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The influence of electronic factors on Pd-mediated cycloisomerization: a systematic investigation of competitive 6-*exo*-dig versus 7-*endo*-dig cyclizations of sugar alkynols

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ABSTRACT

Pd-mediated cycloisomerization of 3-*C*-propargyl-*ribo*- and *allo*furanose derivatives was investigated in detail to understand the influence of electronic factors on the regioselectivity (6-*exo*- vs 7-*endo*) of alkynol cycloisomerization leading either to a six- or seven-membered ring. In general, the 6-*exo*-dig mode of cyclization is facile and is independent of electronic factors. With some of the alkynols, a regioselective (7-*endo*?) hydration of the alkyne unit was observed and this has been attributed to the participation of *C*(3)–OH. When the *C*(3)–OH was protected as its benzyl ether, cycloisomerization of these alkynols occurred exclusively in a 6-*exo*-dig mode resulting in the corresponding [3.2.1]-bicyclic ketals. Additional control experiments conducted were in support of the participation of *C*(3)–OH in regioselective alkyne hydration.

1. Introduction

The intramolecular addition of *C*- and heteroatom nucleophiles across the alkynes falls under the broad category of cycloisomerization reactions.[1] The cycloisomerization is projected as a tool for synthesis of oxygen-containing heterocycles encompassing functionalized furan, pyran, benzopyran, and spiroketal skeletons.[2] Various transition metals like palladium, gold, platinum, tungsten, molybdenum, ruthenium, rhodium, and iridium have been explored as catalysts in cycloisomerization reactions.[3] The key issue of the cycloisomerization reactions is the mode of cyclization, i.e., *exo*-dig versus *endo*-dig.[4] In this context, recently we reported a systematic investigation dealing with the influence of electronic and steric factors over competitive 5-*exo*-dig versus 6-*endo*-dig cyclizations mediated by the $Pd(CH_3CN)_2Cl_2$ complex.[5,6] Using a large set of substrates for the projected cycloisomerization reaction, we noticed that Pd promoted cycloisomerization reactions were substantially influenced by electronic factors, which is in contrast with the base promoted cycloisomerizations.[6] From the results obtained, we concluded that competitive balance between the $-I$ effect of furanose ring and the +M effect of the aryl substituents influences the mode of cyclization. The presence of a +M substituent (–OMe) on the aromatic ring in general enforced a 6-*endo*-dig while the presence of a −M group ($-NO_2$) favored 5-*exo*-dig modes of cyclization. In the cases where the *exo*-mode of ring closure is disfavored due to ring strain we noticed exclusive 6-*endo* cyclization.[6b]

Compared to the competitive 5-*exo*-dig/6-*endo*-dig case, reports concerning the 6-*exo*-dig/7-*endo*-dig cyclizations are less frequent.[7,8] The seminal publications by Utimoto et al. on the Pd-mediated cycloisomerization of ω-alkynols show that 5-*exo* and 6-*exo*-dig cyclizations are more favored over their competitive *endo*-dig cyclizations.[2f] A one pot Sonogashira coupling and cycloisomerization of 3-, 4-, and 5-alkynols with aryl halides were studied by Santelli and co-workers using the *tedicyp* ligand.[7c] In general, 6-*exo*-dig mode of cyclizations was documented and the cyclizations are favored only with electron deficient aryl halides whereas with electron rich aryl halides, only coupling products were isolated. Results published by Luo et al. showed that oxypalladation and cross-coupling of acetylenic alkoxides generally prefer to undergo 6-*exo*-ring closure.[5h] Liu and de Brabander reported regiochemical control in the cycloisomerization of electronically unbiased internal alkynes by selecting appropriate catalysts and conditions.[7d] While our work was in progress, Ley and co-workers reported the selective

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7-*endo* cyclization of alkyne diols by employing $PtCl_4$ as the catalyst.[7e]

In continuation of our interest in the Pd-mediated cycloisomerization of sugar alkynol and the synthesis of natural products having either bridged- or spiro-bicyclic ketal units, we were interested to learn the control of electronic factors over the competitive 6-*exo*-dig versus 7-*endo*-dig modes of cyclization.[6] Herein we describe our investigations in this direction, employing two sets of 3-*C*-propargylfuranosyl derivatives (Fig. 1) **8**–**12**, and **13**–**17**. With the first set of compounds **8**–**12**, the cycloisomerization should lead either to [3.4.0]- or [3.5.0]-dioxabicyclic enol ether derivatives, whereas the formation of fused [3.2.1]- or [4.2.1]-bicyclicacetal derivatives is possible from the second set of compounds **13**–**17** (Fig. 1).

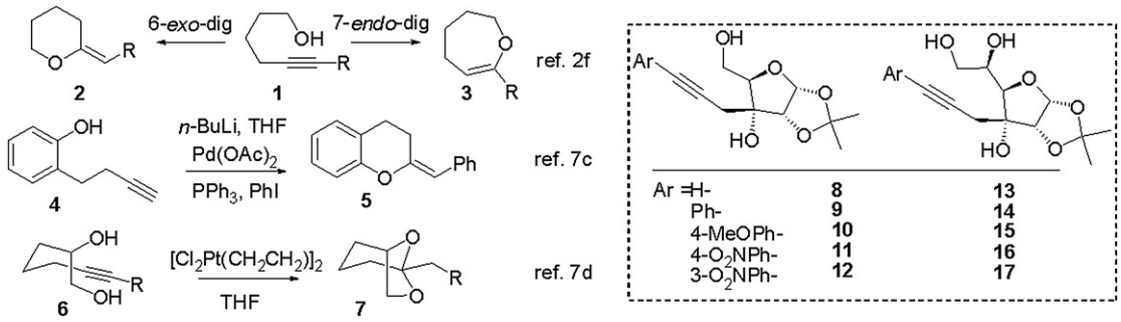


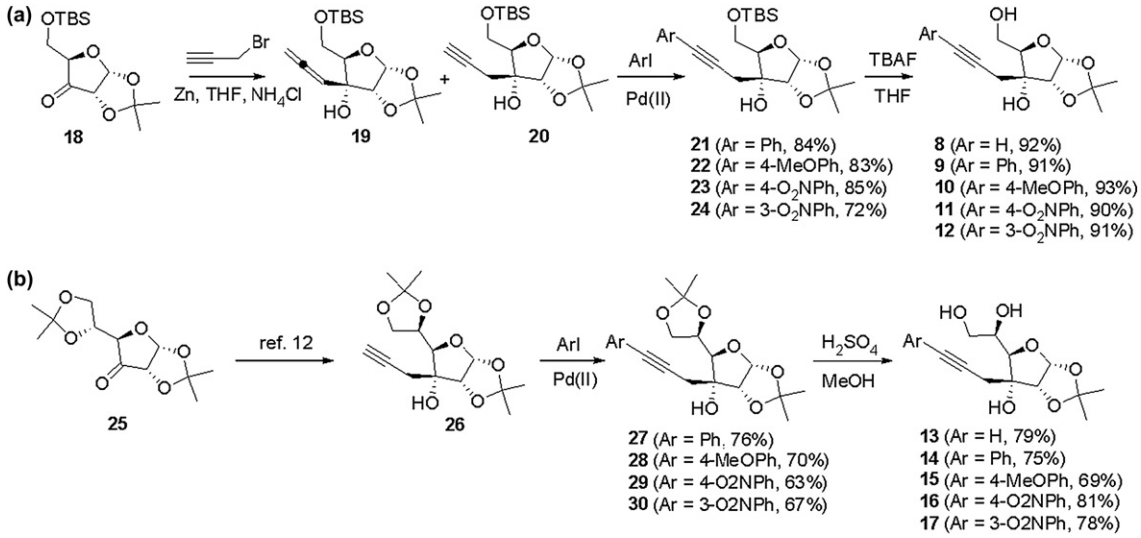
Figure 1. Competitive 6-*exo*-dig versus 7-*endo*-dig cyclizations, some representative examples, and designed substrates **8**–**17**.

2. Results and discussion

The synthesis of the requisite model 3-*C*-propargyl-*ribo*furanose derivatives **8**–**12** started with propargylation of the known 3-ulose derivative **18**[9] under Barbier conditions to afford **20** along with the allene **19** (Scheme 1).[10] The Sonogashira coupling[11] of **20** with different aryl iodides was carried out to obtain compounds **21**–**24**. The TBS group present at *O*-5 of **20**–**24** was subsequently removed by using TBAF/THF to give the first set of cycloisomerization substrates **8**–**12**. The synthesis of the projected cycloisomerization substrates **13**–**17** was carried out in a similar way following the Sonogashira coupling with the 3-*C*-propargyl-*allo*furanose derivative **26** (prepared according to the literature procedure from ulose **25**) (Scheme 1)[12] affording compounds **27**–**30**. The selective hydrolysis of the 5,6-*O*-acetonide group of **26**–**30** with cat. H_2SO_4 in methanol completed the synthesis of the projected cycloisomerization substrates **13**–**17**.

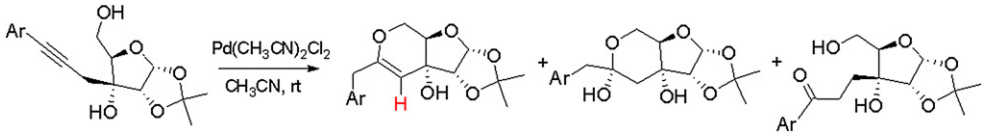
The palladium-catalyzed cycloisomerization reactions of model 3-*C*-propargyl-*ribo*furanose derivatives **8**–**12** were carried out in the presence of $Pd(CH_3CN)_2Cl_2$ in MeCN at room temperature. The results are summarized in Table 1. The parent compound **8** gave exclusively the fused dihydropyran **31** resulting from the double bond isomerization of the intermediate *exo*-methylene derivative.[13] A doublet resonating at 1.79 (d, J=0.8 Hz, 3H) ppm in the ^{1}H NMR spectrum of compound **31** indicated the presence of a methyl group attached to an olefin. There is one additional signal in the downfield region 4.40 (br q, J=0.8 Hz, 1H) ppm along with the sugar ring protons and it was characterized as the internal olefinic proton. The assigned structure of **31** was further supported by the ^{13}C NMR spectrum where signals corresponding to the primary methyl and endocyclic tertiary olefinic-CH and endocyclic quaternary –C appeared at 20.3 (q), 95.0 (d), and 156.2 (s) ppm, respectively.

Cycloisomerization of alkynol **9** (Table 1) afforded the 6-*exo*-product **32** along with small amounts of the hemiketal **33**. The structure of compound **32** was determined with the help of NMR spectroscopy, which shows the characteristic benzylic protons at 3.36 (d, J=16.5 Hz, 1H), 3.40 (d, J=16.5 Hz, 1H) ppm, and endocyclic olefinic proton at 4.40 (br d, J=1.1, Hz, 1H) ppm in ^{1}H NMR (Table 1). Peaks at 40.5 (t) for the benzylic CH_2, at 96.2 (d) for olefinic-CH, and at 158.5 (s) for the quaternary olefinic carbon in ^{13}C NMR indicate the 6-*exo*-dig cyclization with the concomittant isomerization of the double bond. The structure of compound **32** was further confirmed



Scheme 1. Synthesis of (a) 3-*C*-propargyl-*ribo*- (**8**–**12**) and (b) *allo*furanose derivatives (**13**–**17**).

Table 1
Pd-mediated cycloisomerization of alkynols **8**–**12**



	Ar	δ (ppm)		
8	H-	**31** (64%) 4.40	—	—
9	Ph-	**32** (60%) 4.40	**33** (19%)	—
10	4-MeOPh–	**34** (16%) 4.40	—	**35** (55%)
11	4-O_2NPh–	**36** (60%) 4.51	**37** (14%)	—
12	3-O_2NPH–	**38** (53%) 4.53	**39** (13%)	—

from its single crystal X-ray structural analysis.[15–17] The characteristic internal methylene protons of pyran at 1.57 (d, *J*=14.1 Hz, 1H), 1.69 (d, *J*=14.1 Hz, 1H) ppm, and benzylic CH_2 protons at 2.82 (d, *J*=13.6 Hz, 1H), 3.03 (d, *J*=13.6 Hz, 1H) ppm in the ^{1}H NMR spectrum of compound **33** indicated the assigned ketal structure, which was further supported by the ^{13}C NMR spectrum where the characteristic peaks at 37.0 (t) for internal CH_2, 47.5 (t) for benzylic CH_2, 95.5 (s) for hemiketal carbon appeared. With alkynol **10**, cycloisomerization gave the dihydropyran **34** (6-*exo*) and the keto compound **35**. Cycloisomerization of alkynols **11** and **12** gave dihydropyran derivatives **36** and **38** and the hemiketals **37** and **39**, respectively. The dihydropyrans **31**, **32**, **34**, **36**, and **38** and the ketals **33**, **37**, and **39** have similar NMR spectral pattern (Table 1). The single crystal X-ray analyses of (Fig. 2) of *ketals* **37** and **39** unambiguously proved their structures.[15–17]

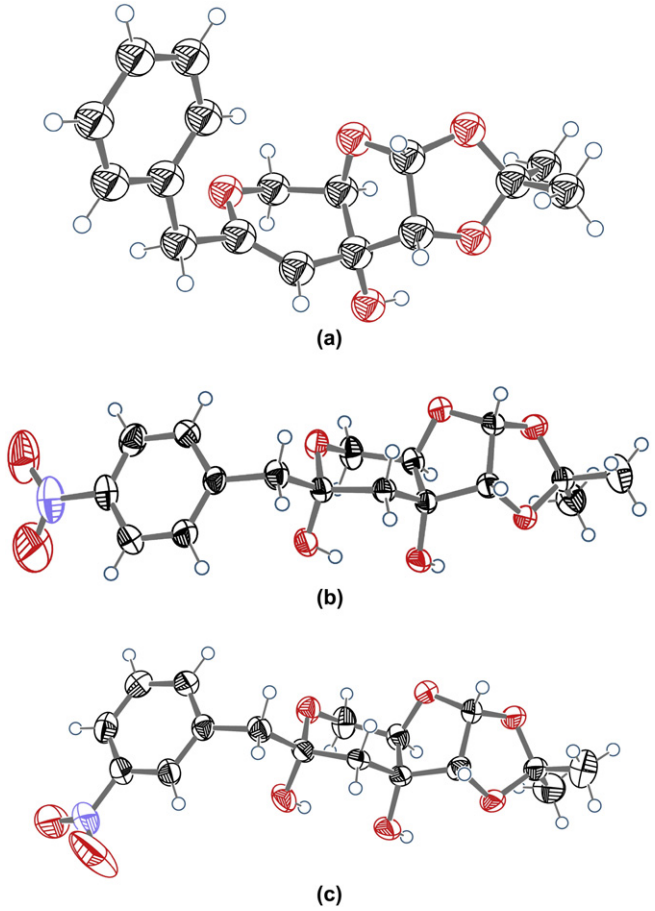
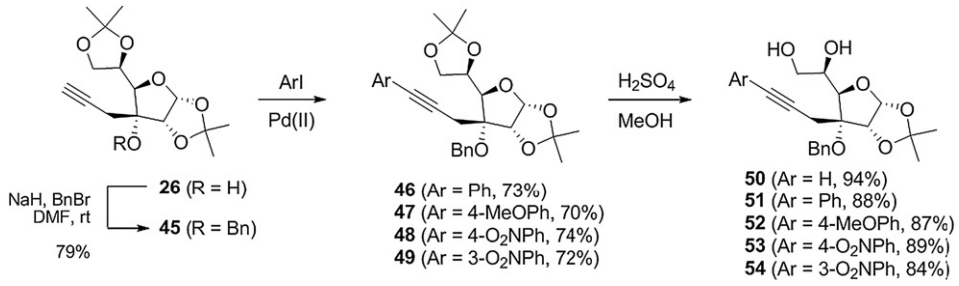


Figure 2. ORTEP structures of compounds (a) **32**, (b) **37**, and (c) **39**.

The results of the $Pd(CH_3CN)_2Cl_2$ catalyzed cycloisomerizations of the 3-*C*-propargyl-*allo*furanose derivatives **13**–**17** are given in Scheme 2. As indicated in Table 2, the cycloisomerization of monosubstituted alkynol **13** gave exclusively [3.2.1]-bicyclic acetal **40**. The appearance of the methylene unit protons separately as doublets at δ 1.62 and 1.95 with a large geminal coupling constant (14.7 Hz) in the ^{1}H NMR spectrum of **40**[14] clearly indicates that this methylene unit has no coupled adjacent-H and thus established the assigned [3.2.1]-bicyclic acetal structure. The presence of a quaternary carbon at 105.3 (s) ppm in the ^{13}C NMR spectrum corresponding to the ketal carbon further confirms the assigned structure to **40**. The cycloisomerization of *p*-nitrophenyl substituted alkynol **16** also gave exclusively the *exo*-cyclic product **43** where the methylene protons resonated as doublets at δ 1.66 and 2.01 with a large geminal coupling constant (14.4 Hz) in the ^{1}H NMR spectrum and the characteristic ketal carbon at 105.7 (s) ppm in the ^{13}C NMR spectrum. The cycloisomerization of alkynols **14**, **15**, and **17**, gave exclusively keto derivatives **41**, **42**, and **44**, respectively. The structure of **41** was deduced from the ^{1}H NMR spectrum where all the four methylene protons resonated separately as dd or ddd between 1.81 and 3.40 ppm thus displaying the through bond connectivity between all of them. The appearance of a quaternary carbon singlet around 200 ppm in the ^{13}C NMR spectrum confirmed the presence of a carbonyl carbon. Characteristic NMR peaks of **41**, **42**, and **44** are given in Table 3.

