at O-5 of **23–29** was subsequently removed by using TBAF/THF to give substrates **8–14**.

The synthesis of the second set of cycloisomerization substrates **15–21** was carried out in a similar manner from ulose **30** (Scheme 2).¹⁷ Following an established sequence for **22**, the protected alkynols **31–37** were prepared by initial addition of alkynyl nucleophiles and Sonogashira coupling reactions of alkynol **31**. The selective hydrolysis of the 5,6-acetonide groups of **31–37** with cat. H_2SO_4 in methanol gave a second set of substrates **15–21**.

2.2. Cycloisomerization of alkynols **8–14**

The Pd-catalyzed cycloisomerization reactions of model 3-C-alkynyl-ribofuranose derivatives **8–14** were carried out in the presence of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ in MeCN at room temperature. The results are summarized in Scheme 3. The parent compound **8** gave exclusively ketal **38** resulting from hydrolysis of the intermediate *exo*-enol. The structure of ketal **38** was supported by spectral and elemental analyses. The characteristic hemiketal carbon singlet appeared at δ 105.6 ppm, thus confirming the assigned structure. Cycloisomerization of alkynol **9** afforded the *endo*-product **39** exclusively, whose structure was supported by spectral and elemental analyses. For example, a broad singlet corresponding to olefinic-H appeared at much higher field (δ 4.40 ppm) in the ^1H NMR spectrum and the olefinic carbons with substantial chemical shift difference [δ 94.1 (d), 159.6 (s)] and upfield OCH_2 triplet at δ 62.9 ppm in the ^{13}C NMR spectrum of compound **39** clearly established the presence of a dihydropyran unit. Compound **39** was found to be susceptible to hydration in CDCl_3 and resulted in the formation of hemiketal **40** as a single anomer. The

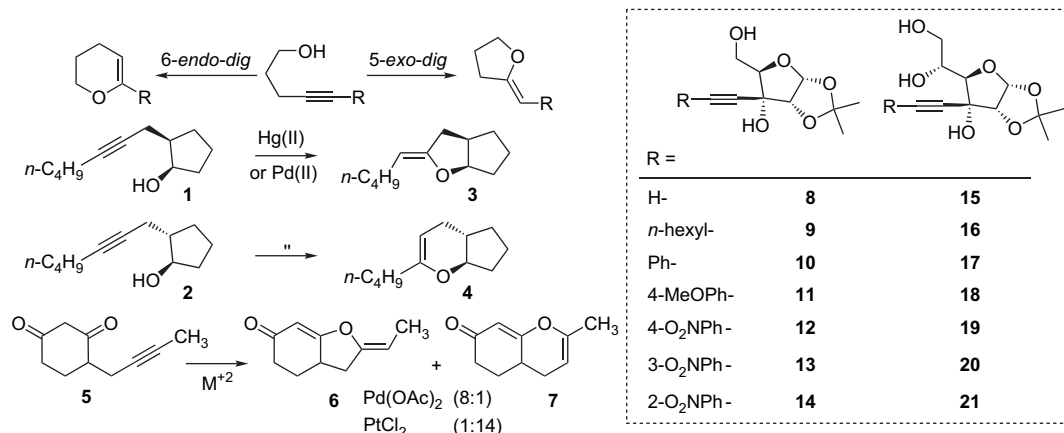
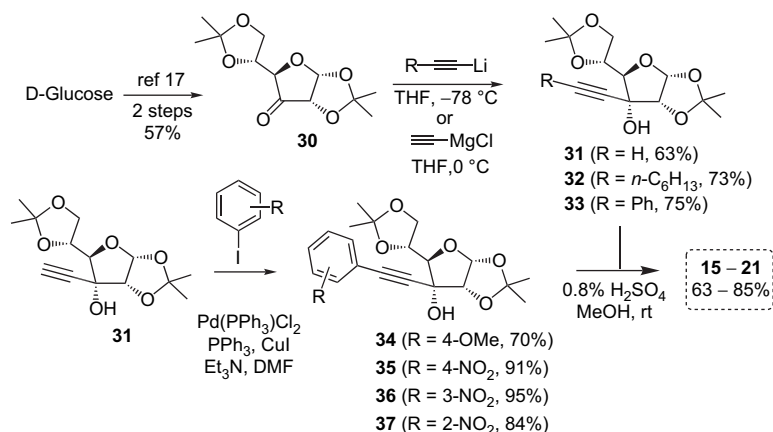
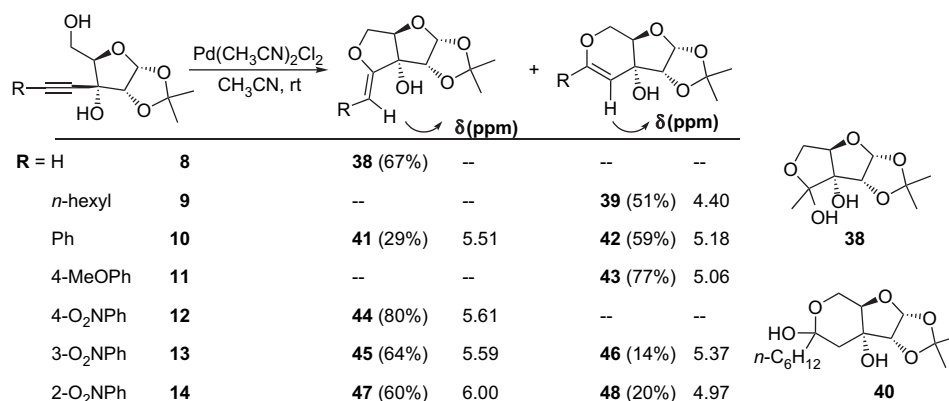


Figure 1. Competitive 5-*exo-dig* and 6-*endo-dig* cyclizations of alkynols, some representative examples, and designed substrates for understanding the electronic control over these cyclizations.

Scheme 2. Synthesis of 3-C-alkynyl-allofuranose derivatives **15–21**.Scheme 3. Cycloisomerization reactions of 3-C-alkynyl-ribofuranose derivatives **8–14**.

spectral data of the resulting product **40** are in accordance with the assigned structure and further supported by single crystal X-ray structural analysis (Fig. 2). While the cycloisomerization of the simple phenylalkynol **10** gave a regiomer mixture of *exo*-product **41** (29%) and the *endo*-product **42** (59%), only formation of *endo*-product **43** was observed with methoxyphenyl alkynol **11**. The structures of the *exo*-product **41** and of the *endo*-product **42** were proposed with the help of ¹H and ¹³C NMR analyses. For example, the characteristic furan ring CH₂ triplet of **41** (δ 71.2 ppm) resonated at 9.6 ppm downfield when compared to corresponding pyran CH₂ triplet of **41** (δ 63.6 ppm) in the ¹³C NMR spectrum. The single crystal X-ray study (Fig. 2) of the *endo*-product **42** unambiguously proved its structure.

The cycloisomerizations of the regiomer nitrophenylalkynols **12–14** are in general fast compared to the other alkynols and afforded 5-*exo*-products exclusively or as the major products. From the cycloisomerization reactions of *o*- and *m*-nitro derivatives **12** and **13**, the *endo*-products **46** and **48**, respectively, could be isolated and characterized. The comparative NMR spectral patterns of **46** and **48** with those of corresponding *endo*-products **40**, **42**, and **43** confirmed their assigned structure. Comparative chemical shifts of *endo*- and *exo*-cyclic enolic-H are given in Scheme 3. In general the olefinic-H of the *endo*-enols (in dihydropyran derivatives **42**, **43**, **46**, **48**)

is found to be more shielded compared to the olefinic-H of corresponding isomeric *exo*-enols (furan derivatives **41**, **44**, **45**, **47**). The single crystal X-ray structural analysis of the *exo*-products **44** and **47** (Table 1) proved their structures unambiguously.

2.3. Cycloisomerization of alkynols **15–21**

The results of the PdCl₂(CH₃CN)₂-catalyzed cycloisomerizations of 3-C-alkynyl-allofuranose derivatives **15–21** are given in Scheme 4. As indicated in Scheme 4, the cycloisomerization of monosubstituted alkynol **15** gave exclusively the known [2.2.1]bicyclic acetal **49**.^{17b} In the case of *n*-hexyl substituted alkynol **16** we exclusively obtained the *endo*-product **50**. The appearance of one of the methylene unit protons separately as doublets at δ 1.60 and 1.93 ppm with large geminal coupling constant (14.9 Hz) in the ¹H NMR spectrum of **50** clearly indicates that this methylene unit has no adjacent-H coupled and thus establishes the assigned [3.2.1] bicyclic acetal structure.¹⁸ With phenyl substituted alkynol **17**, two products **51** and **52** were isolated in 30% and 65% yields, respectively. Considering the similarity in the ¹H NMR spectral pattern of **52** with **50** (two doublets at δ 1.80 and 2.18 with *J*_{gem}=14.6 Hz), we assigned a [3.2.1] bicyclic acetal structure, which was further confirmed by the single crystal structural

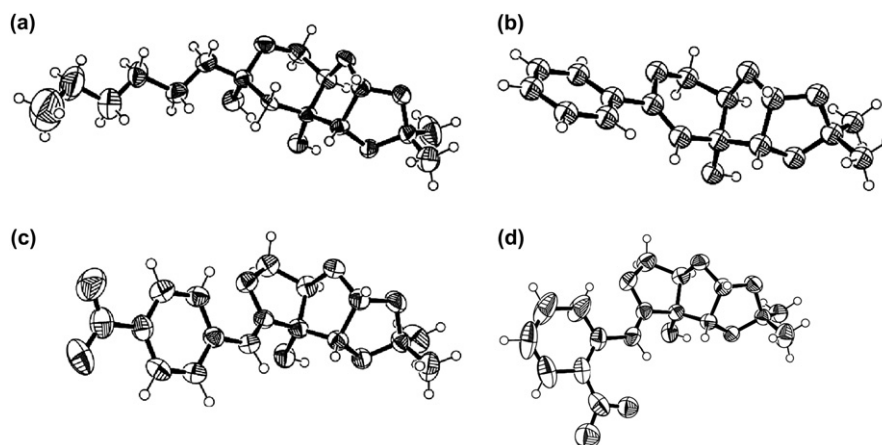


Figure 2. ORTEP structures of (a) compound **40**, (b) compound **42**, (c) compound **44**, and (d) compound **47**.

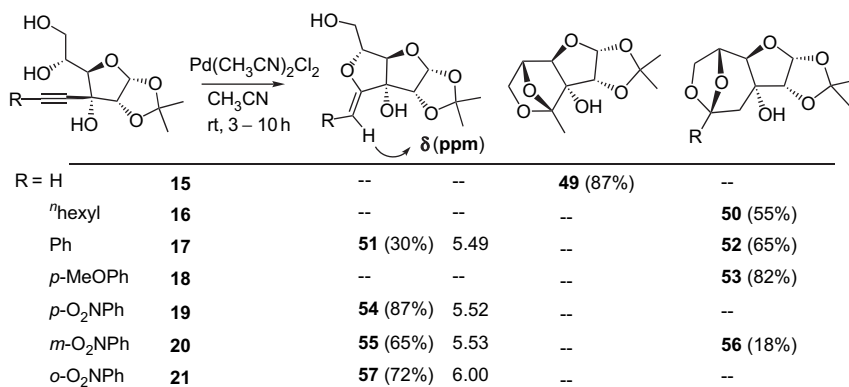
analysis (Fig. 3, Table 1). The appearance of the enolic-H at δ 5.49 ppm in the ^1H NMR spectrum of minor product **51** clearly indicated its *exo*-cyclic nature. The cycloisomerization of *p*- and *o*-nitrophenyl substituted alkynols **19** and **21** gave exclusively *exo*-cyclic products **54** and **57**, respectively; however, *m*-nitro derivative **20** gave small amounts of [3.2.1] bicyclic acetal **56** along with the *exo*-cyclic product **55**. These results are comparable with the results we obtained for the ribose derivatives **8–14**.

From the results obtained with alkynols **8–21**, it is evident that the regioselectivity of ring closure depends upon the nature of the substituents on alkyne. The formation of exclusive 5-*exo*-products from parent alkynols **8** and **15** is expected. In

general terminal alkynes prefer *exo*-mode of approach of the incoming nucleophile in intra- and intermolecular nucleophilic addition reactions.^{1,19} Though the formation of the *endo*-product from the alkynols **9** and **16** contrasts with the results obtained in the cyclization of **1**, the relative inductive effects of the *n*-hexyl and the densely oxygenated furanose ring explain this. In case of aryl-substituted alkynols **10–14** and **17–21**, it is evident from the results obtained that a competitive balance between $-I$ effect of the furanose ring and $+M$ effect of the aryl substituents is operational. These studies reveal that the presence of a $+M$ substituent ($-\text{OMe}$ in our case) on the aromatic ring in general enforces a 6-*endo-dig* while $-M$ group ($-\text{NO}_2$ in our case) favored 5-*exo-dig* modes of

Table 1
Crystal data for compounds **40**, **42**, **44**, **47**, **52**, and **53**^{20–22}

Crystal data	40	42	44	47	52	53
Formula	$\text{C}_{16}\text{H}_{28}\text{O}_6$	$\text{C}_{16}\text{H}_{18}\text{O}_5$	$\text{C}_{16}\text{H}_{17}\text{NO}_7$	$\text{C}_{16}\text{H}_{17}\text{NO}_7$	$\text{C}_{17}\text{H}_{20}\text{O}_6$	$\text{C}_{18}\text{H}_{22}\text{O}_7$
M_r	316.38	290.30	335.31	335.31	320.33	350.36
Crystal size, mm	$0.92 \times 0.08 \times 0.06$	$0.73 \times 0.36 \times 0.14$	$0.56 \times 0.16 \times 0.04$	$0.43 \times 0.41 \times 0.25$	$0.75 \times 0.43 \times 0.37$	$0.77 \times 0.56 \times 0.41$
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$C2$	$P2_1$	$P2_1$	$P2_1$	$P2_12_12_1$
a [Å]	5.460(3)	18.566(7)	5.6459(19)	5.6601(6)	9.003(3)	5.946(2)
b [Å]	10.235(5)	6.108(2)	8.098(3)	9.8552(11)	6.838(2)	14.795(5)
c [Å]	30.624(14)	12.932(5)	17.191(6)	13.9858(15)	12.987(4)	19.346(7)
α [°]	90	90	90	90	90	90
β [°]	90	99.458(6)	91.759(6)	93.574(2)	97.972(5)	90
γ [°]	90	90	90	90	90	90
V [Å ³]	1711.4(13)	1446.5(10)	785.6(5)	778.63(15)	791.8(4)	1702.0(10)
Z	4	4	2	2	2	4
$F(000)$	688	616	352	352	340	744
D calcd [g cm ^{−3}]	1.228	1.333	1.417	1.430	1.344	1.367
μ [mm ^{−1}]	0.093	0.099	0.112	0.113	0.102	0.105
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
$T_{\min}/T_{\max}$	0.9033/0.9945	0.9310/0.9858	0.9396/0.9951	0.9532/0.9716	0.9274/0.9638	0.9233/0.9581
Reflns. collected	15,902	5227	5763	3981	5633	12,270
Unique reflns.	3000	2498	2776	2451	2583	2958
Observed reflns.	2768	2327	2402	2340	2455	2865
No. of parameters	210	196	263	242	215	237
R_1 [$I > 2\sigma(I)$]	0.0771	0.0309	0.0364	0.0307	0.0339	0.0311
WR_2	0.1407	0.0759	0.0665	0.0763	0.0881	0.0776
R_1 (all data)	0.0849	0.0340	0.0450	0.0323	0.0357	0.0320
WR_2 (all data)	0.1435	0.0777	0.0710	0.0777	0.0898	0.0782
Goodness-of-fit	1.272	1.068	1.076	1.055	1.036	1.076
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ^{−3})	+0.226, −0.161	+0.135, −0.112	+0.130, −0.087	+0.116, −0.140	+0.159, −0.159	+0.111, −0.176

Scheme 4. Cycloisomerization reactions of 3-C-alkynyl-allofuranose derivatives **15**–**21**.

cyclization. However, the directional influence of the +M group is strong when it is positioned *para* to the alkyne.

