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A strategy to access fused triazoloquinoline and related nucleoside analogues

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ABSTRACT

Fused triazoloquinolines have been prepared starting from (*E*)-3-(2-nitrophenyl)-1-aryl-prop-2-en-1-ones and sugar or benzyl azides in a sequential [3+2] cycloaddition reaction, followed by one pot Pd–C assisted reduction, cyclization and aromatization. The triazolyl fused quinolines with N^1-glycosyl substituents as unnatural nucleosides have inherent potential to generate a library of compounds for bioevaluations.

1. Introduction

Benzofused aza-heterocycles are a class of compounds endowed with numerous pharmacological properties and considered as 'privileged structures' in medicinal chemistry.[1] Among these heterocycles, quinoline derivatives with planar π-electron deficient ring systems are ubiquitous in nature[2] and encountered in several compounds having great pharmaceutical significance.[3] The 1,2,3-triazole unit, a peptide bond surrogate[4] has wide application in medicinal chemistry[5] as well as in fine chemical industry.[6] Functionalized 1,2,3-triazoles constitute one of the common fragments in biologically active compounds and this has resulted in a wealth of synthetic methodologies for their preparation and incorporation in more complex structures. Moreover, functionalized (benzo/hetero-fused) quinoline analogues are of great interest in synthetic and in medicinal chemistry.[7] In this context 1,2,3-triazoles fused with quinolines (triazoloquinolines), are particularly interesting due to their wide range of biological properties, such as antiviral,[8] antimicrobial,[9] RNA-dependent RNA polymerase inhibitor[10] and anticonvoluscent[11] activity.

At the intersection of heterocyclic and carbohydrate chemistry, synthesis of carbohydrate coupled heterocycles as unnatural nucleoside analogues is an interesting concept in medicinal and bioorganic chemistry. Modifications in the *N*-heterocycle or sugar moieties in nucleosides have led to the evolution of unnatural nucleosides or related analogues, which circumvent the problem of enzymatic degradations of nucleosides.[12] Nucleoside analogues with modified bases have gained importance in organic synthesis[13] due to interesting biological activities[14] and they are known to modulate the properties of DNA to expand the genetic code and creation of a semisynthetic organism.[15] Further such nucleosides, have found applications in DNA probe technology with fluorescent properties,[16] study of DNA damages[17] and as antisense approach and efficiently act as antiviral agents against VZV and HIV.[18]

There are several reports to access these triazoloquinolines, however the methods for directly fused triazoloquinolines are rare.[19] Functional-group tolerance during a chemical transformation has high significance in organic synthesis and more particularly in carbohydrate chemistry and the reactions that follow these criterions allow the design of simpler synthetic routes exempted by the protecting-group operations. In this perspective, reductive cyclization reactions are key to many organic transformations leading to several important bioactive natural products, and clinically useful molecules, such as indoles,[20] 2(1*H*)-indazoles,[21] quinolines,[22] 4(1*H*)-quinolones,[23] quinazolines,[24] benzimidazoles,[25] benzotriazoles[26] and several others.[27]

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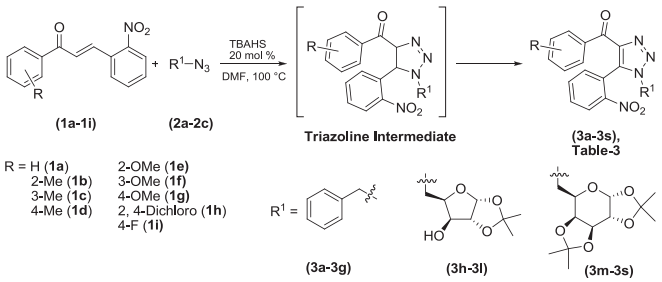
Recently we have been involved in azido sugar chemistry to access new chemotherapeutic agents for different applications. Initially heterocyclic molecules coupled with sugar moiety, were prepared by azide–alkenone cycloaddition chemistry.[28] Herein we report a simple and mild protocol for facile transformation of (*E*)-3-(2-nitrophenyl)-1-aryl-prop-2-en-1-ones into tricyclic heterocyclic fused triazoloquinolines, involving [3+2] cycloaddition of benzyl/sugar azides followed by one pot sequential Pd–C mediated reductive cyclization and aromatization. To the best of our knowledge this is the first report for the synthesis of triazoloquinoline using reductive cyclization in the designed triazolyl methanones.

2. Result and discussion

Our synthetic strategy for tricyclic triazoloquinolines was inspired by the unique versatility of *ortho*-nitroaryl substituted propenones (chalcones), which serve as substrates during dipolar cycloaddition with diverse azides. Reductive cyclization of the resulting *ortho*-nitrophenyl substituted triazolyl methanones has yielded the fused triazoloquinolines. These nucleoside analogues have stereochemical diversity in the monosaccharide used and the stereochemistry of these monosaccharides is conserved throughout the synthetic maneuver.

The strategy begins with the synthesis of readily accessible *ortho*-nitrophenyl substituted propenones (**1a**–**j**).[29] The starting benzyl azide (**2a**) and sugar azides, 5-azido-5-deoxy-1,2-*O*-isoproylidene-α-D-xylofuranose (**2b**), 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**2c**), 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide (**2d**) and 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl azide (**2e**) were prepared from the benzyl bromide and respective monosaccharides, D-xylose, D-glucose and D-galactose by the procedure already reported in the literature.[30] The primary azides (**2a**–**c**) on 1–3 dipolar cycloaddition reaction[31] with different propenones (**1a**–**i**) at 100 °C in presence of 20 mol % of tetrabutylammonium hydrogensulphate (TBAHS) as catalyst in dimethyl formamide (DMF) separately led to the formation of differently substituted triazolyl methanones (**3a**–**s**) in good yields (65–97%) (Scheme 1).



Scheme 1. Synthesis of *ortho*-nitrophenyl substituted triazolyl methanone (**3a**–**s**).

However, the above cycloaddition reaction with anomeric glycosyl azides **2d** and **2e** under same reaction condition was very sluggish and resulted in only 20–25% yield of the desired products **3t** and **3u**, respectively. Therefore, to improve the yield of the products with these anomeric azides, the procedure was reinvestigated with different catalytic systems and results are summarized in Table 1.

Among all the reaction conditions optimized, 20 mol % of tetrabutylammonium hydrogensulphate (TBAHS) as catalyst with 10 mol % *p*-toluene sulphonic acid (*p*-TSA), proved to be the most efficient condition for cycloaddition reaction between propenone **1i** and glucosyl azide **2d** (entry 6, Table 1) with 55% yield of desired product **3t**. The precise role of *p*-TSA in this reaction is not clearly established however, it is presumed to work on the concept of co-operative catalysis. The anomeric glycosyl azides are more reactive as compared to the primary azides and therefore less selective and provide unidentified side products (TLC). *p*-TSA may form the ion pair with the reactive anomeric sugar azide, resulting in its less reactivity and enhanced selectivity to offer better yield of the desired product.

Similarly, galactopyranosyl azide (**2e**) on reaction with propenone **1j** resulted in the desired N^1-galactosyl triazolyl methanone (**3u**) in 50% yield (entry 8, Table 1). Structures of these triazolyl methanones were established on the basis of their analytical data. The stereochemical integrity of compound **3t** and **3u** was maintained during the transformation and none of the isomerization was observed during the course of the reaction (SD).

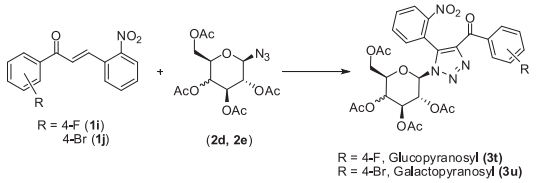
With the above *ortho*-nitrophenyl substituted triazolyl methanones (**3a**–**u**) in our hands, we were ready to perform the key reductive cyclization for the concomitant construction of triazoloquinoline (**4a**–**g**) and unnatural nucleoside analogues (**4h**–**u**) respectively, in good yields. Although the repertoire of reductive cyclization reactions is colossal, however the methodologies that could be advantageous in terms of selectivity, availability, affordability of starting materials, operational simplicity, functional-group tolerance and environmental sustainability is a matter of great interest. Therefore, to maintain the efficiency of the protocol the reductive cyclization reaction was separately optimized on two different substrates; (i) *ortho*-nitrophenyl triazolyl methanone derived from benzyl azide, and (ii) *ortho*-nitrophenyl triazolyl methanone derived from 5-azido-5-deoxy-1,2-*O*-isoproylidene-α-D-xylofuranose, and results are summarized in Table 2.

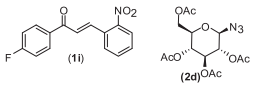
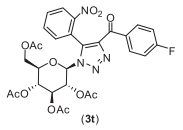
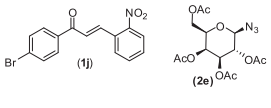
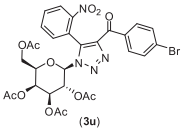
The reaction pattern with the N^1-benzyl- and N^1-xylofuranosyl triazolyl methanones (**3g** and **3j**) for reductive cyclization is almost similar. With Fe powder (3 equiv)/NH_4Cl as catalytic system, a mixture of cyclized products (**4g** and **4j**) and reduced uncyclized amine products (**4g′** and **4j′**) were formed (entries 3 and 8, Table 2). Pd–C/$HCOONH_4$ also provides the same results as Fe powder (3 equiv)/NH_4Cl catalytic system (entries 4 and 9, Table 2). The uncyclized amine product could not be cyclized under above reaction condition even for a prolonged reaction time. Furthermore, increase in catalyst loading also does not affect the course of reaction. $SnCl_2 \cdot 2H_2O$ (10 equiv) as catalyst gave exclusively only the uncyclized reduced products (entries 1 and 6, Table 2) in quantitative yields. Reaction under ultrasonic vibrations also did not affect the cyclization and only uncyclized amines were obtained (entries 1 and 6, Table 2). Formation of uncyclized product in the above reductions may be explained in terms protonation of the substrates (intermediate amine) with the acids generated during reaction and further cyclization would be difficult to achieve with the protonated amine substrate. However, applying H_2 pressure in presence of Pd–C, no such acid is generated and only the cyclized product is obtained (entry 5, Table 2). Thus among all the catalytic systems screened, Pd–C/H_2 under pressure in MeOH was found to be the best one with excellent yield of the cyclized product.

With the above optimized reaction condition for reductive cyclization, first we explored our methodology for differently substituted aromatic heterocyclic systems (**3a**–**g**), where the methodology hold promise and desired products (**4a**–**g**) were obtained in very good yields (87–98%, Table 3). The electronic factor does not play any significant role in reductive cyclization. Further, to see the steric effect, a comparison of the reductive cyclization with 2-, 3-, 4-, Me/OMe substituted substrates in acetophenone ring (**3b**–**g**) was also carried out, without any significant change in the yield of the products with little alteration in time was noted (Table 3). The scope of reaction is well illustrated with variously substituted triazolyl methanones (Table 3).

Next we explored the possibility of preparing unnatural homonucleoside analogues. For this purpose, we set out a model reaction

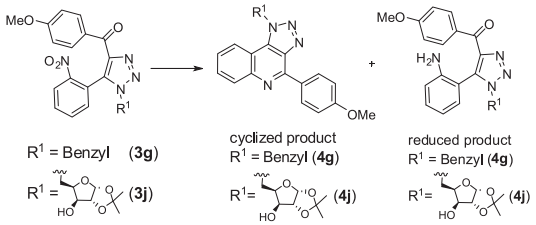
Table 1
Optimization of cycloaddition reaction for glycosyl (anomeric azide) and synthesized molecules (**3t**, **u**)



Entry	Substrate	Product	Catalytic system[a] (mol %)	Time (h)	Yield (%)
1			TBAHS (20)	24	25[b]
2	**1i**+**2d**	**3t**	TBAHS (20)+$AlCl_3$ (10)	16	15[c]
3	**1i**+**2d**	**3t**	TBAHS (20)+$SnCl_4$ (10)	16	15[c]
4	**1i**+**2d**	**3t**	TBAHS (20)+CuI (10)	18	35[b]
5	**1i**+**2d**	**3t**	TBAHS (20)+TBAB (10)	16	25[b]
6	**1i**+**2d**	**3t**	TBAHS (20)+*p*-TSA (10)	18	55
7	**1i**+**2d**	**3t**	*p*-TSA (20)	24	20[b]
8			TBAHS (20)+*p*-TSA (10)	18	50

[a] All the reactions were performed in anhydrous DMF as solvent.
[b] Reaction picture was consistent and incomplete even after several hours.
[c] Reaction was very sluggish and incomplete after several hours.