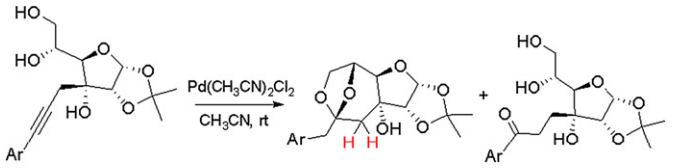
To summarize, the cycloisomerization of 3-*C*-propargyl-*ribo*furanose derivatives **8**, **9**, **11**, and **12** resulted in exclusive 6-*exo*-dig products. With compound **10**, the keto compound **35** was isolated as the major product. The enol ether **34** resulting from a 6-*exo*-dig cyclization followed by isomerization was obtained as the minor product. The cycloisomerization of alkyne diols **13**–**17**, the alkynols **13** and **16** gave the [3.2.1]-bicyclic acetals **40** and **43**, whereas the other three alkynols **14**, **15**, and **16** gave the ketones **41**, **42**, and **44**, respectively. The constitution of these products indicated a regioselective hydration of the internal alkyne resulting exclusively α- to the phenyl ring. The exclusive formation of 6-*exo* products from the phenyl derivative **9** and the 3-NO_2 phenyl derivatives **12** and **17** is interesting since the cyclization of the corresponding substrates without the propagylic –CH_2 (Fig. 3)[6c] gave both 5-*exo* and 6-*endo* products in varying ratios. This indicates a nominal influence of the electronic factors on the regioselectivity of alkynol cylization where the competition is between 6-*exo*- versus 7-*endo* cyclizations, the latter being energetically more demanding. This was supported by the formation of 6-*exo*-product from the PMP derivative **14**.

The formation of the keto compounds **35**, **41**, **42**, and **44**, there are three possibilities that exist (Fig. 4). They are: (a) the hydrolysis of the intermediate 7-*endo* products, (b) the hydration of the alkyne directly,[18] and (c) hydration assisted by the *C*(3)–OH (initial cyclization in a 5-*endo* manner and hydrolysis of intermediate dihydrofuran derivative, *path ii*). However, formation of the keto compounds with the same regioselectivity from PMP and also from



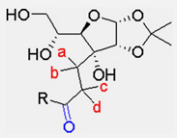
Scheme 2. Synthesis of 3-*O*-benzyl protected 3-*C*-propargyl-*allo*furanose derivatives **50**–**54**.

Table 2
Pd-mediated cycloisomerization of alkynols **13**–**17**



	Ar	δ (ppm)	
13	H–	**40** (70%) (1.62 and 1.95)	—
14	Ph–	—	**41** (66%)
15	4-MeOPh–	—	**42** (60%)
16	4-O_2NPh–	**43** (70%) (1.66 and 2.01)	—
17	3-O_2NPH–	—	**44** (60%)

Table 3
^{1}H and ^{13}C chemical shifts for **41**, **42**, and **44**

R		Ph (**41**)	4-MeOPh (**42**)	3-NO_2Ph (**44**)
	δ_a	1.88	1.87	1.90
	δ_b	2.30	2.30	2.31
	δ_c	3.10	3.04	3.10
	δ_d	3.39	3.33	3.40
	$\delta_{C=O}$	200.0	198.6	199.9

the 3-NO_2 derivative rules out the possibility of both the direct hydration of alkyne unit or hydrolysis of the initially formed 7-*endo*-product. The only option left is the participation of *C*(3)–OH in a 5-*endo* fashion and subsequent hydrolysis.

In order to probe in this direction, we have protected the 3°-OH as its benzyl ether **45** and subjected it to the Sonogashira coupling with the four aryl iodides. Subsequently, the terminal

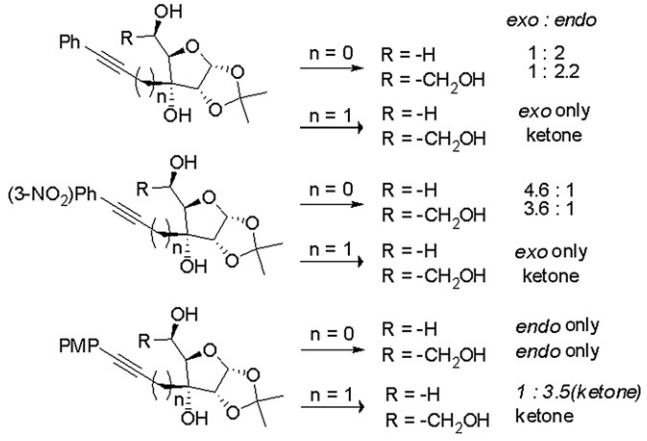


Figure 3. Observed *exo*/*endo* selectivities in the competitive 5-*exo*- versus 6-*endo* and 6-*exo*- versus 7-*endo* cyclization.

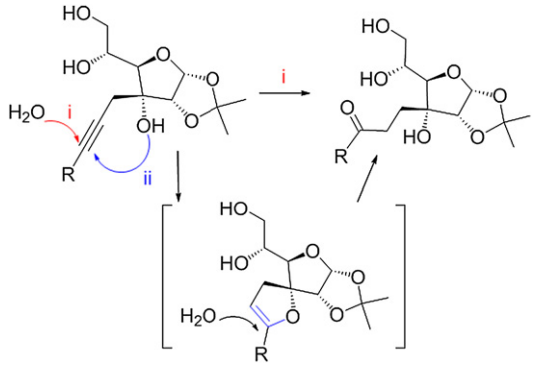
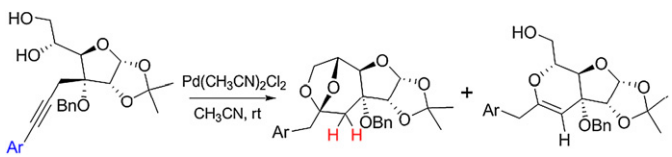


Figure 4. The two possible modes for the formation of ketones **41**, **42**, and **44**.

acetonide of resulting products **45**–**49** was selectively hydrolyzed to prepare the alkyne diols **50**–**54** (Scheme 2). The details of the Pd-mediated cycloisomerization of compounds **50**–**54** are given in Table 4. With all the substrates, we isolated [3.2.1]-bicyclic acetals resulting from the 6-*exo*-dig mode of cyclization (Fig. 5). The exclusive formation of the 6-*exo*-product from **52** is remarkable and suggests the absence of electronic influence on the 6-*exo*- versus 7-*endo* competition, with the former being found to be energetically more facile. These results are in support of the participation of *C*(3)–OH in alkyne hydration. To cross-check this, the acetonides **28** and **47** were exposed to the cycloisomerization conditions (Scheme 3) anticipating hydration at least with the compound **28**. However, the bicyclic ketals **61** and **57** were obtained, respectively, from the alkynes **28** and **47**. The assigned structure for **61** was deduced from the NMR spectral analysis, wherein the four methylene protons resonated separately at 1.52, 2.05–2.21, 2.36–2.54, and 3.69 ppm in the ^{1}H NMR. The exclusive formation of the 6-*exo*-product **61** from the 3-*O*-benzyl derivative could be resulting from the initial hydrolysis of the terminal acetonide group[19] followed by the

Table 4
Pd-mediated cycloisomerization of substrates **50**–**54** and characteristic chemical shifts



	Ar		
50	H–	**55** (82%) (1.37 and 2.33)	—
51	Ph–	**56** (82%) (1.29 and 2.27)	—
52	4-MeOPh–	**57** (81%) (1.27 and 2.24)	—
53	4-O_2NPh–	**58** (68%) (1.38 and 2.32)	—
54	3-O_2NPH–	**59** (67%) (1.35 and 2.33)	**60** (17%)

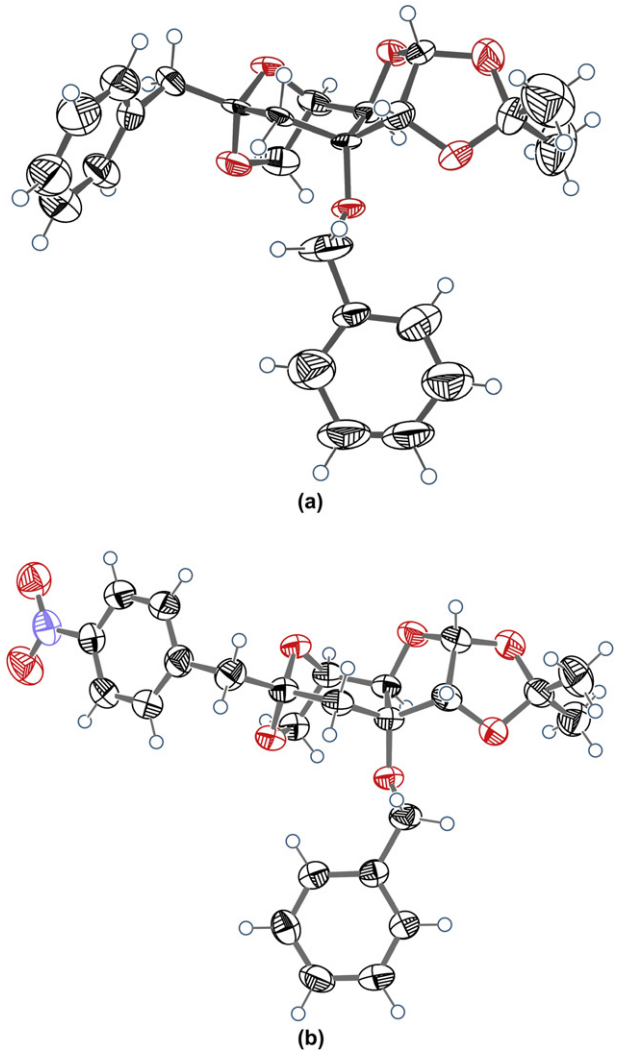
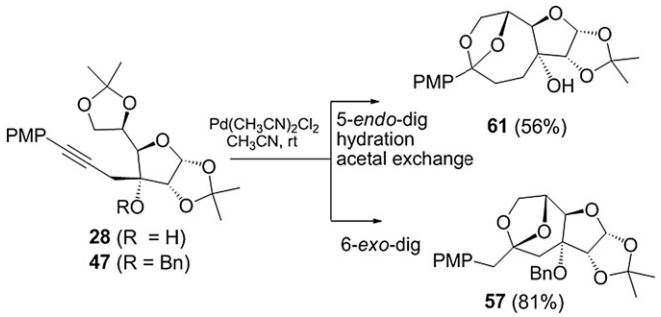


Figure 5. ORTEP structures of compounds (a) **56** and (b) **58**.

cycloisomerization of the intermediate alkynol **52**, both being the reactions catalyzed by the Pd(II) complex. The formation of a [4.2.1]-bicyclic ketal **61** could be explained by initial *C*(3)–OH assisted alkyne hydration of **28** resulting in a ketone, which subsequently would undergo an intramolecular ketal exchange. It is seen that these control experiments with the acetonides provided further evidence of the active role of *C*(3)–OH in alkyne hydration. The formation of keto compounds indicates a competing 5-*endo*-dig cyclization over the 6-*exo*-dig even in the cases where the former is not supported by the electronic factors. The fact that the alkyne hydration was a competitive side reaction in the *allo*-series (**13**–**16**), but not in the *ribo*-series



Scheme 3. Pd-mediated cycloisomerization of acetonides **28** and **47**.

(**8**–**12**) is indicative of the nature of the nucleophile (reactivity of 1°-OH>2°-OH). In the former case (**13**–**16**), the incoming nucleophile in a 6-*exo*-mode is a 2°-OH whereas the same in the latter case (**8**–**12**) is a 1°-OH. In both the instances the competing nucleophile in a 5-*endo* mode is a 3°-OH.

3. Conclusions

In summary, electronic control over the 6-*exo*-dig versus 7-*endo*-dig modes of cyclizations in Pd-mediated cycloisomerization reaction has been studied in detail. The 3-*C*-propargyl *allo*- and *ribo*furanose derivatives, with systematic variation of functional groups at the other side of alkyne, were employed to understand the competitive balance between the inductive effect of the furanose ring and the mesomeric effect of the aryl substituent. Unlike with 3-*C*-alkynyl *allo*- and *ribo*furanose derivatives, where the regioselectivity of the cyclization was in line with the electronic control, with the 3-*C*-propargyl-*ribo* derivatives, we observed complete 6-*exo*-dig selectivity without any electronic interference. However, intermediate *exo*-cyclic enol ethers isomerized to more stable endocyclic enol ethers. With 1,2-*O*-isopropylidene-3-*C*-propargyl-*allo*furanose derivatives, competitive hydration of the alkyne unit with complete regioselectivity was observed. The cycloisomerization of the corresponding 3-*O*-benzyl protected *allo*furanose derivatives revealed that the ketones are resulting from the participation of *C*(3)–OH in a 5-*endo* fashion followed by the hydrolysis of the intermediate dihydrofuran derivative. This was supported by the Pd-mediated cyclization of the selected diacetonides having the PMP group on alkyne and with either *C*(3)–OH free or with the corresponding *O*-benzyl ether. Overall, these results indicate that in the Pd-mediated alkynol cycloisomerizations, the 6-*exo*-dig mode of cyclization is favored over the 7-*endo*-dig mode of cyclization and is not influenced by electronic factors.

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 from Na and benzophenone; DMF 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). Optical rotations were determined on a Jasco DIP-370 digital polarimeter. Specific optical rotations $[\alpha]_D$ are given in 10^{-1} deg cm^2 g^{-1}. ^{1}H and ^{13}C NMR spectroscopy measurements were carried out on Bruker AC 200 MHz or Bruker DRX 500 MHz spectrometers, and TMS was used as internal standard. ^{1}H 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. The multiplicity of ^{13}C NMR signals was assigned with the help of DEPT spectra and the abbreviations used: s=singlet, d=doublet, t=triplet, q=quartet, represent C (quaternary), CH, CH_2, and CH_3, respectively. Mass spectroscopy was carried out on an API QStar Pulsar (Hybrid Quadrupole-TOF LC/MS/MS) spectrometer. Elemental analysis data were obtained on a Thermo Finnigan Flash EA 1112 Series CHNS Analyser.

4.2. Barbier reaction of ketone 18 with propargy bromide

Zn (5.05 g, 77.69 mmol), propargyl bromide (4.15 mL, 46.62 mmol), in THF (50 mL) was stirred vigorously for 30 min, to which a solution of ketone **18** (4.7 g, 15.53 mmol) in THF (50 mL)

was added and the stirring was continued for another 30 min. The reaction mixture was cooled to 0 °C and saturated NH_4Cl (25 mL) was added dropwise for 30 min and stirring was continued overnight. Reaction mixture was filtered through Celite pad and the solvent was evaporated under vacuum and extracted with ethyl acetate, washed with brine, dried (Na_2SO_4), and concentrated. Purification of the crude by column chromatography (10% ethyl acetate in petroleum ether) afforded **19** (1.8 g, 34%) as semi-solid and **20** (2.7 g, 51%) as colorless syrup, respectively.

*4.2.1. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-(propadienyl)-α-D-ribofuranose (**19**).* $[\alpha]_D^{25}$ +14.2 (*c* 1.8, $CHCl_3$). IR ($CHCl_3$): *ν* 3547, 2931, 1957, 1376, 1216, 1086, 838, 757, 668 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 0.07 (s, 6H), 0.88 (s, 9H), 1.34 (s, 3H), 1.59 (s, 3H), 2.76 (br s, 1H), 3.77 (s, 1H), 3.80 (s, 1H), 3.97 (dd, *J*=1.0, 5.4 Hz, 1H), 4.35 (d, *J*=3.7 Hz, 1H), 4.92 (s, 1H), 4.95 (d, *J*=1.1 Hz, 1H), 5.24 (dd, *J*=0.6 6.5 Hz, 1H), 5.69 (d, *J*=3.7 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* −5.4 (q), −5.3 (q), 18.3 (s), 25.9 (q, 3C), 26.6 (q), 26.7 (q), 62.1 (t), 78.0 (s), 78.7 (t), 82.1 (d), 83.3 (d), 90.3 (d), 104.0 (d), 112.7 (s), 207.0 (s) ppm. ESI-MS: *m*/*z* 365.6 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{30}O_5Si$: C, 59.61; H, 8.83. Found: C, 59.54; H, 8.73.

*4.2.2. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-[prop-2′-ynyl]-α-D-ribofuranose (**20**).* $[\alpha]_D^{25}$ +7.6 (*c* 1.3, $CHCl_3$). IR ($CHCl_3$): *ν* 3503, 3311, 2253, 1375, 1255, 1101, 910, 838, 788, 735, 648 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 0.06 (s, 6H), 0.88 (s, 9H), 1.37 (s, 3H), 1.58 (s, 3H), 2.03 (t, *J*=2.6 Hz, 1H), 2.35 (ddd, *J*=0.7, 2.7, 17.1 Hz, 1H), 2.57 (dd, *J*=2.7 17.1 Hz, 1H), 2.79 (br d, *J*=0.8 Hz, 1H), 3.77–3.90 (m, 3H), 4.48 (d, *J*=3.9 Hz, 1H), 5.79 (d, *J*=3.9 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* −5.5 (q), −5.4 (q), 18.2 (s), 22.9 (t), 25.8 (q, 3C), 26.5 (q), 26.6 (q), 60.8 (t), 71.1 (d), 78.1 (s), 79.1 (s), 81.8 (d), 82.0 (d), 103.7 (d), 112.4 (s) ppm. ESI-MS: *m*/*z* 365.6 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{30}O_5Si$: C, 59.61; H, 8.83. Found: C, 59.55; H, 8.75.