Thus, an electronic control exists over the mode of cyclization in Pd-mediated cycloisomerization. The information is significant when compared to the base-mediated cycloisomerization reactions. Recently, base-mediated cycloisomerization of sugar derived alkynols was dealt with in detail by Vasella and co-workers,^{14a,b} who reported that these cycloisomerizations in general prefer either 5- or 6-*exo-dig* mode of cyclization and in case if the *exo*-mode of ring closure is disfavored due to ring strain, isomerization to the allenes is preferred over an alkynol cycloisomerization. Earlier, Padwa's group^{7c,d} had extensively investigated the base-induced cycloisomerization of several (phenylethynyl)aryl-substituted alcohols modulating one of the phenyl ring substituents (Fig. 4).

It has been concluded that 5-*exo-dig* mode of cyclization was exclusively independent of the nature of the aryl substituent. Though they could isolate exclusively the 6-*endo* product in case of substrates bearing a carbonyl group in the *ortho* position of the aromatic ring, it was shown that these apparent 6-*endo* cyclizations are the consequence of a 5-*exo* cyclization

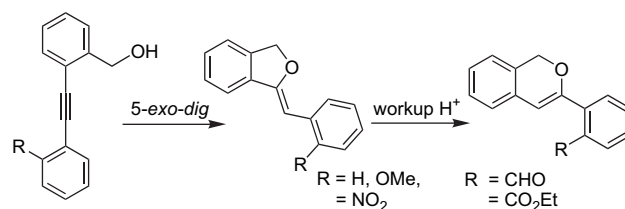


Figure 4. Cycloisomerization of (phenylethynyl)benzyl alcohols.

followed by an acid-catalyzed rearrangement. Along similar lines, Hiroya et al.^{7a} concluded that the regioselectivity in base-mediated cycloisomerization reactions is not influenced by the electronic nature of the functional group on the triple bond, but by steric congestion.

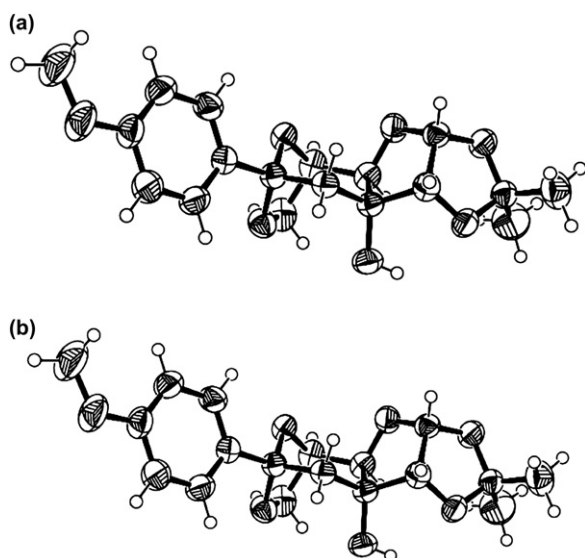
3. Conclusions

In summary, electronic control over the 5-*exo-dig* versus 6-*endo-dig* modes of cyclizations in Pd-mediated cycloisomerization reaction has been studied in detail. 3-C-Alkynyl-allo- and ribofuranose derivatives with systematic variation of functional groups at the opposite side of alkyne were employed to understand the competitive balance between inductive effect of furanose ring and mesomeric effect of aryl substituent. A preference for *endo-dig* cyclization over *exo-dig* is observed, if the aryl substituent is not sufficiently electron withdrawing. At the outset of these studies, a simple access to highly functionalized tetrahydrofuran fused bicyclic acetals and enol ether derivatives was needed and this has been achieved using easily accessible sugar derived alkynols and Pd-mediated coupling and cyclization reactions.

4. Experimental

4.1. General methods

Air and/or moisture sensitive reactions were carried out in anhydrous solvents under an atmosphere of argon in oven-dried glassware. All anhydrous solvents were distilled prior to use: THF and diethyl ether from Na and benzophenone,

Figure 3. ORTEP structures of (a) compound **52** and (b) compound **53**.

CH_2Cl_2 and CH_3CN from CaH_2 , MeOH from Mg cake. Commercial reagents were used without purification. Column chromatography was carried out by using Spectrochem silica gel (60–120 mesh). Specific optical rotations $[\alpha]_{\text{D}}$ are measured at 25 °C and given in $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$. Infrared spectra were recorded in CHCl_3 and are reported in wave number (cm^{-1}). ^1H and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane and coupling constants (J) are reported in hertz (Hz). The following abbreviations are used to designate signal multiplicity: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad.

4.1.1. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-ethynyl- α -D-ribofuranose (**23**)

Mg (1.11 g, 46.3 mmol) was flame dried in a two neck R.B. flask fitted with a reflux condenser and cooled to room temperature in argon atmosphere. Dry THF (30 mL) was introduced followed by a few crystals of iodine. Half of the total volume of $n\text{-BuCl}$ (4.84 mL, 46.3 mmol) was added and the contents were refluxed till the generation of Grignard reagent. Heating was removed and rest of $n\text{-BuCl}$ was added. Stirring was continued at room temperature till all the magnesium was consumed. Then the reaction mixture was cooled to 0 °C and acetylene gas was bubbled into it for 15 min. Ketone **22** (3.5 g, 11.6 mmol) in THF (20 mL) was added at 0 °C and stirred for 30 min. The reaction was quenched with saturated NH_4Cl solution, diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 , concentrated and purified on silica gel (10% ethyl acetate in light petroleum) to give **23** (3.2 g, 84%) as a colorless oil. $[\alpha]_{\text{D}}$ 10.5 (c 1, CHCl_3). IR (CHCl_3): ν 3306, 3019, 2931, 2401, 1514, 1459, 1376, 1163, 1092, 1012 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 0.08 (s, 3H), 0.09 (s, 3H), 0.89 (s, 9H), 1.36 (s, 3H), 1.58 (s, 3H), 2.54 (s, 1H), 3.05 (br s, 1H), 3.91–3.98 (m, 3H), 4.55 (d, $J=3.66$ Hz, 1H), 5.82 (d, $J=3.66$ Hz, 1H). ^{13}C NMR (50 MHz) δ : –5.63 (q), –5.45 (q), 18.11 (s), 25.75 (q, 3C), 26.46 (q), 26.57 (q), 62.68 (t), 75.13 (s), 76.00 (d), 80.43 (s), 80.92 (d), 83.71 (d), 103.98 (d), 113.24 (s). MALDI-TOF (MS): calcd for $\text{C}_{16}\text{H}_{28}\text{O}_5\text{SiNa}$: 351.16, found: 351.14. Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{O}_5\text{Si}$: C, 58.5; H 8.59. Found: C, 58.2; H, 8.11.

4.1.2. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-(oct-1-ynyl)- α -D-ribofuranose (**24**)

To a solution of 1-octyne (273 mg, 2.5 mmol) in THF (10 mL) at –78 °C, $n\text{-BuLi}$ (1.25 mL, 2 mmol, 1.6 M in hexane) was added dropwise. After 1 h, a solution of compound **22** (500 mg, 1.7 mmol) in THF (8 mL) was added and stirring was continued for 6 h at –78 °C. The reaction mixture was quenched with saturated NH_4Cl solution and the aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 , concentrated, and purified by chromatography (10% ethyl acetate in light petroleum) to give **24** (600 mg, 88%) as a syrup. $[\alpha]_{\text{D}}$ 9.7 (c 0.9, CHCl_3). IR (CHCl_3): ν 3537, 3019, 2930, 2857, 2242, 1463, 1375, 1361, 1256, 1217, 1164, 1083, 1007, 873, 838, 667 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 0.07 (s, 3H), 0.08 (s, 3H), 0.87

(t, $J=6.9$ Hz, 3H), 0.89 (s, 9H), 1.24–1.32 (m, 5H), 1.35 (s, 3H), 1.43–1.53 (m, 3H), 1.57 (s, 3H), 2.21 (t, $J=7.0$ Hz, 2H), 2.91 (s, 1H), 3.91–3.94 (m, 3H), 4.47 (d, $J=3.6$ Hz, 1H), 5.79 (d, $J=3.6$ Hz, 1H). ^{13}C NMR (75 MHz) δ : –5.7 (q), –5.5 (q), 13.7 (q), 18.0 (s), 18.4 (t), 22.2 (t), 25.6 (q, 3C), 26.4 (q), 26.5 (q), 28.1 (t), 28.2 (t), 31.0 (t), 63.0 (t), 75.0 (s), 76.8 (s), 81.8 (d), 84.1 (d), 88.3 (s), 103.9 (d), 112.7 (s). Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{O}_5\text{Si}$: C, 64.04; H 9.77. Found: C, 64.15; H, 10.01.

4.1.3. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-phenylethynyl- α -D-ribofuranose (**25**)

To a solution of phenylacetylene (400 mg, 3.9 mmol) in THF (20 mL) at –78 °C, $n\text{-BuLi}$ (2 mL, 3.13 mmol, 1.6 M in hexane) was added dropwise. After 1 h, a solution of compound **22** (790 mg, 2.6 mmol) in THF (10 mL) was added and stirring continued for 3 h at –78 °C. The reaction was quenched by adding saturated NH_4Cl solution, diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified on silica gel (10% ethyl acetate in light petroleum) to afford **25** (920 mg, 81%) as a syrup. $[\alpha]_{\text{D}}$ 2.5 (c 1.5, CHCl_3). IR (CHCl_3): ν 3459, 2929, 2856, 1599, 1492, 1463, 1383, 1254, 1099, 1035, 1001, 880, 836, 690 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 0.09 (s, 3H), 0.10 (s, 3H), 0.90 (s, 9H), 1.38 (s, 3H), 1.62 (s, 3H), 3.14 (s, 1H), 3.99–4.12 (m, 3H), 4.65 (d, $J=3.6$ Hz, 1H), 5.89 (d, $J=3.6$ Hz, 1H), 7.29–7.35 (m, 3H), 7.40–7.45 (m, 2H). ^{13}C NMR (75 MHz) δ : –5.5 (q), –5.3 (q), 18.2 (s), 25.9 (q, 3C), 26.7 (q, 2C), 63.1 (t), 76.0 (s), 81.7 (d), 84.2 (d), 85.7 (s), 87.8 (s), 104.3 (d), 113.4 (s), 121.9 (s), 128.2 (d, 2C), 128.8 (d), 131.8 (d, 2C). Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{O}_5\text{Si}$: C, 65.31; H, 7.97. Found: C, 65.59; H, 7.80.

4.1.4. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-(4-methoxyphenylethynyl)- α -D-ribofuranose (**26**)

4-Iodoanisole (267 mg, 1.14 mmol) was taken in a mixture of Et_3N and DMF (2:1) (5 mL). To this CuI (14 mg, 0.076 mmol), PPh_3 (20 mg, 0.076 mmol), and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (53 mg, 0.076 mmol) were added followed by alkyne (250 mg, 0.76 mmol). Argon was flushed several times and stirred for 2.5 h. After completion, the reaction mixture was diluted with ethyl acetate and the organic layer was washed with water, brine, dried over Na_2SO_4 , and concentrated. Purification of the residue by column chromatography (2:8, EtOAc /light petroleum) afforded **26** (265 mg, 80%) as a white spongy mass. $[\alpha]_{\text{D}}$ 5.1 (c 1, CHCl_3). IR (CHCl_3): ν 3394, 3019, 1607, 1510, 1124, 757, 668 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 0.09 (s, 6H), 0.90 (s, 9H), 1.37 (s, 3H), 1.61 (s, 3H), 3.08 (s, 1H), 3.80 (s, 3H), 3.96–4.1 (m, 3H), 4.62 (d, $J=3.7$ Hz, 1H), 5.87 (d, $J=3.7$ Hz, 1H), 6.81 (d, $J=8.9$ Hz, 2H), 7.34 (d, $J=8.9$ Hz, 2H). ^{13}C NMR (75 MHz) δ : –5.4 (q), –5.2 (q), 18.4 (s), 25.9 (q, 3C), 26.8 (q), 26.9 (q), 55.2 (q), 63.1 (t), 76.1 (s), 81.4 (d), 84.1 (s), 84.2 (d), 87.9 (s), 104.4 (d), 113.4 (s), 113.9 (s), 113.9 (d, 2C), 133.3 (d, 2C), 160.0 (s). MALDI-TOF (MS): calcd for $\text{C}_{23}\text{H}_{34}\text{O}_6\text{SiNa}$:

457.2, found: 457.1. Anal. Calcd for $C_{23}H_{34}O_6Si$: C, 63.56; H 7.89. Found: C, 63.15; H, 8.01.