Table 2
Optimization of reductive cyclization of different substrates under different catalytic conditions



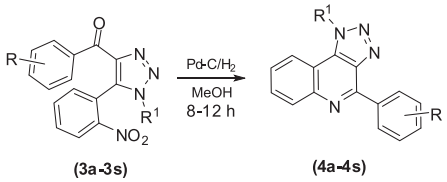
Entry	Substrate	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%) **4g** or **4j**/**4g′** or **4j′**
1	**3g**	$SnCl_2{\cdot}2H_2O$ (10 equiv)	EtOH	80	2	–/90
2	**3g**	$SnCl_2{\cdot}2H_2O$ (10 equiv)[a]	EtOH	30	2	–/93
3	**3g**	Fe powder (3 equiv)/NH_4Cl	EtOH/H_2O	80	14	65/22[b]
4	**3g**	Pd–C/$HCOONH_4$	MeOH	30	19	50/20[b]
5	**3g**	Pd–C/H_2	MeOH	30	8	92/–
6	**3j**	$SnCl_2{\cdot}2H_2O$ (10 equiv)	EtOH	80	2	–/67
7	**3j**	[a]$SnCl_2{\cdot}2H_2O$ (10 equiv)	EtOH	30	2	–/71
8	**3j**	Fe powder (3 equiv)/NH_4Cl	EtOH/H_2O	80	16	60/25
9	**3j**	Pd–C/$HCOONH_4$	MeOH	25	12	63/5[b]
10	**3j**	Pd–C/H_2	MeOH	25	8	83/–
11	**3j**	Pd–C/H_2	EtOH	25	8	72/–
12	**3j**	Pd–C/H_2	EtOAc	25	9	73/–

[a] Reaction was carried out under sonication.
[b] Reaction was incomplete even for a prolonged reaction time.

to validate our hypothesis and gratifyingly the starting carbohydrate derived substrate (**3j**) was efficiently transformed in to the desired triazoloquinoline (**4j**) in promising yield without any side reaction or incomplete conversion (entry10, Table 2). With this encouraging result, we have extended the scope of the methodology with different carbohydrate derived triazoles (**3h**–**s**) to obtain the respective N^1-glycosyl triazoloquinolines (**4h**–**4s**) as homonucleoside analogues in promising yields (80–96%).

Further extension of the scope of the methodology for unnatural nucleoside analogues was also investigated with the anomeric carbon linked *ortho*-nitrophenyl substituted triazolyl methanone (**3t**). The latter was successfully transformed into respective triazoloquinoline glycoside (**4t**), under the above optimized reaction condition. The desired product **4t** was formed in moderate yield (50%) along with the deacetylated nucleoside analogue (**4t′**, yield 10%) during reductive cyclization with Pd–C/H_2 (Scheme 2).

Table 3
Synthesized triazoloquinolines (**4a**–**s**)

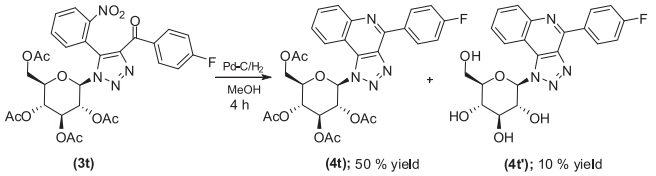


(3a-3s) (4a-4s)

Entry	Compd no.	R	R^1	Time (h)	Yield[a] (%)
1	**4a**	H	Bn	10	94
2	**4b**	2-Me	Bn	13	87
3	**4c**	3-Me	Bn	12	91
4	**4d**	4-Me	Bn	10	98
5	**4e**	2-OMe	Bn	14	87
6	**4f**	3-OMe	Bn	13	90
7	**4g**	4-OMe	Bn	11	97
8	**4h**	3-Me		12	89
9	**4i**	4-Me		11	90
10	**4j**	4-OMe		12	92
11	**4k**	2,4-Dichloro		14	86
12	**4l**	4-Fluoro		11	91
13	**4m**	H		11	85
14	**4n**	2-Me		14	80
15	**4o**	3-Me		13	81
16	**4p**	4-Me		11	96
17	**4q**	2-OMe		13	84
18	**4r**	3-OMe		12	87
19	**4s**	4-OMe		11	93

[a] Isolated yield.

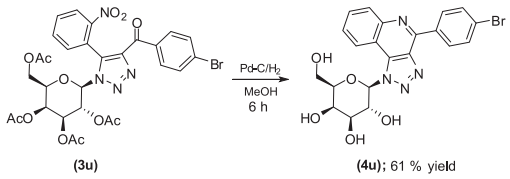
The configuration of the glucose sugar moiety in **4t** was established on the basis of NMR spectrum using the chemical shift, splitting pattern and coupling constants. Coupling constants of H-1′ (d, J=9.40 Hz), H-2′ (t, J=9.60 Hz), H-3′ (t, J=9.60 Hz) and H-4′ (t, J=9.86 Hz) indicated that H-1′, H-2′, H-3′, H-4′ were in the trans orientation (all equatorial). It was further supported by NOE correlations of H-1′ to H-3′, H-2′ to H-4′ and H-1′ to H-5′. Similarly in **4t′** the coupling constant for anomeric proton H-1′ (d, J=9.66 Hz) suggests trans relationship (equatorial) (SD).



(3t) **(4t)**; 50 % yield **(4t′)**; 10 % yield

Scheme 2. Synthesis of unnatural nucleoside (**4t**).

In light of above observation we were keen to synthesize the deacetylated nucleoside analogue **4u** in one pot. For this purpose, we reinvestigated our protocol with substrate **3u** and reaction was run for extended period of time to form the directly deacetylated triazoloquinoline (**4u**) in one pot (Scheme 3). To our pleasant surprise the complete deprotection was observed under reaction condition with improved yield of the desired product (**4u**, 61%) ((debromination was also observed when reaction was carried out for very long time or >10 h) (see ESMS of debrominated product in Supplementary data)).



(3u) **(4u)**; 61 % yield

Scheme 3. Synthesis of unnatural nucleoside (**4u**).

The structure of unnatural nucleosides was established on the basis of their analytical data, further to confirm the structure; several 2D NMR experiments were also carried out, which established the complete correlation of synthesized molecules (SD).

3. Conclusion

In conclusion, we have developed a mild, convenient and compatible strategy for the modular construction of functionalized tricyclic triazoloquinoline and related unnatural nucleoside analogues. First time we demonstrate the application of the reductive cyclization as valuable tool for such one-pot multistep transformation. From the synthetic point of view, this conversion represents a simple approach, a task that otherwise requires several synthetic steps. The scope and functional-group tolerance of the reaction is also well illustrated with a wide range of substrate, however, more optimization with the anomeric sugar azide is still needed, which is currently underway in our group.

4. Experimental section

4.1. General chemistry

Commercially available reagent grade chemicals were used as received. Reactions were monitored by TLC on E. Merck Kieselgel 60 F_{254}, with detection by UV light, spraying a 5% H_2SO_4 ethanolic solution and applying heat. Column chromatography was performed on silica gel (60–120 and 100–200 mesh E. Merck). IR spectra were recorded as thin films or in KBr solution with a Perkin Elmer Spectrum RX-1 (4000–450 cm^{-1}) spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Bruker 200, 300 and 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6. Chemical shift values are reported in

parts per million relative to TMS (tetramethylsilane) as internal reference, unless otherwise stated; s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad); *J* in hertz. HRMS were performed using Quattro II (Micromass). Optical rotation was recorded on Autopol III, S. No. 301, manufactured by Rudolph Research Analytical, USA.

4.2. General procedure for the preparation of triazolyl methanone (3a–s)

*4.2.1. [1-Benzyl-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](phenyl) methanone (**3a**).* (*E*)-1-(2-Phenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1a** (0.79 g, 3.12 mmol) and benzyl azide **2a** (0.50 g, 3.76 mmol) were reacted in presence of 20 mol % TBAHS (0.25 g, 0.75 mmol) as catalyst in DMF (5 mL) at 100 °C for 12 h. After completion of the reaction (TLC), the mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with water to remove DMF and then dried over sodium sulfate (Na_2SO_4) and evaporated under reduced pressure to get the crude mass, which upon purification by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **3a** (1.37 g, 95%) as yellow solid; mp 112–114 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2921, 1646, 1530, 1349 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.41 (2H, d, *J*=7.32 Hz, ArH), 8.28 (1H, d, *J*=8.04 Hz, ArH), 7.72–7.66 (1H, m, ArH), 7.65–7.58 (2H, m, ArH), 7.53–7.48 (2H, m, ArH), 7.33–7.26 (3H, m, ArH), 7.10–7.03 (3H, m, ArH), 5.64 (1H, d, *J*=15.03 Hz, CH_2), 5.36 (1H, d, *J*=15.00 Hz, CH_2); δ_C (75 MHz, $CDCl_3$): 185.2, 148.3, 144.2, 138.5, 136.5, 133.7, 133.1, 132.0, 130.9, 130.8, 128.8, 128.7, 128.1, 128.0, 125.0, 123.0, 52.8; HRMS (ESI): MH^+, found 385.1288. $C_{22}H_{17}N_4O_3$ requires 385.1295.

*4.2.2. [1-Benzyl-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](o-tolyl) methanone (**3b**).* It was obtained by the reaction of (*E*)-1-(*o*-tolyl)-3-(2-nitrophenyl)prop-2-en-1-one **1b** (0.83 g, 3.12 mmol), benzyl azide **2a** (0.50 g, 3.76 mmol) and TBAHS (0.25 g, 0.75 mmol), in DMF (5 mL) at 100 °C for 15 h. Purification by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **3b** (1.34 g, 90%) as light yellow solid; mp 122–124 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2923, 1649, 1528, 1347 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.27 (1H, d, *J*=7.77 Hz, ArH), 7.79 (1H, d, *J*=7.62 Hz, ArH), 7.72–7.62 (2H, m, ArH), 7.43–7.38 (1H, m, ArH), 7.32–7.18 (5H, m, ArH), 7.14 (1H, d, *J*=7.29 Hz, ArH), 7.03 (2H, d, *J*=7.14 Hz, ArH), 5.62 (1H, d, *J*=15.03 Hz, CH_2), 5.36–5.31 (1H, d, *J*=15.03 Hz, CH_2), 2.38 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$): 189.6, 148.0, 144.8, 137.9, 137.7, 137.0, 133.6, 133.2, 132.1, 131.1, 131.0, 130.5, 128.8, 128.7, 127.9, 125.2, 125.1, 122.6, 52.9, 20.3; HRMS (ESI): MH^+, found 399.1445. $C_{23}H_{19}N_4O_3$ requires 399.1452.

*4.2.3. [1-Benzyl-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](m-tolyl) methanone (**3c**).* It was obtained by the reaction of (*E*)-1-(*m*-tolyl)-3-(2-nitrophenyl)prop-2-en-1-one **1c** (0.83 g, 3.12 mmol), benzyl azide **2a** (0.50 g, 3.76 mmol) and TBAHS (0.25 g, 0.75 mmol), in DMF (5 mL) at 100 °C for 14 h. Purification by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **3c** (1.32 g, 88%) as yellow solid; mp 152–155 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2928, 1650, 1531, 1345 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.22 (1H, d, *J*=8.1 Hz, ArH), 8.17 (1H, d, *J*=6.21 Hz, ArH), 8.11 (1H, s, ArH), 7.66–7.53 (2H, m, ArH), 7.35–7.32 (2H, m, ArH), 7.24–7.20 (3H, m, ArH), 7.02–6.98 (3H, m, ArH), 5.59 (1H, d, *J*=15.00 Hz, CH_2), 5.28 (1H, d, *J*=15.03 Hz, CH_2), 2.41 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$): 185.5, 148.3, 144.3, 138.4, 137.7, 136.5, 133.9, 133.7, 133.0, 132.0, 131.1, 130.8, 128.8, 128.6, 128.1, 128.0, 125.0, 123.0, 52.8, 21.4; HRMS (ESI): MH^+, found 399.1447. $C_{23}H_{19}N_4O_3$ requires 399.1452.