4.3. General procedure for Sonogashira coupling

To a solution of alkyne (1 mmol), iodobenzene (1 mmol) in Et_3N (3 mL) and DMF (1.5 mL), TPP was added followed by $Pd(PPh_3)_2Cl_2$ (0.1 mmol), and the reaction mixture was flushed with argon for 30 min. CuI (0.11 mmol) was added and flushed with argon for 10 min and stirred at rt for 12 h. The reaction mixture was partitioned between ethyl acetate, water and the organic layer was separated, washed with brine, dried (Na_2SO_4), and concentrated. The crude residue was purified by column chromatography.

*4.3.1. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-[3′-phenyl-prop-2′-ynyl]-α-D-ribofuranose (**21**).* Reagents: alkyne **20** (500 mg, 1.46 mmol); iodobenzene (0.16 mL, 1.46 mmol); TPP (38 mg, 0.146 mmol); $Pd(PPh_3)_2Cl_2$ (102 mg, 0.146 mmol); CuI (28 mg, 0.146 mmol); Et_3N (5 mL) and DMF (2.5 mL). The crude residue was purified by column chromatography (10% ethyl acetate in petroleum ether) to obtain **21** (515 mg, 84%) as a white solid. Mp 56–57 °C. $[\alpha]_D^{25}$ +22.3 (*c* 1, $CHCl_3$). IR ($CHCl_3$): *ν* 3543, 2954, 1599, 1491, 1375, 1254, 1057, 837, 778, 691 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 0.04 (s, 6H), 0.85 (s, 9H), 1.33 (s, 3H), 1.55 (s, 3H), 2.57 (d, *J*=17.2 Hz, 1H), 2.75 (d, *J*=17.2 Hz, 1H), 2.82 (br s, 1H), 3.83–3.86 (m, 2H), 3.92 (dd, *J*=6.2, 4.0 Hz, 1H), 4.51 (d, *J*=3.9 Hz, 1H), 5.81 (d, *J*=3.9 Hz, 1H), 7.20–7.27 (m, 3H), 7.33–7.40 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* −5.4 (q), −5.2 (q), 18.3 (s), 24.0 (t), 25.9 (q, 3C), 26.7 (q), 26.7 (q), 61.1 (t), 78.6 (s), 82.2 (d, 2C), 83.2 (s), 84.5 (s), 104.0 (d), 112.5 (s), 123.2 (s), 127.9 (d), 128.2 (d, 2C), 131.7 (d, 2C) ppm. ESI-MS: *m*/*z* 441.3 (100%, $[M+Na]^+$). Anal. Calcd for $C_{23}H_{34}O_5Si$: C, 65.99; H, 8.19. Found: C, 65.80; H, 8.32.

*4.3.2. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-[3′-(4-methoxyphenyl)-prop-2′-ynyl]-α-D-ribofuranose (**22**).* Reagents: alkyne **20** (480 mg, 1.40 mmol); iodoanisole (360 mg, 1.54 mmol); TPP (36 mg, 0.14 mmol); $Pd(PPh_3)_2Cl_2$ (98 mg, 0.14 mmol); CuI (26 mg, 0.14 mmol); Et_3N (5 mL) and DMF (2.5 mL). The crude residue was purified by column chromatography (15% ethyl acetate in petroleum ether) afforded **22** (520 mg, 83%) as colorless syrup. $[\alpha]_D^{25}$ +5.3 (*c* 1, $CHCl_3$). IR ($CHCl_3$): *ν* 3500, 2931, 1607, 1510, 1248, 835, 778, 665 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 0.08 (s, 6H), 0.89 (s, 9H), 1.37 (s, 3H), 1.59 (s, 3H), 2.58 (d, *J*=17.1 Hz, 1H), 2.76 (d, *J*=17.1 Hz, 1H), 2.75–2.85 (br s, 1H), 3.79 (s, 3H), 3.85–3.89 (m, 2H), 3.94 (dd, *J*=3.6, 6.5 Hz, 1H), 4.53 (d, *J*=3.9 Hz, 1H), 5.83 (d, *J*=3.9 Hz, 1H), 6.79 (dt, *J*=2.6 8.8 Hz, 2H), 7.33 (dt, *J*=2.6, 8.8 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* −5.5 (q), −5.4 (q), 18.2 (s), 23.8 (t), 25.8 (q, 3C), 26.5 (q), 26.6 (q), 54.9 (q), 61.0 (t), 78.4 (s), 82.2 (d), 82.2 (d), 82.7 (s), 82.8 (s), 103.8 (d), 112.2 (s), 113.6 (d, 2C), 115.2 (s), 132.9 (d, 2C), 159.2 (s) ppm. ESI-MS: *m*/*z* 471.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{24}H_{36}O_6Si$: C, 64.25; H, 8.09. Found: C, 64.13; H, 7.95.

*4.3.3. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-[3′-(4-nitrophenyl)-prop-2′-ynyl]-α-D-ribofuranose (**23**).* Reagents: alkyne **20** (480 mg, 1.40 mmol); 4-iodonitrobenzene (522 mg, 2.1 mmol); TPP (36 mg, 0.14 mmol); $Pd(PPh_3)_2Cl_2$ (98 mg, 0.14 mmol); CuI (26 mg, 0.14 mmol); Et_3N (6 mL) and DMF (3 mL). The residue obtained was purified by column chromatography (15% ethyl acetate in petroleum ether) to give **23** (550 mg, 85%) as yellow syrup. $[\alpha]_D^{25}$ +10.9 (*c* 1, $CHCl_3$). IR ($CHCl_3$): *ν* 3542, 2930, 1594, 1520, 1343, 1106, 838, 751, 688 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 0.08 (s, 6H), 0.90 (s, 9H), 1.39 (s, 3H), 1.60 (s, 3H), 2.64 (d, *J*=17.3 Hz, 1H), 2.85 (d, *J*=17.3 Hz, 1H), 2.85 (br d, *J*=0.6 Hz, 1H), 3.85–3.89 (m, 2H), 3.92 (dd, *J*=3.0, 6.4 Hz, 1H), 4.49 (d, *J*=3.9 Hz, 1H), 5.84 (d, *J*=3.9 Hz, 1H), 7.55 (dt, *J*=2.2, 8.9 Hz, 2H), 8.16 (dt, *J*=2.2, 8.9 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* −5.4 (q), −5.3 (q), 18.3 (s), 24.1 (t), 25.9 (q, 3C), 26.5 (q), 26.7 (q), 60.8 (t), 78.5 (s), 81.4 (s), 82.0 (d, 2C), 90.9 (s), 103.8 (d), 112.6 (s), 123.4 (d, 2C), 130.1 (s), 132.4 (d, 2C), 146.9 (s) ppm. ESI-MS: *m*/*z* 486.2 (100%, $[M+Na]^+$). Anal. Calcd for $C_{23}H_{33}NO_7Si$: C, 59.59; H, 7.17; N, 3.02. Found: C, 59.47; H, 7.14; N, 3.09.

*4.3.4. 1,2-O-Isopropylidene-5-O-(tert-butyldimethylsilyl)-3-C-[3′-(3-nitrophenyl)-prop-2′-ynyl]-α-D-ribofuranose (**24**).* Reagents: alkyne **20** (500 mg, 1.46 mmol); 3-iodonitrobenzene (545 mg, 2.19 mmol); TPP (38 mg, 0.146 mmol); $Pd(PPh_3)_2Cl_2$ (102 mg, 0.14 mmol); CuI (28 mg, 0.146 mmol); Et_3N (8 mL) and DMF (4 mL). The residue obtained was purified by column chromatography (15% ethyl acetate in petroleum ether) gave **24** (490 mg, 72%) as yellow syrup. $[\alpha]_D^{25}$ +9.1 (*c* 1, $CHCl_3$). IR ($CHCl_3$): *ν* 3543, 2930, 1532, 1351, 1100, 838, 758, 673 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 0.09 (s, 6H), 0.90 (s, 9H), 1.39 (s, 3H), 1.60 (s, 3H), 2.62 (d, *J*=17.3 Hz, 1H), 2.84 (d, *J*=17.3 Hz, 1H), 2.85 (d, *J*=0.8 Hz, 1H), 3.86–3.95 (m, 3H), 4.51 (d, *J*=4.0 Hz, 1H), 5.84 (d, *J*=4.0 Hz, 1H), 7.47 (t, *J*=8.0 Hz, 1H), 7.71 (dt, *J*=1.3, 7.7 Hz, 1H), 8.14 (ddd, *J*=1.1, 2.3, 8.2 Hz, 1H), 8.26 (t, *J*=1.9 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* −5.4 (q), −5.3 (q), 18.3 (s), 23.9 (t), 25.9 (q, 3C), 26.5 (q), 26.7 (q), 60.9 (t), 78.4 (s), 80.7 (s), 82.0 (d), 82.1 (d), 88.0 (s), 103.8 (d), 112.6 (s), 122.6 (d), 125.0 (s), 126.4 (d), 129.1 (d), 137.3 (d), 148.0 (s) ppm. ESI-MS: *m*/*z* 486.3 (100%, $[M+Na]^+$). Anal. Calcd for $C_{23}H_{33}NO_7Si$: C, 59.59; H, 7.17; N, 3.02. Found: C, 59.65; H, 7.24; N, 3.12.

4.4. General procedure for the desilylation of compounds 20–24 using TBAF

Silyl ether (1 mmol) was dissolved in THF (10 mL) and cooled to 0 °C. To this, TBAF (1.2 mL, 1.2 mmol, 1 M solution) was added and allowed to stir for 0.5 h while warming the reaction mixture to rt. Solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (50–60% ethyl acetate in petroleum ether) to afford the corresponding alkynol.

*4.4.1. 1,2-O-Isopropylidene-3-C-[prop-2′-ynyl]-α-D-ribofuranose (**8**).* 92% Yield, colorless oil. $[\alpha]_D^{25}$ +20.7 (*c* 1, $CHCl_3$). IR ($CHCl_3$): *ν* 3500, 3301, 2260, 1355, 1245, 1110, 907, 837, 785, 740, 650 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.37 (s, 3H), 1.57 (s, 3H), 2.08 (t, *J*=2.7 Hz, 1H), 2.38 (dd, *J*=2.6, 17.1 Hz, 1H), 2.56 (dd, *J*=2.6, 17.1 Hz, 1H), 2.93 (s, 1H), 3.69–4.04 (m, 4H), 4.48 (d, *J*=3.9 Hz, 1H), 5.81 (d, *J*=3.9 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 22.6 (t), 26.3 (q), 26.4 (q), 59.7 (t), 71.4 (d), 78.1 (s), 78.9 (s), 81.5 (d), 81.7 (d), 103.5 (d), 112.6 (s) ppm. ESI-MS: *m*/*z* 251.3 (100%, $[M+Na]^+$). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.80; H, 7.10.

*4.4.2. 1,2-O-Isopropylidene-3-C-[3′-phenyl-prop-2′-ynyl]-α-D-ribofuranose (**9**).* 91% Yield, white solid. Mp 121–122 °C. $[\alpha]_D^{25}$ +23.7 (*c* 1, $CHCl_3$). IR ($CHCl_3$): *ν* 3449, 3018, 1734, 1490, 1376, 1216, 1110, 875, 755, 667 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.38 (s, 3H), 1.60 (s, 3H), 2.19 (br s, 1H), 2.61 (d, *J*=17.1 Hz, 1H), 2.76 (d, *J*=17.1 Hz, 1H), 2.97 (br s, 1H), 3.80–3.90 (m, 2H), 3.98 (dd, *J*=3.7, 6.4 Hz, 1H), 4.52 (d, *J*=3.9 Hz, 1H), 5.86 (d, *J*=3.9 Hz, 1H), 7.25–7.31 (m, 3H), 7.36–7.43 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 23.9 (t), 26.6 (q), 26.7 (q), 60.2 (t), 78.5 (s), 82.0 (d), 82.3 (d), 83.4 (s), 84.1 (s), 103.8 (d), 112.7 (s), 123.1 (s), 128.1 (d), 128.2 (d, 2C), 131.7 (d, 2C) ppm. ESI-MS: *m*/*z* 327.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.95; H, 6.67.

*4.4.3. 1,2-O-Isopropylidene-3-C-[3′-(4-methoxyphenyl)-prop-2′-ynyl]-α-D-ribofuranose (**10**).* 93% Yield, white solid. Mp 120–121 °C. $[\alpha]_D^{25}$ +23.5 (*c* 1.1, $CHCl_3$). IR ($CHCl_3$): *ν* 3461, 2937, 1606, 1509, 1247, 1031, 833, 755, 667 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.38 (s, 3H), 1.59 (s, 3H), 1.90–1.99 (m, 1H), 2.60 (d, *J*=17.1 Hz, 1H), 2.76 (d, *J*=17.1 Hz, 1H), 2.89 (br s, 1H), 3.79 (s, 3H), 3.86–3.93 (m, 2H), 4.00 (dd, *J*=3.8, 6.6 Hz, 1H), 4.53 (d, *J*=3.9 Hz, 1H), 5.86 (d, *J*=3.9 Hz, 1H), 6.81 (dt, *J*=2.8, 8.8 Hz, 2H), 7.34 (dt, *J*=2.8, 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 23.8 (t), 26.5 (q), 26.5 (q), 55.2 (q), 60.1 (t), 78.5 (s), 81.8 (d), 82.2 (d), 82.4 (s), 83.1 (s), 103.7 (d), 112.6 (s), 113.8 (d, 2C), 115.0 (s), 133.0 (d, 2C), 159.3 (s) ppm. ESI-MS: *m*/*z* 357.0 (100%, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.45; H, 6.47.

*4.4.4. 1,2-O-Isopropylidene-3-C-[3′-(4-nitrophenyl)-prop-2′-ynyl]-α-D-ribofuranose (**11**).* 90% Yield, yellowish syrup. $[\alpha]_D^{25}$ +32.9 (*c* 1, $CHCl_3$). IR ($CHCl_3$): *ν* 3548, 3020, 1594, 1520, 1344, 1215, 855, 757, 668 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.39 (s, 3H), 1.60 (s, 3H), 1.86 (br s, 1H), 2.66 (d, *J*=17.3 Hz, 1H), 2.85 (d, *J*=17.3 Hz, 1H), 2.93 (br s, 1H), 3.86–3.94 (m, 2H), 3.98 (dd, *J*=3.6, 6.8 Hz, 1H), 4.51 (d, *J*=3.9 Hz, 1H), 5.87 (d, *J*=3.9 Hz, 1H), 7.55 (dt, *J*=2.2, 8.9 Hz, 2H), 8.16 (dt, *J*=2.2, 8.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 23.9 (t), 26.4 (q), 26.6 (q), 60.0 (t), 78.4 (s), 81.6 (s), 81.7 (d), 81.9 (d), 90.3 (s), 103.6 (d), 112.8 (s), 123.4 (d, 2C), 129.9 (s), 132.4 (d, 2C), 146.9 (s) ppm. ESI-MS: *m*/*z* 372.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{19}NO_7$: C, 58.45; H, 5.48; N, 4.01. Found: C, 58.25; H, 5.59; N, 4.18.

*4.4.5. 1,2-O-Isopropylidene-3-C-[3′-(3-nitrophenyl)-prop-2′-ynyl]-α-D-ribofuranose (**12**).* 91% Yield, yellow syrup. $[\alpha]_D^{25}$ +25.2 (*c* 1, $CHCl_3$). IR ($CHCl_3$): *ν* 3491, 2991, 1531, 1352, 1216, 1005, 874, 758, 668 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.39 (s, 3H), 1.59 (s, 3H), 2.06 (br s, 1H), 2.62 (d, *J*=17.3 Hz, 1H), 2.81 (d, *J*=17.3 Hz, 1H), 2.96 (br s, 1H), 3.84–3.92 (m, 2H), 3.96 (dd, *J*=3.5, 6.7 Hz, 1H), 4.50 (d, *J*=3.9 Hz, 1H), 5.85 (d, *J*=3.9 Hz, 1H), 7.46 (t, *J*=8.0 Hz, 1H), 7.70 (dt, *J*=1.3, 7.7 Hz, 1H), 8.13 (ddd, *J*=1.1, 2.3, 8.2 Hz, 1H), 8.24 (t, *J*=1.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 23.6 (t), 26.4 (q), 26.5 (q), 59.9 (t), 78.3 (s), 80.9 (s), 81.7 (d), 81.9 (d), 87.4 (s), 103.6 (d), 112.8 (s), 122.8 (d), 124.8 (s), 126.4 (d), 129.2 (d), 137.4 (d), 147.9 (s) ppm. ESI-MS: *m*/*z* 372.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{19}NO_7$: C, 58.45; H, 5.48; N, 4.01. Found: C, 58.28; H, 5.20; N, 4.12.