4.1.5. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-(4-nitrophenylethynyl)- α -D-ribofuranose (27)

To a solution of 4-nitroiodobenzene (341 mg, 1.37 mmol) in 2:1 mixture of Et_3N /DMF (5 mL) were added CuI (17 mg, 0.09 mmol), PPh_3 (24 mg, 0.09 mmol), and $Pd(PPh_3)_2Cl_2$ (64 mg, 0.09 mmol) followed by alkyne **23** (300 mg, 0.913 mmol). The reaction mixture was flushed with argon and stirring was continued for 3 h at 25 °C. Following usual work-up procedure and purification by column chromatography (2:8, $EtOAc$ /light petroleum) gave **27** (321 mg, 78%) as a yellow oil. $[\alpha]_D$ 1.3 (c 0.8, $CHCl_3$). IR ($CHCl_3$): ν 3523, 3020, 2931, 2400, 1595, 1523, 1471, 1346, 1096, 838 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$) δ : 0.09 (s, 6H), 0.90 (s, 9H), 1.39 (s, 3H), 1.62 (s, 3H), 3.21 (s, 1H), 3.97–4.12 (m, 1H), 4.66 (d, $J=3.66$ Hz, 2H), 5.89 (d, $J=3.66$ Hz, 2H), 7.58 (d, $J=8.97$ Hz, 2H), 8.20 (d, $J=8.97$ Hz, 2H). ^{13}C NMR (75 MHz) δ : –5.5 (q), –5.3 (q), 18.3 (s), 25.9 (q, 3C), 26.6 (q), 26.8 (q), 62.9 (t), 76.2 (s), 81.2 (d), 83.8 (d), 85.7 (s), 91.0 (s), 104.3 (d), 113.7 (s), 123.6 (d, 2C), 128.5 (s), 132.5 (d, 2C), 147.5 (s). MALDI-TOF (MS): calcd for $C_{22}H_{31}NO_7$ -SiNa: 472.18, found: 472.28. Anal. Calcd for $C_{22}H_{31}NO_7Si$: C, 58.78; H 6.95; N, 3.12. Found: C, 58.99; H, 6.77; N, 3.14.

4.1.6. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-(3-nitrophenylethynyl)- α -D-ribofuranose (28)

Following a similar procedure as described above, the coupling of 3-nitroiodobenzene (295 mg, 1.19 mmol) and alkyne **23** (260 mg, 0.79 mmol) using CuI (15 mg, 0.079 mmol), PPh_3 (21 mg, 0.079 mmol), and $Pd(PPh_3)_2Cl_2$ (55 mg, 0.079 mmol) afforded **28** (270 mg, 76%) as a colorless oil. $[\alpha]_D$ 2.03 (c 1, $CHCl_3$). IR ($CHCl_3$): ν 3450, 2931, 1533, 1472, 1352, 1258, 1102, 838 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$) δ : 0.10 (s, 6H), 0.9 (s, 9H), 1.39 (s, 3H), 1.62 (s, 3H), 3.2 (s, 1H), 3.98–4.12 (m, 3H), 4.66 (d, $J=3.68$ Hz, 1H), 5.89 (d, $J=3.68$ Hz, 1H), 7.51 (t, $J=8$ Hz, 1H), 7.72 (dt, $J=1.35$, 7.7 Hz, 1H), 8.2 (ddd, $J=1.1$, 2.3, 8.23 Hz, 1H), 8.26–8.28 (m, 1H). ^{13}C NMR (75 MHz) δ : –5.5 (q), –5.3 (q), 18.3 (s), 25.8 (q, 3C), 26.6 (q), 26.7 (q), 62.9 (t), 76.1 (s), 81.2 (d), 83.8 (d), 85.2 (s), 88.6 (s), 104.3 (d), 113.6 (s), 123.6 (s), 123.6 (d), 126.6 (d), 129.4 (d), 137.3 (d), 148.1 (s). MALDI-TOF (MS): calcd for $C_{22}H_{31}NO_7SiNa$: 472.18, found: 472.17. Anal. Calcd for $C_{22}H_{31}NO_7Si$: C, 58.78; H 6.95; N, 3.12. Found: C, 58.83; H, 6.75; N, 3.10.

4.1.7. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-(2-nitrophenylethynyl)- α -D-ribofuranose (29)

Coupling of 2-nitro-iodobenzene (568 mg, 2.28 mmol) and alkyne **23** (500 mg, 1.52 mmol) was carried out by using CuI (29 mg, 0.152 mmol), PPh_3 (40 mg, 0.152 mmol), and $Pd(PPh_3)_2Cl_2$ (107 mg, 0.152 mmol) to procure **29** (555 mg, 81%) after column chromatography (2:8, $EtOAc$ /light petroleum) as a pale yellow oil. $[\alpha]_D$ 1.2 (c 1.0, $CHCl_3$). IR ($CHCl_3$): ν 3526, 3020, 2956, 2410, 1530, 1471, 1346, 1216, 1097 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$) δ : 0.08 (s, 6H),

0.89 (s, 9H), 1.38 (s, 3H), 1.60 (s, 3H), 3.2 (s, 1H), 3.99–4.09 (m, 3H), 4.68 (d, $J=3.66$ Hz, 1H), 5.93 (d, $J=3.66$ Hz, 1H), 7.44–7.63 (m, 3H), 8.04–8.08 (m, 1H). ^{13}C NMR (75 MHz) δ : –5.6 (q), –5.4 (q), 18.2 (s), 25.8 (q, 3C), 26.6 (q), 26.7 (q), 62.9 (t), 76.2 (s), 81.4 (d), 82.9 (s), 83.8 (d), 93.6 (s), 104.3 (d), 113.4 (s), 117.2 (s), 124.7 (d), 129.3 (d), 132.8 (d), 134.7 (d), 149.7 (s). MALDI-TOF (MS): calcd for $C_{22}H_{31}NO_7$ -SiNa: 472.18, found: 472.06. Anal. Calcd for $C_{22}H_{31}NO_7Si$: C, 58.5; H, 8.59; N, 3.12. Found: C, 58.6; H, 8.29; N, 3.14.

4.1.8. 1,2-O-Isopropylidene-3-C-ethynyl- α -D-ribofuranose (8)

A solution of **23** (140 mg, 0.42 mmol) in THF (2 mL) was treated with TBAF (0.5 mL, 0.5 mmol, 1 M in THF) at 0 °C and stirred for 1 h. The reaction mixture was quenched with saturated NH_4Cl solution and partitioned between ethyl acetate and water. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified on silica gel by eluting with 50% ethyl acetate in light petroleum to obtain **8** (75 mg, 82%) as a colorless sticky mass. $[\alpha]_D$ 36.7 (c 1, $CHCl_3$). IR ($CHCl_3$): ν 3305, 3019, 2401, 1519, 1377, 1163, 1019 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$) δ : 1.35 (s, 3H), 1.57 (s, 3H), 2.43 (br s, 1H), 2.59 (s, 1H), 3.29 (br s, 1H), 3.89–3.98 (m, 3H), 4.51 (d, $J=3.7$ Hz, 1H), 5.84 (d, $J=3.7$ Hz, 1H). ^{13}C NMR (50 MHz) δ : 26.5 (q), 26.7 (q), 61.8 (t), 74.7 (s), 76.8 (d), 79.9 (s), 81.5 (d), 83.8 (d), 103.9 (d), 113.5 (s). MALDI-TOF (MS): calcd for $C_{10}H_{14}O_5Na$: 237.07, found: 237.09. Anal. Calcd for $C_{10}H_{14}O_5Si$: C, 56.07; H, 6.59. Found: C, 56.19; H, 6.47.

4.1.9. 1,2-O-Isopropylidene-3-C-oct-1-ynyl- α -D-ribofuranose (9)

A solution of **24** (1 g, 2.4 mmol) in THF (25 mL) and TBAF (2.9 mL, 2.9 mmol, 1 M solution in THF) was stirred at 0 °C for 1 h. Usual workup followed by purification over silica gel (40% ethyl acetate in light petroleum) gave **9** (600 mg, 83%) as a syrup. $[\alpha]_D$ 41 (c 0.5, $CHCl_3$). IR ($CHCl_3$): ν 3460, 3019, 2934, 2860, 2240, 1456, 1377, 1163, 1078, 1008, 873, 668 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$) δ : 0.87 (t, $J=6.9$ Hz, 3H), 1.20–1.31 (m, 6H), 1.34 (s, 3H), 1.43–1.50 (m, 2H), 1.56 (s, 3H), 2.20 (t, $J=7.0$ Hz, 2H), 3.0 (br s, 1H), 3.82–3.95 (m, 3H), 4.44 (d, $J=3.7$ Hz, 1H), 5.81 (d, $J=3.7$ Hz, 1H). ^{13}C NMR (125 MHz) δ : 13.7 (q), 18.3 (t), 22.2 (t), 26.3 (q), 26.4 (q), 28.0 (t), 28.2 (t), 30.9 (t), 61.7 (t), 74.5 (s), 76.0 (s), 81.6 (d), 84.0 (d), 88.9 (s), 103.6 (d), 112.9 (s). MALDI-TOF (MS): calcd for $C_{16}H_{26}O_5Na$: 321.17, found: 321.15. Anal. Calcd for $C_{16}H_{26}O_5$: C, 64.41; H, 8.78. Found: C, 64.55; H, 8.61.

4.1.10. 1,2-O-Isopropylidene-3-C-phenylethynyl- α -D-ribofuranose (10)

A solution of **25** (1.125 g, 2.8 mmol) in THF (25 mL) was treated with TBAF (3.3 mL, 3.3 mmol, 1 M in THF) at 0 °C and stirred for 1 h. Usual workup and purification by column chromatography (50% ethyl acetate in light petroleum) gave **10** (646 mg, 80%) as a colorless solid. $Mp=112$ °C. $[\alpha]_D$ 50.5 (c 1, $CHCl_3$). IR ($CHCl_3$): ν 3436, 2924, 2852, 1612,

1489, 1384, 1083, 1061, 1019, 879, 691 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.40 (s, 3H), 1.62 (s, 3H), 2.98 (s, 1H), 3.93–4.15 (complex AB, 3H), 4.63 (d, $J=3.7$ Hz, 1H), 5.93 (d, $J=3.7$ Hz, 1H), 7.30–7.36 (m, 3H), 7.42–7.47 (m, 2H). ^{13}C NMR (50 MHz) δ : 26.5 (q), 26.7 (q), 62.0 (t), 75.2 (s), 82.0 (d), 84.0 (d), 84.8 (s), 88.2 (s), 103.9 (d), 113.3 (s), 121.4 (s), 128.2 (d, 2C), 128.9 (d), 131.8 (d, 2C). MALDI-TOF (MS): calcd for $\text{C}_{16}\text{H}_{18}\text{O}_5\text{Na}$: 313.11, found: 313.10. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_5$: C, 66.19; H, 6.25. Found: C, 65.96; H, 6.35.

4.1.11. 1,2-O-Isopropylidene-3-C-(4-methoxyphenylethynyl)- α -D-ribofuranose (11**)**

A solution of **26** (200 mg, 0.46 mmol) and 1 M TBAF in THF (0.6 mL, 0.6 mmol) in THF (10 mL) was stirred at 0 °C for 4 h. Usual workup and purification of the crude product by column chromatography (1:1, EtOAc/light petroleum) gave **11** (125 mg, 85%) as a colorless oil. $[\alpha]_{\text{D}}^{25}$ 36.1 (c 1.2, CHCl_3). IR (CHCl_3): ν 3397, 3020, 2395, 1211, 1421, 1037, 926 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.39 (s, 3H), 1.6 (s, 3H), 3.0 (s, 1H), 3.8 (s, 3H), 4.04 (br s, 3H), 4.62 (d, $J=3.75$ Hz, 1H), 5.93 (d, $J=3.75$ Hz, 1H), 6.83 (d, $J=8.9$ Hz, 2H), 7.37 (d, $J=8.9$ Hz, 2H). ^{13}C NMR (75 MHz) δ : 26.6 (q), 26.8 (q), 55.3 (q), 62.3 (t), 75.3 (s), 82.2 (d), 83.12 (s), 84.1 (d), 88.7 (s), 104.2 (d), 113.4 (s), 113.5 (s), 114.0 (d, 2C), 133.5 (d, 2C), 160.2 (s). MALDI-TOF (MS): calcd for $\text{C}_{17}\text{H}_{20}\text{O}_6\text{Na}$: 343.12, found: 343.18. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_6$: C, 63.74; H 6.29. Found: C, 63.51; H, 6.47.

4.1.12. 1,2-O-Isopropylidene-3-C-(4-nitrophenylethynyl)- α -D-ribofuranose (12**)**

Following the procedure as described, treatment of **27** (250 mg, 0.556 mmol) with 1 M TBAF in THF (0.66 mL, 0.66 mmol) followed by usual workup and purification by column chromatography (1:1, EtOAc/light petroleum) gave **12** (158 g, 85%) as a colorless oil. $[\alpha]_{\text{D}}^{25}$ 51.6 (c 1, CHCl_3). IR (CHCl_3): ν 3423, 2917, 1665, 1591, 1377, 1342, 858 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.4 (s, 3H), 1.61 (s, 3H), 3.2 (s, 1H), 4.01–4.11 (m, 3H), 4.64 (d, $J=3.71$ Hz, 1H), 5.95 (d, $J=3.71$ Hz, 1H), 7.61 (d, $J=8.78$ Hz, 2H), 8.18 (d, $J=8.78$ Hz, 2H). ^{13}C NMR (75 MHz) δ : 26.4 (q), 26.8 (q), 62.1 (t), 75.4 (s), 82.2 (d), 83.7 (d), 86.3 (s), 89.8 (s), 104.1 (d), 113.8 (s), 123.6 (d, 2C), 128.2 (s), 132.7 (d, 2C), 147.7 (s). MALDI-TOF (MS): calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7\text{Na}$: 358.09, found: 358.10. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7$: C, 57.31; H, 5.11; N, 4.18. Found: C, 57.28; H, 5.17; N, 4.23.