*4.2.4. [1-Benzyl-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](p-tolyl) methanone (**3d**).* It was obtained by the reaction of (*E*)-1-(*p*-tolyl)-3-(2-nitrophenyl)prop-2-en-1-one **1d** (0.83 g, 3.12 mmol), benzyl azide **2a** (0.50 g, 3.76 mmol) and TBAHS (0.25 g, 0.75 mmol), in DMF (5 mL) at 100 °C for 12 h. Purification by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **3d** (1.45 g, 97%) as yellow solid; mp 136–138 °C, R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2921, 1645, 1530, 1351 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.31 (2H, d, *J*=8.01 Hz, ArH), 8.26 (1H, d, *J*=7.89 Hz, ArH), 7.69–7.56 (2H, m, ArH), 7.29–7.23 (5H, m, ArH), 7.07–7.01 (3H, m, ArH), 5.62 (1H, d, *J*=15.00 Hz, CH_2), 5.32 (1H, d, *J*=15.03 Hz, CH_2), 2.44 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$): 184.9, 148.2, 144.3, 143.8, 138.3, 133.9, 133.7, 133.0, 132.0, 130.9, 128.9, 128.8, 128.6, 127.9, 125.0, 122.9, 52.8, 21.7; HRMS (ESI): MH^+, found 399.1443. $C_{23}H_{19}N_4O_3$ requires 399.1452.

*4.2.5. [1-Benzyl-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](2-methoxyphenyl)methanone (**3e**).* It was obtained by the reaction of (*E*)-1-(2-methoxyphenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1e** (0.88 g, 3.12 mmol), benzyl azide **2a** (0.50 g, 3.76 mmol) and TBAHS (0.25 g, 0.75 mmol), in DMF (5 mL) at 100 °C for 14 h. Purification by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **3e** (1.37 g, 88%) as white solid; mp 96–98 °C; R_f=0.50 (ethyl acetate/hexane, 1:3); ν_{max} (KBr) 2925, 1651, 1529, 1345, 1214 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.17 (1H, dd, J_1=8.07 Hz, J_2=1.20 Hz, ArH), 7.62–7.50 (2H, m, ArH), 7.49–7.46 (1H, dd, J_1=7.56 Hz, J_2=1.59 Hz, ArH), 7.42–7.36 (1H, m, ArH), 7.22–7.15 (3H, m, ArH), 7.05 (1H, dd, J_1=7.35 Hz, J_2=1.41 Hz, ArH), 6.98–6.93 (3H, m, ArH), 6.90 (1H, d, *J*=8.34 Hz, ArH), 5.59 (1H, d, *J*=15.06 Hz, CH_2), 5.24 (1H, d, *J*=15.09 Hz, CH_2), 3.73 (3H, s, OCH_3); δ_C (75 MHz, $CDCl_3$): 187.8, 158.2, 148.0, 145.1, 136.5, 133.9, 133.0, 132.6, 132.5, 130.8, 130.3, 128.7, 128.5, 128.2, 127.8, 125.0, 122.5, 120.2, 111.6, 55.6, 52.8; HRMS (ESI): MNa^+, found 437.1213. $C_{23}H_{18}N_4O_4Na$ requires 437.1220.

*4.2.6. [1-Benzyl-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](3-methoxyphenyl)methanone (**3f**).* It was obtained by the reaction of (*E*)-1-(3-methoxyphenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1f** (0.88 g, 3.12 mmol), benzyl azide **2a** (0.50 g, 3.76 mmol) and TBAHS (0.25 g, 0.75 mmol), in DMF (5 mL) at 100 °C for 13 h. Purification by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **3f** (1.15 g, 90%) as yellow solid; mp 88–90 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2929, 1650, 1531, 1351, 1218 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.30 (1H, d, *J*=7.26, ArH), 8.15 (1H, d, *J*=6.99, ArH), 7.89 (1H, s, ArH), 7.73–7.68 (1H, m, ArH), 7.65–7.60 (1H, m, ArH), 7.42 (1H, t, *J*=6.87, ArH), 7.31–7.29 (3H, m, ArH), 7.17–7.14 (1H, m, ArH), 7.07 (3H, br, ArH), 5.67 (1H, d, *J*=14.91, CH_2), 5.34 (1H, d, *J*=15.06, CH_2), 3.90 (3H, s, OCH_3); δ_C (75 MHz, $CDCl_3$): 184.9, 159.4, 148.3, 144.3, 138.5, 137.6, 133.7, 132.9, 132.0, 130.8, 129.1, 128.8, 128.6, 128.0, 125.0, 123.9, 123.0, 120.4, 114.1, 55.2, 52.8; HRMS (ESI): MNa^+, found 437.1211. $C_{23}H_{18}N_4O_4Na$ requires 437.1220.

*4.2.7. [1-Benzyl-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](4-methoxyphenyl)methanone (**3g**).* It was obtained by the reaction of (*E*)-1-(4-Methoxyphenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1g** (0.88 g, 3.12 mmol), benzyl azide **2a** (0.50 g, 3.76 mmol) and TBAHS (0.25 g, 0.75 mmol), in DMF (5 mL) at 100 °C for 12 h. Purification by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **3g** (1.42 g, 91%) as yellow solid; mp 94–96 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2928, 1644, 1529, 1349, 1262 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.26 (1H, d, *J*=7.92 Hz, ArH), 8.11 (1H, d, *J*=7.56 Hz, ArH), 7.84 (1H, s, ArH), 7.69–7.57 (2H, m, ArH), 7.38 (1H, t, *J*=7.92 Hz, ArH), 7.28–7.23 (3H, m, ArH), 7.13–7.11 (1H, m, ArH), 7.05–7.01 (3H, m, ArH), 5.62 (1H, d, *J*=14.97 Hz, CH_2), 5.31 (1H, d, *J*=15.00 Hz, CH_2), 3.85 (3H, s, OCH_3); δ_C (75 MHz, $CDCl_3$): 184.9, 159.5, 148.3, 144.3, 137.7, 133.7, 133.0, 132.1, 130.9, 129.1, 128.8, 128.6, 128.0, 125.0, 123.8, 120.3,

114.2, 55.2, 52.8; HRMS (ESI): MH^+, found 415.1394 $C_{23}H_{19}N_4O_4$ requires 415.1401.

*4.2.8. [1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](m-tolyl)methanone (**3h**).* It was obtained by the reaction of (*E*)-1-(*m*-tolyl)-3-(2-nitrophenyl)prop-2-en-1-one **1c** (1.49 g, 4.60 mmol), 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose **2b** (1.00 g, 4.60 mmol) and TBAHS (0.31 g, 0.92 mmol), in DMF (10 mL) at 100 °C for 17 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (20% ethyl acetate/hexane), yielded the titled compound **3h** (1.47 g, 66%) as yellow solid; mp 76–78 °C; R_f=0.50 (ethyl acetate/hexane, 1:2); $[\alpha]_D^{30}$ −58 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 3432, 2929, 1646, 1531, 1347, 1071 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.29 (1H, br, ArH), 8.08–8.05 (2H, m, ArH), 7.74 (2H, br, ArH), 7.47–7.27 (3H, m, ArH), 5.86 (1H, br, H-1′), 5.28 (1H, s, OH), 4.73 (1H, br, CH_2), 4.55–4.52 (2H, m, CH_2 and H-2′), 4.37–4.26 (2H, m, H-4′ and H-3′), 2.39 (3H, s, CH_3), 1.26 (6H, s, 2× $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 185.9, 148.6, 143.5, 139.5, 138.1, 136.3, 134.2, 133.7, 132.6, 131.6, 131.5, 131.0, 128.0, 125.2, 122.2, 112.2, 105.0, 85.1, 78.2, 74.5, 46.0, 26.3, 21.3, 14.4; HRMS (ESI): MH^+, found 481.1713. $C_{24}H_{25}N_4O_7$ requires 481.1718.

Note: (For numbering of the proton see the Supplementary data).

*4.2.9. [1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](p-tolyl)methanone (**3i**).* It was obtained by the reaction of (*E*)-1-(*p*-tolyl)-3-(2-nitrophenyl)prop-2-en-1-one **1d** (1.49 g, 4.60 mmol), 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose **2b** (1.00 g, 4.60 mmol) and TBAHS (0.31 g, 0.92 mmol), in DMF (10 mL) at 100 °C for 16 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (20% ethyl acetate/hexane), yielded the titled compound **3i** (1.51 g, 68%) as yellow solid; mp 78–80 °C; R_f=0.50 (ethyl acetate/hexane, 1:2); $[\alpha]_D^{30}$ −66 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 3435, 2926, 1642, 1530, 1350, 1074 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.33–8.30 (1H, m, ArH), 8.27–8.20 (2H, m, ArH), 7.78–7.71 (2H, m, ArH), 7.25–7.23 (3H, m, ArH), 5.84–5.81 (1H, m, H-1′), 4.65–4.59 (1H, m, CH_2), 4.54–4.50 (1H, m, CH_2), 4.31–4.23 (3H, m, H-2′, H-4′ and H-3″), 2.42 (3H, s, CH_3), 1.36 (3H, s, $C(CH_3)_2$), 1.28 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 184.5, 143.8, 139.1, 133.4, 132.3, 131.3, 131.2, 130.9, 128.9, 125.4, 125.2, 122.5, 112.0, 105.1, 85.0, 46.1, 26.8, 26.2, 21.7; HRMS (ESI): MH^+, found 481.1717. $C_{24}H_{25}N_4O_7$ requires 481.1718.

*4.2.10. [1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](4-methoxyphenyl)methanone (**3j**).* It was obtained by the reaction of (*E*)-1-(4-methoxyphenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1g** (1.32 g, 4.60 mmol), 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose **2b** (1.00 g, 4.60 mmol) and TBAHS (0.31 g, 0.92 mmol), in DMF (10 mL) at 100 °C for 15 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (20% ethyl acetate/hexane), yielded the titled compound **3j** (1.67 g, 72%) as yellow solid; mp 68–70 °C; R_f=0.50 (ethyl acetate/hexane, 1:2); $[\alpha]_D^{30}$ −61 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 3438, 2928, 1645, 1533, 1351, 1077 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.36–8.23 (3H, m, ArH), 7.73–7.68 (2H, m, ArH), 7.45–7.34 (1H, m, ArH), 6.92–6.90 (2H, m, ArH), 5.82–5.81 (1H, m, H-1′), 4.70–4.63 (1H, m, CH_2), 4.57–4.48 (2H, m, CH_2 and H-2′), 4.34–4.18 (2H, m, H-4′ and H-3′), 3.87 (3H, s, OCH_3), 1.36 (3H, s, $C(CH_3)_2$), 1.27 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 183.6, 163.9, 149.1, 143.7, 139.1, 133.4, 133.2, 132.5, 131.3, 125.3, 122.5, 113.5, 111.9, 105.0, 85.2, 79.0, 74.4, 55.2, 45.8, 26.9, 26.2; HRMS (ESI): MH^+, found 497.1658. $C_{24}H_{25}N_4O_8$ requires 497.1667.