4.5. Sonogashira coupling of alkynol 26 with aryl iodides

*4.5.1. 1,2:5,6-Di-O-isopropylidene-3-C-[3′-phenyl-prop-2′-ynyl]-α-D-allofuranose (**27**).* Reagents: alkyne **26** (500 mg, 1.68 mmol); iodobenzene (514 mg, 2.52 mmol); TPP (44 mg, 0.168 mmol); $Pd(PPh_3)_2Cl_2$ (118 mg, 0.168 mmol); CuI (32 mg, 0.168 mmol); Et_3N (6 mL) and DMF (3 mL). The crude residue was purified by column chromatography (10% ethyl acetate in petroleum ether) to obtain **27** (480 mg, 76%) as a yellow solid. Mp 117–124 °C. $[\alpha]_D^{25}$ +5.80 (*c* 0.8, $CHCl_3$). IR ($CHCl_3$): *ν* 3020, 2936, 1384, 1216, 1084, 758, 669 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.35 (s, 3H), 1.36 (s, 3H), 1.45 (s, 3H), 1.59 (s, 3H), 2.75 (d, *J*=17.1 Hz, 1H), 2.88 (s, 1H), 2.94 (d, *J*=17.1 Hz, 1H), 3.84 (d, *J*=8.3 Hz, 1H), 3.93 (dd, *J*=5.0, 8.3 Hz, 1H), 4.09–4.27 (m, 2H), 4.57 (d, *J*=3.8 Hz, 1H), 5.80 (d, *J*=3.8 Hz, 1H), 7.24–7.30 (m, 3H), 7.34–7.41 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 24.6 (t), 25.3 (q), 26.5 (q), 26.7 (q, 2C), 67.9 (t), 73.4 (d), 79.0 (s), 82.0 (d), 82.7 (d), 83.3 (s), 84.0 (s), 104.0 (d), 109.7 (s), 112.6 (s), 123.1 (s), 128.0 (d), 128.2 (d, 2C), 131.5 (d, 2C) ppm. ESI-MS: *m*/*z* 397.3 (100%, $[M+Na]^+$). Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.19; H, 7.16.

*4.5.2. 1,2:5,6-Di-O-isopropylidene-3-C-[3′-(4-methoxyphenyl)-prop-2′-ynyl]-α-D-allofuranose (**28**).* Reagents: alkyne **26** (380 mg, 1.27 mmol); 1-iodo-4-methoxybenzene (291 mg, 1.42 mmol); TPP (33 mg, 0.127 mmol); $Pd(PPh_3)_2Cl_2$ (89 mg, 0.127 mmol); CuI (24 mg, 0127 mmol); Et_3N (6 mL), and in DMF (3 mL) the coupling product **28** (360 mg, 70%) was obtained as colorless oil. $[\alpha]_D^{25}$ +8.8 (*c* 1.1, $CHCl_3$). IR ($CHCl_3$): *ν* 3528, 3019, 1607, 1510, 1480, 1375, 1216, 1181, 835, 758 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.35 (s, 3H), 1.36 (s, 3H), 1.44 (s, 3H), 1.59 (s, 3H), 2.74 (d, *J*=17.0 Hz, 1H), 2.86 (d, *J*=16.9 Hz, 1H), 2.86 (s, 1H) 3.78 (s, 3H), 3.84 (d, *J*=8.3 Hz, 1H), 3.93 (dd, *J*=5.1, 8.34 Hz, 1H), 4.08–4.27 (m, 2H), 4.56 (d, *J*=3.8 Hz, 1H), 5.79 (d, *J*=3.8 Hz, 1H), 6.79 (dt, *J*=2.4, 8.8 Hz, 2H), 7.31 (dt, *J*=2.8, 8.8 Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 24.7 (t), 25.4 (q), 26.6 (q), 26.8 (q, 2C), 55.2 (q), 68.1 (t), 73.5 (d), 79.2 (s), 82.1 (d), 82.3 (s), 82.8 (d), 90.8 (s), 104.2 (d), 109.8 (s), 112.7 (s), 113.9 (d, 2C), 115.3 (s), 133.0 (d, 2C), 159.4 (s) ppm. ESI-MS: *m*/*z* 427.3 (100%, $[M+Na]^+$). Anal. Calcd for $C_{22}H_{28}O_7$: C, 65.33; H, 6.98. Found: C, 65.29; H, 6.81.

*4.5.3. 1,2:5,6-Di-O-isopropylidene-3-C-[3′-(4-nitrophenyl)-prop-2′-ynyl]-α-D-allofuranose (**29**).* Reagents: alkyne **26** (426 mg, 1.43 mmol); iodo-4-nitrobenzene (533 mg, 2.14 mmol); TPP (37 mg, 0.143 mmol); $Pd(PPh_3)_2Cl_2$ (100 mg, 0.143 mmol); CuI (27 mg, 0.143 mmol); Et_3N (6 mL) and DMF (3 mL). The crude residue was purified by column chromatography (10% ethyl acetate in petroleum ether) to obtain **29** (380 mg, 63%) as a colorless gum. $[\alpha]_D^{25}$ 0.0 (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): *ν* 3330, 2925, 1607, 1510, 1737, 1594, 1343, 1081, 855, 758 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.32 (s, 3H), 1.35 (s, 3H), 1.42 (s, 3H), 1.57 (s, 3H), 2.72 (d, *J*=17.2 Hz, 1H), 2.93 (s, 1H), 2.98 (d, *J*=17.2 Hz, 1H), 3.79 (dt, *J*=2.7, 8.4 Hz, 1H), 3.90 (dt, *J*=3.3, 7.6 Hz, 1H), 4.06–4.18 (m, 2H), 4.52 (d, *J*=3.8 Hz, 1H), 5.76 (d, *J*=3.8 Hz, 1H), 7.50 (dt, *J*=2.4, 8.8 Hz, 2H), 8.11 (dt, *J*=2.3, 8.6 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 24.6 (t), 25.3 (q), 26.6 (q), 26.7 (q), 26.7 (q), 68.0 (t), 73.4 (d), 79.0 (s), 81.8 (d), 81.8 (s), 82.5 (d), 90.4 (s), 103.9 (d), 109.9 (s), 112.8 (s), 123.5 (d, 2C), 130.0 (s), 132.4 (d, 2C), 146.9 (s) ppm. ESI-MS: *m*/*z* 442.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{21}H_{25}NO_8$: C, 60.14; H, 5.96; N, 3.34. Found: C, 60.01; H, 5.86; N, 3.22.

*4.5.4. 1,2:5,6-Di-O-isopropylidene-3-C-[3′-(3-nitrophenyl)-prop-2′-ynyl]-α-D-allofuranose (**30**).* Reagents: alkyne **26** (320 g, 1.07 mmol); 1-iodo-3-nitrobenzene (399 mg, 1.60 mmol); TPP (28 mg, 0.107 mmol); $Pd(PPh_3)_2Cl_2$ (50 mg, 0.107 mmol); CuI (20 mg, 0.107 mmol); Et_3N (5 mL) and DMF (2.5 mL). The crude residue was purified by column chromatography (10% ethyl acetate in petroleum

ether) to obtain **30** (300 mg, 67%) as a thick liquid. $[\alpha]_D^{25}$ +3.1 (*c* 1.8, $CHCl_3$). IR ($CHCl_3$): *ν* 3552, 3020, 1532, 1375, 1216, 1075, 758, 669 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.33 (s, 3H), 1.36 (s, 3H), 1.43 (s, 3H), 1.58 (s, 3H), 2.71 (d, *J*=17.2 Hz, 1H), 2.94 (s, 1H), 2.97 (d, *J*=16.9 Hz, 1H), 3.81 (dt, *J*=2.8, 8.4 Hz, 1H), 3.91 (dt, *J*=2.9, 7.5 Hz, 1H), 4.07–4.20 (m, 2H), 4.54 (d, *J*=3.9 Hz, 1H), 5.77 (d, *J*=3.8 Hz, 1H), 7.44 (t, *J*=7.9 Hz, 1H), 7.67 (dt, *J*=1.5, 7.5 Hz, 1H), 8.10 (ddd, *J*=1.2, 2.4, 8.3 Hz, 1H), 8.20 (t, *J*=1.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 24.1 (t), 25.0 (q), 26.3 (q), 26.4 (q), 26.4 (q), 67.7 (t), 73.1 (d), 78.7 (s), 80.7 (s), 81.5 (d), 82.3 (d), 87.4 (s), 103.6 (d), 109.5 (s), 112.5 (s), 122.4 (d), 124.7 (s), 126.1 (d), 129.0 (d), 137.1 (d), 147.7 (s) ppm. ESI-MS: *m*/*z* 442.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{21}H_{25}NO_8$: C, 60.14; H, 5.96; N, 3.34. Found: C, 59.99; H, 6.03; N, 3.22.

4.6. General procedure for the acetonide hydrolysis of compounds 26–30

A solution of alkyne (1 mmol) in MeOH (30 mL) was treated with dil H_2SO_4 (15 mL, 0.8% in water) dropwise and stirred at rt for 5 h. The reaction mixture was quenched with $NaHCO_3$ (2.5 g), concentrated under reduced pressure. The residue was portioned between ethyl acetate/water and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried ($NaSO_4$) and concentrated. The crude residue was purified by column chromatography (60–80% ethyl acetate in petroleum ether) to obtain the alkyne diols **13**–**17**.

*4.6.1. 1,2-O-isopropylidene-3-C-[prop-2′-ynyl]-α-D-allofuranose (**13**).* 79% Yield, colorless syrup. $[\alpha]_D^{25}$ +25.8 (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): *ν* 3449, 2986, 1987, 1375, 1245, 1047, 874, 758, 669 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.35 (s, 3H), 1.58 (s, 3H), 2.09 (t, *J*=2.6 Hz, 1H), 2.50 (dd, *J*=2.6, 17.2 Hz, 1H), 2.78 (dd, *J*=2.6, 17.2 Hz, 1H), 3.21 (br s, 1H), 3.54–3.81 (m, 4H), 3.81 (br s, 2H), 4.50 (d, *J*=3.8 Hz, 1H), 5.73 (d, *J*=3.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 23.1 (t), 26.5 (q 2C), 64.3 (t), 70.0 (d), 70.7 (d), 71.6 (s), 79.0 (d), 82.4 (d), 93.1 (s), 103.9 (d), 109.8 (s) ppm. ESI-MS: *m*/*z* 259.1 (100%, $[M+1]^+$). Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.81; H, 7.02. Found: C, 55.73; H, 7.25.

*4.6.2. 1,2-O-Isopropylidene-3-C-[3′-(phenyl)-prop-2′-ynyl]-α-D-allofuranose (**14**).* 75% Yield, white solid. Mp 115–119 °C. $[\alpha]_D^{25}$ +22.7 (*c* 1, $CHCl_3$). IR ($CHCl_3$): *ν* 3439, 3020, 1385, 1216, 1084, 757, 669 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.34 (s, 3H), 1.57 (s, 3H), 2.75 (d, *J*=17.2 Hz, 1H), 2.97 (d, *J*=17.2 Hz, 1H), 3.29 (br s, 3H), 3.66–3.89 (m, 4H), 4.55 (d, *J*=3.7 Hz, 1H), 5.79 (d, *J*=3.7 Hz, 1H), 7.25–7.28 (m, 3H), 7.37–7.42 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 24.1 (t), 26.5 (q), 26.5 (q), 64.3 (t), 70.1 (d), 79.2 (d), 79.3 (s), 82.4 (d), 83.4 (s), 84.2 (s), 103.7 (d), 112.8 (s), 123.0 (s), 128.1 (d), 128.2 (d, 2C), 131.6 (d, 2C) ppm. ESI-MS: *m*/*z* 357.2 (100%, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.56; H, 6.79.

*4.6.3. 1,2-O-Isopropylidene-3-C-[3′-(4-methoxyphenyl)-prop-2′-ynyl]-α-D-allofuranose (**15**).* 69% Yield, colorless solid. Mp 130–132 °C. $[\alpha]_D^{25}$ +21.9 (*c* 1.3, $CHCl_3$). IR ($CHCl_3$): *ν* 3477, 3019, 1464, 1384, 1246, 1034, 728, 669 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.37 (s, 3H), 1.59 (s, 3H), 2.67 (br s, 1H), 2.76 (d, *J*=17.0 Hz, 1H), 2.94 (d, *J*=17.0 Hz, 1H), 3.08 (br s, 1H), 3.70 (dd, *J*=4.8, 11.5 Hz, 1H), 3.79 (s, 3H), 3.81–3.87 (m, 2H), 3.72 (br s, 1H), 3.94–4.02 (m, 1H), 4.52 (d, *J*=3.9 Hz, 1H), 5.79 (d, *J*=3.9 Hz, 1H), 6.80 (dt, *J*=8.9, 2.1 Hz, 2H), 7.33 (d, *J*=8.9, 2.6 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 24.1 (t), 26.5 (q), 26.6 (q), 55.2 (q), 64.4 (t), 70.0 (d), 79.3 (d), 79.4 (s), 82.5 (s), 82.5 (d), 83.3 (s), 103.7 (d), 112.8 (s) 113.9 (d, 2C), 115.0 (s), 133.0 (d, 2C), 159.5 (s) ppm. ESI-MS: *m*/*z* 387.2 (100%, $[M+Na]^+$). Anal. Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.59; H, 6.71.

*4.6.4. 1,2-O-Isopropylidene-3-C-[3′-(4-nitrophenyl)-prop-2′-ynyl]-α-D-allofuranose (**16**).* 81% Yield, colorless gum. $[\alpha]_D^{25}$ +16.5 (*c* 0.8, $CHCl_3$). IR ($CHCl_3$): *ν* 3436, 3020, 1595, 1345, 1216, 1084, 750, 669 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.36 (s, 3H), 1.58 (s, 3H), 2.77 (d, *J*=17.3 Hz, 1H), 3.05 (d, *J*=17.3 Hz, 1H), 3.47 (br s, 3H), 3.68–3.88 (m, 4H), 4.54 (d, *J*=3.8 Hz, 1H), 5.80 (d, *J*=3.9 Hz, 1H), 7.53 (dt, *J*=2.1, 8.8 Hz, 2H), 8.13 (dt, *J*=2.2, 8.8 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 24.1 (t), 26.4 (q, 2C), 64.3 (t), 70.1 (d), 79.0 (d), 79.2 (s), 81.8 (s), 82.1 (d), 90.3 (s), 103.6 (d), 112.9 (s), 123.5 (d, 2C), 129.9 (s), 132.4 (d, 2C), 146.9 (s) ppm. ESI-MS: *m*/*z* 402.0 (100%, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{21}NO_8$: C, 56.99; H, 5.58; N, 3.69. Found: C, 56.83; H, 5.47; N, 3.64.

*4.6.5. 1,2-O-Isopropylidene-3-C-[3′-(3-nitrophenyl)-prop-2′-ynyl]-α-D-allofuranose (**17**).* Colorless gum. $[\alpha]_D^{25}$ +41.1 (*c* 2.0, $CHCl_3$). IR ($CHCl_3$): *ν* 3436, 3081, 1520, 1376, 1217, 1097, 758, 669 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.36 (s, 3H), 1.58 (s, 3H), 2.74 (d, *J*=17.3 Hz, 1H), 3.05 (d, *J*=17.3 Hz, 1H), 3.37 (br s, 3H), 3.67–3.88 (m, 4H), 4.56 (d, *J*=3.9 Hz, 1H), 5.79 (d, *J*=3.8 Hz, 1H), 7.44 (t, *J*=7.8 Hz, 1H), 7.69 (dt, *J*=1.3, 7.8 Hz, 1H), 8.10 (ddd, *J*=1.0, 2.3, 8.2 Hz, 1H), 8.21 (t, *J*=1.9 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 24.1 (t), 26.5 (q), 26.5 (q), 64.3 (t), 70.1 (d), 79.2 (d), 79.3 (s), 82.4 (d), 83.3 (s), 84.2 (s), 103.7 (d), 112.8 (s), 123.0 (s), 128.1 (s), 128.2 (d, 2C), 131.6 (d, 2C) ppm. ESI-MS: *m*/*z* 402.3 (100%, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{21}NO_8$: C, 56.99; H, 5.58; N, 3.69. Found: C, 56.81; H, 5.08; N, 3.52.

4.7. Pd-mediated cyclization of alkynols 8–17

*4.7.1. 1,2-O-Isopropylidene-3-C-(2′-hydroxy-prop-1-enyl)-2′,5-anhydro-α-D-ribofuranose (**31**).* A solution of **8** (90 mg, 0.39 mmol) and $Pd(CH_3CN)_2Cl_2$ (10 mg, 0.04 mmol) in acetonitrile (10 mL) was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and purified by silica gel chromatography (15% ethyl acetate in petroleum ether) to obtain **31** (58 mg, 64%) as syrup. $[\alpha]_D^{25}$ −31.3 (*c* 2.5, $CHCl_3$). IR ($CHCl_3$): *ν* 3432, 3019, 1672, 1376, 1216, 1116, 876, 756, 667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.35 (s, 3H), 1.56 (s, 3H), 1.79 (d, *J*=0.8 Hz, 3H), 2.89 (br s 1H), 3.90 (dd, *J*=1.2, 12.6 Hz, 2H), 4.19 (d, *J*=3.7 Hz, 1H), 4.31 (dd, *J*=1.6, 12.6 Hz, 1H), 4.40 (br q, *J*=0.8 Hz, 1H), 5.72 (d, *J*=3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 20.3 (q), 26.8 (q), 27.0 (q), 63.1 (t), 71.3 (s), 76.9 (d), 83.5 (d), 95.0 (d), 104.2 (d), 112.7 (s), 156.2 (s) ppm. ESI-MS: *m*/*z* 251.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.83; H, 7.05.

*4.7.2. Pd-mediated cyclization of **9**.* A solution of **9** (100 mg, 0.33 mmol) and $Pd(CH_3CN)_2Cl_2$ (8 mg, 0.03 mmol) in acetonitrile (10 mL) was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and the residue obtained was purified by silica gel chromatography (20%, 30% ethyl acetate in petroleum ether) to obtain **32** (60 mg, 60%) and **33** (20 mg, 19%) as colorless solids.