4.1.13. 1,2-O-Isopropylidene-3-C-(3-nitrophenylethynyl)- α -D-ribofuranose (13**)**

A solution of **28** (210 mg, 0.47 mmol) and 1 M TBAF (0.56 mL, 0.56 mmol) in THF (10 mL) was stirred for 2 h at 0 °C. After completion, the reaction mixture was worked up as described above and the crude product was purified by column chromatography (1:1, EtOAc/light petroleum) to obtain **13** (126 mg, 80%) as a colorless oil. $[\alpha]_{\text{D}}^{25}$ –1.7 (c 1.5, CHCl_3). IR (CHCl_3): ν 3466, 3078, 2923, 1531, 1459, 1354, 1050, 884 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.39 (s,

3H), 1.61 (s, 3H), 2.9 (br s, 2H), 3.98–4.09 (m, 3H), 4.63 (d, $J=3.7$ Hz, 1H), 5.93 (d, $J=3.7$ Hz, 1H), 7.51 (t, $J=8.0$ Hz, 1H), 7.74 (dt, $J=1.4$, 7.8 Hz, 1H), 8.19 (ddd, $J=1.15$, 2.18, 8.3 Hz, 1H), 8.28 (t, $J=1.9$ Hz, 1H). ^{13}C NMR (75 MHz) δ : 25.7 (q), 25.9 (q), 61.2 (t), 74.7 (s), 81.4 (d), 83.47 (d), 84.2 (s), 88.1 (s), 95.3 (s), 103.4 (d), 112.4 (s), 122.8 (d), 125.7 (d), 129.0 (d), 136.8 (d), 147.4 (s). MALDI-TOF (MS): calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7\text{Na}$: 358.09, found: 358.1. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7$: C, 57.31; H 5.11; N, 4.18. Found: C, 57.35; H, 5.19; N, 4.15.

4.1.14. 1,2-O-Isopropylidene-3-C-(2-nitrophenylethynyl)- α -D-ribofuranose (14**)**

A solution of **29** (300 mg, 0.667 mmol) in THF (10 mL) was cooled to 0 °C. TBAF (1 M) in THF (0.8 mL, 0.8 mmol) was added dropwise and stirring continued for 2 h. After completion, the reaction mixture was treated with saturated NH_4Cl solution and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 , concentrated, and purified by column chromatography (1:1, EtOAc/light petroleum) to obtain **14** (185 mg, 83%) as a colorless oil. $[\alpha]_{\text{D}}^{25}$ 36.7 (c 1, CHCl_3). IR (CHCl_3): ν 3427, 3020, 1609, 1473, 1377, 1346, 1164, 1047, 872 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.38 (s, 3H), 1.60 (s, 3H), 2.28 (br s, 1H), 3.34 (s, 1H), 3.99–4.09 (m, 3H), 4.67 (d, $J=3.7$ Hz, 1H), 5.96 (d, $J=3.7$ Hz, 1H), 7.45–7.68 (m, 3H), 8.07 (br d, $J=8.1$ Hz, 1H). ^{13}C NMR (75 MHz) δ : 26.6 (q), 26.8 (q), 62.0 (t), 75.6 (s), 82.2 (d), 83.5 (s), 83.9 (d), 92.9 (s), 104.2 (d), 113.6 (s), 117.1 (s), 124.8 (d), 129.5 (d), 133.0 (d), 135.0 (d), 149.7 (s). MALDI-TOF (MS): calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7\text{Na}$: 358.09, found: 357.99. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7$: C, 57.31; H 5.11; N, 4.18. Found: C, 57.15; H, 4.98; N, 4.35.

4.1.15. 1,2:5,6-Di-O-isopropylidene-3-C-ethynyl- α -D-allofuranose (31**)**

As described for compound **23**, at 0 °C to a solution of ketone **30** (5 g, 19.35 mmol) in THF (25 mL) was added ethynyl MgCl [generated from Mg (1.86 g, 77.43 mmol) and $n\text{-BuCl}$ (8.1 mL, 77.4 mmol)] and stirred for 30 min. Usual workup and purification by column chromatography (10% ethyl acetate in light petroleum) gave **31** (3.5 g, 63%). $[\alpha]_{\text{D}}^{25}$ 7.9 (c 2.5, CHCl_3) [lit.^{17b} $[\alpha]_{\text{D}}^{25}$ 9.5 (c 1, CHCl_3)]. ^1H NMR (400 MHz, CDCl_3) δ : 1.35 (s, 6H), 1.44 (s, 3H), 1.58 (s, 3H), 2.64 (s, 1H), 3.09 (s, 1H), 3.82 (d, $J=8.2$ Hz, 1H), 4.0 (dd, $J=4.6$, 8.8 Hz, 1H), 4.12 (dd, $J=6.2$, 8.8 Hz, 1H), 4.4 (ddd, $J=5.6$, 6.1, 8.2 Hz, 1H), 4.58 (d, $J=3.5$ Hz, 1H), 5.78 (d, $J=3.5$ Hz, 1H). ^{13}C NMR (50 MHz) δ : 25.1 (q), 26.5 (q), 26.6 (q, 2C), 66.8 (t), 74.6 (d), 75.6 (s), 76.8 (s), 76.8 (d), 80.9 (d), 84.1 (d), 103.9 (d), 109.4 (s), 113.2 (s). Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_6$: C, 59.14; H 7.09. Found: C, 59.03; H, 7.14.

4.1.16. 1,2:5,6-Di-O-isopropylidene-3-C-(oct-1-ynyl)- α -D-allofuranose (32**)**

Compound **32** was prepared by treating the ketone **30** (1 g, 3.9 mmol) with lithium salt of 1-octyne prepared from 1-octyne (640 mg, 5.8 mmol) and $n\text{-BuLi}$ (2.9 mL, 4.6 mmol, 1.6 M in hexane) stirring at –78 °C for 5 h followed by usual

workup. The resulting residue was purified by silica gel chromatography (20% ethyl acetate in light petroleum) to afford **32** (1.04 g, 73%) as thick syrup. $[\alpha]_D^{25}$ 6.7 (*c* 1.6, CHCl_3). ^1H NMR (200 MHz, CDCl_3) δ : 0.87 (t, $J=6.7$ Hz, 3H), 1.24–1.30 (m, 6H), 1.34 (s, 6H), 1.43 (s, 3H), 1.48–1.51 (m, 2H), 1.57 (s, 3H), 2.23 (t, $J=7.0$ Hz, 2H), 3.82 (d, $J=7.6$ Hz, 1H), 3.99 (dd, $J=5.1$, 8.6 Hz, 1H), 4.09 (dd, $J=6.2$, 8.6 Hz, 1H), 4.36 (ddd, $J=5.1$, 6.2, 7.6 Hz, 1H), 4.51 (d, $J=3.6$ Hz, 1H), 5.75 (d, $J=3.6$ Hz, 1H). ^{13}C NMR (75 MHz) δ : 14.0 (q), 18.7 (t), 22.5 (t), 25.2 (q), 26.7 (q, 3C), 28.3 (t), 28.4 (t), 31.2 (t), 66.8 (t), 74.9 (d), 75.7 (s), 77.8 (s), 81.2 (d), 84.4 (d), 89.7 (s), 104.0 (d), 109.3 (s), 113.4 (s). Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{O}_6$: C, 65.19; H, 8.75. Found: C, 65.30; H, 8.78.

4.1.17. 1,2:5,6-Di-*O*-isopropylidene-3-*C*-phenylethynyl- α -*D*-allofuranose (**33**)

Compound **33** was prepared by treating the ketone **30** (1 g, 3.9 mmol) with lithium salt of phenylacetylene prepared from phenylacetylene (593 mg, 5.8 mmol) and *n*-BuLi (2.9 mL, 4.6 mmol, 1.6 M in hexane) at -78°C for 1 h followed by usual workup and purification on silica gel column (20% ethyl acetate in light petroleum) gave **33** (1.05 g, 75%). $[\alpha]_D^{25}$ -8.4 (*c* 0.4, CHCl_3). IR (CHCl_3): ν 3684, 3543, 3019, 2992, 2938, 2230, 1599, 1520, 1069, 1042, 873, 841, 625 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.37 (s, 3H), 1.38 (s, 3H), 1.46 (s, 3H), 1.61 (s, 3H), 3.11 (s, 1H), 3.93 (d, $J=7.6$ Hz, 1H), 4.06 (dd, $J=5.2$, 8.7 Hz, 1H), 4.15 (dd, $J=6.1$, 8.7 Hz, 1H), 4.47 (ddd, $J=5.2$, 6.1, 7.6 Hz, 1H), 4.67 (d, $J=3.6$ Hz, 1H), 5.85 (d, $J=3.6$ Hz, 1H), 7.29–7.35 (m, 3H), 7.42–7.47 (m, 2H). ^{13}C NMR (75 MHz) δ : 25.1 (q), 26.5 (q, 2C), 26.6 (q), 66.7 (t), 74.8 (d), 76.1 (s), 81.5 (d), 84.1 (d), 85.7 (s), 88.4 (s), 104.1 (d), 109.3 (s), 113.5 (s), 121.6 (s), 128.2 (d, 2C), 128.8 (d), 131.7 (d, 2C). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_6$: C, 66.65; H, 6.71. Found: C, 66.45; H, 6.43.

4.1.18. 1,2:5,6-Di-*O*-isopropylidene-3-*C*-(4-methoxyphenylethynyl)- α -*D*-allofuranose (**34**)

A solution of alkyne **31** (0.5 g, 1.76 mmol), *p*-iodoanisole (620 mg, 2.64 mmol), Et_3N (10 mL), CuI (67 mg, 0.35 mmol), PPh_3 (46 mg, 0.17 mmol), and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (123 mg, 0.17 mmol) in DMF (5 mL) was flushed with argon for 30 min and stirred for 10 h. The reaction mixture was diluted with ethyl acetate, washed with water, brine, dried over Na_2SO_4 , and concentrated. The residue was purified on silica gel column (30% ethyl acetate in light petroleum) to obtain **34** (481 mg, 70%) as a solid. $\text{Mp}=120^\circ\text{C}$. $[\alpha]_D^{25}$ -7.1 (*c* 1, CHCl_3). IR (CHCl_3): ν 3437, 3019, 2936, 1606, 1511, 1384, 1216, 1070, 1034, 834, 668 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.37 (s, 6H), 1.46 (s, 3H), 1.61 (s, 3H), 3.13 (s, 1H), 3.80 (s, 3H), 3.96 (d, $J=7.5$ Hz, 1H), 4.07 (dd, $J=5.2$, 8.7 Hz, 1H), 4.15 (dd, $J=6.1$, 8.7 Hz, 1H), 4.49 (br ddd, $J=5.2$, 6.1, 7.6 Hz, 1H), 4.67 (d, $J=3.4$ Hz, 1H), 5.86 (d, $J=3.4$ Hz, 1H), 6.83 (d, $J=8.9$ Hz, 2H), 7.37 (d, $J=8.9$ Hz, 2H). ^{13}C NMR (125 MHz) δ : 25.1 (q), 26.6 (q), 26.7 (q, 2C), 55.3 (q), 66.9 (t), 74.9 (d), 76.2 (s), 81.4 (d), 84.1 (d), 84.2 (s), 88.8 (s), 104.2 (d), 109.5 (s), 113.6 (s), 113.7 (s), 114.0 (d, 2C), 133.3 (d, 2C), 160.1 (s). MALDI-TOF (MS):

calcd for $\text{C}_{21}\text{H}_{26}\text{O}_7\text{Na}$: 413.16, found: 413.22. Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{O}_7$: C, 64.60; H, 6.71. Found: C, 64.43; H, 6.90.

4.1.19. 1,2:5,6-Di-*O*-isopropylidene-3-*C*-(4-nitrophenylethynyl)- α -*D*-allofuranose (**35**)

To a solution of 4-nitroiodobenzene (328 mg, 1.3 mmol) in $\text{Et}_3\text{N}/\text{DMF}$ (6 mL, 2:1) were successively added CuI (33 mg, 0.176 mmol), PPh_3 (23 mg, 0.088 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (62 mg, 0.088 mmol), and alkyne **31** (250 mg, 0.88 mmol). The reaction mixture was flushed with argon for 30 min and the stirring continued for 5 h. After usual workup, the residue was chromatographed on silica gel (40% ethyl acetate in light petroleum) to procure **35** (324 mg, 91%) as a syrup. $[\alpha]_D^{25}$ -20.5 (*c* 1.5, CHCl_3). IR (CHCl_3): ν 3447, 3020, 1596, 1523, 1384, 1347, 1071, 855, 669 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.37 (s, 3H), 1.39 (s, 3H), 1.47 (s, 3H), 1.62 (s, 3H), 3.22 (s, 1H), 3.92 (d, $J=8.1$ Hz, 1H), 4.05 (dd, $J=4.8$, 8.8 Hz, 1H), 4.15 (dd, $J=6.1$, 8.8 Hz, 1H), 4.43 (ddd, $J=4.8$, 6.1, 8.1 Hz, 1H), 4.70 (d, $J=3.6$ Hz, 1H), 5.87 (d, $J=3.6$ Hz, 1H), 7.61 (br d, $J=8.9$ Hz, 2H), 8.20 (br d, $J=8.9$ Hz, 2H). ^{13}C NMR (50 MHz) δ : 25.1 (q), 26.6 (q, 2C), 26.7 (q), 67.0 (t), 74.8 (d), 76.4 (s), 81.0 (d), 83.8 (d), 86.4 (s), 90.8 (s), 104.0 (d), 109.7 (s), 113.8 (s), 123.5 (d, 2C), 128.2 (s), 132.6 (d, 2C), 147.5 (s). MALDI-TOF (MS): calcd for $\text{C}_{20}\text{H}_{23}\text{O}_8\text{NNa}$: 428.13, found: 428.17. Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{O}_8\text{N}$: C, 59.25; H, 5.72; N, 3.46. Found: C, 59.55; H, 5.69; N, 3.48.