*4.2.11. [1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](2,4-dichlorophenyl)methanone (**3k**).* It was obtained by the reaction of (*E*)-1-(2,4-dichlorophenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1h** (1.49 g, 4.60 mmol), 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (1.00 g, 4.60 mmol) **2b** and TBAHS (0.31 g, 0.92 mmol), in DMF (10 mL) at 100 °C for 17 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (20% ethyl acetate/hexane), yielded the titled compound **3k** (1.61 g, 65%) as yellow solid; mp 82–84 °C, R_f=0.50 (ethyl acetate/hexane, 1:2); $[\alpha]_D^{30}$ −37 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 3436, 2929, 1641, 1531, 1348, 1074 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.35–8.29 (1H, m, ArH), 7.83–7.76 (2H, m, ArH), 7.54–7.44 (3H, m, ArH), 7.34–7.25 (1H, m, ArH), 5.82–5.78 (1H, m, H-1′), 4.65–4.58 (1H, m, CH_2), 4.54–4.46 (1H, m, CH_2), 4.27–4.17 (3H, m, H-2′, H-4′ and H-3′), 1.37 (3H, s, $C(CH_3)_2$), 1.26 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$):184.5, 148.7, 137.5, 135.6, 133.8, 133.1, 132.5, 131.7, 131.6, 131.1, 130.2, 128.2, 126.8, 125.6, 112.0, 105.0, 85.0, 78.9, 78.1, 74.4, 46.0, 26.8, 26.3; HRMS (ESI): MH^+, found 535.0778. $C_{23}H_{21}Cl_2N_4O_7$ requires 535.0782.

*4.2.12. [1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](4-fluorophenyl)methanone (**3l**).* It was obtained by the reaction of (*E*)-1-(4-fluorophenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1i** (1.26 g, 4.64 mmol), 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose **2b** (1.00 g, 4.60 mmol) and TBAHS (0.31 g, 0.92 mmol), in DMF (10 mL) at 100 °C for 15 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (20% ethyl acetate/hexane), yielded the titled compound **3l** (1.57 g, 71%) as white solid; mp 86–88 °C; R_f=0.50 (ethyl acetate/hexane, 1:2); $[\alpha]_D^{30}$ −68 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 3432, 2927, 1646, 1533, 1347, 1078 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.42–8.36 (2H, m, ArH), 7.80–7.73 (2H, m, ArH), 7.49 (1H, dd, J_1=7.17 Hz, J_2=1.92 Hz, ArH), 7.39–7.36 (1H, m, ArH), 7.17–7.11 (2H, m, ArH), 5.90 (1H, m, H-1″), 4.76–4.70 (1H, m, CH_2), 4.58–4.53 (1H, m, CH_2), 4.36 (1H, s, H-2′), 4.32–4.27 (2H, m, H-4′ and H-3′), 1.30 (3H, s, $C(CH_3)_2$), 1.27 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 184.0, 164.6 (d, $^1J_{CF}$=247.00 Hz), 148.7, 143.7, 139.8, 133.9, 133.5, 132.4, 131.6 (d, $^3J_{CF}$=7.50 Hz), 125.2, 122.1, 115.3 (d, $^2J_{CF}$=22.50 Hz), 112.2, 105.0, 85.2, 78.9, 74.5, 46.5, 26.8, 26.2; HRMS (ESI): MH^+, found 485.1461. $C_{23}H_{22}FN_4O_7$ requires 485.1467.

*4.2.13. [1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](phenyl)methanone (**3m**).* It was obtained by the reaction of (*E*)-1-phenyl-3-(2-nitrophenyl)prop-2-en-1-one **1a** (0.89 g, 3.50 mmol), 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **2c** (1.00 g, 3.50 mmol) and TBAHS (0.24 g, 0.70 mmol), in DMF (10 mL) at 100 °C for 13 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **3m** (1.39 g, 74%) as yellow solid; mp 62–64 °C; R_f=0.50 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{30}$ +105 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2929, 1648, 1531, 1346, 1077 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.34–8.31 (3H, m, ArH), 7.75–7.69 (2H, m, ArH), 7.57–7.52 (2H, m, ArH), 7.50–7.46 (2H, m, ArH), 5.44 (1H, d, *J*=4.68 Hz, H-1′), 4.65–4.61 (2H, m, CH_2), 4.46–4.44 (1H, m, H-3′), 4.33–4.31 (1H, m, H-2′), 4.25–4.20 (2H, m, H-4′ and H-5″), 1.31–1.23 (9H, m, 3× $C(CH_3)_2$), 1.16 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 186.0, 148.6, 139.9, 136.6, 133.1, 133.1, 133.0, 130.9, 130.7, 128.2, 128.2, 124.8, 122.8, 109.7, 109.4, 70.9, 70.8, 70.4, 67.0, 48.1, 26.0, 25.7, 25.0, 24.3; HRMS (ESI): MH^+, found 537.1971. $C_{27}H_{29}N_4O_8$ requires 537.1980.

*4.2.14. [1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](o-tolyl)methanone (**3n**).* It was obtained by the reaction of (*E*)-1-(*o*-tolyl)-3-(2-nitrophenyl)prop-2-en-1-one **1b** (0.94 g, 3.50 mmol), 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (1.00 g, 3.50 mmol) and TBAHS (0.24 g, 0.70 mmol), in DMF (10 mL) at 100 °C for 16 h. The crude product was purified by column

chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **3n** (1.35 g, 70%) as yellow solid; mp 82–84 °C; R_f=0.50 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{30}$ +65 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2928, 1646, 1530, 1344, 1071 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.30 (1H, d, *J*=8.16 Hz, ArH), 7.74–7.69 (3H, m, ArH), 7.57–7.54 (1H, m, ArH), 7.51–7.49 (1H, m, ArH), 7.26–7.19 (2H, m, ArH), 5.41 (1H, d, *J*=4.59 Hz, H-1′), 4.61–4.57 (2H, m, CH_2), 4.37–4.35 (1H, m, H-3′), 4.30–4.27 (2H, m, H-2′ and H-4′), 4.19 (1H, m, H-5′), 2.34 (3H, s, CH_3), 1.32–1.25 (9H, m, 3× $C(CH_3)_2$), 1.15 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$):189.9, 148.7, 137.8, 133.2, 132.8, 130.9, 130.4, 129.7, 129.2, 128.3, 127.5, 125.1, 124.9, 122.7, 109.6, 109.3, 71.5, 70.9, 70.4, 67.0, 48.0, 26.1, 25.7, 25.0, 24.3, 20.3; HRMS (ESI): MH^+, found 551.2130. $C_{28}H_{31}N_4O_8$ requires 551.2136.

*4.2.15. [1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](m-tolyl)methanone (**3o**).* It was obtained by the reaction of (*E*)-1-(*m*-tolyl)-3-(2-nitrophenyl)prop-2-en-1-one **1c** (0.94 g, 3.50 mmol), 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **2c** (1.00 g, 3.50 mmol) and TBAHS (0.24 g, 0.70 mmol), in DMF (10 mL) at 100 °C for 15 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **3o** (1.39 g, 72%) as yellow solid; mp 84–86 °C; R_f=0.50 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{30}$ +84 (*c* 0.1, $CHCl_3$); ν_{max} (KBr), 2924, 1642, 1534, 1343, 1073 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.31 (1H, d, *J*=7.74 Hz, ArH), 8.18–8.12 (1H, m, ArH), 8.09 (1H, s, ArH), 7.76–7.66 (2H, m, ArH), 7.53 (1H, d, *J*=7.74 Hz, ArH), 7.38–7.34 (2H, m, ArH), 5.42 (1H, d, *J*=3.72 Hz, H-1′), 4.66–4.57 (2H, m, CH_2), 4.43–4.39 (1H, m, H-3″), 4.30–4.29 (1H, m, H-2′), 4.22–4.17 (2H, m, H-4′ and H-5″), 2.41 (3H, s, CH_3), 1.30–1.22 (12H, m, 4× $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 184.5, 148.7, 143.4, 139.7, 137.5, 136.7, 133.7, 133.1, 132.8, 132.0, 131.1, 130.6, 128.2, 128.0, 124.8, 123.1, 109.5, 109.3, 70.8, 70.8, 67.0, 48.0, 26.1, 25.7, 25.0, 24.3, 21.4; HRMS (ESI): MH^+, found 551.2128. $C_{28}H_{31}N_4O_8$ requires 551.2136.

*4.2.16. [1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](p-tolyl)methanone (**3p**).* It was obtained by the reaction of (*E*)-1-(*p*-tolyl)-3-(2-nitrophenyl)prop-2-en-1-one **1d** (0.94 g, 3.5 mmol), 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **2c** (1.00 g, 3.50 mmol) and TBAHS (0.24 g, 0.70 mmol), in DMF (10 mL) at 100 °C for 14 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **3p** (1.45 g, 75%) as yellow solid; mp 56–59 °C; R_f=0.50 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{30}$ +66 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2928, 1644, 1531, 1344, 1075 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.30–8.25 (3H, m, ArH), 7.75–7.65 (2H, m, ArH), 7.53 (1H, dd, J_1=7.26 Hz, J_2=1.86 Hz, ArH), 7.25–7.24 (2H, m, ArH), 5.41 (1H, d, *J*=5.10 Hz, H-1″), 4.65–4.58 (2H, m, CH_2), 4.42–4.36 (1H, m, H-3′), 4.29–4.27 (1H, m, H-2′), 4.21–4.18 (2H, m, H-4′ and H-5′), 2.41 (3H, s, CH_3), 1.30–1.21 (12H, m, 4× $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 185.1, 148.7, 143.6, 139.6, 134.2, 133.1, 132.8, 130.9, 130.7, 128.9, 128.8, 125.2, 124.7, 123.1, 109.6, 109.3, 70.8, 70.4, 67.0, 48.0, 26.0, 25.7, 25.0, 24.3, 21.7; HRMS (ESI): MNa^+, found 573.1965. $C_{28}H_{30}N_4O_8Na$ requires 573.1956.

*4.2.17. [1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](2-methoxyphenyl)methanone (**3q**).* It was obtained by the reaction of (*E*)-1-(2-methoxyphenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1e** (0.99 g, 3.50 mmol), 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **2c** (1.00 g, 3.50 mmol) and TBAHS (0.24 g, 0.70 mmol), in DMF (10 mL) at 100 °C for 15 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **3q** (1.38 g, 70%) as yellow solid; mp 58–60 °C; R_f=0.50 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{30}$ +88 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2926, 1646, 1533, 1343, 1076 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.07 (1H, d, *J*=8.49 Hz, ArH), 7.80–7.79 (1H, m, ArH), 7.65–7.59 (2H, m, ArH), 7.50–7.49 (1H, m, ArH), 7.38–7.35 (2H, m, ArH), 7.13–7.11 (1H, m, ArH), 5.46 (1H, d, *J*=4.89 Hz, H-1′), 4.61–4.58 (2H, m, CH_2), 4.29–4.18 (4H, m, H-3″, H-2′, H-4′ and H-5′), 3.79 (3H, s, OCH_3), 1.34–1.31 (12H, m, 4× $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 183.2, 157.4, 148.3, 141.2, 132.3, 130.9, 130.6, 130.3, 130.2, 129.2, 128.8, 127.9, 124.7, 120.4, 119.9, 111.5, 109.6, 108.6, 71.5, 71.0, 66.5, 57.1, 42.3, 26.0, 25.9, 24.9, 24.3; HRMS (ESI): MH^+, found 567.2089. $C_{28}H_{31}N_4O_9$ requires 567.2086.