*4.7.2.1. 1,2-O-Isopropylidene-3-C-(2′-hydroxy-2′-benzyl-E-vinyl)-2′,5-anhydro]-α-D-ribofuranose (**32**).* Mp 118–119 °C. $[\alpha]_D^{25}$ −67.8 (*c* 1, $CHCl_3$). IR ($CHCl_3$): *ν* 3533, 3019, 1669, 1376, 1216, 1115, 875, 756, 668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.35 (s, 3H), 1.57 (s, 3H), 2.89 (br s, 1H), 3.36 (d, *J*=16.5 Hz, 1H), 3.40 (d, *J*=16.5 Hz, 1H), 3.84 (d, *J*=12.3 Hz, 1H), 3.92 (br d, *J*=1.1 Hz, 1H), 4.16 (d, *J*=3.7 Hz, 1H), 4.33 (dd, *J*=1.4, 12.4 Hz, 1H), 4.40 (br d, *J*=1.1, Hz, 1H), 5.71 (d, *J*=3.7 Hz, 1H), 7.18–7.29 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 26.8 (q), 27.0 (q), 40.5 (t), 63.4 (t), 71.3 (s), 77.1 (d), 83.4 (d), 96.2 (d), 104.2 (d), 112.7 (s), 126.5 (d), 128.4 (d, 2C), 129.0 (d, 2C), 137.0 (s), 158.5 (s) ppm. ESI-MS: *m*/*z* 327.0 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.10; H, 6.78.

*4.7.2.2. Crystallographic data for **32**.* $C_{17}H_{20}O_5$: *M*=304.33, crystal dimensions 0.65×0.25×0.11 mm^3, orthorhombic, space group $P\ 2_12_12_1$, *a*=6.0693(14), *b*=12.689(3), *c*=20.174(5) Å,

V=1553.7 (6) Å^3, Z=4, ρ_{calcd}=1.301 g cm^{-3}, μ (Mo Kα)=0.095 mm^{-1}, F(000)=648, $2\theta_{max}$=50.00°, T=297(2) K, 7855 reflections collected, 2722 unique, 2507 observed ($I>2\sigma(I)$) reflections, 202 refined parameters, R value 0.0323, $wR2$=0.0697 (all data R=0.0362, $wR2$=0.0725), S=1.101, minimum and maximum transmission 0.9410 and 0.9893; maximum and minimum residual electron densities +0.117 and −0.137 e Å^{-3}.

*4.7.2.3. 1,2-O-Isopropylidene-3-C-(2′-oxo-3′-phenyl-propyl)-α-D-ribofuranose-(2′-C,5-O)-hemiketal (**33**).* Mp 144–145 °C. $[\alpha]_D^{25}$ −8.4 (*c* 1, $CHCl_3$). IR ($CHCl_3$): ν 3522, 3019, 1684, 1376, 1216, 1010, 875, 756, 668 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 3H), 1.55 (s, 3H), 1.57 (d, J=14.1 Hz, 1H), 1.69 (d, J=14.1 Hz, 1H), 2.82 (d, J=13.6 Hz, 1H), 3.03 (d, J=13.6 Hz, 1H), 3.20 (br s, 1H), 3.69 (s, 1H), 3.81 (s, 1H), 3.96 (d, J=13.8 Hz, 1H), 4.06 (d, J=3.7 Hz, 1H), 4.12 (dd, J=1.8, 13.8 Hz, 1H), 5.74 (d, J=3.7 Hz, 1H), 7.21–7.28 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.5 (q, 2C), 37.0 (t), 47.5 (t), 57.6 (t), 74.1 (d), 74.5 (s), 82.7 (d), 95.5 (s), 103.7 (d), 112.8 (s), 126.9 (d), 128.2 (d, 2C), 130.9 (d, 2C), 135.1 (s) ppm. ESI-MS: m/z 345.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.28; H, 6.82.

*4.7.3. Pd-mediated cyclization of **10**.* A solution of **10** (120 mg, 0.36 mmol) and $Pd(CH_3CN)_2Cl_2$ (9 mg, 0.04 mmol) in acetonitrile (10 mL) was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and residue obtained was purified by silica gel chromatography (20%, 60% ethyl acetate in petroleum ether) to obtain **34** (20 mg, 16%) and **35** (70 mg, 55%) as colorless syrups.

*4.7.3.1. 1,2-O-Isopropylidene-3-C-[2′-hydroxy-2′-(4-methoxybenzyl)-E-vinyl]-2′,5-anhydro-α-D-ribofuranose (**34**).* $[\alpha]_D^{25}$ −49.8 (*c* 1.2, $CHCl_3$). IR ($CHCl_3$): ν 3479, 2926, 1741, 1669, 1512, 1248, 875, 757, 666 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.35 (s, 3H), 1.57 (s, 3H), 2.89 (br s, 1H), 3.29 (d, J=16.0 Hz, 1H), 3.37 (d, J=17.3 Hz, 1H), 3.78 (s, 3H), 3.84 (dd, J=0.9, 12.4 Hz, 1H), 3.94 (dd, J=1.6, 3.0 Hz, 1H), 4.19 (d, J=3.7 Hz, 1H), 4.34 (ddd, J=0.6, 2.0, 12.4 Hz, 1H), 4.40 (d, J=0.9 Hz, 1H), 5.73 (d, J=3.7 Hz, 1H), 6.82 (dt, J=2.98.7 Hz, 2H), 7.11 (dt, J=2.9, 8.7 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.7 (q), 27.0 (q), 39.6 (t), 55.2 (q), 63.4 (t), 71.3 (s), 77.1 (d), 83.4 (d), 95.9 (d), 104.2 (d), 112.8 (s), 113.8 (d, 2C), 129.0 (s), 130.0 (d, 2C), 158.3 (s), 159.0 (s) ppm. ESI-MS: m/z 357.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.58; H, 6.55.

*4.7.3.2. 1,2-O-Isopropylidene-3-C-[3′-oxo-3′-(4-methoxyphenyl)-propyl]-α-D-ribofuranose (**35**).* $[\alpha]_D^{25}$ +13.3 (*c* 2.3, $CHCl_3$). IR ($CHCl_3$): ν 3491, 2936, 1673, 1601, 1512, 1171, 877, 755, 666 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.34 (s, 3H), 1.57 (s, 3H), 1.89 (dd, J=6.3, 8.5 Hz, 1H), 1.94 (dd, J=8.2, 6.5 Hz, 1H), 2.85 (br s, 1H), 2.99 (ddd, J=17.7, 8.1, 6.2 Hz, 1H), 3.25 (ddd, J=6.3, 8.3, 17.7 Hz, 1H), 3.78–3.84 (m, 2H), 3.86 (s, 3H), 3.94 (dd, J=4.1 6.6 Hz, 1H), 4.22 (d, J=3.9 Hz, 1H), 5.81 (d, J=3.9 Hz, 1H), 6.91 (dt, J=2.9, 8.9 Hz, 2H), 7.94 (dt, J=2.9, 8.9 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.5 (t), 26.4 (q, 2C), 31.9 (t), 55.4 (q), 60.5 (t), 78.6 (s), 81.0 (d), 82.7 (d), 103.6 (d), 112.5 (s), 113.7 (d, 2C), 129.7 (s), 130.3 (d, 2C), 163.5 (s), 198.3 (s) ppm. ESI-MS: m/z 375.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{24}O_7$: C, 61.35; H, 6.86. Found: C, 61.30; H, 6.82.

*4.7.4. Pd-mediated cyclization of **11**.* A solution of **11** (100 mg, 0.29 mmol) and $Pd(CH_3CN)_2Cl_2$ (7 mg, 0.03 mmol) in acetonitrile (10 mL) was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and the crude residue obtained was purified by silica gel chromatography (25%, 30% ethyl acetate in petroleum ether) to obtain **36** (60 mg, 60%) as yellow syrup and **37** (15 mg, 14%) as yellow solid.

*4.7.4.1. 1,2-O-Isopropylidene-3-C-[2′-hydroxy-2′-(4-nitrobenzyl)-E-vinyl]-2′,5-anhydro-α-D-ribofuranose (**36**).* $[\alpha]_D^{25}$ −61.0 (*c* 2, $CHCl_3$). IR ($CHCl_3$): ν 3505, 2988, 2923, 1671, 1519, 1347, 1064, 875, 733, 648 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.35 (s, 3H), 1.56 (s, 3H), 2.99 (br s, 1H), 3.43 (d, J=16.3 Hz, 1H), 3.51 (d, J=16.3 Hz, 1H), 3.84 (dd, J=0.8, 12.4 Hz, 1H), 3.93 (dd, J=1.8, 3.2 Hz, 1H), 4.21 (d, J=3.7 Hz, 1H), 4.34 (ddd, J=0.6, 2.0, 12.4 Hz, 1H), 4.52 (d, J=1.8 Hz, 1H), 5.73 (d, J=3.7 Hz, 1H), 7.36 (dt, J=2.5, 8.7 Hz, 2H), 8.13 (dt, J=2.5, 8.7 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.6 (q), 26.8 (q), 40.3 (t), 63.5 (t), 71.2 (s), 76.7 (d), 83.1 (d), 97.2 (d), 104.0 (d), 112.9 (s), 123.6 (d, 2C), 129.6 (d, 2C), 144.8 (s), 146.8 (s), 156.7 (s) ppm. ESI-MS: m/z 372.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{19}NO_7$: C, 58.45; H, 5.48; N, 4.01. Found: C, 58.40; H, 5.43; N, 4.02.

*4.7.4.2. 1,2-O-Isopropylidene-3-C-[2′-oxo-3′(4-nitrophenyl)-propyl]-α-D-ribofuranose-(2′-C,5-O)-hemiketal (**37**).* Mp 149–150 °C. $[\alpha]_D^{25}$ −11.6 (*c* 1.2, $CHCl_3$). IR ($CHCl_3$): ν 3397, 2923, 1597, 1511, 1345, 1043, 862, 733, 648 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 3H), 1.55 (s, 3H), 1.61 (d, J=14.1 Hz, 1H), 1.71 (d, J=14.1 Hz, 1H), 2.96 (d, J=13.6 Hz, 1H), 3.10 (d, J=13.6 Hz, 1H), 3.08 (br s, 1H), 3.67 (br s, 1H), 3.99 (d, J=14.0 Hz, 1H), 4.07 (d, J=3.8 Hz, 1H), 4.12 (dd, J=2.2, 14.0 Hz, 1H), 4.44 (s, 1H), 5.78 (d, J=3.8 Hz, 1H), 7.47 (dt, J=2.4, 8.7 Hz, 2H), 8.14 (dt, J=2.4, 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.3 (q), 26.4 (q), 37.0 (t), 47.1 (t), 57.5 (t), 73.7 (d), 74.7 (s), 82.1 (d), 95.1 (s), 103.6 (d), 113.0 (s), 123.1 (d, 2C), 131.7 (d, 2C), 143.4 (s), 147.0 (s) ppm. ESI-MS: m/z 390.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{21}NO_8$: C, 55.58; H, 5.76; N, 3.81. Found: C, 55.55; H, 5.74; N, 3.75.

*4.7.4.3. Crystallographic data for **37**.* $C_{17}H_{21}NO_8$: M=367.35, crystal dimensions 0.77×0.31×0.18 mm^3, monoclinic, space group $P2_1$, a=5.4991(14), b=17.126(4), c=9.123(2) Å, β=95.765(4), V=854.9(4) Å^3, Z=2, ρ_{calcd}=1.427 g cm^{-3}, μ (Mo Kα)=0.114 mm^{-1}, F(000)=388, $2\theta_{max}$=50.00°, T=297(2) K, 6696 reflections collected, 3262 unique, 3100 observed ($I>2\sigma(I)$) reflections, 297 refined parameters, R value 0.0355, $wR2$=0.0881 (all data R=0.0374, $wR2$=0.0902), S=1.045, minimum and maximum transmission 0.9172 and 0.9797; maximum and minimum residual electron densities +0.295 and −0.138 e Å^{-3}.

*4.7.5. Pd-mediated cyclization of **12**.* A solution of **12** (150 mg, 0.43 mmol) and $Pd(CH_3CN)_2Cl_2$ (11 mg, 0.04 mmol) in acetonitrile (15 mL) was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and the residue obtained was purified by silica gel chromatography (25%, 30% ethyl acetate in petroleum ether) to obtain **38** (80 mg, 53%) as yellow syrup and **39** (20 mg, 13%) as yellow solid.

*4.7.5.1. 1,2-O-Isopropylidene-3-C-[2′-hydroxy-2′-(3-nitrobenzyl)-E-vinyl]-2′,5-anhydro-α-D-ribofuranose (**38**).* $[\alpha]_D^{25}$ −49.7 (*c* 2, $CHCl_3$). IR ($CHCl_3$): ν 3506, 2989, 1671, 1530, 1351, 1215, 874, 756, 667 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.36 (s, 3H), 1.57 (s, 3H), 2.98 (s, 1H), 3.44 (d, J=16.4 Hz, 1H), 3.52 (d, J=16.4 Hz, 1H), 3.86 (dd, J=0.9, 12.4 Hz, 1H), 3.94 (dd, J=1.8, 3.2 Hz, 1H), 4.23 (d, J=3.7 Hz, 1H), 4.35 (ddd, J=0.6, 2.0, 12.4 Hz, 1H), 4.53 (d, J=1.9 Hz, 1H), 5.78 (d, J=3.7 Hz, 1H), 7.46 (dt, J=2.5, 8.6 Hz, 1H), 7.54 (dt, J=1.4, 7.7 Hz, 1H), 8.06–8.11 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.6 (q), 26.8 (q), 40.0 (t), 63.4 (t), 71.2 (s), 76.7 (d), 83.1 (d), 97.2 (d), 104.0 (d), 112.8 (s), 121.7 (d), 123.6 (d), 129.2 (d), 135.0 (d), 139.2 (s), 148.2 (s), 156.7 (s) ppm. ESI-MS: m/z 372.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{19}NO_7$: C, 58.45; H, 5.48; N, 4.01. Found: C, 58.41; H, 5.42. N, 3.99.

*4.7.5.2. 1,2-O-Isopropylidene-3-C-[2′-oxo-3′-(3-nitrophenyl)-propyl]-α-D-ribofuranose-(2′-C,5-O)-hemiketal (**39**).* Mp 152–153 °C. $[\alpha]_D^{25}$ −14.0 (*c* 1.5, $CHCl_3$). IR ($CHCl_3$): ν 3478, 2929, 1529, 1351, 1216, 1052, 876, 757, 667 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 3H), 1.55 (s, 3H), 1.61 (d, J=14.0 Hz, 1H), 1.73 (d, J=14.0 Hz, 1H), 2.94 (d, J=13.6 Hz, 1H), 3.10 (d, J=13.6 Hz, 1H), 3.11 (br s, 1H), 3.68 (br s, 1H), 3.98 (d, J=14.0 Hz, 1H), 4.08 (s, 1H), 4.13 (dd, J=2.1, 12.4 Hz, 1H), 4.45 (s, 1H), 5.79 (d, J=3.8 Hz, 1H), 7.44 (t, J=7.9 Hz, 1H), 7.66 (dt, J=1.2,

7.7 Hz, 1H), 8.10 (ddd, *J*=1.1, 2.3, 8.1 Hz, 1H), 8.16 (t, *J*=1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.2 (q), 26.3 (q), 36.9 (t), 46.9 (t), 57.5 (t), 73.7 (d), 74.6 (s), 82.1 (d), 95.0 (s), 103.6 (d), 112.9 (s), 121.8 (d), 125.6 (d), 128.8 (d), 137.1 (d), 137.6 (s), 148.0 (s) ppm. ESI-MS: *m*/*z* 390.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{17}H_{21}NO_8$: C, 55.58; H, 5.76; N, 3.81. Found: C, 55.53; H, 5.70; N, 3.75.

4.7.5.3. Crystallographic data for ***39***. $C_{17}H_{21}NO_8$: *M*=367.35, crystal dimensions 0.97×0.05×0.03 mm^3, orthorhombic, space group $P\,2_12_12_1$, *a*=5.5126(16), *b*=16.461(5), *c*=19.369(6) Å, *V*=1757.5(9) Å^3, *Z*=4, ρ_{calcd}=1.388 g cm^{-3}, μ (Mo Kα)=0.111 mm^{-1}, *F*(000)=776, $2\theta_{max}$=50.00°, *T*=297(2) K, 8849 reflections collected, 3087 unique, 2292 observed ($I>2\sigma(I)$) reflections, 237 refined parameters, *R* value 0.0494, *wR*2=0.0852 (all data *R*=0.0770, *wR*2=0.0945), *S*=1.029, minimum and maximum transmission 0.8999 and 0.9965; maximum and minimum residual electron densities +0.173 and −0.178 e Å^{-3}.

4.7.6. Pd-mediated cyclization of ***13***. To a solution of **13** (100 mg, 0.39 mmol) in acetonitrile (20 mL) was added $Pd(CH_3CN)_2Cl_2$ (22 mg, 0.08 mmol) and the reaction mixture was stirred at rt under argon atmosphere for 1 h. The reaction mixture was concentrated and purified by silica gel chromatography (40% ethyl acetate in petroleum ether) to obtain **40** (70 mg, 70%) as a white solid.