4.1.20. 1,2:5,6-Di-*O*-isopropylidene-3-*C*-(3-nitrophenylethynyl)- α -*D*-allofuranose (**36**)

Preparation of **36** was carried out by treating **31** (260 mg, 0.91 mmol) with 3-nitroiodobenzene (341 mg, 1.37 mmol), CuI (35 mg, 0.18 mmol), PPh_3 (24 mg, 0.09 mmol), and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (63 mg, 0.09 mmol) and stirring the contents for 5 h followed by usual workup and chromatographic purification (30% ethyl acetate in light petroleum) to obtain **36** (352 mg, 95%) as a liquid. $[\alpha]_D^{25}$ -14.0 (*c* 1, CHCl_3). IR (CHCl_3): ν 3537, 3020, 2992, 1534, 1455, 1384, 1354, 1164, 1071, 928, 841, 623 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.37 (s, 3H), 1.38 (s, 3H), 1.47 (s, 3H), 1.61 (s, 3H), 3.21 (s, 1H), 3.91 (d, $J=8.0$ Hz, 1H), 4.05 (dd, $J=4.8$, 8.7 Hz, 1H), 4.15 (dd, $J=6.1$, 8.7 Hz, 1H), 4.44 (ddd, $J=4.8$, 6.1, 8.0 Hz, 1H), 4.69 (d, $J=3.6$ Hz, 1H), 5.86 (d, $J=3.6$ Hz, 1H), 7.52 (t, $J=8.1$ Hz, 1H), 7.75 (dt, $J=1.3$, 7.7 Hz, 1H), 8.20 (ddd, $J=1.1$, 2.3, 8.2 Hz, 1H), 8.09 (br t, $J=1.8$ Hz, 1H). ^{13}C NMR (50 MHz) δ : 25.1 (q), 26.5 (q, 2C), 26.6 (q), 66.9 (t), 74.8 (d), 76.2 (s), 81.0 (d), 83.9 (d), 85.8 (s), 88.4 (s), 104.0 (d), 109.6 (s), 113.7 (s), 123.3 (s), 123.6 (d), 126.5 (d), 129.4 (d), 137.3 (d), 147.9 (s). MALDI-TOF (MS): calcd for $\text{C}_{20}\text{H}_{23}\text{O}_8\text{NNa}$: 428.13, found: 428.17. Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{O}_8\text{N}$: C, 59.25; H, 5.72; N, 3.46. Found: C, 58.98; H, 5.46; N, 3.18.

4.1.21. 1,2:5,6-Di-*O*-isopropylidene-3-*C*-(4-nitrophenylethynyl)- α -*D*-allofuranose (**37**)

The preparation of **37** was carried out by treating **31** (250 mg, 0.88 mmol) with 2-nitroiodobenzene (326 mg, 1.3 mmol), CuI (33 mg, 0.176 mmol), PPh_3 (23 mg,

0.088 mmol), and Pd(PPh₃)₂Cl₂ (62 mg, 0.088 mmol) in Et₃N/DMF (6 mL, 2:1) as described earlier for 5 h. The residue was chromatographed on silica gel (20% ethyl acetate in light petroleum) to afford **37** (300 mg, 84%) as a colorless oil. [α]_D –16.1 (*c* 1.9, CHCl₃). IR (CHCl₃): ν 3437, 3020, 1530, 1385, 1352, 1084, 1029, 929, 668 cm^{–1}. ¹H NMR (200 MHz, CDCl₃) δ : 1.37 (s, 3H), 1.39 (s, 3H), 1.47 (s, 3H), 1.61 (s, 3H), 3.22 (s, 1H), 3.9 (d, *J*=8.2 Hz, 1H), 4.02 (br dd, *J*=4.9, 8.8 Hz, 1H), 4.12 (br dd, *J*=6.1, 8.8 Hz, 1H), 4.44–4.54 (m, 1H), 4.72 (d, *J*=3.6 Hz, 1H), 5.89 (d, *J*=3.6 Hz, 1H), 7.47–7.69 (m, 3H), 8.1 (d, *J*=8.0 Hz, 1H). ¹³C NMR (50 MHz) δ : 25.0 (q), 26.6 (q), 26.7 (q, 2C), 67.1 (t), 74.8 (d), 76.5 (s), 81.2 (d), 83.6 (s), 84.0 (d), 93.6 (s), 104.1 (d), 109.5 (s), 113.6 (s), 117.1 (s), 124.7 (d), 129.4 (d), 132.8 (d), 134.8 (d), 149.6 (s). MALDI-TOF (MS): calcd for C₂₀H₂₃NO₈Na: 428.13, found: 428.17. Anal. Calcd for C₂₀H₂₃NO₈: C, 59.25; H, 5.72; N, 3.46. Found: C, 59.01; H, 5.61; N, 3.28.

4.1.22. 1,2-O-Isopropylidene-3-C-ethynyl- α -D-allofuranose (**15**)

Compound **31** (170 mg, 0.6 mmol) and 0.8% H₂SO₄ (1 mL) in MeOH (4 mL) were stirred for 12 h. The reaction mixture was neutralized with NaHCO₃ and extracted with ethyl acetate. The combined organic phase was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel chromatography (90% ethyl acetate in light petroleum) to give **15** (100 mg, 68%) as colorless thick liquid. [α]_D 53.8 (*c* 1, CHCl₃). IR (CHCl₃): ν 3445, 3251, 3020, 2941, 1603, 1386, 1166, 1107, 1072, 1017, 874, 669 cm^{–1}. ¹H NMR (200 MHz, D₂O) δ : 1.39 (s, 3H), 1.58 (s, 3H), 3.63 (dd, *J*=5.9, 12.0 Hz, 1H), 3.8 (dd, *J*=2.7, 12.0 Hz, 1H), 3.91 (d, *J*=8.6 Hz, 1H), 4.04 (ddd, *J*=2.7, 5.8, 8.5 Hz, 1H), 4.75 (d, *J*=3.7 Hz, 1H), 5.93 (d, *J*=3.7 Hz, 1H). ¹³C NMR (50 MHz, D₂O) δ : 27.3 (q, 2C), 65.2 (t), 72.7 (d), 77.2 (s), 80.4 (d), 85.9 (d), 105.1 (d), 115.9 (s). MALDI-TOF (MS): calcd for C₁₁H₁₆O₆Na: 267.084, found: 267.09. Anal. Calcd for C₁₁H₁₆O₆: C, 54.09; H, 6.60. Found: C, 54.34; H, 6.47.

4.1.23. 1,2-O-Isopropylidene-3-C-(oct-1-ynyl)- α -D-allofuranose (**16**)

Compound **16** was prepared by treating **32** (500 mg, 1.4 mmol) with 0.8% H₂SO₄ (5 mL) for 15 h followed by usual workup. The residue was chromatographed on silica gel (80% ethyl acetate in light petroleum) to obtain **16** (352 mg, 79%) as a solid. Mp=76 °C. [α]_D 31.8 (*c* 1.3, CHCl₃). IR (CHCl₃): ν 3400, 3019, 2933, 1644, 1428, 1377, 1163, 1076, 1045, 1007, 929, 872, 668 cm^{–1}. ¹H NMR (200 MHz, CDCl₃) δ : 0.87 (t, *J*=6.8 Hz, 3H), 1.28–1.32 (m, 6H), 1.35 (s, 3H), 1.45–1.52 (m, 2H), 1.57 (s, 3H), 2.24 (t, *J*=7.0 Hz, 2H), 2.57 (br s, 1H), 2.96 (d, *J*=4 Hz, 1H), 3.47 (s, 1H), 3.69–3.9 (m, 3H), 4.0–4.10 (m, 1H), 4.51 (d, *J*=3.6 Hz, 1H), 5.77 (d, *J*=3.6 Hz, 1H). ¹³C NMR (75 MHz) δ : 13.9 (q), 18.7 (t), 22.4 (t), 26.6 (q, 2C), 28.4 (t), 28.5 (t), 31.2 (t), 63.9 (t), 71.8 (d), 76.2 (s), 76.8 (s), 79.6 (d), 84.4 (d), 90.2 (s), 103.9 (d), 113.5 (s). MALDI-TOF (MS): calcd

for C₁₇H₂₈O₆Na: 351.18, found: 351.17. Anal. Calcd for C₁₇H₂₈O₆: C, 62.17; H, 8.59. Found: C, 62.15; H, 8.36.

4.1.24. 1,2-O-Isopropylidene-3-C-phenylethynyl- α -D-allofuranose (**17**)

A solution of **33** (500 mg, 1.4 mmol) in MeOH (20 mL) and dil H₂SO₄ (5 mL, 0.8% in water) was stirred at 25 °C for 15 h, quenched with NaHCO₃, and concentrated. The residue was partitioned between ethyl acetate and water and the aqueous layer was extracted with ethyl acetate. The combined organic phase was dried over Na₂SO₄, concentrated, and purified by column chromatography (80% ethyl acetate in light petroleum) to obtain **17** (312 mg, 70%) as white solid. Mp=126 °C. [α]_D 40.1 (*c* 1, CHCl₃). IR (CHCl₃): ν 3468, 3019, 1385, 1039, 929, 874, 669 cm^{–1}. ¹H NMR (200 MHz, CDCl₃) δ : 1.35 (s, 3H), 1.59 (s, 3H), 3.37 (br s, 3H), 3.73 (dd, *J*=4.9, 11.8 Hz, 1H), 3.87 (dd, *J*=3.1, 11.8 Hz, 1H), 3.96 (d, *J*=8.6 Hz, 1H), 4.15 (ddd, *J*=3.1, 4.9, 8.3 Hz, 1H), 4.66 (d, *J*=3.6 Hz, 1H), 5.84 (d, *J*=3.7 Hz, 1H), 7.28–7.32 (m, 3H), 7.42–7.47 (m, 2H). ¹³C NMR (50 MHz) δ : 26.6 (q, 2C), 64.0 (t), 71.8 (d), 76.6 (s), 79.6 (d), 84.1 (d), 85.4 (s), 88.8 (s), 103.9 (d), 113.7 (s), 121.4 (s), 128.4 (d, 2C), 129.0 (d), 132.0 (d, 2C). MALDI-TOF (MS): calcd for C₁₇H₂₀O₆Na: 343.13, found: 343.09. Anal. Calcd for C₁₇H₂₀O₆: C, 63.74; H, 6.29. Found: C, 63.74; H, 6.05.

4.1.25. 1,2-O-Isopropylidene-3-C-(4-methoxyphenylethynyl)- α -D-allofuranose (**18**)

Compound **34** (100 mg, 0.26 mmol) and 0.8% H₂SO₄ (1 mL) in MeOH (4 mL) were stirred for 12 h, neutralized with NaHCO₃, and worked up as usual to give a residue which was purified on silica gel (80% ethyl acetate in light petroleum) to afford **18** (72 mg, 80%) as a white solid. Mp=116 °C. [α]_D 42.3 (*c* 1, CHCl₃). IR (CHCl₃): ν 3404, 3019, 1606, 1511, 1250, 1106, 1035, 930, 874, 834 cm^{–1}. ¹H NMR (200 MHz, CDCl₃) δ : 1.35 (s, 3H), 1.58 (s, 3H), 3.10 (br s, 2H), 3.72–3.78 (m, 2H), 3.77 (s, 3H), 3.83 (br s, 1H), 3.91 (d, *J*=8.6 Hz, 1H), 4.07–4.17 (m, 1H), 4.62 (d, *J*=3.6 Hz, 1H), 5.81 (d, *J*=3.6 Hz, 1H), 6.79 (d, *J*=8.8 Hz, 2H), 7.37 (d, *J*=8.8 Hz, 2H). ¹³C NMR (50 MHz, CDCl₃) δ : 26.7 (q, 2C), 55.2 (q), 64.0 (t), 71.8 (d), 76.7 (s), 79.6 (d), 84.1 (s), 84.2 (d), 88.8 (s), 103.9 (d), 113.6 (s, 2C), 114.0 (d, 2C), 133.5 (d, 2C), 160.2 (s). MALDI-TOF (MS): calcd for C₁₈H₂₂O₇Na: 373.13, found: 373.14. Anal. Calcd for C₁₈H₂₂O₇: C, 61.71; H, 6.33. Found: C, 61.55; H, 6.27.

4.1.26. 1,2-O-Isopropylidene-3-C-(4-nitrophenylethynyl)- α -D-allofuranose (**19**)

Compound **19** (75% yield) was prepared by adopting similar reaction condition as reported for **31**. Mp=139 °C. [α]_D 36.9 (*c* 1, CH₃OH). IR (CHCl₃): ν 3419, 3020, 1594, 1522, 1377, 1346, 1020, 929, 855, 669 cm^{–1}. ¹H NMR (200 MHz, CDCl₃/DMSO-*d*₆) δ : 1.30 (s, 3H), 1.53 (s, 3H), 3.49 (br s, 1H), 3.62 (br d, *J*=10.7 Hz, 1H), 3.79 (br d, *J*=10.7 Hz, 1H), 3.93 (br d, *J*=8.9 Hz, 1H), 3.98–4.08 (m, 2H), 4.50 (s, 1H), 4.62 (d, *J*=3.6 Hz, 1H), 5.78 (d, *J*=3.6 Hz, 1H), 7.55 (br d, *J*=8.4 Hz, 2H), 8.10 (br d, *J*=8.4 Hz, 2H). ¹³C NMR

(50 MHz, CDCl₃) δ : 26.2 (q), 26.3 (q), 63.8 (t), 71.7 (d), 76.4 (s), 79.0 (d), 83.8 (d), 85.5 (s), 91.8 (s), 103.5 (d), 113.3 (s), 123.1 (d, 2C), 128.4 (s), 132.4 (d, 2C), 147.0 (s). MALDI-TOF (MS): calcd for C₁₇H₁₉NO₈Na: 388.10, found: 388.11. Anal. Calcd for C₁₇H₁₉NO₈: C, 55.89; H, 5.24; N, 3.83. Found: C, 56.08; H, 5.37; N, 3.62.