*4.2.18. [1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](3-methoxyphenyl)methanone (**3r**).* It was obtained by the reaction of (*E*)-1-(3-methoxyphenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1e** (0.99 g, 3.50 mmol), 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **2c** (1.00 g, 3.50 mmol) and TBAHS (0.24 g, 0.70 mmol), in DMF (10 mL) at 100 °C for 15 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **3r** (1.46 g, 74%) as yellow solid; mp 60–62 °C; R_f=0.50 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{30}$ +128 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2928, 1643, 1531, 1341, 1073 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.32 (1H, dd, J_1=7.56 Hz, J_2=1.41 Hz, ArH), 8.09 (1H, d, 7.86 Hz, ArH), 7.82–7.78 (1H, m, ArH), 7.74–7.69 (2H, m, ArH), 7.53 (1H, d, 2.22 Hz, ArH), 7.39–7.37 (1H, m, ArH), 7.12–7.09 (1H, m, ArH), 5.41 (1H, d, *J*=4.74 Hz, H-1″), 4.62–4.59 (2H, m, CH_2), 4.43–4.41 (1H, m, H-3′), 4.30–4.27 (1H, m, H-2′), 4.22–4.19 (2H, m, H-4′ and H-5′), 3.83 (3H, s, OCH_3), 1.30 (3H, s, $C(CH_3)_2$), 1.28 (3H, s, $C(CH_3)_2$), 1.22 (3H, s, $C(CH_3)_2$), 1.15 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 185.5, 159.6, 149.2, 143.5, 140.0, 138.0, 133.2, 130.8, 129.1, 125.2, 124.8, 123.0, 120.3, 114.1, 109.6, 109.4, 70.9, 70.8, 70.4, 67.0, 55.3, 48.1, 26.0, 25.7, 25.0, 24.3; HRMS (ESI): MH^+, found 567.2089. $C_{28}H_{31}N_4O_9$ requires 567.2086.

*4.2.19. [1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](4-methoxyphenyl)methanone (**3s**).* It was obtained by the reaction of (*E*)-1-(4-methoxyphenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1g** (0.99 g, 3.50 mmol), 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **2c** (1.00 g, 3.50 mmol) and TBAHS (0.24 g, 0.70 mmol), in DMF (10 mL) at 100 °C for 13 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **3s** (1.44 g, 73%) as yellow solid; mp 54–56 °C; R_f=0.50 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{30}$ +94 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2926, 1642, 1530, 1343, 1071 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.32 (1H, d, *J*=7.50 Hz, ArH), 8.10 (1H, d, *J*=7.86 Hz, ArH), 7.79 (1H, m, ArH), 7.73–7.69 (2H, m, ArH), 7.53 (1H, d, *J*=7.47 Hz, ArH), 7.39–7.34 (2H, m, ArH), 5.40 (1H, d, *J*=4.71 Hz, H-1′), 4.61–4.58 (2H, m, CH_2), 4.42–4.36 (1H, m, H-3′), 4.28–4.15 (3H, m, H-2′, H-4′ and H-5′), 3.84 (3H, s, OCH_3), 1.30–1.21 (12H, m, 4× $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 184.5, 163.9, 149.0, 143.5, 139.5, 133.6, 133.0, 132.1, 131.3, 129.6, 125.1, 123.1, 113.7, 109.7, 109.4, 70.9, 70.8, 70.4, 67.0, 55.4, 48.1, 26.0, 25.7, 25.0, 24.3; HRMS (ESI): MH^+, found 567.2090. $C_{28}H_{31}N_4O_9$ requires 567.2086.

*4.2.20. [1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](4-fluorophenyl)methanone (**3t**).* It was obtained by the reaction of (*E*)-1-(4-fluorophenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1i** (0.72 g, 2.68 mmol), 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide **2d** (1.00 g, 2.68 mmol), TBAHS (0.18 g, 0.53 mmol) and *p*-TSA (0.05 g, 0.27 mmol), in DMF (10 mL) at 100 °C for 18 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (25% ethyl acetate/hexane), yielded the titled compound **3t** (0.94 g, 55%) as yellow solid; mp 65–68 °C; R_f=0.50 (ethyl acetate/hexane, 3:2); $[\alpha]_D^{30}$ +62 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2925, 1651, 1530, 1338,

1070 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.13 (1H, d, J=6.75 Hz, ArH), 7.85 (1H, t, J=6.75 Hz, ArH), 7.68–7.66 (3H, m, ArH), 7.13–7.01 (3H, m, ArH), 5.26–5.10 (3H, m, H-1′, H-2′ and H-3′), 5.05–4.98 (1H, m, H-4″), 4.29–4.08 (3H, m, H-5′ and CH_2), 2.03–1.97 (12H, m, 4× $-COCH_3$); δ_C (75 MHz, $CDCl_3$): 188.7, 170.5, 170.1, 170.0, 169.3, 163.3 (d, $^1J_{CF}$=250.32 Hz), 148.1, 135.2, 133.3, 132.6 (d, $^3J_{CF}$=7.95 Hz), 131.1, 130.7, 130.1, 130.0, 124.5, 115.1 (d, $^2J_{CF}$=22.50 Hz), 83.6, 73.9, 73.0, 72.6, 68.4, 62.1, 20.7, 20.7, 20.5, 20.5; HRMS (ESI): MH^+, found 643.1678. $C_{29}H_{28}FN_4O_{12}$ requires 643.1682.

*4.2.21. [1-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-5-(2-nitrophenyl)-1H-1,2,3-triazol-4-yl](4-bromophenyl)methanone (**3u**).* It was obtained by the reaction of (*E*)-1-(4-Bromophenyl)-3-(2-nitrophenyl)prop-2-en-1-one **1j** (0.89 g, 2.68 mmol), 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl azide **2e** (1.00 g, 2.68 mmol), TBAHS (0.18 g, 0.53 mmol) and *p*-TSA (0.05 g, 0.27 mmol), in DMF (10 mL) at 100 °C for 18 h. The crude product was purified by column chromatography using 60–120 mesh silica gel (25% ethyl acetate/hexane), yielded the titled compound **3u** (0.94 g, 50%) as yellow solid; mp 78–80 °C; R_f=0.50 (ethyl acetate/hexane, 3:2); $[\alpha]_D^{30}$ +71 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2926, 1653, 1533, 1341, 1074 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 7.71–7.66 (4H, m, ArH), 7.53–7.48 (3H, m, ArH), 7.13 (1H, br, ArH), 5.43–5.27 (2H, m, H-1′ and H-2′), 5.10 (1H, m, H-3′), 4.91–4.88 (1H, m, H-4′), 4.18–4.00 (3H, m, H-5′ and CH_2), 2.09–1.97 (12H, m, 4× $-COCH_3$); δ_C (50 MHz, $CDCl_3$):184.0, 170.0, 169.7, 168.9, 168.7, 148.8, 143.9, 139.9, 134.9, 133.2, 132.2, 131.6, 128.8, 125.2, 121.8, 84.7, 75.0, 72.5, 69.6, 67.4, 61.5, 20.5, 20.4, 20.1; HRMS (ESI): MH^+, found 703.0876. $C_{29}H_{28}BrN_4O_{12}$ requires 703.0882.

4.3. General procedure for the preparation of 1-benzyl-4-phenyl-1*H*-[1,2,3]triazolo[4,5-*c*]quinoline (4a)

A mixture of triazolyl methanone **3a** (0.20 g, 0.52 mmol) and 5% palladium on charcoal (0.10 g) in dry methanol (10 mL) was stirred under a hydrogen atmosphere at room temperature for 10 h. The reaction mixture was filtered through Celite and the solvent evaporated under vacuum to give the crude product, which was purified by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the title compound **4a** (0.16 g, 94%) as white solid; mp 72–74 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2926, 1519 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.87–8.84 (2H, m, ArH), 8.31 (1H, d, J=8.25 Hz, ArH), 8.03 (1H, d, J=7.68 Hz, ArH), 7.74–7.68 (1H, m, ArH), 7.64–7.55 (3H, m, ArH), 7.51–7.46 (1H, m, ArH), 7.35–7.27 (3H, m, ArH), 7.18–7.15 (2H, m, ArH), 6.25 (2H, s, CH_2); δ_C (75 MHz, $CDCl_3$): 151.4, 145.5, 139.9, 136.6, 134.4, 134.3, 130.8, 130.4, 129.9, 129.6, 129.2, 128.6, 128.5, 127.0, 126.4, 121.7, 114.7, 53.8; HRMS (ESI): MH^+, found 337.1441. $C_{22}H_{17}N_4$ requires 337.1448.

*4.3.1. 1-Benzyl-4-(o-tolyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4b**).* It was obtained by the reductive cyclization of **3b** (0.20 g, 0.50 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **4b** (0.15 g, 87%) as white solid; mp 140–142 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2926, 1521, 769 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.35 (1H, d, J=8.10 Hz, ArH), 8.11 (1H, d, J=8.10 Hz, ArH), 7.83–7.74 (2H, m, ArH), 7.57 (1H, t, J=7.77 Hz, ArH), 7.43 (3H, s, ArH), 7.37–7.35 (3H, m, ArH), 7.25–7.23 (2H, m, ArH), 6.28 (2H, s, CH_2), 2.50 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$): 154.8, 145.5, 140.5, 137.1, 136.2, 134.4, 133.6, 131.0, 130.9, 130.8, 129.5, 129.3, 129.2, 128.5, 127.0, 126.4, 125.7, 121.7, 114.6, 53.7, 20.6; HRMS (ESI): MH^+, found 351.1607. $C_{23}H_{19}N_4$ requires 351.1604.

*4.3.2. 1-Benzyl-4-(m-tolyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4c**).* It was obtained by the reductive cyclization of **3c** (0.20 g, 0.50 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **4c** (0.16 g, 91%) as white solid; mp 128–130 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr), 2927, 1518, 765 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.72–8.67 (2H, m, ArH), 8.33 (1H, d, J=8.19 Hz, ArH), 8.02 (1H, d, J=7.92 Hz, ArH), 7.73 (1H, t, J=7.20 Hz, ArH), 7.54–7.46 (2H, m, ArH), 7.39–7.28 (4H, m, ArH), 7.20–7.18 (2H, m, ArH), 6.27 (2H, s, CH_2), 2.58 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$): 151.5, 145.5, 139.9, 138.0, 136.5, 134.4, 134.2, 131.2, 130.9, 130.3, 129.4, 129.2, 128.4, 127.3, 126.7, 126.3, 121.6, 114.6, 53.7, 21.7; HRMS (ESI): MH^+, found 351.1606. $C_{23}H_{19}N_4$ requires 351.1604.

*4.3.3. 1-Benzyl-4-(p-tolyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4d**).* It was obtained by the reductive cyclization of **3d** (0.20 g, 0.50 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **4d** (0.17 g, 98%) as white solid; mp 182–184 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2926, 1519, 771 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.85 (2H, d, J=7.77 Hz, ArH), 8.28 (1H, d, J=8.16 Hz, ArH), 7.98 (1H, d, J=7.92 Hz, ArH), 7.69 (1H, t, J=7.20 Hz, ArH), 7.44–7.41 (3H, m, ArH), 7.33–7.30 (3H, m, ArH), 7.18–7.16 (2H, m, ArH), 6.23 (2H, s, CH_2), 2.51 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$): 151.1, 145.5, 140.4, 139.8, 134.5, 134.1, 133.9, 130.7, 129.9, 129.2, 129.2, 128.4, 126.5, 126.3, 121.5, 114.5, 53.6, 21.6; HRMS (ESI): MH^+, found 351.1613. $C_{23}H_{19}N_4$ requires 351.1604.

*4.3.4. 1-Benzyl-4-(2-methoxyphenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4e**).* It was obtained by the reductive cyclization of **3e** (0.20 g, 0.48 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **4e** (0.15 g, 87%) as white solid; mp 174–177 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2928, 1521, 1218, 768 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 8.32 (1H, d, J=8.32 Hz, ArH), 8.03 (1H, d, J=8.20 Hz, ArH), 7.72–7.66 (2H, m, ArH), 7.51–7.47 (2H, m, ArH), 7.34–7.27 (3H, m, ArH), 7.19–7.18 (2H, m, ArH), 7.14–7.10 (2H, m, ArH), 6.22 (2H, s, CH_2), 3.83 (3H, s, OCH_3); δ_C (100 MHz, $CDCl_3$): 158.1, 153.2, 146.1, 141.0, 134.8, 133.5, 131.5, 131.3, 131.2, 129.5, 129.5, 128.6, 127.1, 126.8, 126.7, 122.0, 121.1, 115.2, 112.0, 56.0, 53.9; HRMS (ESI): MH^+, found 367.1554. $C_{23}H_{19}N_4O$ requires 367.1553.

*4.3.5. 1-Benzyl-4-(3-methoxyphenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4f**).* It was obtained by the reductive cyclization of **3f** (0.20 g, 0.48 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **4f** (0.16 g, 90%) as white solid; mp 146–148 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 2927, 1518, 1219, 762 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 8.52 (1H, d, J=7.56 Hz, ArH), 8.44 (1H, s, ArH), 8.27 (1H, d, J=8.24 Hz, ArH), 7.97 (1H, d, J=8.08 Hz, ArH), 7.70–7.66 (1H, m, ArH), 7.51–7.43 (2H, m, ArH), 7.30–7.28 (3H, m, ArH), 7.16–7.14 (2H, m, ArH), 7.09 (1H, d, J=8.16 Hz, ArH), 6.21 (2H, s, CH_2), 3.97 (3H, s, OCH_3); δ_C (100 MHz, $CDCl_3$): 159.8, 151.0, 145.4, 139.9, 137.8, 134.4, 134.2, 130.9, 129.4, 129.4, 129.2, 128.4, 126.8, 126.3, 122.6, 121.5, 117.0, 114.6, 114.3, 55.3, 53.7; HRMS (ESI): MH^+, found 367.1553. $C_{23}H_{19}N_4O$ requires 367.1553.

*4.3.6. 1-Benzyl-4-(4-methoxyphenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4g**).* It was obtained by the reductive cyclization of **3g** (0.20 g, 0.48 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (10% ethyl acetate/hexane), yielded the titled compound **4g** (0.17 g, 97%) as white solid; mp 134–136 °C; R_f=0.50 (ethyl acetate/hexane, 1:4); ν_{max} (KBr), 2926, 1519, 1217, 772 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.57 (1H, d, J=7.62 Hz, ArH), 8.49 (1H, s, ArH), 8.34 (1H, d, J=8.28 Hz, ArH), 8.05

(1H, d, J=8.07 Hz, ArH), 7.74 (1H, t, J=7.14 Hz, ArH), 7.56–7.49 (2H, m, ArH), 7.35–7.33 (3H, m, ArH), 7.21–7.19 (2H, m, ArH), 7.13 (1H, d, J=6.66 Hz, ArH), 6.28 (2H, s, CH_2), 4.01 (3H, s, OCH_3); δ_C (75 MHz, $CDCl_3$): 159.9, 151.0, 145.5, 139.9, 137.9, 134.5, 131.0, 129.5, 129.2, 128.5, 126.9, 126.3, 122.6, 121.5, 117.1, 114.8, 114.4, 55.3, 53.8; HRMS (ESI): MH^+, found 367.1553. $C_{23}H_{19}N_4O$ requires 367.1553.

*4.3.7. [1-Benzyl-5-(2-aminophenyl)-1H-1,2,3-triazol-4-yl](4-methoxyphenyl)methanone (**4g′**).* (A) *With $SnCl_2\cdot 2H_2O$*: To a stirred solution of **3g** (0.10 g, 0.24 mmol) in ethanol (5 mL), $SnCl_2\cdot 2H_2O$ (0.54 g, 2.40 mmol) was added. The reaction mixture was stirred at 80 °C for 2 h. After completion of reaction (TLC), it was neutralized with sodium bicarbonate. After neutralization, it was filtered through Celite and the solvent evaporated under vacuum to give the crude product, which was diluted with water and extracted with ethyl acetate. The organic layer was collected, dried over sodium sulfate (Na_2SO_4) and evaporated under reduced pressure to get the crude mass, which upon purification by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4g′** (0.08 g, 90%) as white solid.

(B) *With $SnCl_2\cdot 2H_2O$ under ultrasonic irradiation*: Above procedure was repeated under ultrasonic irradiation at 30 °C, yielded the titled compound **4g′** (0.09 g, 93%) as white solid.

(C) *With Iron powder and ammonium chloride*: Iron powder (0.04 g, 0.72 mmol) and ammonium chloride (0.008 g, 0.140 mmol) was added to a stirred solution of **3g** (0.10 g, 0.24 mmol) in a mixture of ethanol (5 mL) and water (0.5 mL). The reaction mixture was stirred at 80 °C for 14 h. After completion of reaction (TLC), it was filtered through Celite and the solvent evaporated under reduced pressure to give the crude product, which was purified by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4g′** (0.02 g, 22%) as white solid.

(D) *With Pd–C and ammonium formate*: Ammonium formate (0.08 g, 1.20 mmol) was added to a stirred solution of **3g** (0.10 g, 0.24 mmol) in dry methanol. The reaction mixture was stirred at 30 °C for 19 h. After completion of reaction (TLC), it was filtered through Celite and the solvent evaporated under reduced pressure to give the crude product, which was purified by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4g′** (0.019 g, 20%) as white solid; mp 146–148 °C; R_f=0.45 (ethyl acetate/hexane, 1:4); ν_{max} (KBr) 3432, 2926, 1647, 1216, 768 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 7.94 (1H, d, J=7.62 Hz, ArH), 7.41–7.32 (4H, m, ArH), 7.24 (1H, d, J=6.48 Hz, ArH), 7.17–7.06 (4H, m, ArH), 6.87 (1H, t, J=7.26 Hz, ArH), 6.67 (1H, t, J=7.23 Hz, ArH), 6.26 (2H, s, CH_2), 3.94 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$): 184.5, 159.4, 141.2, 140.8, 130.5, 130.0, 129.4, 129.2, 128.8, 126.5, 126.4, 123.8, 122.6, 122.4, 116.9, 116.1, 115.0, 55.5, 54.1; HRMS (ESI): MH^+, found 385.1654. $C_{23}H_{21}N_4O_2$ requires 385.1659.

*4.3.8. 1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-4-(m-tolyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4h**).* It was obtained by the reductive cyclization of **3h** (0.20 g, 0.42 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (25% ethyl acetate/hexane), yielded the titled compound **4h** (0.16 g, 89%) as white solid; mp 228–232 °C; R_f=0.50 (ethyl acetate/hexane, 2:3); $[\alpha]_D^{30}$ −46 (c 0.1, DMSO); ν_{max} (KBr) 3463, 2926, 1217, 763 cm^{-1}; δ_H (300 MHz, DMSO-d_6): 8.67–8.64 (3H, m, ArH), 8.35 (1H, d, J=8.13 Hz, ArH), 7.94 (1H, t, J=7.80 Hz ArH), 7.83 (1H, t, J=7.98 Hz, ArH), 7.57 (1H, t, J=7.56 Hz, ArH), 7.47 (1H, d, J=7.47 Hz, ArH), 5.92–5.91 (2H, m, H-1′ and OH), 5.47–5.31 (2H, m, CH_2), 4.77–4.72 (1H, m, H-4′), 4.59 (1H, d, J=3.60 Hz, H-2′), 4.39–4.36 (1H, m, H-3′), 2.53 (3H, s, CH_3), 1.26 (3H, s, $C(CH_3)_2$), 1.23 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 150.4, 145.2, 139.1, 138.2, 136.7, 134.9, 131.6, 130.6, 130.4, 130.2, 129.0, 127.7, 127.3, 123.2, 115.3, 111.4, 105.0, 85.6, 79.4, 74.1, 49.8, 27.0, 26.5, 21.7; HRMS (ESI): MH^+, found 433.1864. $C_{24}H_{25}N_4O_4$ requires 433.1870.

*4.3.9. 1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-4-(p-tolyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4i**).* It was obtained by the reductive cyclization of **3i** (0.20 g, 0.42 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (25% ethyl acetate/hexane), yielded the titled compound **4i** (0.18 g, 90%) as white solid; mp 232–234 °C; R_f=0.50 (ethyl acetate/hexane, 2:3); $[\alpha]_D^{30}$ −44 (c 0.1, DMSO); ν_{max} (KBr) 3461, 2927, 1218, 770 cm^{-1}; δ_H (300 MHz, DMSO-d_6): 8.76 (2H, d, J=8.16 Hz, ArH), 8.59 (1H, d, J=8.19 Hz, ArH), 8.27 (1H, d, J=8.13 Hz, ArH), 7.88 (1H, t, J=7.53 Hz, ArH), 7.76 (1H, t, J=7.71 Hz, ArH), 7.45 (2H, d, J=8.19 Hz, ArH), 5.88–5.86 (2H, m, H-1″ and OH), 5.42–5.29 (2H, m, CH_2), 4.72–4.70 (1H, m, H-4′), 4.56 (1H, d, J=3.54 Hz, H-2′), 4.35–4.33 (1H, m, H-3′), 2.44 (3H, s, CH_3), 1.22 (3H, s, $C(CH_3)_2$), 1.19 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 150.1, 145.1, 140.8, 139.0, 134.8, 133.9, 130.4, 130.3, 129.8, 129.6, 127.5, 123.1, 115.1, 111.3, 104.9, 85.6, 79.4, 74.0, 49.7, 27.0, 26.4, 21.5; HRMS (ESI): MH^+, found 433.1863. $C_{24}H_{25}N_4O_4$ requires 433.1870.

*4.3.10. 1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-4-(4-methoxyphenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4j**).* It was obtained by the reductive cyclization of **3j** (0.20 g, 0.40 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (25% ethyl acetate/hexane), yielded the titled compound **4j** (0.17 g, 92%) as white solid; mp 242–244 °C; R_f=0.50 (ethyl acetate/hexane, 2:3); $[\alpha]_D^{30}$ −56 (c 0.1, DMSO); ν_{max} (KBr) 3462, 2927, 1219, 771 cm^{-1}; δ_H (300 MHz, DMSO-d_6): 8.84 (2H, d, J=8.88 Hz, ArH), 8.54 (1H, d, J=8.16 Hz, ArH), 8.21 (1H, d, J=8.16 Hz, ArH), 7.83 (1H, t, J=7.72 Hz, ArH), 7.71 (1H, t, J=7.84 Hz, ArH), 7.18 (2H, d, J=8.92 Hz, ArH), 5.88 (1H, d, J=3.56 Hz, H-1′), 5.87 (1H, d, J=4.92 Hz, OH), 5.38–5.24 (2H, m, CH_2), 4.71–4.68 (1H, m, H-4″), 4.56 (1H, d, J=3.60 Hz, H-2″), 4.35 (1H, dd, J_1=4.60, J_2=3.00, H-3″) 3.87 (3H, s, OCH_3), 1.21 (3H, s, $C(CH_3)_2$), 1.18 (3H, s, $C(CH_3)_2$); δ_C (50 MHz, $CDCl_3$): 161.2, 149.2, 144.7, 138.4, 134.3, 130.9, 129.8, 129.8, 128.7, 126.7, 122.5, 114.5, 114.0, 110.8, 104.4, 85.1, 78.9, 73.5, 55.3, 49.2, 26.5, 25.9; HRMS (ESI): MH^+, found 449.1820. $C_{24}H_{25}N_4O_5$ requires 449.1819.

*4.3.11. [1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-5-(2-aminophenyl)-1H-1,2,3-triazol-4-yl](4-methoxyphenyl)methanone (**4j′**).* (A) *With $SnCl_2\cdot 2H_2O$*: To a stirring solution of **3j** (0.10 g, 0.20 mmol) in ethanol (5 mL), $SnCl_2\cdot 2H_2O$ (0.45 g, 2.00 mmol) was added. The reaction mixture was stirred at 80 °C for 2 h. After completion of reaction (TLC), it was neutralized with sodium bicarbonate. After neutralization, it was filtered through Celite and the solvent evaporated under vacuum to give the crude product, which was diluted with water and extracted with ethyl acetate. The organic layer was collected, dried over sodium sulfate (Na_2SO_4) and evaporated under reduced pressure to get the crude mass, which upon purification by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4j′** (0.06 g, 67%) as white solid.

(B) *With $SnCl_2\cdot 2H_2O$ under ultrasonic irradiation*: Above procedure was repeated under ultrasonic irradiation at 30 °C, yielded the titled compound **4j′** (0.07 g, 71%) as white solid.

(C) *With Iron powder and ammonium chloride*: To a stirred solution of **3j** (0.100 g, 0.200 mmol) in a mixture of ethanol (5 mL) and water (0.5 mL), iron powder (0.034 g, 0.600 mmol) and ammonium chloride (0.006 g, 0.120 mmol) were added. The reaction mixture was stirred at 80 °C for 16 h. After completion of reaction (TLC), it was filtered through Celite and the solvent evaporated under reduced pressure to give the crude product, which was purified by column chromatography using 60–120 mesh silica gel (15% ethyl

acetate/hexane), yielded the titled compound **4j′** (0.024 g, 25%) as white solid.

(D) *With Pd–C and ammonium formate*: To a stirred solution of **3j** (0.100 g, 0.200 mmol) in dry methanol, ammonium formate (0.076 g, 1.000 mmol) was added. The reaction mixture was stirred at 25 °C for 12 h. After completion of reaction (TLC), it was filtered through Celite and the solvent evaporated under reduced pressure to give the crude product, which was purified by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4j′** (0.005 g, 5%) as white solid; mp 187–189 °C; R_f=0.45 (ethyl acetate/hexane, 2:3); $[\alpha]_D^{30}$ −26 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 3431, 2926, 1219, 771 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.88 (1H, br, ArH), 8.47 (1H, br, ArH), 8.26–8.24 (2H, m, ArH), 7.74–7.69 (2H, m, ArH), 7.07 (2H, br, ArH), 5.90 (1H, br, H-1′), 5.15 (2H, br, CH_2), 4.77 (1H, br, H-4′), 4.48 (1H, br, H-2′), 4.07 (1H, br, H-3′), 3.85 (3H, s, OCH_3), 1.36 (3H, s, $C(CH_3)_2$), 1.24 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 184.3, 161.7, 140.7, 139.8, 133.2, 130.8, 129.2, 128.1, 123.0, 121.9, 120.6, 115.1, 113.7, 112.2, 105.2, 85.6, 79.7, 74.3, 55.6, 49.3, 26.9, 26.3; HRMS (ESI): MH^+, found 467.1917. $C_{24}H_{27}N_4O_6$ requires 467.1925.

*4.3.12. 1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-4-(2,4-dichlorophenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4k**).* It was obtained by the reductive cyclization of **3k** (0.20 g, 0.42 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (25% ethyl acetate/hexane) as eluent, yielded the titled compound **4k** (0.16 g, 86%) as white solid; mp 224–226 °C; R_f=0.50 (ethyl acetate/hexane, 2:3); $[\alpha]_D^{30}$ −2 (*c* 0.1, DMSO); ν_{max} (KBr) 3462, 2928, 1218, 768 cm^{-1}; δ_H (300 MHz, DMSO-d_6+$CDCl_3$): 8.69 (1H, d, *J*=7.89 Hz, ArH), 8.32 (1H, d, *J*=7.86 Hz, ArH), 7.88–7.83 (1H, m, ArH), 7.80–7.71 (2H, m, ArH), 7.63–7.58 (1H, m, ArH), 7.50 (1H, d, *J*=7.86 Hz, ArH), 5.94 (1H, br, H-1′), 5.35–5.33 (2H, m, CH_2), 4.82 (1H, br, H-4′), 4.59 (1H, br, H-2′), 4.34 (1H, s, H-3′), 1.36 (3H, s, $C(CH_3)_2$), 1.27 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 145.1, 139.3, 135.5, 134.2, 134.0, 132.8, 130.5, 129.8, 129.5, 127.5, 126.9, 122.5, 115.4, 111.4, 104.8, 85.4, 79.8, 74.0, 49.4, 26.6, 26.1; HRMS (ESI): MH^+, found 487.0928. $C_{23}H_{21}Cl_2N_4O_4$ requires 487.0934.

*4.3.13. 1-(5-Deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-4-(4-fluorophenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4l**).* It was obtained by the reductive cyclization of **3l** (0.20 g, 0.41 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (25% ethyl acetate/hexane), yielded the titled compound **4l** (0.16 g, 91%) as white solid; mp 214–217 °C; R_f=0.50 (ethyl acetate/hexane, 2:3); $[\alpha]_D^{30}$ −39 (*c* 0.1, DMSO); ν_{max} (KBr) 3462, 2928, 1218, 768 cm^{-1}; δ_H (400 MHz, DMSO-d_6): 8.91–8.87 (2H, m, ArH), 8.61 (1H, d, *J*=8.16 Hz, ArH), 8.27 (1H, d, *J*=8.24 Hz, ArH), 7.89 (1H, t, *J*=7.40 Hz, ArH), 7.78 (1H, t, *J*=7.60, ArH), 7.47 (2H, t, *J*=8.80 Hz, ArH), 6.21 (1H, br, OH), 5.86 (1H, d, *J*=3.40 Hz, H-1′), 5.42 (1H, dd, J_1=14.92 Hz, J_2=3.72 Hz, CH_2), 5.33–5.27 (1H, m, CH_2), 4.69–4.67 (1H, m, H-4′), 4.56 (1H, d, *J*=3.44 Hz, H-2′), 4.35 (1H, d, *J*=1.88 Hz, H-3″), 1.20 (3H, s, $C(CH_3)_2$), 1.18 (3H, s, $C(CH_3)_2$); δ_C (100 MHz, $CDCl_3$): 162.4 (d, $^1J_{CF}$=252.00 Hz), 148.4, 144.5, 138.4, 134.5, 132.7, 131.6 (d, $^3J_{CF}$=10.00 Hz), 130.0, 127.3, 122.7, 115.7, (d, $^2J_{CF}$=20.00 Hz), 114.7, 110.8, 104.5, 85.1, 79.1, 73.5, 49.4, 26.5, 26.0; HRMS (ESI): MH^+, found 437.1626. $C_{23}H_{22}FN_4O_4$ requires 437.1620.

*4.3.14. 1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-4-phenyl-1H-[1,2,3]triazolo[4,5-c]quinoline (**4m**).* It was obtained by the reductive cyclization of **3m** (0.20 g, 0.35 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4m** (0.15 g, 85%) as white solid; mp 68–70 °C; R_f=0.50 (ethyl acetate/hexane, 1:3); $[\alpha]_D^{30}$ −184 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2925, 1212, 1070, 761 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.89–8.86 (2H, m, ArH), 8.57 (1H, d, *J*=8.07 Hz, ArH), 8.42 (1H, d, *J*=8.04 Hz, ArH), 7.87–7.82 (1H, m, ArH), 7.71–7.59 (4H, m, ArH), 5.47 (1H, d, *J*=4.89 Hz, H-1′), 5.34 (2H, d, *J*=6.69 Hz, CH_2), 4.75–4.71 (1H, dd, J_1=7.89 Hz, J_2=2.37 Hz, H-3′), 4.61 (1H, t, *J*=6.60 Hz, H-2′), 4.42–4.39 (1H, dd, J_1=7.89 Hz, J_2=1.53 Hz, H-4′), 4.37–4.35 (1H, m, H-5′), 1.70 (3H, s, $C(CH_3)_2$), 1.45 (3H, s, $C(CH_3)_2$), 1.31 (3H, s, $C(CH_3)_2$), 1.26 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 151.5, 145.7, 139.4, 136.8, 135.1, 130.8, 130.3, 129.9, 129.5, 128.6, 126.6, 122.1, 115.2, 109.9, 109.0, 70.8, 70.4, 67.4, 50.1, 26.1, 25.8, 24.7, 24.4; HRMS (ESI): MH^+, found 489.2123. $C_{27}H_{29}N_4O_5$ requires 489.2132.

*4.3.15. 1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-4-(o-tolyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4n**).* It was obtained by the reductive cyclization of **3n** (0.20 g, 0.36 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4n** (0.14 g, 80%) as white solid; mp 58–60 °C; R_f=0.50 (ethyl acetate/hexane, 1:3); $[\alpha]_D^{30}$ −99 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2928, 1212, 762 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.59 (1H, d, *J*=8.01 Hz, ArH), 8.38 (1H, d, *J*=8.19 Hz, ArH), 7.84–7.81 (2H, m, ArH), 7.73–7.68 (1H, m, ArH), 7.43 (3H, br, ArH), 5.46 (1H, d, *J*=4.92 Hz, H-1′), 5.31–5.27 (2H, m, CH_2), 4.72 (1H, dd, J_1=7.89 Hz, J_2=2.37 Hz, H-3′), 4.60 (1H, t, *J*=6.03 Hz, H-2′), 4.39–4.32 (2H, m, H-4′ and H-5′), 2.50 (3H, s, CH_3), 1.69 (3H, s, $C(CH_3)_2$), 1.44 (3H, s, $C(CH_3)_2$), 1.33 (3H, s, $C(CH_3)_2$), 1.30 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 154.8, 145.6, 139.9, 137.2, 136.3, 134.4, 130.9, 129.3, 129.2, 126.6, 125.6, 122.1, 115.1, 109.8, 108.8, 70.9, 70.4, 67.4, 50.1, 29.7, 26.2, 25.8, 24.8, 24.4, 20.7; HRMS (ESI): MH^+, found 503.2294. $C_{28}H_{31}N_4O_5$ requires 503.2289.

*4.3.16. 1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-4-(m-tolyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4o**).* It was obtained by the reductive cyclization of **3o** (0.20 g, 0.36 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4o** (0.15 g, 81%) as white solid; mp 52–54 °C; R_f=0.50 (ethyl acetate/hexane, 1:3); $[\alpha]_D^{30}$ −106 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2926, 1217, 1070, 771 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.66–8.62 (2H, m, ArH), 8.47 (1H, d, *J*=8.13 Hz, ArH), 8.33 (1H, d, *J*=8.25 Hz, ArH), 7.76 (1H, t, *J*=7.95 Hz, ArH), 7.59 (1H, t, *J*=7.83 Hz, ArH), 7.46 (1H, t, *J*=7.62 Hz, ArH), 7.33 (1H, d, *J*=7.47 Hz, ArH), 5.40 (1H, d, *J*=4.95 Hz, H-1′), 5.27–5.21 (2H, m, CH_2), 4.65 (1H, dd, J_1=7.89 Hz, J_2=2.31 Hz, H-3″), 4.55 (1H, t, *J*=7.11 Hz, H-2′), 4.31–4.25 (2H, m, H-4′ and H-5″), 2.53 (3H, s, CH_3), 1.62 (3H, s, $C(CH_3)_2$), 1.37 (3H, s, $C(CH_3)_2$), 1.25 (6H, s, 2× $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 151.6, 145.7, 139.4, 137.8, 136.6, 134.9, 131.1, 130.9, 130.4, 129.3, 128.4, 127.4, 126.4, 122.0, 115.1, 109.8, 108.8, 70.8, 70.8, 70.4, 67.2, 50.0, 29.7, 26.1, 25.8, 24.8, 24.4, 21.7; HRMS (ESI): MH^+, found 503.2293. $C_{28}H_{31}N_4O_5$ requires 503.2289.

*4.3.17. 1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-4-(p-tolyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4p**).* It was obtained by the reductive cyclization of **3p** (0.20 g, 0.36 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4p** (0.17 g, 96%) as white solid; mp 84–87 °C; R_f=0.50 (ethyl acetate/hexane, 1:3); $[\alpha]_D^{30}$ −105 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2927, 1216, 1069, 770 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.82 (2H, d, *J*=8.07 Hz, ArH), 8.56 (1H, d, *J*=8.22 Hz, ArH), 8.40 (1H, d, *J*=8.28 Hz, ArH), 7.84 (1H, t, *J*=7.47 Hz, ArH), 7.67 (1H, t, *J*=7.65 Hz, ArH), 7.48 (2H, d, *J*=8.01 Hz, ArH), 5.49 (1H, d, *J*=4.89 Hz, H-1″), 5.34 (2H, d, *J*=6.66 Hz, CH_2), 4.75 (1H, dd, J_1=7.86 Hz, J_2=2.10 Hz, H-3′), 4.62 (1H, t, *J*=6.18 Hz, H-2′), 4.42–4.36 (2H, m, H-4′ and H-5′), 2.53 (3H, s, CH_3), 1.71 (3H, s, $C(CH_3)_2$), 1.46 (3H, s, $C(CH_3)_2$), 1.32 (3H, s, $C(CH_3)_2$), 1.27 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 151.4, 145.7, 140.5, 139.4, 135.0, 134.0, 130.7, 129.8, 129.4, 126.4, 122.1, 115.1, 109.9, 108.9, 70.8, 70.4, 67.4, 50.1, 26.1, 25.8, 24.8, 24.4, 21.5; HRMS (ESI): MH^+, found 503.2293. $C_{28}H_{31}N_4O_5$ requires 503.2289.

4.3.18. 1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-4-(2-methoxyphenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline

*(**4q**).* It was obtained by the reductive cyclization of **3q** (0.20 g, 0.35 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4q** (0.15 g, 84%) as white solid; mp 78–80 °C; R_f=0.50 (ethyl acetate/hexane, 1:3); $[\alpha]_D^{30}$ −92 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2929, 1218, 1071, 764 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.51 (1H, d, *J*=8.13 Hz, ArH), 8.35 (1H, d, *J*=8.25 Hz, ArH), 7.77 (1H, t, *J*=7.29 Hz, ArH), 7.68–7.61 (2H, m, ArH), 7.49–7.44 (1H, m, ArH), 7.14–7.07 (2H, m, ArH), 5.42 (1H, d, *J*=4.92 Hz, H-1′), 5.30–5.14 (2H, m, CH_2), 4.65–4.62 (1H, dd, J_1=7.89 Hz, J_2=2.28 Hz, H-3′), 4.54 (1H, t, *J*=6.18 Hz, H-2′), 4.31–4.27 (2H, m, H-4′ and H-5′), 3.80 (3H, s, OCH_3), 1.63 (3H, s, $C(CH_3)_2$), 1.37 (3H, s, $C(CH_3)_2$), 1.27 (3H, s, $C(CH_3)_2$), 1.22 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 157.9, 152.8, 145.9, 140.1, 134.0, 131.3, 130.9, 130.8, 129.2, 126.6, 122.1, 120.8, 115.4, 111.8, 109.8, 108.8, 70.8, 70.4, 67.4, 55.7, 55.0, 26.1, 25.9, 24.8, 24.4; HRMS (ESI): MH^+, found 519.2243. $C_{28}H_{31}N_4O_6$ requires 519.2238.

*4.3.19. 1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-4-(3-methoxyphenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4r**).* It was obtained by the reductive cyclization of **3r** (0.20 g, 0.35 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (15% ethyl acetate/hexane), yielded the titled compound **4r** (0.16 g, 87%) as white solid; mp 72–74 °C; R_f=0.50 (ethyl acetate/hexane, 1:3); $[\alpha]_D^{30}$ −113 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2926, 1217, 1070, 771 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.54–8.50 (2H, m, ArH), 8.47–8.46 (1H, m, ArH), 8.39 (1H, d, *J*=8.22 Hz, ArH), 7.84–7.79 (1H, m, ArH), 7.66 (1H, t, *J*=7.26 Hz, ArH), 7.53 (1H, t, *J*=8.01 Hz, ArH), 7.14 (1H, dd, J_1=8.19 Hz, J_2=2.49 Hz, ArH), 5.46 (1H, d, *J*=4.95 Hz, H-1′), 5.36–5.23 (2H, m, CH_2), 4.71 (1H, dd, J_1=7.89 Hz, J_2=2.40 Hz, H-3′), 4.60–4.56 (1H, m, H-2′), 4.38–4.32 (2H, m, ArH, H-4′ and H-5′), 4.02 (3H, s, OCH_3), 1.68 (3H, s, $C(CH_3)_2$), 1.43 (3H, s, $C(CH_3)_2$), 1.30 (3H, s, $C(CH_3)_2$), 1.25 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 159.8, 151.1, 145.6, 139.4, 138.0, 135.0, 131.0, 129.4, 129.3, 126.5, 122.7, 122.0, 117.0, 115.2, 114.3, 109.8, 108.8, 70.8, 70.8, 70.4, 67.3, 55.3, 50.0, 26.1, 25.8, 24.8, 24.4; HRMS (ESI): MH^+, found 519.2241. $C_{28}H_{31}N_4O_6$ requires 519.2238.

*4.3.20. 1-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-yl)-4-(4-methoxyphenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4s**).* It was obtained by the reductive cyclization of **3s** (0.20 g, 0.35 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel with 15% ethyl acetate/hexane as eluent, yielded the titled compound **4s** (0.17 g, 93%) as white solid; mp 80–82 °C; R_f=0.50 (ethyl acetate/hexane, 1:3); $[\alpha]_D^{30}$ −96 (*c* 0.1, $CHCl_3$); ν_{max} (KBr) 2926, 1218, 1069, 771 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.93 (2H, d, *J*=8.46 Hz, ArH), 8.45 (1H, d, *J*=7.35 Hz, ArH), 8.30 (1H, d, *J*=7.92 Hz, ArH), 7.75 (1H, t, *J*=6.99 Hz, ArH), 7.60–7.58 (1H, m, ArH), 7.12 (2H, d, *J*=8.46 Hz, ArH), 5.44 (1H, d, *J*=4.32 Hz, H-1″), 5.25–5.18 (2H, m, CH_2), 4.67 (1H, d, *J*=6.54 Hz, H-3′), 4.55 (1H, br, H-2′), 4.33–4.30 (2H, m, H-4′ and H-5′), 3.93 (3H, s, OCH_3), 1.64 (3H, s, $C(CH_3)_2$), 1.39 (3H, s, $C(CH_3)_2$), 1.27 (3H, s, $C(CH_3)_2$), 1.22 (3H, s, $C(CH_3)_2$); δ_C (75 MHz, $CDCl_3$): 161.5, 150.7, 145.7, 139.2, 134.8, 131.5, 130.6, 129.5, 129.2, 126.0, 121.9, 114.9, 113.8, 109.7, 108.8, 70.8, 70.8, 70.4, 67.2, 55.2, 50.0, 26.1, 25.8, 24.7, 24.3; HRMS (ESI): MH^+, found 519.2248. $C_{28}H_{31}N_4O_6$ requires 519.2238.

4.4. General procedure for the preparation of 1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-(4-fluorophenyl)-1*H*-[1,2,3]triazolo[4,5-*c*]quinoline (4t)

It was obtained by the reductive cyclization of **3t** (0.20 g, 0.31 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (25% ethyl acetate/hexane), yielded the titled compound **4t** (0.09 g, 50%) as white solid; mp 102–104 °C; R_f=0.50 (ethyl acetate/hexane, 2:3); $[\alpha]_D^{30}$ +92 (*c* 0.1, DMSO); ν_{max} (KBr) 2926, 1721, 1216, 1071, 773 cm^{-1}; δ_H (300 MHz, DMSO-d_6): 8.88–8.84 (2H, m, ArH), 8.61 (1H, d, *J*=8.31 Hz, ArH), 8.35 (1H, d, *J*=8.35 Hz, ArH), 7.99 (1H, t, *J*=7.60 Hz, ArH), 7.92 (1H, t, *J*=7.60 Hz, ArH), 7.48 (2H, m, ArH), 7.24 (1H, d, *J*=9.40 Hz, H-1′), 6.07 (1H, t, *J*=9.60 Hz, H-2′), 5.82 (1H, t, *J*=9.60 Hz, H-3′), 5.34 (1H, t, *J*=9.86 Hz, H-4′), 4.81–4.78 (1H, m, H-5′), 4.27 (1H, dd, J_1=12.58 Hz, J_2=5.72 Hz, H-6a′), 4.13 (1H, dd, J_1=12.58, J_2=1.52, H-6b′), 2.09 (3H, s, $-COCH_3$), 2.00 (3H, s, $-COCH_3$), 1.92 (3H, s, $-COCH_3$), 1.75 (3H, s, $-COCH_3$); δ_C (75 MHz, DMSO-d_6): 170.4, 169.9, 169.4, 168.6, 162.2 (d, $^1J_{CF}$=246.00 Hz), 149.2, 145.2, 137.9, 136.1, 132.0 (d, $^3J_{CF}$=8.58 Hz), 131.1, 130.3, 128.2, 123.5, 115.7(d, $^2J_{CF}$=21.55 Hz), 114.0, 84.0, 73.6, 72.7, 69.1, 67.6, 61.6, 20.5, 20.2, 19.9; HRMS (ESI): MH^+, found 595.1845. $C_{29}H_{28}FN_4O_9$ requires 595.1835.

*4.4.1. 1-(β-D-Glucopyranosyl)-4-(4-fluorophenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4t′**).* It was obtained by the reductive cyclization of **3t** (0.20 g, 0.31 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (2% methanol/chloroform), yielded the titled compound **4t′** (0.01 g, 10%) as white solid; mp 203–205 °C; R_f=0.50 (methanol/chloroform, 1:24); $[\alpha]_D^{30}$ +32 (*c* 0.1, MeOH); ν_{max} (KBr) 3463, 2926, 1218, 1070, 771 cm^{-1}; δ_H (300 MHz, DMSO-d_6): 8.98–8.93 (2H, m, ArH), 8.75 (1H, d, *J*=7.80 Hz, ArH), 8.37 (1H, d, *J*=7.80 Hz, ArH), 7.98 (1H, t, *J*=7.41 Hz, ArH), 7.85 (1H, t, *J*=7.41 Hz, ArH), 7.55 (2H, t, *J*=8.91 Hz, ArH), 6.42 (1H, d, *J*=9.66 Hz, H-1′), 5.48 (3H, br, 3× OH), 4.78 (1H, br, OH), 4.32–4.26 (1H, m, H-2″), 3.92–3.80 (2H, m, H-3′ and H-4′), 3.70–3.59 (3H, m, H-5′ and CH_2); δ_C (75 MHz, DMSO-d_6): 162.9 (d, $^1J_{CF}$=247.32 Hz), 149.5, 146.0, 139.0, 135.5, 133.1, 132.3(2C) (d, $^3J_{CF}$=7.50 Hz), 130.8, 128.2, 116.1(2C) (d, $^2J_{CF}$=22.50 Hz), 114.8, 80.5, 77.4, 71.4(2C), 69.9, 61.0; HRMS (ESI): MH^+, found 427.1409. $C_{21}H_{20}FN_4O_5$ requires 427.1412.

*4.4.2. 1-(β-D-Galactopyranosyl)-4-(4-bromophenyl)-1H-[1,2,3]triazolo[4,5-c]quinoline (**4u**).* It was obtained by the reductive cyclization of **3u** (0.20 g, 0.28 mmol). The purification of crude product by column chromatography using 60–120 mesh silica gel (2% methanol/chloroform), yielded the titled compound **4u** (0.08 g, 61%) as white solid; mp 193–195 °C; R_f=0.50 (methanol/chloroform, 1:24); $[\alpha]_D^{30}$ +64 (*c* 0.1, MeOH); ν_{max} (KBr) 3461, 2927, 1217, 1071, 773 cm^{-1}; δ_H (300 MHz, DMSO-d_6): 9.15 (1H, br, ArH), 8.83 (2H, d, *J*=8.07 Hz, ArH), 8.32 (1H, d, *J*=8.07 Hz, ArH), 7.89–7.87 (2H, m, ArH), 7.75–7.64 (2H, m, ArH), 6.31 (1H, d, *J*=9.18 Hz, H-1″), 5.39 (2H, br, 2× OH), 4.87 (1H, br, OH), 4.45 (1H, br, OH), 4.07–4.00 (2H, m, H-2′, H-3′), 3.78 (4H, m, H-4′, H-5′, CH_2); δ_C (75 MHz, DMSO-d_6): 156.7, 148.7, 145.5, 139.4, 135.8, 132.2, 131.8, 130.7, 130.3, 129.9, 129.1, 128.1, 124.9, 115.1, 79.3, 74.0, 68.9, 68.2, 60.9; HRMS (ESI): MH^+, found 487.0607. $C_{21}H_{20}BrN_4O_5$ requires 487.0612.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.07.088.

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