*4.7.6.1. 1,2-O-Isopropylidene-3-C-(2′-oxopropyl)]-α-D-allofuranose-(2′-C,5-O,6-O)-ketal (**40**).* Mp 139–140 °C. $[\alpha]_D^{25}$ −3.8 (*c* 2.2, $CHCl_3$). IR ($CHCl_3$): ν 3538, 3020, 1386, 1216, 1052, 730, 669 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.32 (s, 3H), 1.45 (s, 3H), 1.54 (s, 3H), 1.62 (d, *J*=14.7 Hz, 1H), 1.95 (d, *J*=14.7 Hz, 1H), 3.04 (s, 1H), 3.70 (s, 1H), 3.82 (dd, *J*=5.9, 7.1 Hz, 1H), 4.05 (d, *J*=3.7 Hz, 1H), 4.13 (d, *J*=7.2 Hz, 1H), 4.65 (d, *J*=5.4 Hz, 1H), 5.82 (d, *J*=3.5 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.0 (q), 26.6 (q), 26.8 (q), 41.8 (t), 65.2 (t), 73.7 (d), 74.8 (s), 77.6 (d), 83.7 (d), 103.9 (d), 105.3 (s), 112.7 (s) ppm. ESI-MS: *m*/*z* 281.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.81; H, 7.02. Found: C, 55.67; H, 7.26.

4.7.7. Pd-mediated cyclization of ***14***. To a solution of **14** (130 mg, 0.39 mmol) in acetonitrile (10 mL) was added $Pd(CH_3CN)_2Cl_2$ (11 mg, 0.04 mmol) and the reaction mixture was stirred at rt under argon atmosphere for 2 h. The reaction mixture was concentrated and purified by silica gel chromatography (40% ethyl acetate in petroleum ether) to obtain **41** (90 mg, 66%) as a colorless syrup.

*4.7.7.1. 1,2-O-Isopropylidene-3-C-[3′-oxo-3′-(phenyl)-propyl]-α-D-allofuranose (**41**).* $[\alpha]_D^{25}$ +35.4 (*c* 2.0, $CHCl_3$). IR ($CHCl_3$): ν 3439, 3020, 1683, 1385, 1216, 1083, 758, 669 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.31 (s, 3H), 1.56 (s, 3H), 1.88 (ddd, *J*=5.7, 8.3, 14.5 Hz, 1H), 2.29 (br s, 1H), 2.30 (ddd, *J*=6.1, 8.5, 14.5 Hz, 1H), 3.09 (br s, 1H), 3.10 (ddd, *J*=5.7, 8.2, 14.1 Hz, 1H), 3.39 (ddd, *J*=6.1, 8.5, 14.5 Hz, 1H), 3.40 (br s, 1H), 3.65 (dd, *J*=3.7, 10.9 Hz, 1H), 3.80–3.86 (m, 3H), 4.25 (d, *J*=3.8 Hz, 1H), 5.74 (d, *J*=3.7 Hz, 1H), 7.39–7.67 (m, 3H), 7.93–7.98 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.4 (t), 26.3 (q), 26.5 (q), 32.4 (t), 64.5 (t), 69.8 (d), 79.2 (s), 79.4 (d), 80.9 (d), 103.4 (d), 112.7 (s), 128.0 (d, 2C), 128.6 (d, 2C), 133.2 (d), 136.6 (s), 200.0 (s) ppm. ESI-MS: *m*/*z* 375.3 (100%, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{24}O_7$: C, 61.35; H, 6.86. Found: C, 61.19; H, 7.04.

4.7.8. Pd-mediated cyclization of ***15***. To a solution of **15** (40 mg, 0.11 mmol) in acetonitrile (10 mL) was added $Pd(CH_3CN)_2Cl_2$ (11 mg, 0.04 mmol) and the reaction mixture was stirred at rt under argon atmosphere for 4 h. Usual work followed by purification of crude by silica gel chromatography (40% ethyl acetate in petroleum ether) afforded **42** (25 mg, 60%) as a gum.

*4.7.8.1. 1,2-O-Isopropylidene-3-C-[3′-oxo-3′-(4-methoxyphenyl)-propyl]-α-D-allofuranose (**42**).* $[\alpha]_D^{25}$ +12.0 (*c* 0.8, $CHCl_3$). IR ($CHCl_3$): ν 3437, 2927, 1671, 1376, 1218, 1084, 771, 669 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.31 (s, 3H), 1.55 (s, 3H), 1.87 (ddd, *J*=5.9, 8.3, 14.5 Hz, 1H), 2.30 (ddd, *J*=6.2, 8.2, 14.7 Hz, 1H), 3.04 (ddd, *J*=5.9, 8.2, 14.1 Hz, 1H), 3.05 (br s, 1H), 3.29 (br s, 1H), 3.33 (ddd, *J*=6.2, 8.3, 14.8 Hz, 1H), 3.65 (dd, *J*=3.7, 10.8 Hz, 1H), 3.75–3.85 (m, 3H), 3.83 (s, 3H), 3.83 (br s, 1H), 4.25 (d, *J*=3.8 Hz, 1H), 5.73 (d, *J*=3.8 Hz, 1H), 6.90 (dt, *J*=2.7, 8.9 Hz, 2H), 7.95 (dt, *J*=2.7, 8.9 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.6 (t), 26.3 (q), 26.5 (q), 31.9 (t), 55.4 (q), 64.6 (t), 69.8 (d), 79.2 (s), 79.5 (d), 80.9 (d), 103.5 (d), 112.6 (s), 113.7 (d, 2C), 129.6 (s), 130.3 (d, 2C), 163.5 (s), 198.6 (s) ppm. ESI-MS: *m*/*z* 405.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{19}H_{26}O_8$: C, 59.68; H, 6.85. Found: C, 59.72; H, 6.70.

4.7.9. Pd-mediated cyclization of ***16***. To a solution of **16** (100 mg, 0.26 mmol) in acetonitrile (20 mL) was added $Pd(CH_3CN)_2Cl_2$ (22 mg, 0.08 mmol) and the reaction mixture was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and the crude was purified by silica gel chromatography (35% ethyl acetate in petroleum ether) to procure **43** (70 mg, 70%) as pale yellow oil.

*4.7.9.1. 1,2-O-Isopropylidene-3-C-[2′-oxo-3′-(4-nitrophenyl)-propyl]-α-D-allofuranose-(2′-C,5-O,6-O)-ketal (**43**).* $[\alpha]_D^{25}$ +16.9 (*c* 2.2, $CHCl_3$). IR ($CHCl_3$): ν 3462, 2985, 1638, 1374, 1241, 1047, 847, 634 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.35 (s, 3H), 1.56 (s, 3H), 1.66 (d, *J*=14.4 Hz, 1H), 2.01 (d, *J*=14.4 Hz, 1H), 3.04 (d, *J*=0.9 Hz, 1H), 3.10 (d, *J*=16.3 Hz, 1H), 3.17 (d, *J*=16.3 Hz, 1H), 3.55 (dd, *J*=5.7, 7.2 Hz, 1H), 3.71 (br s, 1H), 4.09 (d, *J*=3.7 Hz, 1H), 4.14 (d, *J*=7.2 Hz, 1H), 4.62 (d, *J*=5.2 Hz, 1H), 5.85 (d, *J*=3.7 Hz, 1H), 7.44 (dt, *J*=2.2, 8.7 Hz, 2H), 8.12 (d, *J*=2.3, 8.7 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.6 (q), 26.7 (q), 41.1 (t), 42.8 (t), 65.6 (t), 73.7 (d), 74.9 (s), 78.0 (d), 83.7 (d), 104.0 (d), 105.7 (s), 112.9 (s), 123.0 (d, 2C), 131.5 (d, 2C), 142.7 (s), 147.0 (s) ppm. ESI-MS: *m*/*z* 402.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{21}NO_8$: C, 56.99; H, 5.58; N, 3.69. Found: C, 56.84; H, 5.49; N, 3.44.

4.7.10. Pd-mediated cyclization of ***17***. To a solution of **17** (80 mg, 0.21 mmol) in acetonitrile (10 mL) was added $Pd(CH_3CN)_2Cl_2$ (11 mg, 0.04 mmol) and the reaction mixture was stirred at rt under argon atmosphere for 6 h. Usual workup and purification of the crude by silica gel chromatography (40% ethyl acetate in petroleum ether) gave **44** (50 mg, 60%) as yellow oil.

*4.7.10.1. 1,2-O-Isopropylidene-3-C-[3′-oxo-3′-(3-nitrophenyl)-propyl]-α-D-allofuranose (**44**).* $[\alpha]_D^{25}$ +11.4 (*c* 1.8, $CHCl_3$). IR ($CHCl_3$): ν 3439, 3020, 1683, 1385, 1216, 1083, 758, 669 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.32 (s, 3H), 1.56 (s, 3H), 1.90 (ddd, *J*=5.8, 8.3, 14.5 Hz, 1H), 2.31 (ddd, *J*=6.2, 8.3, 14.8 Hz, 1H), 2.33 (br s, 1H), 3.10 (ddd, *J*=5.9, 8.3, 14.3 Hz, 1H), 3.11 (br s, 1H), 3.39 (br s, 1H), 3.40 (ddd, *J*=6.4, 8.5, 14.6 Hz, 1H), 3.66 (dd, *J*=4.5, 11.4 Hz, 1H), 3.79–3.91 (m, 3H), 4.26 (d, *J*=3.8 Hz, 1H), 5.75 (d, *J*=3.8 Hz, 1H), 7.32 (ddd, *J*=1.5, 6.1, 7.7 Hz, 1H), 7.45 (dt, *J*=2.2, 7.4, Hz, 1H), 7.77 (ddt, *J*=6.1, 8.5, 14.5 Hz, 1H), 7.96 (dt, *J*=1.2, 6.9 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.4 (t), 26.4 (q), 26.5 (q), 32.4 (t), 64.5 (t), 69.8 (d), 79.2 (s), 79.5 (d), 80.9 (d), 103.5 (d), 112.7 (s), 124.9 (d), 128.0 (d), 128.6 (d), 133.2 (s), 138.6 (d), 153.3 (s), 200.0 (s) ppm. ESI-MS: *m*/*z* 420.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{23}NO_9$: C, 54.40; H, 5.83; N, 3.52. Found: C, 54.58; H, 5.58; N, 3.29.

4.8. Synthesis of 1,2:5,6-di-*O*-isopropylidine-3-*O*-benzyl-3-*C*-(prop-2′-ynyl)-α-D-*allo*furanose (45)

To a solution of alcohol **26** (1.5 g, 5.03 mmol) in dry DMF (15 mL), NaH (181 mg, 7.54 mmol) was added portionwise at 0 °C and stirred for 30 min, followed by benzyl bromide (0.720 mL, 6.03 mmol). After stirring for additional 12 h at rt, the reaction

mixture was quenched at 0 °C by adding satd Na_2SO_4, poured into water, and extracted with ethyl acetate. The combined organic phases were washed with water, brine, dried (Na_2SO_4), and concentrated. Purification of the crude by column chromatography (15% ethyl acetate in petroleum ether) yielded the benzyl derivative **45** (1.37 g, 70%) as colorless oil. R_f (20% EtOAc/pet. ether) 0.4. $[\alpha]_D^{25}$ +45.2 (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): ν 3284, 3089, 3065, 2987, 2933, 2220, 1606, 1455, 1382, 844 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.34 (s, 3H), 1.37 (s, 3H), 1.39 (s, 3H), 1.60 (s, 3H), 2.13 (t, *J*=2.8 Hz, 1H), 2.63 (dd, *J*=2.7 Hz, 17.3 Hz, 1H), 2.82 (dd, *J*=2.7 Hz, 17.3 Hz, 1H), 4.01 (dd, *J*=5.3 Hz, 8.5 Hz, 1H), 4.10 (dd, *J*=6.0 Hz, 8.5 Hz, 1H), 4.18 (d, *J*=7.3 Hz, 1H), 4.25 (dt, *J*=5.8 Hz, 7.3 Hz, 1H), 4.76 (d, *J*=3.8 Hz, 1H), 4.78 (d, *J*=11.5 Hz, 1H), 4.87 (d, *J*=11.3 Hz, 1H), 5.81 (d, *J*=3.8 Hz, 1H), 7.26 (t, *J*=3.5 Hz, 1H), 7.32 (t, *J*=7.0 Hz, 2H), 7.40 (d, *J*=7.0 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21 (t), 25.3 (q), 26.6 (q), 26.8 (q), 27.0 (q), 67.4 (t), 67.5 (t), 72.1 (s), 73.4 (d), 79.1 (d), 81.6 (d), 82.3 (d), 83.7 (s), 104.4 (d), 109.5 (s), 112.8 (s), 127.2 (d, 3C), 128.0 (d, 2C), 138 (s) ppm. ESI-MS: *m*/*z* 411.52 (100%, $[M+Na]^+$), 427.51 (89%, $[M+K]^+$). Anal. Calcd for $C_{22}H_{28}O_6$: C, 68.02; H, 7.27. Found: C, 68.12; H, 7.06.

4.9. Sonogashira coupling of compound 45 with aryliodides

*4.9.1. 1,2:5,6-Di-O-isopropylidine-3-O-benzyl-3-C-([3′-phenyl-prop-2′-ynyl])-α-D-allofuranose (**46**).* Reagents: alkyne **45** (250 mg, 0.643 mmol); iodobenzene (0.11 mL, 0.961 mmol); TPP (17 mg, 0.0643 mmol); $Pd(PPh_3)_2Cl_2$ (45 mg, 0.0643 mmol); CuI (12 mg, 0.0643 mmol); Et_3N (5 mL) and DMF (2.5 mL). The crude residue was purified by column chromatography (10% ethyl acetate in petroleum ether) to obtain **46** (221 mg, 73%) as a yellow syrup. R_f (30% EtOAc/pet. ether) 0.6. $[\alpha]_D^{25}$ +63.2 (*c* 2.0, $CHCl_3$). IR ($CHCl_3$): ν 3063, 2987, 2935, 2223, 1953, 1731, 1677, 1598, 1491, 1454, 1372, 844, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 3H), 1.36 (s, 3H), 1.39 (s, 3H), 1.59 (s, 3H), 2.83 (d, *J*=17.1 Hz, 1H), 3.00 (d, *J*=17.1 Hz, 1H), 4.01–4.05 (m, 1H), 4.11 (dt, *J*=2.2, 6.3 Hz, 1H), 4.21 (d, *J*=7.0 Hz, 1H), 4.31–4.36 (m, 1H), 4.77 (d, *J*=3.5 Hz, 1H), 4.82 (d, *J*=11.3 Hz, 1H), 4.92 (d, *J*=11.3 Hz, 1H), 5.85 (d, *J*=3.5 Hz, 1H), 7.28–7.32 (m, 6H), 7.36–7.38 (m, 2H), 7.41 (d, *J*=7.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.5 (t), 25.3 (q), 26.6 (q), 26.8 (q), 27.0 (q), 67.4 (t), 67.5 (t), 73.5 (d), 81.8 (d), 82.5 (d), 83.7 (s), 84.1 (s), 84.5 (s), 104.4 (d), 109.4 (s), 112.8 (s), 123.0 (s), 127.0 (d), 127.2 (d, 2C), 128.0 (d, 2C), 128.1 (d), 128.3 (d, 2C), 131.4 (d, 2C) 138.9 (s) ppm. ESI-MS (*m*/*z*): 487.57 (47%, $[M+Na]^+$), 503.55 (100%, $[M+K]^+$). Anal. Calcd for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94. Found: C, 72.47; H, 6.71.

*4.9.2. 1,2:5,6-Di-O-isopropylidine-3-O-benzyl-3-C-([3′-(4-methoxyphenyl)-prop-2′-ynyl])-α-D-allofuranose (**47**).* Reagents: alkyne **45** (200 mg, 0.515 mmol); iodoanisole (181 mg, 0.772 mmol); TPP (13 mg, 0.0515 mmol); $Pd(PPh_3)_2Cl_2$ (36 mg, 0.0515 mmol); CuI (10 mg, 0.0515 mmol); Et_3N (5 mL) and DMF (2.5 mL). The crude residue was purified by column chromatography (15% ethyl acetate in petroleum ether) afforded **47** (178 mg, 70%) as colorless syrup. R_f (30% EtOAc/pet. ether) 0.6. $[\alpha]_D^{25}$ +50.0 (*c* 2.5, $CHCl_3$). IR ($CHCl_3$): ν 3065, 2988, 2540, 2222, 1725, 1666, 1606, 1455, 1373, 1170, 1075, 834, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 3H), 1.37 (s, 3H), 1.41 (s, 3H), 1.61 (s, 3H), 2.82 (d, *J*=17.2 Hz, 1H), 2.99 (d, *J*=17.2 Hz, 1H), 3.80 (s, 3H), 4.04 (dd, *J*=5.5, 8.3 Hz, 1H), 4.23 (dd, *J*=6.0, 8.3 Hz, 1H), 4.26 (d, *J*=7.3 Hz, 1H), 4.33–4.37 (m, 1H), 4.78 (d, *J*=3.8 Hz, 1H), 4.83 (d, *J*=11.3 Hz, 1H), 4.93 (d, *J*=11.3 Hz, 1H), 5.84 (d, *J*=3.8 Hz, 1H), 6.82 (br d, *J*=8.8 Hz, 2H), 7.26 (d, *J*=7.3 Hz, 1H), 7.30–7.33 (m, 4H), 7.43 (br d, *J*=7.3 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.5 (t), 25.4 (q), 26.6 (q), 26.8 (q), 27.0 (q), 55.2 (q), 67.3 (t), 67.5 (t), 73.5 (d), 81.9 (d), 82.6 (d), 82.9 (s), 83.5 (s), 84.1 (s), 104.4 (d), 109.4 (s), 112.8 (s), 113.9 (d, 2C), 115.2 (s), 127.1 (d), 127.2 (d, 2C), 128.0 (d, 2C), 132.8 (d, 2C), 138.9 (s), 159.4 (s) ppm. ESI-MS (*m*/*z*): 495.63 (18%, $[M+1]^+$), 517.68 (100%, $[M+Na]^+$). Anal. Calcd for $C_{29}H_{34}O_7$: C, 70.43; H, 6.93. Found: C, 70.61; H, 6.78.

*4.9.3. 1,2:5,6-Di-O-isopropylidine-3-O-benzyl-3-C-[3′-(4-nitrophenyl)-prop-2′-ynyl]-α-D-allofuranose (**48**).* Reagents: alkyne **45** (350 mg, 0.901 mmol); 4-iodonitrobenzene (336 mg, 1.351 mmol); TPP (24 mg, 0.0901 mmol); $Pd(PPh_3)_2Cl_2$ (63 mg, 0.0901 mmol); CuI (17 mg, 0.0901 mmol); Et_3N (6 mL) and DMF (3 mL). The crude residue was purified by column chromatography (10% ethyl acetate in petroleum ether) to give **48** (339 mg, 74%) as yellow syrup. R_f (20% EtOAc/pet. ether) 0.4. $[\alpha]_D^{25}$ +27.9 (*c* 1.9, $CHCl_3$). IR ($CHCl_3$): ν 3065, 2930, 2223, 1667, 1594, 1519, 1345, 1217, 1060, 855, 755 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.34 (s, 3H), 1.39 (s, 3H), 1.41 (s, 3H), 1.62 (s, 3H), 2.89 (d, *J*=17.4 Hz, 1H), 3.09 (d, *J*=17.4 Hz, 1H), 4.00–4.31 (m, 4H), 4.76 (d, *J*=3.8 Hz, 1H), 4.84 (d, *J*=11.2 Hz, 1H), 4.93 (d, *J*=11.2 Hz, 1H), 5.84 (d, *J*=3.8 Hz, 1H), 7.28–7.33 (m, 2H), 7.36–7.45 (m, 3H), 7.50 (br dt, *J*=2.1, 8.9 Hz, 2H), 8.16 (br dt, *J*=2.1, 8.9 Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.7 (t), 25.3 (q), 26.5 (q), 26.7 (q), 26.9 (q), 67.5 (t, 2C), 73.4 (d), 81.5 (d), 82.1 (s), 82.7 (d), 84.1 (s), 90.6 (s), 104.1 (d), 109.5 (s), 112.9 (s), 123.5 (d, 2C), 127.1 (d, 2C), 127.2 (d), 128.0 (d, 2C), 129.9 (s), 132.2 (d, 2C), 138.7 (s), 146.9 (s) ppm. ESI-MS (*m*/*z*): 509.77 (13%, $[M+1]^+$), 532.76 (100%, $[M+Na]^+$). Anal. Calcd for $C_{28}H_{31}NO_8$: C, 66.00; H, 6.13; N, 2.75. Found: C, 65.83; H, 6.33; N, 2.86.

*4.9.4. 1,2:5,6-Di-O-isopropylidine-3-O-benzyl-3-C-[3′-(3-nitrophenyl)-prop-2′-ynyl]-α-D-allofuranose (**49**).* Reagents: alkyne **45** (350 mg, 0.901 mmol); 3-iodonitrobenzene (336 mg, 1.351 mmol); TPP (24 mg, 0.0901 mmol); $Pd(PPh_3)_2Cl_2$ (63 mg, 0.0901 mmol); CuI (17 mg, 0.0901 mmol); Et_3N (6 mL) and DMF (3 mL). The crude residue was purified by column chromatography (10% ethyl acetate in petroleum ether) gave **49** (320 mg, 72%) as yellow syrup. R_f (20% EtOAc/pet. ether) 0.4. $[\alpha]_D^{25}$ +50.9 (*c* 1.5, $CHCl_3$). IR ($CHCl_3$): ν 3066, 2989, 2933, 2402, 2229, 1730, 1573, 1532, 1351, 1217, 1075, 875, 845, 756 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.35 (s, 3H), 1.39 (s, 3H), 1.42 (s, 3H), 1.62 (s, 3H), 2.87 (d, *J*=17.4 Hz, 1H), 3.07 (d, *J*=17.4 Hz, 1H), 4.01–4.38 (m, 4H), 4.76 (d, *J*=3.8 Hz, 1H), 4.84 (d, *J*=11.2 Hz, 1H), 4.94 (d, *J*=11.2 Hz, 1H), 5.84 (d, *J*=3.8 Hz, 1H), 7.28–7.37 (m, 3H), 7.41–7.46 (m, 2H), 7.49 (d, *J*=8.1 Hz, 1H), 7.62 (dt, *J*=1.3, 7.8 Hz, 1H), 8.14 (ddd, *J*=1.1, 2.3, 8.1 Hz, 1H), 8.21 (t, *J*=1.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.5 (t), 25.3 (q), 26.5 (q), 26.7 (q), 26.9 (q), 67.5 (t), 67.6 (t), 73.4 (d), 81.4 (s), 81.5 (d), 82.7 (d), 84.0 (s), 87.7 (s), 104.1 (d), 109.5 (s), 112.9 (s), 122.8 (d), 124.8 (s), 126.2 (d), 127.0 (d, 2C), 127.2 (d), 128.0 (d, 2C), 129.3 (d), 137.2 (d), 138.7 (s), 148.0 (s) ppm. ESI-MS (*m*/*z*): 509.77 (13%, $[M+1]^+$), 532.76 (100%, $[M+Na]^+$). Anal. Calcd for $C_{28}H_{31}NO_8$: C, 66.00; H, 6.13; N, 2.75. Found: C, 65.83; H, 6.16; N, 2.66.

4.10. The acetonide hydrolysis of compounds 46–50

A solution of alkyne (1 mmol) in MeOH (30 mL) was treated with dil. H_2SO_4 (15 mL, 0.8% in water) dropwise and stirred at rt for 5 h. The reaction mixture was quenched with $NaHCO_3$ (2.5 g), concentrated under reduced pressure. The residue was portioned between ethyl acetate/water and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried ($NaSO_4$) and concentrated. The crude residue was purified by column chromatography (30–60% ethyl acetate in petroleum ether) to obtain the alkyne diols **50**–**54**.

*4.10.1. 1,2-O-Isopropylidine-3-O-benzyl-3C-propynyl-α-D-allofuranose (**50**).* 94% Yield as colorless gum. R_f (20% EtOAc/pet. ether) 0.1. $[\alpha]_D^{25}$ +31.2 (*c* 2.4, $CHCl_3$). IR ($CHCl_3$): ν 3488, 3304, 3065, 2988, 2119, 1953, 1724, 1666, 1455, 1384, 872, 755 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.37 (s, 3H), 1.61 (s, 3H), 2.22 (t, *J*=2.8 Hz, 1H), 2.71 (dd, *J*=2.7, 17.3 Hz, 1H), 2.77 (dd, *J*=2.7, 17.3 Hz, 1H), 2.84 (br s, 1H), 3.66 (dd, *J*=5.2, 11.5 Hz, 1H), 3.78 (dd, *J*=3.0, 11.5 Hz, 1H), 3.95–3.97 (m, 1H), 4.07 (t, *J*=8.8 Hz, 1H), 4.65 (d, *J*=3.8 Hz, 1H), 4.74 (d,

J=10.4 Hz, 1H), 4.85 (d, J=10.4 Hz, 1H), 5.76 (d, J=3.8 Hz, 1H), 7.27–7.30 (d, J=7.4 Hz, 1H), 7.34 (t, J=7.7 Hz, 2H), 7.40 (d, J=7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3 (t), 26.6 (q, 2C), 64.3 (t), 68.1 (t), 69.5 (d), 72.6 (s), 78.7 (d), 78.9 (d), 81.4 (d), 84.3 (s), 104.0 (d), 113.2 (s), 127.7 (d), 127.8 (d, 2C), 128.3 (d, 2C), 137.6 (s) ppm. ESI-MS: m/z 349.41 (2%, $[M+1]^+$), 371.42 (100%, $[M+Na]^+$). Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.68; H, 6.78.

*4.10.2. 1,2-O-Isopropylidine-3-O-benzyl-3C-[3′-(phenyl)-prop-2α-ynyl]-α-D-allofuranose (**51**).* 88% Yield, colorless syrup. R_f (30% EtOAc/pet. ether) 0.2. $[\alpha]_D^{25}$ +71.8 (c 0.4, $CHCl_3$). IR ($CHCl_3$): ν 3480, 2925, 1725, 1598, 1217, 1087, 1026, 873.58, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (s, 3H), 1.62 (s, 3H), 2.32 (br s, 1H), 2.89 (d, J=2.3 Hz, 1H), 2.93 (d, J=17.3 Hz, 1H), 2.98 (d, J=17.3 Hz, 1H), 3.70 (dd, J=4.3, 11.3 Hz, 1H), 3.81 (dd, J=2.2, 11.3 Hz, 1H), 4.04–4.08 (m, 1H), 4.12 (d, J=8.8 Hz, 1H), 4.68 (d, J=3.8 Hz, 1H), 4.79 (d, J=10.3 Hz, 1H), 4.92 (d, J=10.3 Hz, 1H), 5.81 (d, J=3.8 Hz, 1H), 7.28–7.33 (m, 6H), 7.38–7.43 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2 (t), 26.7 (q), 26.7 (q), 64.4 (t), 68.2 (t), 69.6 (d), 78.9 (d), 81.6 (d), 84.1 (s), 84.2 (s), 84.7 (s), 104.1 (d), 113.2 (s), 122.6 (s), 127.8 (d), 127.9 (d, 2C), 128.3 (d, 2C), 128.3 (d), 128.4 (d, 2C), 131.5 (d, 2C), 137.9 (s) ppm. ESI-MS (m/z): 425.54 (3%, $[M+1]^+$), 447.55 (100%, $[M+Na]^+$). Anal. Calcd for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65. Found: C, 70.54; H, 6.48.

*4.10.3. 1,2-O-Isopropylidine-3-O-benzyl-3C-[3′-(4-methoxyphenyl)-prop-2′-ynyl]-α-D-allofuranose (**52**).* 87% Yield, colorless syrup. R_f (30% EtOAc/pet. ether) 0.2. $[\alpha]_D^{25}$ +61. 2 (c 1.7, $CHCl_3$). IR ($CHCl_3$): ν 3542, 3013, 2934, 2541, 2403, 2050, 1727, 1606, 1510, 873, 833, 755 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (s, 3H), 1.62 (s, 3H), 2.38 (br s, 1H), 2.90 (d, J=17.8 Hz, 1H), 2.92 (s, 1H), 2.95 (d, J=17.8 Hz, 1H), 3.70 (d, J=9.5 Hz, 1H), 3.80 (s, 3H), 4.08 (br s, 1H), 4.09 (s, 1H), 4.66 (d, J=3.8 Hz, 1H), 4.78 (d, J=10.3 Hz, 1H), 4.92 (d, J=10.3 Hz, 1H), 5.80 (d, J=3.8 Hz, 1H), 6.82 (d, J=8.8 Hz, 2H), 7.28–7.35 (m, 5H), 7.42 (d, J=6.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2 (t), 26.7 (q), 26.7 (q), 55.2 (q), 64.4 (t), 68.1 (t), 69.6 (d), 79.0 (d), 81.7 (d), 82.5 (s), 84.0 (s), 84.7 (s), 104.1 (d), 113.2 (s), 114.0 (d, 2C), 114.7 (s), 127.7 (d), 127.8 (d, 2C), 128.3 (d, 2C), 132.9 (d, 2C), 137.7 (s), 159.6 (s) ppm. ESI-MS (m/z): 455.62 (12%, $[M+1]^+$), 477.62 (100%, $[M+Na]^+$). Anal. Calcd for $C_{26}H_{30}O_7$: C, 68.71; H, 6.65. Found: C, 68.91; H, 6.35.

*4.10.4. 1,2-O-Isopropylidine-3-O-benzyl-3C-[3′-(4-nitrophenyl)-prop-2′-ynyl]-α-D-allofuranose (**53**).* 89% Yield, yellow syrup. R_f (30% EtOAc/pet. ether) 0.2. $[\alpha]_D^{25}$ +31.3 (c 1.1, $CHCl_3$). IR ($CHCl_3$): ν 3471, 3013, 2926, 2453, 1929, 1733, 1606, 1518, 1350, 1225, 1119, 875, 856, 758 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.40 (s, 3H), 1.64 (s, 3H), 2.83 (br s, 1H), 2.99 (d, J=17.6 Hz, 1H), 3.01 (d, J=17.6 Hz, 1H), 3.71 (dd, J=4.7, 11.5 Hz 1H), 3.82 (dd, J=3.3, 11.5 Hz 1H), 4.05–4.08 (m, 1H), 4.13 (d, J=8.8 Hz, 1H), 4.66 (d, J=3.8 Hz, 1H), 4.82 (d, J=10.4 Hz, 1H), 4.87 (d, J=10.4, 1H), 5.82 (d, J=3.8 Hz, 1H), 7.30–7.35 (m, 3H), 7.40 (d, J=8.0 Hz, 2H), 7.51 (d, J=8.8 Hz, 2H), 8.16 (d, J=8.8 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 22.3 (t), 26.7 (q, 2C), 64.4 (t), 68.2 (t), 69.7 (d), 78.8 (d), 81.7 (s), 82.5 (s), 84.8 (s), 89.9 (d), 104.1 (d), 113.5 (s), 123.6 (d, 2C), 127.7 (d, 2C), 127.9 (d), 128.4 (d, 2C), 129.5 (s), 132.4 (d, 2C), 137.5 (s), 147.1 (s) ppm. ESI-MS (m/z): 492.53 (100%, $[M+Na]^+$). Anal. Calcd for $C_{25}H_{27}NO_8$: C, 63.96; H, 5.80; N, 2.98. Found: C, 63.73; H, 5.90; N, 2.74.

*4.10.5. 1,2-O-Isopropylidine-3-O-benzyl-3C-[3′-(3-nitrophenyl)-prop-2′-ynyl]-α-D-allofuranose (**54**).* 84% Yield, yellow syrup. R_f (30% EtOAc/pet. ether) 0.2. $[\alpha]_D^{25}$ +49.5 (c 1.1, $CHCl_3$). IR ($CHCl_3$): ν 3479, 3085, 2928, 2229, 1671, 1606, 1530, 1455, 1374, 1167, 1083, 875, 756 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.4 (s, 3H), 1.64 (s, 3H), 1.88 (br s, 1H), 2.42 (br s, 1H), 2.97 (d, J=17.6 Hz, 1H), 3.03 (d, J=17.6 Hz, 1H), 3.71 (dd, J=4.6, 11.5 Hz, 1H), 3.82 (dd, J=3.1, 11.5 Hz, 1H), 4.05–4.07 (m, 1H), 4.14 (d, J=8.8 Hz, 1H), 4.68 (d, J=3.6 Hz, 1H), 4.83 (d, J=10.4 Hz, 1H), 4.89 (d, J=10.4 Hz, 1H), 5.83 (d, J=3.6 Hz, 1H), 7.30 (d, J=7.1 Hz, 1H), 7.34 (t, J=7.7 Hz, 2H), 7.42 (d, J=7.4 Hz, 2H), 7.48 (t, J=8.0 Hz, 1H), 7.67 (d, J=7.4 Hz, 1H), 8.16 (dd, J=8.2 Hz, 2.0 Hz, 1H), 8.21 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.2 (t), 26.7 (q, 2C), 64.4 (t), 68.2 (t), 69.7 (d), 78.8 (d), 81.5 (s), 81.7 (d), 84.7 (s), 87.1 (s), 104.1 (d), 113.4 (s), 123.1 (d), 124.5 (s) 126.3 (d), 127.7 (d, 2C), 127.9 (d), 128.4 (d, 2C), 129.4 (d), 137.4 (d), 137.5 (s), 148.0 (s) ppm. ESI-MS (m/z): 492.53 (100%, $[M+Na]^+$). Anal. Calcd for $C_{25}H_{27}NO_8$: C, 63.96; H, 5.80; N, 2.98. Found: C, 64.83; H, 5.67; N, 2.72.

4.11. Pd-mediated cyclization of alkynols 50–54

*4.11.1. 1,2-O-Isopropylidine-3-O-benzyl-3C-[3′-(2-oxypropyl])-α-D-allofuranose-(2′-C,5-O,6-O)-ketal (**55**).* To a solution of **50** (115 mg, 0.33 mmol) in acetonitrile (6 mL) was added $Pd(CH_3CN)_2Cl_2$ (42 mg, 0.165 mmol) and the reaction mixture was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and purified by silica gel chromatography (15% ethyl acetate in petroleum ether) to obtain **55** (97 mg, 84%) as a white solid. R_f (20% EtOAc/pet. ether) 0.2. Mp 143–145 °C. $[\alpha]_D^{25}$ +6.5 (c 0.8, $CHCl_3$). IR ($CHCl_3$): ν 3063, 2986, 1731, 1606, 1384, 1155, 1057, 866, 742 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (d, J=14.9 Hz, 1H), 1.38 (s, 3H), 1.53 (s, 3H), 1.59 (s, 3H), 2.33 (d, J=14.9 Hz, 1H), 3.83 (dd, J=6.1, 6.8 Hz, 1H), 4.01 (s, 1H), 4.21 (d, J=6.9 Hz, 1H), 4.31 (d, J=3.6 Hz, 1H), 4.55 (d, J=10.5 Hz, 1H), 4.63 (d, J=10.5 Hz, 1H), 4.68 (d, J=3.6 Hz, 1H), 5.01 (d, J=3.6 Hz, 1H), 7.28 (t, J=7.4 Hz, 1H), 7.34 (t, J=7.1 Hz, 2H), 7.45 (d, J=7.1 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.2 (q), 26.9 (q), 27.1 (q), 35.8 (t), 65.1 (t), 66.5 (t), 74.0 (d), 77.8 (d), 80.4 (s), 83.0 (d), 104.8 (s), 104.9 (d), 113.2 (s), 127.4 (d), 127.7 (d, 2C), 128.2 (d, 2C), 138.4 (s) ppm. ESI-MS: (m/z) 371.34 (100%, $[M+Na]^+$), 387.33 (42%, $[M+K]^+$). Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.23; H, 6.64.

*4.11.2. 1,2-O-Isopropylidene-3-O-benzyl-3C-[2′-oxo-3′-phenyl-propyl]-α-D-allofuranose-(2′-C,5-O,6-O)-ketal (**56**).* To a solution of **51** (97 mg, 0.2284 mmol) in acetonitrile (10 mL) was added $Pd(CH_3CN)_2Cl_2$ (29 mg, 0.112 mmol) and the reaction mixture was stirred at rt under argon atmosphere for 2 h. The reaction mixture was concentrated and purified by silica gel chromatography (15% ethyl acetate in petroleum ether) to obtain **56** (80 mg, 82%) as a yellow color solid. R_f (30% EtOAc/pet. ether) 0.5. Mp 141–143 °C. $[\alpha]_D^{25}$ +47.0 (c 0.4, $CHCl_3$). IR ($CHCl_3$): ν 3063, 2952, 1734, 1605, 1455, 1059, 1021, 873, 754, 699 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.29 (d, J=14.9 Hz, 1H), 1.35 (s, 3H), 1.57 (s, 3H), 2.27 (d, J=14.9 Hz, 1H), 3.08 (d, J=14.3 Hz, 1H), 3.11 (d, J=14.3 Hz, 1H), 3.72 (dd, J=5.9 Hz, 6.7 Hz, 1H), 4.00 (s, 1H), 4.20 (d, J=6.9 Hz, 1H), 4.25 (d, J=3.6 Hz, 1H), 4.47 (d, J=10.5 Hz, 1H), 4.52 (d, J=10.5 Hz, 1H), 4. 67 (dd, J=1.1, 5.1 Hz, 1H), 5.85 (d, J=3.5 Hz, 1H), 7.24–7.28 (m, 3H), 7.29–7.35 (m, 5H), 7.38–7.40 (m, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.8 (q), 27.1 (q), 34.3 (t), 43.8 (t), 65.3 (t), 66.6 (t), 73.9 (d), 78.0 (d), 80.5 (s), 83.0 (d), 104.9 (d), 105.9 (s), 113.1 (s), 126.6 (d), 127.4 (d), 127.8 (d, 2C), 128.0 (d, 2C), 128.1 (d, 2C), 130.4 (d, 2C), 135.4 (s), 138.3 (s) ppm. ESI-MS (m/z): 447.40 (100%, $[M+Na]^+$). 463.38 (87%, $[M+K^+]$). Anal. Calcd for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65. Found: C, 70.44; H, 6.85.

*4.11.2.1. Crystallographic data for **56**.* $C_{25}H_{28}O_6$: M=424.47, crystal dimensions 0.59×0.19×0.04 mm^3, orthorhombic, space group $P2_12_12_1$, a=6.174(2), b=9.766(4), c=37.152(14) Å, V=2240.2(15) Å^3, Z=4, ρ_{calcd}=1.259 g cm^{-3}, μ (Mo Kα)=0.089 mm^{-1}, F(000)=904, $2\theta_{max}$=50.00°, T=297(2) K, 11,062 reflections collected, 3937 unique, 3769 observed ($I>2\sigma(I)$) reflections, 282 refined parameters, R value 0.1143, $wR2$=0.2463 (all data R=0.1271, $wR2$=0.2533), S=1.247, minimum and maximum transmission 0.9964 and 0.9495; maximum and minimum residual electron densities +0.583 and −0.272 e Å^{-3}.

*4.11.3. 1,2-O-Isopropylidine-3-O-benzyl-3C-[2′-oxo-3′-(4-methoxyphenyl) propyl]-α-D-allofuranose-(2′-C,5-O,6-O)-ketal (**57**).* To a solution of **52** (100 mg, 0.220 mmol) in acetonitrile (6 mL) was added $Pd(CH_3CN)_2Cl_2$ (28 mg, 0.108 mmol) and the reaction mixture was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and the crude was purified by silica gel chromatography (15% ethyl acetate in petroleum ether) to procure **57** (90 mg, 90%) as white solid. R_f (20% EtOAc/pet. ether) 0.3. Mp 127–129 °C. $[\alpha]_D^{25}$ +27.6 (*c* 0.7, $CHCl_3$). IR ($CHCl_3$): *ν* 3064, 2932, 1889, 1723, 1612, 1373, 1301, 1114, 1059, 873, 833, 755 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): *δ* 1.27 (d, *J*=14.8 Hz, 1H), 1.34 (s, 3H), 1.57 (s, 3H), 2.24 (d, *J*=14.8 Hz, 1H), 3.02 (s, 2H), 3.71 (t, *J*=6.33 Hz, 1H), 3.78 (s, 3H), 3.99 (s, 1H), 4.18 (d, *J*=6.9 Hz, 1H), 4.24 (d, *J*=3.6 Hz, 1H), 4.47 (d, *J*=10.7 Hz, 1H), 4.51 (d, *J*=10.7 Hz, 1H), 4.65 (d, *J*=4.6 Hz, 1H), 5.84 (d, *J*=3.6 Hz, 1H), 6.83 (d, *J*=8.5 Hz, 2H), 7.25 (d, *J*=8.8 Hz, 2H), 7.30–7.33 (m, 2H), 7.39 (d, *J*=7.2 Hz, 2H), 7.47–7.51 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 26.8 (q), 27.1 (q), 34.2 (t), 42.9 (t), 55.1 (q), 65.3 (t), 66.6 (t), 73.9 (d), 78.0 (d), 80.5 (s), 83.0 (d), 104.9 (d), 105.9 (s), 113.1 (s) 113.5 (d, 2C), 127.4 (d), 127.5 (s), 127.7 (d, 2C), 128.1 (d, 2C), 131.3 (d, 2C), 138.4 (s), 158.4 (s) ppm. ESI-MS (*m*/*z*): 477.41 (100%, $[M+Na]^+$), 493.39 (55%, $[M+K]^+$). Anal. Calcd for $C_{26}H_{30}O_7$: C, 68.71; H, 6.65. Found: C, 68.59; H, 6.81.

*4.11.4. 1,2-O-Isopropylidine-3-O-benzyl-3C-[2′-oxo-3′-(4-nitrophenyl)propyl]-α-D-allofuranose-(2′-C,5-O,6-O)-ketal (**58**).* A solution of **53** (150 mg, 0.319 mmol) and $Pd(CH_3CN)_2Cl_2$ (41 mg, 0.158 mmol) in acetonitrile (6 mL) was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and the residue obtained was purified by silica gel chromatography (15%, 18% ethyl acetate in petroleum ether) to obtain **58** (103 mg, 68%) as yellow solid. R_f (20% EtOAc/pet. ether) 0.3. Mp 173–175 °C. $[\alpha]_D^{25}$ +14.4 (*c* 0.5, $CHCl_3$). IR ($CHCl_3$): *ν* 3070, 2925, 1929, 1732, 1606, 1518, 1349, 1225, 1119, 1018, 876, 747 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): *δ* 1.37 (s, 3H), 1.38 (d, *J*=14.6 Hz, 1H), 1.58 (s, 3H), 2.32 (d, *J*=14.6 Hz, 1H), 3.17 (s, 2H), 3.58 (t, *J*=6.3 Hz, 1H), 4.01 (s, 1H), 4.19 (d, *J*=7.1 Hz, 1H), 4.31 (d, *J*=3.3 Hz, 1H), 4.54 (d, *J*=10.7 Hz, 1H), 4.56 (d, *J*=10.7 Hz, 1H), 4.63 (d, *J*=4.4 Hz, 1H), 5.90 (d, *J*=3.3 Hz, 1H), 7.29 (d, *J*=7.1 Hz, 1H), 7.34 (t, *J*=7.1 Hz, 2H), 7.41 (d, *J*=7.1 Hz, 2H), 7.50 (d, *J*=8.8 Hz, 2H), 8.13 (d, *J*=8.8 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 26.9 (q), 27.1 (q), 35.0 (t), 43.0 (t), 65.5 (t), 66.7 (t), 73.9 (d), 77.8 (d), 80.6 (s), 82.9 (d), 104.9 (d), 105.3 (s), 113.3 (s), 123.1 (d, 2C), 127.5 (d), 127.6 (d, 2C), 128.2 (d, 2C), 131.5 (d, 2C), 138.2 (s), 142.9 (s), 146.9 (s) ppm. ESI-MS (*m*/*z*): 493.70 (80%, $[M+Na]^+$), 508.56 (100%, $[M+K]^+$). Anal. Calcd for $C_{25}H_{27}NO_8$: C, 63.96; H, 5.80; N, 2.98. Found: C, 64.24; H, 5.60; N, 2.81.

*4.11.4.1. Crystallographic data for **58**.* $C_{25}H_{27}NO_8$: *M*=469.48, crystal dimensions 0.46×0.14×0.09 mm^3, orthorhombic, space group $P\,2_12_12_1$. *a*=5.9696(9), *b*=16.175(2), *c*=23.804(4) Å, *V*=2298.5(6) $Å^3$, *Z*=4, ρ_{calcd}=1.357 g cm^{-3}, *μ* (Mo Kα)=0.102 mm^{-1}, *F*(000)=992, $2\theta_{max}$=50.00°, *T*=297(2) K, 18,048 reflections collected, 4519 unique, 4519 observed ($I>2\sigma(I)$) reflections, 309 refined parameters, *R* value 0.0488, *wR*2=0.1076 (all data *R*=0.0539, *wR*2=0.1099), *S*=1.216, minimum and maximum transmission 0.9912 and 0.9547; maximum and minimum residual electron densities +0.209 and −0.138 e $Å^{-3}$.

*4.11.5. Pd-mediated cyclization of **54**.* A solution of **54** (90 mg, 0.192 mmol) and $Pd(CH_3CN)_2Cl_2$ (25 mg, 0.096 mmol) in acetonitrile (6 mL) was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and the residue obtained was purified by silica gel chromatography (15%, 18% ethyl acetate in petroleum ether) to obtain **59** (64 mg, 71%) as yellow solid and **60** (15 mg, 17%) as yellow oil.

*4.11.5.1. 1,2-O-Isopropylidine-3-O-benzyl-3C-[2′-oxo-3′-(3-nitrophenyl)-propyl]-α-D-allofuranose-(2′-C,5-O,6-O)-ketal (**59**).* R_f (20% EtOAc/pet. ether) 0.3. Mp 95–97 °C. $[\alpha]_D^{25}$ +15.9 (*c* 0.9, $CHCl_3$). IR ($CHCl_3$): *ν* 3066, 2926, 1727, 1607, 1529, 1350, 1167, 1060, 873, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.35 (d, *J*=14.3 Hz, 1H), 1.37 (s, 3H), 1.39 (d, *J*=14.6 Hz, 1H), 1.58 (s, 3H), 3.18 (s, 2H), 3.58 (t, *J*=6.0 Hz, 1H), 4.02 (br s, 1H), 4.19 (d, *J*=7.0 Hz, 1H), 4.32 (d, *J*=3.5 Hz, 1H), 4.54 (d, *J*=10.8 Hz, 1H), 4.57 (d, *J*=10.8 Hz, 1H), 4.83 (dd, *J*=1.7, 5.5 Hz, 1H), 5.90 (d, *J*=3.5 Hz, 1H), 7.29 (d, *J*=7.3 Hz, 1H), 7.34 (t, *J*=7.5 Hz, 2H), 7.41 (d, *J*=7.3 Hz, 2H), 7.45 (t, *J*=8.1 Hz, 1H), 7.68 (d, *J*=7.8 Hz, 1H), 8.10 (dd, *J*=1.3, 8.3 Hz, 1H), 8.21 (t, *J*=1.8 Hz 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 26.8 (q), 27.1 (q), 34.9 (t), 42.7 (t), 65.5 (t), 66.7 (t), 73.9 (d), 77.8 (d), 80.5 (s), 82.9 (d), 104.9 (d), 105.2 (s), 113.3 (s), 121.8 (d), 125.4 (d), 127.5 (d), 127.6 (d, 2C), 128.2 (d, 2C), 128.7 (d), 136.9 (d), 137.1 (s), 138.2 (s), 147.9 (s) ppm. ESI-MS (*m*/*z*): 492.56 (50%, $[M+Na]^+$), 508.54 (100%, $[M+K]^+$). Anal. Calcd for $C_{25}H_{27}NO_8$: C, 63.96; H, 5.80; N, 2.98. Found: C, 63.74; H, 5.60; N, 2.78.

*4.11.5.2. 1,2-O-Isopropylidene-3-O-benzyl-3C-[2′-hydroxy-2′-(3-nitro-benzyl)-E-vinyl]-2′,5-anhydro-α-D-allofuranose (**60**).* R_f (20% EtOAc/pet. ether) 0.2. $[\alpha]_D^{25}$ +32.2 (*c* 1.3, $CHCl_3$). IR ($CHCl_3$): *ν* 3456, 3016, 2929, 1719, 1531, 1375, 1215, 1090, 887, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.37 (s, 3H), 1.58 (s, 3H), 1.88 (br s, 1H), 3.18 (s, 2H), 3.58 (dd, *J*=6.8, 6.0 Hz, 1H), 4.02 (br s, 1H), 4.12 (q, *J*=7.3 Hz, 1H), 4.19 (d, *J*=7.3 Hz, 1H), 4.32 (d, *J*=3.5 Hz, 1H), 4.53 (d, *J*=10.8 Hz, 1H), 4.57 (d, *J*=10.8 Hz, 1H), 4.63 (dd, *J*=1.8, 5.3 Hz, 1H), 5.91 (d, *J*=3.5 Hz, 1H), 7.32 (d, *J*=7.0 Hz, 1H), 7.34 (t, *J*=7.0 Hz, 2H), 7.41 (d, *J*=7.0 Hz, 2H), 7.45 (t, *J*=8.0 Hz, 1H), 7.69 (d, *J*=7.8 Hz, 1H), 8.11 (dd, *J*=1.5, 8.0 Hz, 1H), 8.22 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 26.9 (q), 27.1 (q), 42.8 (t), 65.5 (t), 66.7 (t), 73.97 (d), 77.2 (d), 77.9 (d), 80.6 (s), 82.9 (d), 104.9 (d), 105.2 (s), 113.3 (s), 121.8 (d), 125.5 (d), 127.5 (d), 127.7 (d, 2C), 128.2 (d, 2C), 128.7 (d), 136.9 (d), 137.1 (s), 138.2 (s), 148.0 (s) ppm. ESI-MS (*m*/*z*): 491.41 (34%, $[M+Na]^+$), 508.41 (100%, $[M+K]^+$). Anal. Calcd for $C_{25}H_{27}NO_8$: C, 63.96; H, 5.80; N, 2.98. Found: C, 63.64; H, 5.66; N, 2.77.

4.12. Pd-mediated cyclization of 28

To a solution of **28** (50 mg, 0.12 mmol) in acetonitrile (10 mL) was added $Pd(CH_3CN)_2Cl_2$ (11 mg, 0.04 mmol) and the reaction mixture was stirred at rt under argon atmosphere for 6 h. The reaction mixture was concentrated and purified by silica gel chromatography (35% ethyl acetate in petroleum ether) to obtain **61** (28 mg, 56%) as a white solid.

*4.12.1. 1,2-O-Isopropylidene-3-C-[3′-oxo-3′-(4-methoxyphenyl) propyl]-α-D-allofuranose-(3′-C,5-O,6-O)-ketal (**61**).* Mp 175–178 °C. $[\alpha]_D^{25}$ −29.4 (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): *ν* 3439, 3020, 1620, 1339, 1216, 929, 758, 669 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): *δ* 1.36 (s, 3H), 1.52 (dd, *J*=5.0, 12.6 Hz, 1H), 1.61 (s, 3H), 2.05–2.21 (m, 2H), 2.36–2.54 (m, 1H), 3.69 (d, *J*=8.3 Hz, 1H), 3.72 (d, *J*=8.2 Hz, 1H), 3.79 (s, 3H), 3.98 (br s, 1H), 4.03 (d, *J*=8.7 Hz, 1H), 4.20 (d, *J*=3.5 Hz, 1H), 4.80 (br d, *J*=5.3 Hz, 1H), 5.80 (d, *J*=3.7 Hz, 1H), 6.84 (dt, *J*=2.3, 8.9 Hz, 2H), 7.41 (dt, *J*=2.7, 8.9 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 26.2 (q), 26.7 (q), 28.4 (t), 36.6 (t), 55.2 (q), 65.5 (t), 76.7 (d), 79.5 (s), 81.7 (d), 85.9 (d), 102.7 (d), 110.7 (s), 112.8 (s), 113.5 (d, 2C), 125.8 (d, 2C), 135.0 (s), 159.4 (s) ppm. ESI-MS: *m*/*z* 365.1 (100%, $[M+H]^+$). Anal. Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.58; H, 6.62.

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