4.1.27. 1,2-O-Isopropylidene-3-C-(3-nitrophenylethynyl)- α -D-allofuranose (**20**)

Following a similar procedure reported for the deprotection of **31**, triol **20** (347 mg, 77%) was obtained by deprotection of **36** (500 mg, 1.23 mmol). [α]_D 35.7 (c 1, MeOH). IR (CHCl₃): ν 3433, 3020, 2935, 1533, 1385, 1164, 1353, 1084, 1040, 929, 872, 624 cm⁻¹. ¹H NMR (200 MHz, CDCl₃) δ : 1.40 (s, 3H), 1.62 (s, 3H), 2.70 (br s, 1H), 3.57 (br s, 1H), 3.79 (dd, J =4.8, 11.5 Hz, 1H), 3.93 (dd, J =3.3, 11.5 Hz, 1H), 3.97 (d, J =8.0 Hz, 1H), 4.14–4.22 (m, 1H), 4.71 (d, J =3.6 Hz, 1H), 5.91 (d, J =3.6 Hz, 1H), 7.53 (t, J =8.0 Hz, 1H), 7.78 (dt, J =1.4, 7.7 Hz, 1H), 8.21 (ddd, J =1.1, 2.3, 8.3 Hz, 1H), 8.31 (br t, J =1.9 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ : 26.0 (q), 26.1 (q), 63.5 (t), 71.4 (d), 76.1 (s), 78.8 (d), 83.7 (d), 84.7 (s), 89.2 (s), 103.2 (d), 112.8 (s), 122.8 (d), 123.2 (s), 126.0 (d), 129.0 (d), 137.1 (d), 147.4 (s). MALDI-TOF (MS): calcd for C₁₇H₁₉NO₈Na: 388.10, found: 388.09. Anal. Calcd for C₁₇H₁₉NO₈: C, 55.89; H, 5.24; N, 3.83. Found: C, 55.90; H, 5.43; N, 3.57.

4.1.28. 1,2-O-Isopropylidene-3-C-(2-nitrophenylethynyl)- α -D-allofuranose (**21**)

Compound **21** (73%) was prepared by adopting similar reaction condition as reported for **31**. [α]_D 26.0 (c 1, MeOH). IR (CHCl₃): ν 3401, 2924, 1610, 1527, 1384, 1217, 1084, 1030, 930 cm⁻¹. ¹H NMR (200 MHz, CDCl₃) δ : 1.39 (s, 3H), 1.6 (s, 3H), 2.47 (br s, 1H), 3.06 (br s, 1H), 3.76 (dd, J =4.8, 11.7 Hz, 1H), 3.91 (dd, J =3.2, 11.7 Hz, 1H), 4.01 (d, J =8.2 Hz, 1H), 4.20 (ddd, J =3.2, 4.8, 8.2 Hz, 1H), 4.74 (d, J =3.6 Hz, 1H), 5.93 (d, J =3.6 Hz, 1H), 7.50 (ddd, J =1.8, 7.3, 8.0 Hz, 1H), 7.61 (dt, J =1.5, 7.5 Hz, 1H), 7.69 (dd, J =1.8, 7.6 Hz, 1H), 8.08 (dd, J =1.3, 8.0 Hz, 1H). ¹³C NMR (75 MHz) δ : 26.6 (q, 2C), 64.1 (t), 71.8 (d), 76.7 (s), 79.8 (d), 83.5 (s), 84.1 (d), 94.1 (s), 104.0 (d), 113.7 (s), 117.2 (s), 124.6 (d), 129.4 (d), 133.0 (d), 135.1 (d), 149.6 (s). MALDI-TOF (MS): calcd for C₁₇H₁₉NO₈Na: 388.10, found: 388.09. Anal. Calcd for C₁₇H₁₉NO₈: C, 55.89; H, 5.24; N, 3.83. Found: C, 55.80; H, 5.33; N, 3.74.

4.1.29. Pd-mediated cyclization of **8**

A solution of **8** (60 mg, 0.28 mmol) and PdCl₂(CH₃CN)₂ (7 mg, 0.028 mmol) in dry CH₃CN (4 mL) under argon atmosphere was stirred at 25 °C for 1 h. The crude product was purified by column chromatography on silica gel (30% ethyl acetate in light petroleum) to obtain **38** (44 mg, 67%) as a colorless liquid.

1,2-O-Isopropylidene-3-C-(1'-acetyl)- α -D-ribofuranose-(1'-C,5-O)-hemiketal (**38**): [α]_D 56.7 (c 0.75, CHCl₃). IR (CHCl₃): ν 3466, 3019, 2991, 1456, 1384, 1165, 1087, 1025 cm⁻¹. ¹H NMR (200 MHz, CDCl₃) δ : 1.39 (s, 3H),

1.48 (s, 3H), 1.57 (s, 3H), 2.51 (s, 1H), 3.01 (s, 1H), 4.02 (dd, J =1.64, 10.48 Hz, 1H), 4.19 (dd, J =5.05, 10.48 Hz, 1H), 4.43 (m, 1H), 4.51 (d, J =3.79 Hz, 1H), 5.89 (d, J =3.79 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ : 21.8 (q), 26.9 (q), 27.2 (q), 70.8 (t), 78.9 (d), 86.6 (d), 89.3 (s), 105.6 (s), 108.1 (d), 112.4 (s). MALDI-TOF (MS): calcd for C₁₀H₁₆O₆Na: 255.08, found: 255.12. Anal. Calcd for C₁₀H₁₆O₆: C, 51.72; H 6.94. Found: C, 51.79; H, 7.13.

4.1.30. Pd-mediated cyclization of **9**

A solution of **9** (200 mg, 0.67 mmol) and PdCl₂(CH₃CN)₂ (17 mg, 0.067 mmol) in dry CH₃CN (6 mL) was stirred under argon for 32 h. Usual workup followed by chromatographic purification (30% ethyl acetate in light petroleum) gave **39** (51 mg, 51%) and unreacted **9** (100 mg).

1,2-O-Isopropylidene-3-C-(2'-hydroxy-oct-1-enyl)-2',5-anhydro- α -D-ribofuranose (**39**): [α]_D 35.2 (c 0.25, CHCl₃). IR (CHCl₃): ν 3381, 3019, 2930, 1376, 1163, 1124, 1066, 668 cm⁻¹. ¹H NMR (200 MHz, CDCl₃) δ : 0.87 (t, J =6.8 Hz, 3H), 1.26–1.28 (m, 6H), 1.36 (s, 3H), 1.42–1.57 (m, 2H), 1.57 (s, 3H), 2.05 (t, J =7.2 Hz, 2H), 2.86 (s, 1H), 3.83 (br dd, J =0.8, 12.3 Hz, 1H), 3.90–3.91 (m, 1H), 4.19 (d, J =3.6 Hz, 1H), 4.33 (br dd, J =1.6, 12.3 Hz, 1H), 4.40 (br s, 1H), 5.70 (d, J =3.6 Hz, 1H). ¹³C NMR (125 MHz) δ : 13.9 (t), 22.4 (t), 26.3 (t), 26.6 (q), 26.9 (q), 28.6 (t), 31.4 (t), 34.0 (t), 62.9 (t), 71.1 (s), 76.6 (d), 83.4 (d), 94.1 (d), 104.0 (d), 112.6 (s), 159.6 (s). MALDI-TOF (MS): calcd for C₁₆H₂₆O₅Na: 321.17, found: 321.18. Anal. Calcd for C₁₆H₂₆O₅: C, 64.41; H, 8.78. Found: C, 64.65; H, 8.60.

4.1.31. 1,2-O-Isopropylidene-3-C-(2'-oxooctyl)- α -D-ribofuranose-(2'-C,5-O)-hemiketal (**40**)

[α]_D -3.7 (c 0.4, CHCl₃). IR (CHCl₃): ν 3516, 3019, 2930, 1422, 1376, 1105, 1051, 1005, 877 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ : 0.85 (t, J =6.6 Hz, 3H), 1.23–1.29 (m, 6H), 1.32 (s, 3H), 1.35–1.42 (m, 2H), 1.51 (d, J =14.1 Hz, 1H), 1.54 (s, 3H), 1.56–1.59 (m, 2H), 1.77 (d, J =14.1 Hz, 1H), 3.66 (s, 1H), 3.91 (d, J =13.8 Hz, 1H), 4.05 (d, J =3.7 Hz, 1H), 4.11 (dd, J =2.2, 14.0 Hz, 1H), 4.16 (br s, 1H), 5.74 (d, J =3.7 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ : 14.1 (q), 22.6 (t), 22.7 (t), 26.4 (q), 26.5 (q), 29.5 (t), 31.8 (t), 36.8 (t), 41.6 (t), 57.3 (t), 74.0 (d), 74.6 (s), 82.6 (d), 95.5 (s), 103.6 (d), 112.7 (s). MALDI-TOF (MS): calcd for C₁₆H₂₈O₆Na: 339.18, found: 339.18. Anal. Calcd for C₁₆H₂₈O₆: C, 60.74; H, 8.98. Found: C, 60.32; H, 9.02.

4.1.32. Pd-mediated cyclization of **10**

The reaction of **10** (100 mg, 0.34 mmol) and PdCl₂-(CH₃CN)₂ (9 mg, 0.034 mmol) in dry CH₃CN (6 mL) was carried out as described earlier for 48 h at 25 °C followed by chromatography on silica (10% ethyl acetate in light petroleum) to obtain **41** (29 mg, 29%) as a colorless oil.

1,2-O-Isopropylidene-3-C-(1'-hydroxy-2'-phenyl-Z-vinyl)-1',5-anhydro- α -D-ribofuranose (**41**): [α]_D 21.3 (c 0.3, CHCl₃). IR (CHCl₃): ν 3393, 3020, 1495, 1385, 1165, 1143, 1083, 1060, 1011, 978, 876 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ : 1.42 (s, 3H), 1.62 (s, 3H), 3.15 (s, 1H), 4.35 (dd, J =2.7,

10.4 Hz, 1H), 4.43 (d, $J=10.4$ Hz, 1H), 4.46 (d, $J=2.7$ Hz, 1H), 4.62 (d, $J=3.8$ Hz, 1H), 5.51 (s, 1H), 5.88 (d, $J=3.8$ Hz, 1H), 7.13 (t, $J=7.3$ Hz, 1H), 7.27 (t, $J=7.7$ Hz, 2H), 7.57 (d, $J=7.7$ Hz, 2H). ^{13}C NMR (125 MHz) δ : 27.1 (q), 27.3 (q), 73.2 (t), 83.2 (d), 83.8 (d), 87.1 (s), 103.3 (d), 105.8 (d), 113.2 (s), 126.3 (d), 128.3 (2d, 4C), 135.2 (s), 155.7 (s). MALDI-TOF (MS): calcd for $\text{C}_{16}\text{H}_{18}\text{O}_5\text{Na}$: 313.11, found: 313.14. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_5$: C, 66.19; H, 6.25. Found: C, 66.10; H, 6.47.

Further elution with 20% ethyl acetate in light petroleum gave **42** (59 mg, 59%) as white solid.

1,2-*O*-Isopropylidene-3-*C*-(2'-hydroxy-2'-phenyl-*Z*-vinyl)-2',5-anhydro- α -D-ribofuranose (**42**): mp=103 °C. $[\alpha]_{\text{D}} -58.2$ (c 0.3, CHCl_3). IR (CHCl_3): ν 3531, 3019, 2928, 1451, 1384, 1164, 1116, 1087, 1056, 1009, 895, 874, 693, 668, 623 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.37 (s, 3H), 1.60 (s, 3H), 3.05 (s, 1H), 4.02 (br s, 1H), 4.05 (s, 1H), 4.32 (d, $J=3.6$ Hz, 1H), 4.54 (br d, $J=12.2$ Hz, 1H), 5.18 (s, 1H), 5.74 (d, $J=3.6$ Hz, 1H), 7.31–7.32 (m, 3H), 7.58–7.60 (m, 2H). ^{13}C NMR (125 MHz) δ : 26.8 (q), 27.1 (q), 63.6 (t), 71.7 (s), 77.4 (d), 83.5 (d), 95.1 (d), 104.2 (d), 112.8 (s), 125.2 (d, 2C), 128.2 (d, 2C), 129.2 (d), 134.3 (s), 155.5 (s). MALDI-TOF (MS): calcd for $\text{C}_{16}\text{H}_{18}\text{O}_5\text{Na}$: 313.11, found: 313.11. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_5$: C, 66.19; H, 6.25. Found: C, 66.40; H, 6.23.

4.1.33. Pd-mediated cyclization of **11**

Alkyne **11** (130 mg, 0.406 mmol) was taken in CH_3CN in argon atmosphere. $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (10 mg, 0.04 mmol) was added to it. After completion of reaction the reaction mixture was concentrated and purified by column chromatography (4:6, EtOAc/hexane). The product **43** was obtained as white crystalline solid (0.100 g, 77%).

1,2-*O*-Isopropylidene-3-*C*-[2'-hydroxy-2'-(4-methoxy-phenyl)-*Z*-vinyl]-2',5-anhydro- α -D-ribofuranose (**43**): mp=110.8 °C. $[\alpha]_{\text{D}} -77.16$ (c 1, CHCl_3). IR (CHCl_3): ν 3480, 2989, 1651, 1455, 1249, 1056, 898 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.37 (s, 3H), 1.59 (s, 3H), 3.02 (s, 1H), 3.80 (s, 3H), 4.02–4.05 (m, 2H), 4.31 (d, $J=3.66$ Hz, 1H), 4.53 (ddd, $J=0.68$, 2.1, 12.48 Hz, 1H), 5.06 (d, $J=1.86$ Hz, 1H), 5.75 (d, $J=3.66$ Hz, 1H), 6.83 (d, $J=8.9$ Hz, 2H), 7.51 (d, $J=8.9$ Hz, 2H). ^{13}C NMR (75 MHz) δ : 26.76 (q), 27.00 (q), 55.18 (q), 63.48 (t), 71.72 (d), 77.32 (d), 83.49 (d), 93.32 (d), 104.22 (d), 112.79 (s), 113.47 (d, 2C), 126.57 (d, 2C), 126.83 (s), 155.24 (s), 160.35 (s). MALDI-TOF (MS): calcd for $\text{C}_{17}\text{H}_{20}\text{O}_6\text{Na}$: 343.12, found: 343.18. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_6$: C, 63.74; H, 6.29. Found: C, 64.03; H, 6.47.

4.1.34. Pd-mediated cyclization of **12**

A solution of alkyne **12** (50 mg, 0.15 mmol) and $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (4 mg, 0.015 mmol) in CH_3CN (6 mL) was stirred under argon atmosphere at 25 °C for 12 h. After completion of reaction the reaction mixture was concentrated and purified by column chromatography (4:6, EtOAc/light petroleum) to afford **44** (40 mg, 80%) as yellow crystalline solid.

1,2-*O*-Isopropylidene-3-*C*-[1'-hydroxy-2'-(4-nitro-phenyl)-*Z*-vinyl]-1',5-anhydro- α -D-ribofuranose (**44**): mp=220.4 °C.

$[\alpha]_{\text{D}} 42.9$ (c 1, CHCl_3). IR (CHCl_3): ν 3458, 3019, 1674, 1592, 1508, 1344, 1257, 1150, 1060, 878 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 1.43 (s, 3H), 1.63 (s, 3H), 3.34 (s, 1H), 4.40–4.56 (m, 3H), 4.62 (d, $J=3.87$ Hz, 1H), 5.61 (s, 1H), 5.91 (d, $J=3.87$ Hz, 1H), 7.70 (d, $J=8.95$ Hz, 2H), 8.14 (d, $J=8.95$ Hz, 2H). ^{13}C NMR (75 MHz) δ : 26.9 (q), 27.1 (q), 74.2 (t), 82.7 (d), 83.2 (d), 87.5 (s), 101.3 (d), 105.7 (d), 113.5 (s), 123.7 (d, 2C), 128.4 (d, 2C), 142.1 (s), 145.4 (s), 159.8 (s). MALDI-TOF (MS): calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7\text{Na}$: 358.09, found: 358.15. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7$: C, 57.3; H, 5.11; N, 4.18. Found: C, 57.9; H, 5.24; N, 4.006.

4.1.35. Pd-mediated cyclization of **13**

Alkyne **13** (50 mg, 0.15 mmol) and $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (4 mg, 0.015 mmol) were taken in CH_3CN (5 mL) and stirred under argon for 12 h. After completion of reaction the reaction mixture was concentrated and purified by column chromatography (30% ethyl acetate in light petroleum) to obtain **45** (32 mg, 64%) as yellow syrup.

1,2-*O*-Isopropylidene-3-*C*-[1'-hydroxy-2'-(3-nitro-phenyl)-*Z*-vinyl]-1',5-anhydro- α -D-ribofuranose (**45**): $[\alpha]_{\text{D}} 16.4$ (c 1.8, CHCl_3). IR (CHCl_3): ν 3502, 3021, 2991, 1673, 1528, 1459, 1376, 1351, 1165, 1085, 1012, 876 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ : 1.42 (s, 3H), 1.62 (s, 3H), 3.32 (s, 1H), 4.42 (dd, $J=2.8$, 10.5 Hz, 1H), 4.50 (m, 2H), 4.62 (d, $J=3.8$ Hz, 1H), 5.59 (s, 1H), 5.91 (d, $J=3.8$ Hz, 1H), 7.42 (t, $J=8.0$ Hz, 1H), 7.84 (d, $J=7.8$ Hz, 1H), 7.98 (ddd, $J=0.78$, 2.01, 8.17 Hz, 1H), 8.46 (s, 1H). ^{13}C NMR (100 MHz) δ : 26.9 (q), 27.0 (q), 73.9 (t), 82.8 (d), 83.4 (d), 87.3 (s), 100.9 (d), 105.7 (d), 113.4 (s), 120.7 (d), 122.6 (d), 128.9 (d), 133.8 (d), 136.9 (s), 148.4 (s), 158.4 (s). MALDI-TOF (MS): calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7\text{Na}$: 358.09, found: 358.15. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7$: C, 57.31; H 5.11; N, 4.18. Found: C, 57.22; H, 5.03; N, 4.09.

Further elution (35% ethyl acetate in light petroleum) gave **46** (7 mg, 14%) as a colorless oil.

1,2-*O*-Isopropylidene-3-*C*-[2'-hydroxy-2'-(3-nitro-phenyl)-*Z*-vinyl]-2',5-anhydro- α -D-ribofuranose (**46**): $[\alpha]_{\text{D}} -41.5$ (c 0.5, CHCl_3). IR (CHCl_3): ν 3478, 3019, 2927, 2855, 1654, 1533, 1451, 1350, 1118, 1057, 1020, 874 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ : 1.40 (s, 3H), 1.62 (s, 3H), 3.14 (s, 1H), 4.09–4.12 (m, 2H), 4.39 (d, $J=3.65$ Hz, 1H), 4.62 (br d, $J=12.5$ Hz, 1H), 5.37 (s, 1H), 5.80 (d, $J=3.65$ Hz, 1H), 7.52 (t, $J=8.03$ Hz, 1H), 7.93 (d, $J=7.9$ Hz, 1H), 8.19 (d, $J=8.0$ Hz, 1H), 8.48 (s, 1H). ^{13}C NMR (100 MHz) δ : 26.8 (q), 26.9 (q), 63.9 (t), 71.5 (s), 77.2 (d), 83.1 (d), 97.4 (d), 104.2 (d), 113.1 (s), 120.3 (d), 123.8 (d), 129.3 (d), 130.9 (d), 136.0 (s), 148.4 (s), 153.2 (s). MALDI-TOF (MS): calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7\text{Na}$: 358.09, found: 358.12. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7$: C, 57.31; H 5.11; N, 4.18. Found: C, 57.19; H, 4.91; N, 3.98.

4.1.36. Pd-mediated cyclization of **14**

A solution of alkyne **14** (50 mg, 0.15 mmol) and $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (4 mg, 0.015 mmol) in CH_3CN (5 mL) was stirred under argon atmosphere for 12 h. After completion of

reaction, the reaction mixture was concentrated and purified by column chromatography (40% ethyl acetate in light petroleum) to obtain **47** (30 mg, 60%) as yellow crystalline solid.

1,2-*O*-Isopropylidene-3-*C*-[1'-hydroxy-2'-(2-nitro-phenyl)-*Z*-vinyl]-1',5-anhydro- α -D-ribofuranose (**47**): mp=163.4 °C. $[\alpha]_D^{25}$ 17.4 (*c* 1.5, CHCl₃). IR (CHCl₃): ν 3401, 3020, 1605, 1522, 1423, 1347, 1165, 1086, 1018 cm⁻¹. ¹H NMR (200 MHz, CDCl₃) δ : 1.37 (s, 3H), 1.56 (s, 3H), 3.22 (s, 1H), 4.35 (d, *J*=2.4 Hz, 1H), 4.36 (s, 1H), 4.41 (d, *J*=2.4 Hz, 1H), 4.59 (d, *J*=3.86 Hz, 1H), 5.84 (d, *J*=3.86 Hz, 1H), 6.02 (s, 1H), 7.18 (ddd, *J*=1.4, 7.44, 8.18 Hz, 1H), 7.45 (ddd, *J*=1.3, 7.6, 8.3 Hz, 1H), 7.8 (dd, *J*=1.39, 8.21 Hz, 1H), 8.1 (dd, *J*=1.37, 8.08 Hz, 1H). ¹³C NMR (75 MHz) δ : 27.0 (q), 27.1 (q), 73.9 (t), 82.7 (d), 83.3 (d), 87.4 (s), 96.5 (d), 105.7 (d), 113.4 (s), 124.5 (d), 126.5 (d), 129.6 (s), 130.6 (d), 132.4 (d), 147.4 (s), 159.2 (s). MALDI-TOF (MS): calcd for C₁₆H₁₇NO₇Na: 358.09, found: 358.10. Anal. Calcd for C₁₆H₁₇NO₇: C, 57.31; H, 5.11; N, 4.18. Found: C, 57.43; H, 5.25; N, 4.92.

Further elution (35% ethyl acetate in light petroleum) gave **48** (10 mg, 20%) as colorless oil.

1,2-*O*-Isopropylidene-3-*C*-[2'-hydroxy-2'-(2-nitro-phenyl)-*Z*-vinyl]-2',5-anhydro- α -D-ribofuranose (**46**): $[\alpha]_D^{25}$ 95.8 (*c* 0.8, CHCl₃). IR (CHCl₃): ν 3493, 3020, 2928, 1663, 1609, 1449, 1357, 1100, 999, 897 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ : 1.40 (s, 3H), 1.61 (s, 3H), 3.01 (s, 1H), 3.99 (br d, *J*=12.0 Hz, 1H), 4.04–4.08 (m, 1H), 4.32 (d, *J*=3.7 Hz, 1H), 4.43 (dd, *J*=1.0, 12.3 Hz, 1H), 4.97 (d, *J*=1.76 Hz, 1H), 5.85 (d, *J*=3.7 Hz, 1H), 7.44–7.57 (m, 3H), 7.82 (m, 1H). ¹³C NMR (100 MHz) δ : 26.9 (q), 27.1 (q), 64.6 (t), 71.6 (s), 77.8 (d), 83.2 (d), 100.1 (d), 104.3 (d), 113.0 (s), 124.2 (d), 129.9 (d), 130.3 (d), 130.5 (s), 132.2 (d), 148.9 (s), 154.2 (s). MALDI-TOF (MS): calcd for C₁₆H₁₇NO₇Na: 358.09, found: 358.04. Anal. Calcd for C₁₆H₁₇NO₇: C, 57.31; H, 5.11; N, 4.18. Found: C, 57.51; H, 4.95; N, 4.30.

4.1.37. Pd-mediated cyclization of **15**

A solution of **15** (50 mg, 0.21 mmol) and PdCl₂(CH₃CN)₂ (5 mg, 0.02 mmol) in CH₃CN (4 mL) was stirred at 25 °C for 10 h under argon atmosphere. The reaction mixture was concentrated and chromatographed on silica gel (40% ethyl acetate in light petroleum) to obtain **49** (44 mg, 87%) as a solid.

1,2-*O*-Isopropylidene-[3-*C*,5-*O*,6-*O*(methylmethylidene)]- α -D-allofuranose (**49**): mp=159 °C. $[\alpha]_D^{25}$ -40.1 (*c* 1, CHCl₃) [lit.^{17d} $[\alpha]_D^{25}$ -34.4 (*c* 0.9, CHCl₃)]. IR (CHCl₃): ν 3491, 2995, 2942, 1456, 1378, 1239, 1216, 1160, 1100, 1009, 936 cm⁻¹. ¹H NMR (200 MHz, CDCl₃) δ : 1.40 (s, 3H), 1.56 (s, 6H), 3.19 (s, 1H), 3.60–3.69 (m, 2H), 4.16 (s, 1H), 4.32 (d, *J*=3.9 Hz, 1H), 4.50 (br d, *J*=3.0 Hz, 1H), 5.86 (d, *J*=3.9 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ : 13.4 (q), 27.4 (q, 2C), 64.9 (t), 81.6 (d), 81.9 (d), 88.0 (s), 88.7 (d), 107.1 (d), 107.6 (s), 114.0 (s). MALDI-TOF (MS): calcd for C₁₁H₁₆O₆Na: 267.08, found: 267.10. Anal. Calcd for C₁₁H₁₆O₆: C, 54.09; H, 6.60. Found: C, 53.88; H, 6.69.

4.1.38. Pd-mediated cyclization of **16**

Compound **50** was prepared as described earlier treating **16** (200 mg, 0.61 mmol) and PdCl₂(CH₃CN)₂ (15 mg, 0.061 mmol) in dry CH₃CN (10 mL) under argon at 25 °C for 24 h, followed by chromatography on silica gel (30% ethyl acetate in light petroleum) to obtain **50** (50 mg, 55%) based on recovered **16** (110 mg).

1,2-*O*-Isopropylidene-3-*C*-(2'-oxooctyl)- α -D-allofuranose-(2'-*C*,5-*O*,6-*O*)-ketal (**50**): $[\alpha]_D^{25}$ -1.2 (*c* 0.8, CHCl₃). IR (CHCl₃): ν 3406, 3019, 2957, 2927, 1495, 1457, 1384, 1164, 1100, 1081, 1050, 695 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ : 0.86 (t, *J*=6.7 Hz, 3H), 1.23–1.31 (m, 6H), 1.35 (s, 3H), 1.39–1.44 (m, 2H), 1.57 (s, 3H), 1.60 (d, *J*=14.5 Hz, 1H), 1.69–1.72 (m, 2H), 1.93 (d, *J*=14.5 Hz, 1H), 3.05 (br s, 1H), 3.75 (s, 1H), 3.80 (dd, *J*=5.7, 7.1 Hz, 1H), 4.09 (d, *J*=3.7 Hz, 1H), 4.17 (d, *J*=7.2 Hz, 1H), 4.67 (br d, *J*=5.2 Hz, 1H), 5.85 (d, *J*=3.7 Hz, 1H). ¹³C NMR (125 MHz) δ : 14.1 (q), 22.5 (t), 22.6 (t), 26.7 (q), 26.9 (t), 29.4 (d), 31.7 (t), 37.2 (t), 40.9 (t), 65.5 (t), 73.8 (d), 75.0 (s), 78.1 (d), 84.0 (d), 104.0 (d), 107.0 (s), 112.8 (s). MALDI-TOF (MS): calcd for C₁₇H₂₈O₆Na: 351.18, found: 351.19. Anal. Calcd for C₁₇H₂₈O₆: C, 62.17; H, 8.59. Found: C, 62.46; H, 8.71.

4.1.39. Pd-mediated cyclization of **17**

Compound **17** (100 mg, 0.31 mmol) and PdCl₂(CH₃CN)₂ (8 mg, 0.031 mmol) in dry CH₃CN (6 mL) were stirred under argon for 7 h at 25 °C. The reaction mixture was concentrated and purified on silica gel (10% ethyl acetate in light petroleum) to obtain **51** (30 mg, 30%) as colorless oil and **52** (65 mg, 65%) as yellow solid.

1,2-*O*-Isopropylidene-3-*C*-(1'-hydroxy-2'-phenyl-*Z*-vinyl)-1',5-anhydro- α -D-allofuranose (**51**): $[\alpha]_D^{25}$ 24.9 (*c* 1.3, CHCl₃). IR (CHCl₃): ν 3415, 2928, 2854, 1751, 1671, 1599, 1494, 1449, 1375, 1083, 1023, 872, 696 cm⁻¹. ¹H NMR (200 MHz, CDCl₃) δ : 1.40 (s, 3H), 1.62 (s, 3H), 3.82 (dd, *J*=4.4, 12.1 Hz, 1H), 3.90 (dd, *J*=3.9, 12.1 Hz, 1H), 4.22 (br s, 1H), 4.46 (s, 1H), 4.60 (t, *J*=4.2 Hz, 1H), 4.63 (d, *J*=3.7 Hz, 1H), 5.49 (s, 1H), 5.84 (d, *J*=3.7 Hz, 1H), 7.10–7.17 (m, 1H), 7.25–7.32 (m, 2H), 7.55–7.59 (m, 2H). ¹³C NMR (75 MHz) δ : 27.1 (q), 27.3 (q), 62.6 (t), 83.8 (d), 85.6 (d), 86.1 (d), 86.7 (s), 102.7 (d), 105.8 (d), 113.5 (s), 126.3 (d), 128.2 (d), 128.3 (d, 3C), 135.3 (s), 156.8 (s). MALDI-TOF (MS): calcd for C₁₇H₂₀O₆Na: 343.13, found: 343.11. Anal. Calcd for C₁₇H₂₀O₆: C, 63.74; H, 6.29. Found: C, 64.01; H, 6.54.

1,2-*O*-Isopropylidene-3-*C*-(2'-oxo-2'-phenylethyl)- α -D-allofuranose-(2'-*C*,5-*O*,6-*O*)-ketal (**52**): mp=123 °C. $[\alpha]_D^{25}$ -2.2 (*c* 1, CHCl₃). IR (CHCl₃): ν 3515, 2986, 2899, 1450, 1384, 1374, 1053, 1011, 890, 872, 700 cm⁻¹. ¹H NMR (200 MHz, CDCl₃) δ : 1.29 (s, 3H), 1.52 (s, 3H), 1.80 (d, *J*=14.6 Hz, 1H), 2.18 (d, *J*=14.6 Hz, 1H), 3.08 (br s, 1H), 3.76 (s, 1H), 3.89 (br dd, *J*=5.2, 7.3 Hz, 1H), 4.03 (d, *J*=3.6 Hz, 1H), 4.26 (d, *J*=7.3 Hz, 1H), 4.79 (d, *J*=5.2 Hz, 1H), 5.82 (d, *J*=3.6 Hz, 1H), 7.22–7.30 (m, 3H), 7.46–7.50 (m, 2H). ¹³C NMR (75 MHz) δ : 26.7 (q), 27.0 (q), 43.3 (t), 65.6 (t), 74.3 (d), 75.2 (s), 78.1 (d), 84.1 (d), 104.2 (d), 106.2 (s), 112.9 (s), 125.1 (d, 2C), 128.2 (d, 2C), 128.5 (d), 139.9 (s).

MALDI-TOF (MS): calcd for $C_{17}H_{20}O_6Na$: 343.13, found: 343.12. Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.99; H, 6.48.

4.1.40. Pd-mediated cyclization of **18**

A solution of **18** (50 mg, 0.14 mmol) and $PdCl_2(CH_3CN)_2$ (4 mg, 0.014 mmol) in dry CH_3CN (4 mL) was stirred at 25 °C for 3 h and concentrated. The residue was purified on silica gel (50% ethyl acetate in light petroleum) to give **53** (41 mg, 82%) as white solid.

1,2-*O*-Isopropylidene-3-*C*-[2'-oxo-2'-(4-methoxyphenyl)-ethyl]- α -D-allofuranose-(2'-*C*,5-*O*,6-*O*)-ketal (**53**): mp=168 °C. $[\alpha]_D^{25}$ 2.6 (c 1.25, $CHCl_3$). IR ($CHCl_3$): ν 3019, 1516, 1249, 1177, 1084, 1052, 873, 802, 669 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$) δ : 1.37 (s, 3H), 1.60 (s, 3H), 1.89 (d, $J=14.6$ Hz, 1H), 2.27 (d, $J=14.6$ Hz, 1H), 3.17 (s, 1H), 3.79 (s, 3H), 3.84 (br s, 1H), 3.98 (dd, $J=5.7, 7.2$ Hz, 1H), 4.13 (br d, $J=3.7$ Hz, 1H), 4.33 (dd, $J=0.8, 7.2$ Hz, 1H), 4.87 (br d, $J=5.4$ Hz, 1H), 5.91 (d, $J=3.7$ Hz, 1H), 6.87 (br d, $J=8.9$ Hz, 2H), 7.48 (br d, $J=8.9$ Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 26.7 (q), 26.9 (q), 43.0 (t), 55.2 (q), 65.6 (t), 74.2 (d), 75.2 (s), 77.9 (d), 83.8 (d), 104.0 (d), 106.1 (s), 112.9 (s), 113.5 (d, 2C), 126.4 (d, 2C), 132.1 (s), 159.7 (s). MALDI-TOF (MS): calcd for $C_{18}H_{22}O_7Na$: 373.13, found: 373.11. Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.71; H, 6.33. Found: C, 61.77; H, 6.22.

4.1.41. Pd-mediated cyclization of **19**

Compound **19** (100 mg, 0.27 mmol) and $PdCl_2(CH_3CN)_2$ (7 mg, 0.027 mmol) in dry CH_3CN (4 mL) were stirred under argon atmosphere at 25 °C for 5 h and concentrated. The residue was purified on silica gel (50% ethyl acetate in light petroleum) to obtain **54** (87 mg, 87%) as a yellow oil.

1,2-*O*-Isopropylidene-3-*C*-[1'-hydroxy-2'-(4-nitro-phenyl)-Z-vinyl]-1',5-anhydro- α -D-ribofuranose (**54**): $[\alpha]_D^{25}$ 33.8 (c 1.5, $CHCl_3$). IR ($CHCl_3$): ν 3437, 3020, 2938, 1781, 1661, 1593, 1513, 1376, 1341, 1216, 1165, 1086, 1027, 861 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$) δ : 1.40 (s, 3H), 1.61 (s, 3H), 3.14 (br s, 1H), 3.88 (dd, $J=3.7, 12.1$ Hz, 1H), 4.01 (dd, $J=3.4, 12.1$ Hz, 1H), 4.50 (s, 2H), 4.64 (d, $J=3.7$ Hz, 1H), 4.69 (t, $J=3.7$ Hz, 1H), 5.52 (s, 1H), 5.84 (d, $J=3.7$ Hz, 1H), 7.61 (d, $J=8.9$ Hz, 2H), 8.01 (d, $J=8.9$ Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 27.0 (q), 27.2 (q), 62.5 (t), 83.5 (d), 85.2 (d), 87.0 (s), 87.2 (d), 100.4 (d), 105.6 (d), 113.8 (s), 123.7 (d, 2C), 128.3 (d, 2C), 142.3 (s), 145.1 (s), 161.4 (d). MALDI-TOF (MS): calcd for $C_{17}H_{19}NO_8Na$: 388.10, found: 388.12. Anal. Calcd for $C_{17}H_{19}NO_8$: C, 55.89; H, 5.24; N, 3.83. Found: C, 56.08; H, 5.16; N, 3.71.

4.1.42. Pd-mediated cyclization of **20**

The reaction of **20** (100 mg, 0.27 mmol) and $PdCl_2(CH_3CN)_2$ (7 mg, 0.027 mmol) in dry CH_3CN (4 mL) was carried out as described earlier to procure **55** (65 mg, 65%) and **56** (18 mg, 18%).

1,2-*O*-Isopropylidene-3-*C*-[1'-hydroxy-2'-(3-nitro-phenyl)-Z-vinyl]-1',5-anhydro- α -D-ribofuranose (**55**): $[\alpha]_D^{25}$ 7.4 (c 1.5, $CHCl_3$). IR ($CHCl_3$): ν 3535, 3020, 1609, 1529, 1384, 1346, 1164, 1083, 842 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$) δ : 1.40 (s,

3H), 1.61 (s, 3H), 3.03 (br s, 1H), 3.88 (dd, $J=3.8, 12.0$ Hz, 1H), 4.0 (br dd, $J=3.4, 12.0$ Hz, 1H), 4.50 (s, 1H), 4.51 (s, 1H), 4.64 (d, $J=3.7$ Hz, 1H), 4.69 (t, $J=3.8$ Hz, 1H), 5.53 (s, 1H), 5.84 (d, $J=3.7$ Hz, 1H), 7.39 (t, $J=8.0$ Hz, 1H), 7.79 (dt, $J=1.3, 7.8$ Hz, 1H), 7.92 (ddd, $J=1.0, 2.3, 8.2$ Hz, 1H), 8.42 (t, $J=1.9$ Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 26.9 (q), 27.2 (q), 62.5 (t), 83.5 (d), 85.3 (d), 86.7 (d), 86.8 (s), 100.1 (d), 105.6 (d), 113.8 (s), 120.6 (d), 122.6 (d), 129.0 (d), 133.8 (d), 137.0 (s), 148.3 (s), 159.7 (s). MALDI-TOF (MS): calcd for $C_{17}H_{19}NO_8Na$: 388.10, found: 388.09. Anal. Calcd for $C_{17}H_{19}NO_8$: C, 55.89; H, 5.24; N, 3.83. Found: C, 55.85; H, 5.43; N, 3.87.

1,2-*O*-Isopropylidene-3-*C*-[2'-oxo-2'-(3-nitrophenyl)-ethyl]- α -D-allofuranose-(2'-*C*,5-*O*,6-*O*)-ketal (**56**): $[\alpha]_D^{25}$ 3.7 (c 0.8, $CHCl_3$). IR ($CHCl_3$): ν 3400, 3020, 1533, 1385, 1352, 1165, 1084, 1053, 992, 890 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$) δ : 1.39 (s, 3H), 1.61 (s, 3H), 1.90 (d, $J=14.6$ Hz, 1H), 2.28 (d, $J=14.6$ Hz, 1H), 3.18 (s, 1H), 3.85 (s, 1H), 4.01 (dd, $J=5.9, 7.0$ Hz, 1H), 4.15 (d, $J=3.7$ Hz, 1H), 4.40 (d, $J=7.3$ Hz, 1H), 4.92 (d, $J=5.4$ Hz, 1H), 5.94 (d, $J=3.7$ Hz, 1H), 7.55 (t, $J=8.1$ Hz, 1H), 7.91 (d, $J=7.8$ Hz, 1H), 8.21 (dd, $J=1.2, 8.1$ Hz, 1H), 8.47 (br t, $J=1.8$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 26.8 (q), 26.9 (q), 43.0 (t), 65.9 (t), 74.5 (d), 75.2 (s), 77.9 (d), 83.7 (d), 104.2 (d), 105.3 (s), 113.1 (s), 120.8 (d), 123.6 (d), 129.3 (d), 131.4 (d), 141.9 (s), 148.3 (s). MALDI-TOF (MS): calcd for $C_{17}H_{19}NO_8Na$: 388.10, found: 388.08. Anal. Calcd for $C_{17}H_{19}NO_8$: C, 55.89; H, 5.24; N, 3.83. Found: C, 56.17; H, 5.53; N, 3.48.

4.1.43. Pd-mediated cyclization of **21**

A solution of **21** (50 mg, 0.14 mmol) and $PdCl_2(CH_3CN)_2$ (4 mg, 0.014 mmol) in dry CH_3CN (4 mL) was stirred under argon atmosphere for 5 h at 25 °C. The reaction mixture was concentrated and the residue chromatographed on silica (30% ethyl acetate in light petroleum) to obtain **57** (36 mg, 72%) as yellow oil.

1,2-*O*-Isopropylidene-3-*C*-[1'-hydroxy-2'-(2-nitrophenyl)-Z-vinyl]-1',5-anhydro- α -D-ribofuranose (**57**): $[\alpha]_D^{25}$ 76.9 (c 0.5, $CHCl_3$). IR ($CHCl_3$): ν 3435, 3020, 1729, 1662, 1523, 1376, 1346, 1165, 1085, 1027, 873 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$) δ : 1.42 (s, 3H), 1.62 (s, 3H), 3.88 (dd, $J=4.3, 12.1$ Hz, 1H), 3.96 (dd, $J=3.8, 12.1$ Hz, 1H), 4.49 (br s, 1H), 4.62 (t, $J=4.2$ Hz, 1H), 4.69 (d, $J=3.7$ Hz, 1H), 5.89 (d, $J=3.7$ Hz, 1H), 6.0 (s, 1H), 7.27 (ddd, $J=1.4, 7.4, 8.4$ Hz, 1H), 7.52 (ddd, $J=1.4, 7.6, 8.9$ Hz, 1H), 7.83 (dd, $J=1.3, 8.2$ Hz, 1H), 7.99 (dd, $J=1.3, 8.0$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 27.0 (q), 27.3 (q), 62.6 (t), 83.5 (d), 85.4 (d), 86.9 (s), 86.9 (d), 96.1 (d), 105.8 (d), 113.8 (s), 124.5 (d), 126.7 (d), 129.6 (s), 130.9 (d), 132.4 (d), 147.7 (s), 160.0 (s). MALDI-TOF (MS): calcd for $C_{17}H_{19}NO_8Na$: 388.10, found: 388.11. Anal. Calcd for $C_{17}H_{19}NO_8$: C, 55.89; H, 5.24; N, 3.83. Found: C, 55.91; H, 5.39; N, 3.73.

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- X-ray intensity data for all the compounds were collected on a Bruker SMART APEX CCD diffractometer with *omega* and *phi* scan modes, λ Mo $K\alpha=0.71073$ Å at $T=297(2)$ K. All the data were corrected for Lorentzian, polarization, and absorption effects using Bruker's SAINT and SADABS programs. The crystal structure is solved by direct method using SHELXS-97 and the refinement was performed by full matrix least squares of F^2 using SHELXL-97.²¹
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- Only cell parameters are reported herein (Table 1); a full structural analysis will be published elsewhere. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as deposition nos. CCDC-649447 (**40**), CCDC-296444 (**42**), CCDC-649448 (**44**), CCDC-649449 (**47**), CCDC-296445 (**52**), and CCDC-649450 (**53**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk].