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Synthesis of 1,2,3-Triazoles from Azide-Derivatised Aminocyclitols by Catalytic Diazo Transfer and CuAAC Click Chemistry

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Cu^{II}-catalysed diazo transfer and Cu^{I}-catalysed azide–alkyne 1,3-dipolar cycloaddition (CuAAC) "click chemistry" were used to synthesis C_7N aminocyclitol-derivatised 1,2,3-triazoles. In the course of this work, the -N=N- moiety was transferred onto C_7N aminocyclitols such as validamine, valienamine and valiolamine by employing imidazole-1-sulfonyl azide as the diazo transfer reagent with catalysis by Cu^{II}, Zn^{II} and Ni^{II}, in moderate to good yields. The obtained azidocyclitols were coupled with various terminal alkynes under modified Meldal's conditions with good to excellent yields. The stereo- and regiochemistry of the products were confirmed by 2D-NMR (NOESY and HMBC). One-pot syntheses of the corresponding 1,2,3-triazoles, as safer and more efficient procedures, were also investigated and gave moderate to good yields.

1. Introduction

Carbasugars (also known as pseudosugars) are attractive in the context of new drug discovery.[1] It has been postulated that their structural resemblance to the parent sugars should facilitate their recognition by enzymes or other biological systems in place of the related *true* sugars.[2] Meanwhile, the replacement of the oxygen atom with a methylene group in the framework should make these compounds more stable toward endogenous degradative enzymes, as well as leading to interesting biological properties, mainly as antibiotics and glycosidase inhibitors.[3]

C_7N aminocyclitols such as valienamine (**1**), validamine (**2**) and valiolamine (**3**),[4] important compounds related to carbasugars, were first isolated as fragments of the validamycins and fully characterised as possessing greater or lesser degrees of enzyme inhibitory activity toward certain glycosidases (Figure 1). In the light of this discovery, hundreds of analogues have been synthesised and their biological activities have been evaluated, resulting in the discovery of several pharmaceutical leads.[4a] The most representative example was voglibose (**4**),[5] a clinically useful drug in the treatment of diabetes.[6]

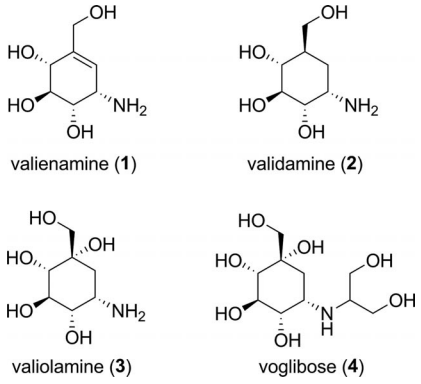

Figure 1. Structures of aminocyclitols and voglibose.

During the last few years there has been increasing interest in the use of "copper-catalysed azide–alkyne cycloaddition" (CuAAC),[7] the most extensively utilised reaction in "click chemistry".[8] In carbohydrate chemistry, CuAAC reactions have come to be increasingly applied for diversification or modification of carbohydrates and syntheses of neoglycoconjugates directed towards the understanding of biological pathways, mechanisms and drug discovery,[9] including the generation of potential substrates or inhibitors for a range of different enzymes.[10,3b] For instance, β-linked 1-glycosyl-4-phenyltriazoles **5** and **6** (Figure 2), prepared from β-glycosyl azides and phenylacetylene by CuAAC, were assessed for inhibitory activity against three different β-glycosidases.[11] Moreover, organic compounds bearing triazole derivatives of other different pharmacodynamic nuclei were found to display various forms of biological activity, including anti-HIV activity,[12] selective β_3 adrenergic

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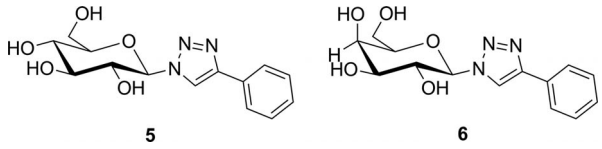
receptor inhibition[13] and antibacterial activity,[14] perhaps due in part to their ability to mimic certain aspects of a peptide bond.



5 6

Figure 2. Potential glycosidase inhibitors synthesised by "click chemistry".

To the best of our knowledge, there is no reported research on the diversification of aminocyclitols through CuAAC modification. In continuation of our ongoing study of C_7N aminocyclitols,[15] here we report a new and facile procedure for the modification of aminocyclitols by diazo transfer and CuAAC.

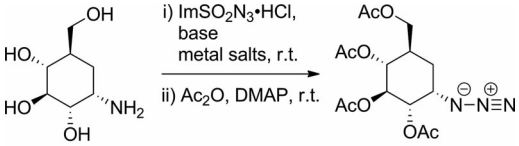
2. Results and Discussion

Our initial investigations focused on the introduction of the azide group, a component regularly used in CuAAC, into the substrates. Most commonly, an azide group is introduced into a molecule by nucleophilic displacement of a nucleofuge by an azide ion.[16] In contrast with that approach is diazo transfer, in which an –N=N– moiety is transferred onto an existing amine group, with retention of configuration, rather than the entire azido group being incorporated into a molecule.[17] The first diazo transfer onto an amino sugar, by use of trifluoromethanesulfonyl azide (TfN_3), was reported in 1991 by Vasella et al.[18] and was further improved by Wong et al.[19] Although powerful, this procedure presents several disadvantages, such as difficulty in the isolation of TfN_3 and the requirement for an excess of toxic and costly triflic anhydride, which prohibit the application of this protocol on a large scale. In 2007, Goddard-Borger reported the synthesis of imidazole-1-sulfonyl azide hydrochloride as an efficient and shelf-stable diazo transfer reagent by a simple one-pot procedure.[20] This reagent, as an efficient alternative to TfN_3, converted a diverse range of amines into the corresponding azides with excellent yields.

In order to make full use of the existing amino groups on aminocyclitols and for the sake of operational safety, we thus decided to use imidazole-1-sulfonyl azide as the diazo transfer reagent in our reseach. Initially, according to the available reports from Wong (TfN_3 with Cu^{II}, Ni^{II} or Zn^{II} as catalyst)[19a] and Goddard-Borger ($ImSO_2N_3$·HCl with Cu^{II} as catalyst)[20] for the diazo transfer, the reaction conditions were optimised systematically and various bases and transition metal salts were scanned (Table 1) with use of validamine (**2**) as the model substrate.

Bases added in this procedure not only neutralised the hydrogen chloride from $ImSO_2N_3$·HCl, but also played an essential role in the reaction between the amino group in the substrate and the azide group in the $ImSO_2N_3$ under the influence of the metal catalyst. Inorganic bases, including $KHCO_3$ (Table 1, Entry 1), Na_2CO_3 (Table 1, Entry 2) and K_2CO_3 (Table 1, Entries 3–9), and organic bases, such as triethylamine (TEA) (Table 1, Entries 10–11) and *N*,*N*-diisopropylethylamine (DIPEA, Table 1, Entries 12–15), were screened. The results demonstrated that K_2CO_3 gave the highest yield (Table 1, Entries 3–5) and was a little better than DIPEA (Table 1, Entries 12–15).

Table 1. Survey of the catalytic diazo transfer reation.



2 7

Entry[a]	Base	Metal salt	Solvent	Yield [%][b]
1	$KHCO_3$	$CuSO_4·5H_2O$	MeOH	54
2	Na_2CO_3	$CuSO_4·5H_2O$	MeOH	38
3	K_2CO_3	$CuSO_4·5H_2O$	MeOH	88
4	K_2CO_3	$Zn(OAc)_2$	MeOH	78
5	K_2CO_3	$Ni(NO_3)_2·6H_2O$	MeOH	63
6	K_2CO_3	$CuSO_4·5H_2O$	THF	23
7	K_2CO_3	$CuSO_4·5H_2O$	toluene	trace
8	K_2CO_3	$CuSO_4·5H_2O$	CH_2Cl_2	41
9	K_2CO_3	$CuSO_4·5H_2O$	DMF	72
10	TEA	$CuSO_4·5H_2O$	MeOH	82
11	TEA	$Zn(OAc)_2$	MeOH	76
12	DIPEA	$ZnCl_2$	MeOH	70
13	DIPEA	$CuSO_4·5H_2O$	MeOH	85
14	DIPEA	$CuSO_4·5H_2O$	DMF	82
15	DIPEA	$Ni(NO_3)_2·6H_2O$	DMF	67

[a] Conditions: **2** (1.0 mmol), $ImSO_2N_3$·HCl (1.2 equiv.), base (2.0 equiv.), cat. (0.05 equiv.), room temp., 12 h. [b] Isolated yields after peracetylation under conventional conditions.

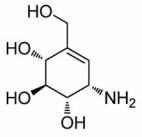
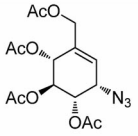
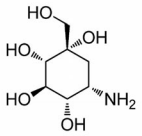
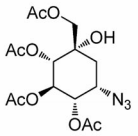
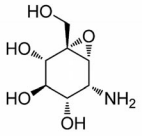
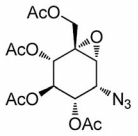
As catalysts, various metal salts, including Cu^{II}, Ni^{II} or Zn^{II}, were examined. Copper sulfate (Table 1, Entries 3 and 13) was found to be better than zinc acetate (Table 1, Entry 4), zinc chloride (Table 1, Entry 12) and nickel nitrate (Table 1, Entries 5 and 15), and this result was similar to that reported by Wong.[19a]

Finally, solvent screening revealed that MeOH was the most suitable solvent when either K_2CO_3 (Table 1, Entry 3) or DIPEA (Table 1, Entry 13) was employed as base, due to its good dissolving capacity for validamine, relative to other solvents such as THF (Table 1, Entry 6), toluene (Table 1, Entry 7) or CH_2Cl_2 (Table 1, Entry 8). In addition, DMF, as a highly polar solvent, also gave a good yield of product, when accompanied by copper sulfate and DIPEA (Table 1, Entry 14).

With the optimal conditions (Table 1, Entry 3) in hand, the substrate scope of this reaction was examined with other C_7N aminocyclitols, including valienamine (**1**), valiolamine (**2**) and valienamine epoxide (**10**). The results are listed in Table 2.

Even though the protocol for diazo transfer with imidazole-1-sulfonyl azide has been utilised extensively in the

Table 2. Synthesis of different aminocyclitol-derived azides by catalytic diazo transfer.

Entry	Substrate	Product	Reaction time (h)	Yield[a] (%)
1	 1	 8	12	92
2	 3	 9	12	82
3	 10	 11	12	73

[a] Isolated yields.

modification of amino acids[21] and proteins,[22] to the best of our knowledge this transformation has not been applied to aminocyclitols. However, the reaction is expected to proceed by a mechanism very similar to that reported by Wong et al.[19b]

During the characterisation of azide **8**, it was found that Ogawa et al. had obtained **8** as early as 1985, in the total synthesis of (+)-valienamine.[23] Unexpectedly, although the spectroscopic data (^{1}H NMR, see Experimental Section) for **8** were identical to those for the corresponding racemate reported in the literature,[23a] the physical properties [white solid and $[a]_D^{25}$ = +103.7 (c = 0.98, $CHCl_3$)] of our product were very different from those of Ogawa's optically active **8** [syrup and $[a]_D^{20}$ = +40 (c = 1.0, $CHCl_3$)]![23b] In order to confirm the structure of **8**, X-ray crystallographic analysis of a single crystal was carried out, as shown in Figure 3. The result demonstrated that the product we obtained had the same structure as we expected. Therefore, it could be concluded that the specific optical rotation reported by Ogawa et al. has a relatively large error, which might be caused either by partial racemisation of the product or by residual solvent.

Since the discovery of the CuAAC reaction, a large number of different sets of reaction conditions and various forms of Cu^I catalyst have been reported.[7a] In carbohydrate chemistry, combinations such as i) Cu^{II} and sodium ascorbate,[24a–24c,11b,24d–24f] ii) Cu^{II} and Cu^0,[25] iii) Cu^{II} and ascorbic acid[26] and iv) Cu^I and base[11a,27] have been developed. Moreover, besides conventional heating methods, microwave irradiation has also been introduced to accelerate the reaction with sluggish substrates.[27a,11b]

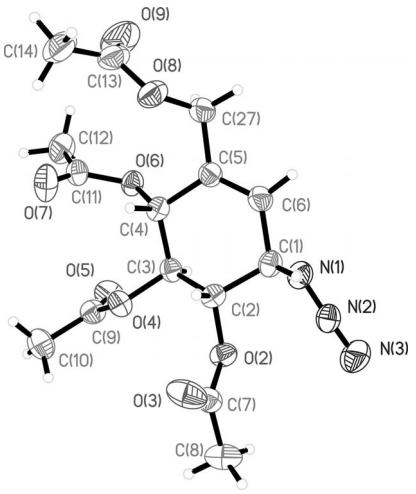


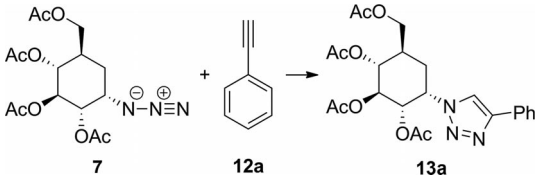
Figure 3. ORTEP drawing of valienamine azide tetraacetate (**8**).

Initially, we adopted a method based on the procedure first described by Sharpless that involves 0.05 mol equiv. of $CuSO_4$ plus 0.2 mol equiv. of sodium ascorbate (NaAsc) as a catalyst, in a 1:1 tBuOH/H_2O solvent mixture at room temperature. Testing these conditions for coupling between peracetylated validamine azide and phenylacetylene revealed a low level of conversion into the desired product (Table 3, Entry 1), even at a higher temperature (Table 3, Entries 2 and 3). Therefore, two variations of these conditions (referred to as Methods I and II) were employed, allowing significant improvement of the cycloaddition yields of the target products. In Method I, which was a modification of Sharpless's procedure, the reactions were conducted in non-redistilled DMF at 100 °C in the presence of DIPEA. The yield of product was improved to 88% in 8 h (Table 3, Entry 5). In Method II, Meldal's conditions (CuX/base) were adopted; different CuXs such as CuI (Table 3, Entries 6–8), CuBr (Table 3, Entry 9) and CuCl (Table 3, Entry 10) were scanned in the presence of Et_3N or DIPEA. The results demonstrated that DMF was still the most suitable solvent, and CuI/DIPEA (Table 3, Entry 7) was shown to be the best combination in this reaction. It should be noted that all the reactions afford single regioisomers (as judged by ^{1}H NMR spectroscopy). The stereo- and regiochemistry of the product, established by 2D-NMR spectroscopy, is discussed in detail below. With optimised conditions in hand, we next sought to define the scope of the azidocyclitols and terminal alkynes (Table 4, below).

During the purification of products, it was found that the solubilities of the triazoles in MeOH were very low, and that after washing with small amounts of MeOH, the solids obtained were found to be analytically pure by TLC and NMR analyses (^{1}H and ^{13}C). The yields of products in this simplified procedure were only slightly smaller than those obtained after purification by column chromatography (from 94% to 87%).

Subsequently, the substrate scope of this reaction was also examined. As highlighted in Table 4, a variety of ter-

Table 3. Survey of the cycloaddition conditions.



7 12a 13a

Entry	Catalyst	Reductant or base	Solvent/time	*T* [°C]	Yield [%][a]
1	$CuSO_4 \cdot 5H_2O$ (0.05 equiv.)	NaAsc (0.2 equiv.)	H_2O/*t*BuOH (1:1)/48 h	room temp.	30
2	$CuSO_4 \cdot 5H_2O$ (0.05 equiv.)	NaAsc (0.2 equiv.)	H_2O/*t*BuOH (1:1)/24 h	80	48
3	$CuSO_4 \cdot 5H_2O$ (0.05 equiv.)	NaAsc (0.2 equiv.)	toluene/24 h	80	56
4	$CuSO_4 \cdot 5H_2O$ (0.05 equiv.)	NaAsc (0.2 equiv.)	DMF/12 h	100	73
5	$CuSO_4 \cdot 5H_2O$ (0.05 equiv.)	NaAsc (0.2 equiv.), DIPEA (1.0 equiv.)	DMF/8 h	100	88
6	CuI (0.1 equiv.)	DIPEA (1.0 equiv.)	toluene/12 h	80	82
7	CuI (0.1 equiv.)	DIPEA (1.0 equiv.)	DMF/6 h	100	94 (87)
8	CuI (0.1 equiv.)	TEA (1.0 equiv.)	DMF/12 h	100	81
9	CuBr (0.1 equiv.)	DIPEA (1.0 equiv.)	DMF/24 h	100	70
10	CuCl (0.1 equiv.)	DIPEA (1.0 equiv.)	DMF/24 h	100	59

[a] Isolated yields after column chromatography; simplified procedure in parentheses.

minal alkynes **12** could react efficiently with azide **7** to give the corresponding products in good yields after isolation (Table 4, Entries 1–10). Azides **8**, **9** and **11** could also react smoothly with terminal alkynes to give moderate to good yields (Table 4, Entries 11–30). Moreover, it was found that the substituents on phenylacetylene had no evident effect on the yields of corresponding products. This conclusion was consistent with the characteristics of CuAAC.

With regard to the stereo- and regiochemistry of the products (discussed here for the example of **15a**: α-configuration of triazole, phenyl group in the triazole 4′-position), especially those obtained at the relatively high temperatures corresponding to those used in uncatalysed Huisgen-type cycloaddition, which provides mixtures of 1,4- and 1,5-triazole regioisomers, these were unambiguously established by NOESY and HMBC (Figure 4) experiments. Indeed, the ^{1}H 2D-NOESY spectrum shows correlations between 5′-H and 6-H and between 2-H and 2′′-H (Figure 5), and the ^{1}H-^{13}C HMBC experiment shows cross coupling between 5′-H and C-6, C-4′ and C-1′′ (Figure 6), in accordance with the proposed structure for **15a**.

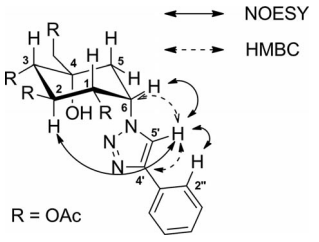
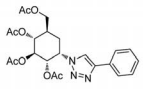
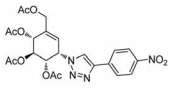
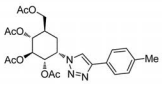
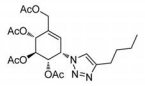
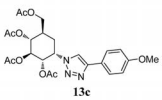
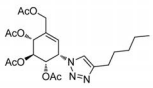
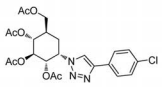
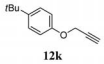
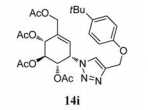
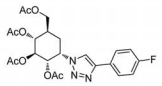
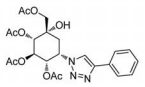
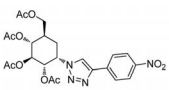
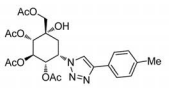
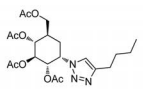
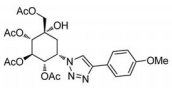
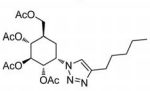
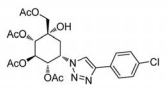
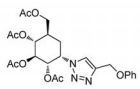
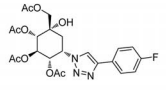
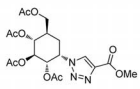
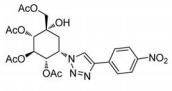
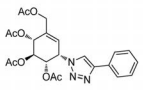
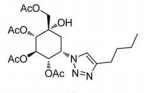
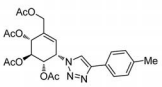
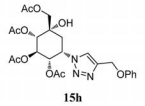
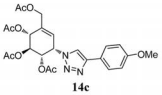
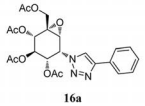
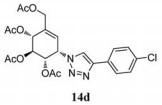
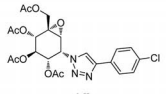
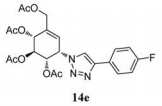


Figure 4. Significant NOESY and HMBC correlations in compound **15a**.

Although organic azides are stable under most reaction conditions, those of low molecular weight or containing several azide units tend to be explosive and are difficult to handle. Thus, some procedures to generate azides in situ with subsequent azide–alkyne cycloaddition have been reported.[28] In order to circumvent laborious purification by chromatography, we attempted to develop a convenient one-pot procedure for generating triazoles directly from amines and avoiding the isolation of the azide intermediates. Wittmann et al.[28c] reported a one-pot, two-step procedure, in which the first step was the generation of a series of azides from various primary amines by use of TfN_3 in combination with $CuSO_4$ and solid sodium hydrogen carbonate and the second step involved the addition of a terminal acetylene along with sodium ascorbate and the Cu^I-stabilising ligand TBTA. Even though Wittmann's procedure is highly optimised, there are several practical limitations to its employment in parallel or combinatorial synthesis, such as the use of TfN_3 and microwave irradiation for the CuAAC. An improved one-pot procedure utilising imidazole-1-sulfonyl azide hydrochloride as a substitute for TfN_3 has been reported by Smith et al.[28d] Although this procedure is experimentally simple and suitable for parallel chemistry, in particular avoiding the safety concerns associated with earlier procedures, the substrate scope of the method is very narrow. Moreover, in Smith's procedure, sodium ascorbate is added along with $CuSO_4$ in the first step, and could reduce Cu^{II} into Cu^I immediately, decreasing the efficiency of Cu^{II}-catalysed diazo transfer and resulting in the low yields for electron-deficient amines.

According to the optimal conditions for diazo transfer (Table 1) and CuAAC (Table 3), the combination of copper sulfate (0.05 equiv.) and DIPEA (2.0 equiv.) was chosen for the first-step reaction in DMF. After consumption of the aminocyclitol (TLC monitoring), sodium ascorbate (0.2 equiv.) was added to the reaction mixture to reduce the Cu^{II} into Cu^I, followed by the addition of the terminal alkyne. Finally, the triazole was acetylated under conventional conditions, and the desired product could be purified by

Table 4. Synthesis of different aminocyclitol-derived 1,2,3-triazoles.

Entry	Azide	Alkyne	Product	Yield[a] (%)	Entry	Azide	Alkyne	Product	Yield[a] (%)
1	**7**	 **12a**	 **13a**	87	16	**8**	**12f**	 **14f**	95
2	**7**	 **12b**	 **13b**	92	17	**8**	**12g**	 **14g**	84
3	**7**	 **12c**	 **13c**	82	18	**8**	**12h**	 **14h**	86
4	**7**	 **12d**	 **13d**	89	19	**8**	 **12k**	 **14i**	85
5	**7**	 **12e**	 **13e**	90	21	**9**	**12a**	 **15a**	88
6	**7**	 **12f**	 **13f**	93	22	**9**	**12b**	 **15b**	84
7	**7**	 **12g**	 **13g**	89	24	**9**	**12c**	 **15c**	82
8	**7**	 **12h**	 **13h**	91	23	**9**	**12d**	 **15d**	81
9	**7**	 **12i**	 **13i**	89	24	**9**	**12e**	 **15e**	85
10	**7**	 **12j**	 **13j**	86	25	**9**	**12f**	 **15f**	91
11	**8**	**12a**	 **14a**	92	26	**9**	**12g**	 **15g**	91
12	**8**	**12b**	 **14b**	93	27	**9**	**12i**	 **15h**	85
13	**8**	**12c**	 **14c**	87	28	**11**	**12a**	 **16a**	92
14	**8**	**12d**	 **14d**	91	29	**11**	**12d**	 **16b**	94
15	**8**	**12e**	 **14e**	89	30	**11**	**12g**	**16c**	92

[a] Isolated yields.

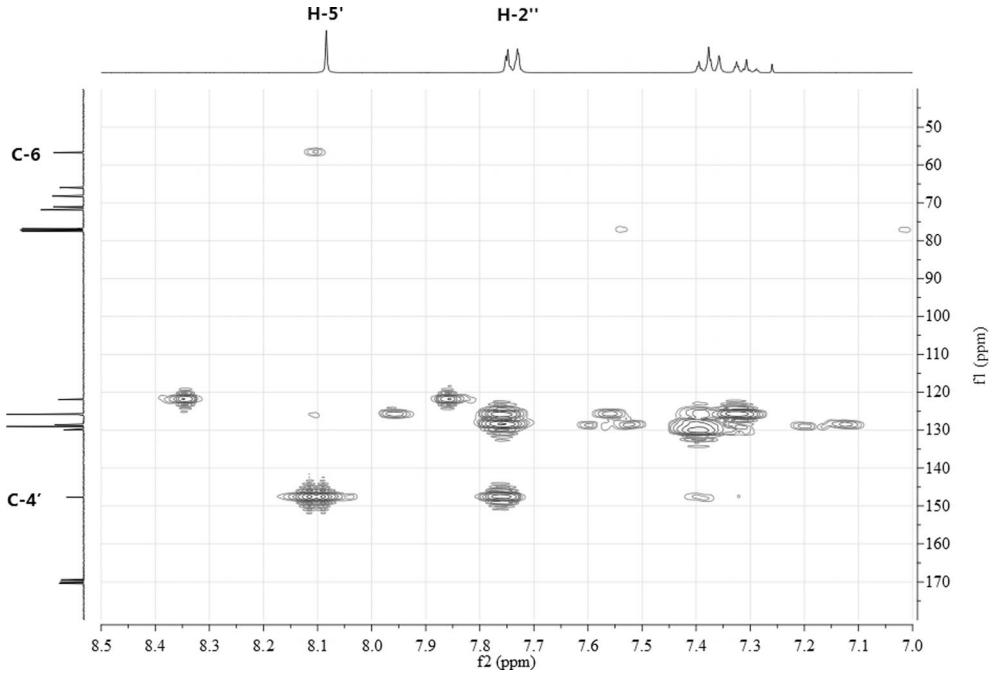


Figure 5. Expansion of the NOESY spectrum in the aromatic region.

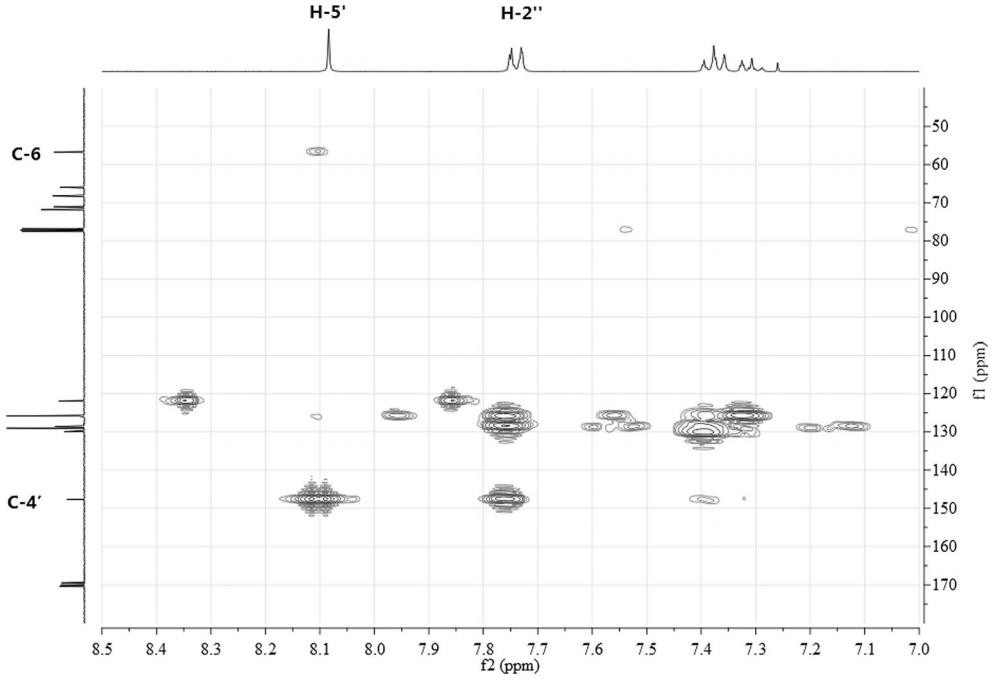


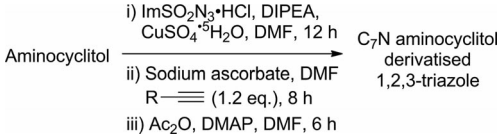
Figure 6. Expansion of the HMBC spectrum in the aromatic region.

the simplified procedure described above. The results with different substrates are listed in Table 5. The one-pot synthesis of triazolylaminocyclitols circumvented the need for purification of hazardous azides by chromatography and met the requirement of "click chemistry".

3. Conclusion

In conclusion, we have synthesised C_7N aminocyclitol derivatives of 1,2,3-triazoles by Cu^{II}-catalysed diazo transfer and CuAAC. A diazo moiety is transferred onto a C_7N

Table 5. One-pot synthesis of triazolylaminocyclitols.



Entry	Aminocyclitol	R–≡	Product	Yield [%][a]
1	**2**	**12a**	**13a**	76
2	**2**	**12b**	**13b**	80
3	**2**	**12c**	**13c**	75
4	**2**	**12d**	**13d**	72
5	**2**	**12e**	**13e**	73
6	**2**	**12f**	**13f**	83
7	**2**	**12g**	**13g**	83
8	**2**	**12h**	**13h**	82
9	**2**	**12i**	**13i**	81
10	**2**	**12j**	**13j**	76
11	**1**	**12a**	**14a**	86
12	**1**	**12b**	**14b**	85
13	**1**	**12c**	**14c**	76
14	**1**	**12d**	**14d**	80
15	**1**	**12e**	**14e**	78
16	**1**	**12f**	**14f**	89
17	**1**	**12g**	**14g**	72
18	**1**	**12h**	**14h**	76
19	**1**	**12k**	**14i**	75
20	**3**	**12a**	**15a**	75
21	**3**	**12b**	**15b**	78
22	**3**	**12c**	**15c**	72
23	**3**	**12d**	**15d**	73
24	**3**	**12e**	**15e**	74
25	**3**	**12f**	**15f**	83
26	**3**	**12g**	**15g**	80
27	**3**	**12i**	**15h**	78

[a] Isolated yields.

aminocyclitol derivative, such as validamine, valienamine or valiolamine, by employing imidazole-1-sulfonyl azide as the diazo transfer reagent with catalysis by Cu^{II} in moderate to good yields. The azidocyclitols can be linked with various terminal alkynes under Meldal's conditions with good to excellent yields. To circumvent laborious purification of products by chromatography, one-pot variants of the syntheses, as safer and more efficient procedures, were also investigated and gave moderate to good yields.

4. Experimental Section

4.1. General Methods: Melting points were determined with an X4-Data microscope melting point apparatus and are uncorrected. Optical rotation values were measured with a PerkinElmer P241 polarimeter operating at 589 nm. Infrared (IR) spectra were recorded with a Bruker Vector22 FT-IR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were measured at 400 MHz (^{1}H) or at 100 MHz (^{13}C) with a Bruker Avance DRX 400 spectrometer; HRMS were recorded with a Bruker MicroTOF-QII mass instrument (ESI). All reactions were monitored by analytical thin-layer chromatography (TLC, Merck) with detection by spraying with dodecamolybdophosphoric acid in ethanol (5%, w/v) or ninhydrin in ethanol (5%, w/v) and subsequent heating. Silica gel (300–400 mesh) was used for flash chromatography. All reagents and solvents were general reagent grade unless otherwise stated.

4.2. General Procedure for Preparation of Azide-Derivatised Aminocyclitols: Imidazole-1-sulfonyl azide hydrochloride (2.52 g, 12.0 mmol) was added to the aminocyclitol (10.0 mmol), K_2CO_3 (2.35 g, 17.0 mmol) and $CuSO_4 \cdot 5H_2O$ (25 mg, 0.1 mmol) in MeOH (25 mL), and the mixture was stirred at room temp. for 12 h. It was then concentrated and co-evaporated with toluene (20 mL × 2). Acetic anhydride was added to the residue in pyridine, and the mixture was stirred overnight. It was then concentrated under reduced pressure, diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were washed with hydrochloric acid (5%, 50 mL × 2), $NaHCO_3$ (5%, 50 mL × 2) and brine (50 mL × 2), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Flash chromatography gave the azide.

4.2.1 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-azidocyclohexane-1,2,3-triyl Triacetate (7): White crystalline solid (88%), m.p. 63.3–64.8 °C. $[\alpha]_D^{25}$ = +33.7 (*c* = 1.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.43 (t, *J* = 9.9 Hz, 1 H, 2-H), 5.00 (dd, *J* = 10.2, 3.5 Hz, 1 H, 1-H), 4.96 (dd, *J* = 10.2, 8.6 Hz, 1 H, 3-H), 4.17 (dd, *J* = 6.4, 3.3 Hz, 1 H, 6-H), 4.10 (dd, *J* = 11.5, 4.7 Hz, 1 H, C*H*HOAc), 3.90 (dd, *J* = 11.5, 3.1 Hz, 1 H, CH*H*OAc), 2.36–2.22 (m, 1 H, 4-H), 2.10 (s, 3 H, CH_3COO), 2.05 (s, 3 H, CH_3COO), 2.03 (s, 3 H, CH_3COO), 2.01 (s, 3 H, CH_3COO), 1.96 (dt, *J* = 14.7, 3.7 Hz, 1 H, 5-H), 1.75–1.61 (m, 1 H, 5-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.69 (CH_3COO), 169.97 (2 C, CH_3COO), 169.89 (CH_3COO), 73.63 (C-3), 71.30 (C-2), 71.12 (C-1), 62.80 (C-6), 58.86 (CH_2OAc), 34.68 (C-4), 28.98 (C-5), 20.69 (CH_3COO), 20.58 (CH_3COO), 20.57 (CH_3COO), 20.45 (CH_3COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2927, 2100, 1741, 1369, 1237, 1210, 1035, 967, 918, 726 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 121 (55), 122 (42), 138 (43), 181 (33), 198 (35), 240 (16), 312 (81), 330 (8), 372 (17) $[M]^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{15}H_{21}N_3NaO_8$ $[M + Na]^+$ 394.1226; found 394.1227.

4.2.2 (1*S*,2*S*,3*R*,6*S*)-4-(Acetoxymethyl)-6-azidocyclohex-4-ene-1,2,3-triyl Triacetate (8): White crystalline solid (92%), m.p. 58.6–59.2 °C. $[\alpha]_D^{25}$ = +103.7 (*c* = 0.98, $CHCl_3$) [ref.[23b] syrup and $[\alpha]_D^{20}$ = +40 (*c* = 1.0, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.95 (dd, *J* = 5.6, 1.0 Hz, 1 H, 5-H), 5.66 (d, *J* = 7.1 Hz, 1 H, 3-H), 5.50 (dd, *J* = 10.6, 7.2 Hz, 1 H, 2-H), 5.18 (dd, *J* = 10.6, 4.3 Hz, 1 H, 1-H), 4.70 (d, *J* = 13.4 Hz, 1 H, CH*H*OAc), 4.42 (d, *J* = 13.4 Hz, 1 H, C*H*HOAc), 4.42 (dd, *J* = 4.5, 5.7 Hz, 1 H, 6-H), 2.13 (s, 3 H, CH_3COO), 2.06 (s, 6 H, CH_3COO), 2.04 (s, 3 H, CH_3COO) ppm.[23a] ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.21 (CH_3COO), 169.04 (CH_3COO), 168.89 (CH_3COO), 168.82 (CH_3COO), 135.48 (C-4), 122.41 (C-5), 68.98 (C-1), 68.80 (C-3), 68.58 (C-2), 61.59 (CH_2OAc), 55.70 (C-6), 19.64 (2 C, CH_3COO), 19.58 (CH_3COO), 19.45 (CH_3COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2961, 2104, 1743, 1365, 1213, 1045, 977, 919, 867, 752 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 123 (64), 137 (45), 138 (36), 165 (82), 180 (38), 207 (36), 310 (44), 327 (46), 370 (1) $[M + 1]^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{15}H_{19}N_3NaO_8$ $[M + Na]^+$ 392.1070; found 392.1074.

CCDC-969693 (for **8**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.2.3 (1*S*,2*R*,3*S*,4*S*,6*S*)-4-(Acetoxymethyl)-6-azido-4-hydroxycyclohexane-1,2,3-triyl Triacetate (9): White crystalline solid (82%), m.p. 117.3–118.7 °C (ref.[29] 122.8–124.2 °C). $[\alpha]_D^{25}$ = –13.4 (*c* = 1.00, $CHCl_3$) [ref.[29] $[\alpha]_D^{20}$ = –13.2 (*c* = 2.00, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.64 (t, *J* = 10.2 Hz, 1 H, 2-H), 5.04 (dd, *J* = 10.4, 3.9 Hz, 1 H, 1-H), 5.01 (d, *J* = 10.2 Hz, 1 H, 3-H), 4.21

(q, J = 3.5 Hz, 1 H, 6-H), 3.95 (d, J = 11.4 Hz, 1 H, C*H*HOAc), 3.66 (d, J = 11.4 Hz, 1 H, CH*H*OAc), 3.39 (s, 1 H, O*H*), 2.08 (d, J = 3.0 Hz, 1 H, 5-H), 2.05 (s, 3 H, CH_3COO), 2.01 (s, 3 H, CH_3COO), 2.00 (s, 3 H, CH_3COO), 1.95 (s, 3 H, CH_3COO), 1.91 (d, J = 3.6 Hz, 1 H, 5-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.23 (CH$_3$*C*OO), 168.96 (CH$_3$*C*OO), 168.84 (CH$_3$*C*OO), 168.70 (CH$_3$*C*OO), 72.32 (C-4), 72.11 (C-3), 70.90 (C-2), 67.54 (C-1), 64.64 (*C*H$_2$OAc), 57.31 (C-6), 32.27 (C-5), 19.73 (*C*H$_3$COO), 19.54 (*C*H$_3$COO), 19.50 (*C*H$_3$COO), 19.40 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2927, 2105, 1739, 1375, 1229, 1162, 1038, 914, 810, 744 cm^{-1}. MS (EI): m/z (%) = 43 (100), 73 (32), 96 (22), 115 (89), 124 (25), 138 (43), 157 (85), 180 (49), 370 (88), 388 (8) [M + 1]$^+$. HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{21}N_3NaO_9$ [M + Na]$^+$ 410.1175; found 410.1176.

4.2.4 (1*R*,2*S*,3*R*,4*S*,5*R*,6*R*)-1-(Acetoxymethyl)-5-azido-7-oxabicyclo[4.1.0]heptane-2,3,4-triyl Triacetate (11): White crystalline solid (73%), m.p. 84.8–85.8 °C. $[\alpha]_D^{25}$ = +50.1 (c = 0.58, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.47 (d, J = 8.3 Hz, 1 H, 3-H), 5.28 (dd, J = 10.7, 8.3 Hz, 1 H, 2-H), 4.91 (dd, J = 10.7, 6.0 Hz, 1 H, 1-H), 4.29 (dd, J = 5.7, 4.9 Hz, 1 H, 6-H), 4.28 (d, J = 12.3 Hz, 1 H, C*H*HOAc), 3.81 (d, J = 12.3 Hz, 1 H, CH*H*OAc), 3.49 (d, J = 4.8 Hz, 1 H, 5-H), 2.05 (s, 3 H, CH_3COO), 2.05 (s, 3 H, CH_3COO), 2.02 (s, 3 H, CH_3COO), 1.95 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.06 (CH$_3$*C*OO), 168.99 (CH$_3$*C*OO), 168.95 (CH$_3$*C*OO), 168.33 (CH$_3$*C*OO), 68.76 (C-2), 68.60 (C-3), 66.63 (*C*H$_2$OAc), 60.82 (C-1), 59.35 (C-4), 56.18 (C-5), 54.47 (C-6), 19.55 (*C*H$_3$COO), 19.49 (*C*H$_3$COO), 19.48 (*C*H$_3$COO), 19.25 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2101, 1747, 1431, 1366, 1228, 1204, 1116, 1035, 742, 657 cm^{-1}. MS (EI): m/z (%) = 43 (100), 98 (55), 125 (46), 126 (48), 135 (59), 153 (73), 154 (94), 196 (78), 316 (32), 386 (2) [M + 1]$^+$. HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{19}N_3NaO_9$ [M + Na]$^+$ 408.1019; found 408.1022.

4.3 General Procedure for Synthesis of Aminocyclitol Triazoles by CuAAC. Method A: A solution of the appropriate azide (0.25 mmol) and CuI (5.0 mg, 0.025 mmol, 0.1 equiv.) in degassed DMF (5 mL) was stirred under nitrogen. The appropriate alkyne (0.30 mmol, 1.2 equiv.) was then added, followed by the addition of DIPEA (32.0 mg, 0.25 mmol, 1.0 equiv.). The solution was stirred at 100 °C under nitrogen, and the reaction was complete within 6 h as monitored by TLC (DCM/EtOAc 4:1). The mixture was allowed to cool to room temp. and then diluted with EtOAc (80 mL). The organic layer was washed with hydrochloric acid (5%, 50 mL × 3), $NaHCO_3$ (5%, 50 mL × 3) and brine (50 mL × 2), dried with anhydrous Na_2SO_4 and concentrated to dryness to afford a solid residue, which was washed with iced MeOH (2 mL) for alkynes **12a**–**f** or iced hexane (2 mL) for alkynes **12g**–**k**. After solvent removal under vacuum, the obtained solids were found to be analytically pure by TLC and NMR analyses (^{1}H and ^{13}C). **Method B:** Imidazole-1-sulfonyl azide hydrochloride (63.0 mg, 12.0 mmol) was added to the aminocyclitol (0.25 mmol), DIPEA (65.0 mg, 0.5 mmol) and $CuSO_4 \cdot 5H_2O$ (4.0 mg, 0. 025 mmol) in degassed DMF (5 mL) and the mixture was stirred at room temp. for 12 h. Sodium ascorbate (20.0 mg, 0.1 mmol) and the selected alkyne (0.30 mmol, 1.2 equiv.) were added to the reaction mixture, which was stirred at 100 °C under nitrogen for 8 h. Acetic anhydride (160 mg, 1.5 mmol) and DMAP (5 mg) were added to the residue, which was stirred overnight. The mixture was diluted with H_2O (10 mL) and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with hydrochloric acid (5%, 10 mL × 2), $NaHCO_3$ (5%, 10 mL × 2) and brine (10 mL × 2), dried with anhydrous Na_2SO_4, filtered and concentrated to dryness to afford a solid residue, which was washed with iced MeOH (2 mL).

4.3.1 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)cyclohexane-1,2,3-triyl Triacetate (13a): This compound was prepared from **7** (93 mg, 0.25 mmol) and phenylacetylene (31 mg, 0.30 mmol) by **Method A** (103 mg, 87%) or from **2** by **Method B** (90 mg, 76%), as colourless needles, m.p. 227.3–228.1 °C. $[\alpha]_D^{25}$ = +87.6 (c = 1.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (dd, J = 5.1, 3.3 Hz, 2 H, Ar-H), 7.72 (s, 1 H, triazole H), 7.36 (t, J = 7.5 Hz, 2 H, Ar-H), 7.32–7.24 (m, 1 H, Ar-H), 5.72 (t, J = 9.7 Hz, 1 H, 2-H), 5.13 (dd, J = 10.0, 5.2 Hz, 1 H, 1-H), 5.10 (dd, J = 4.8, 3.2 Hz, 1 H, 3-H), 5.09 (dd, J = 6.2, 3.1 Hz, 1 H, 6-H), 4.10 (dd, J = 11.6, 4.7 Hz, 1 H, C*H*HOAc), 3.86 (dd, J = 11.6, 3.0 Hz, 1 H, CH*H*OAc), 2.99 (ddd, J = 13.8, 9.6, 3.8 Hz, 1 H, 4-H), 2.43–2.26 (m, 1 H, 5-H), 2.12–2.02 (m, 1 H, 5-H), 1.98 (s, 3 H, CH_3COO), 1.98 (s, 3 H, CH_3COO), 1.92 (s, 3 H, CH_3COO), 1.88 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.75 (CH$_3$*C*OO), 169.18 (CH$_3$*C*OO), 169.07 (CH$_3$*C*OO), 168.50 (CH$_3$*C*OO), 146.09 (triazole-C$_{quat}$), 129.09 (Ar-C$_{quat}$), 127.92 (Ar-C), 127.42 (Ar-C), 124.73 (Ar-C), 120.40 (triazole-C), 70.82 (C-3), 70.19 (C-2), 70.16 (C-1), 61.76 (C-6), 55.92 (*C*H$_2$OAc), 34.80 (C-4), 28.30 (C-5), 19.73 (*C*H$_3$COO), 19.62 (*C*H$_3$COO), 19.58 (*C*H$_3$COO), 19.56 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3046, 1734, 1436, 1382, 1228, 1032, 971, 894, 763, 694 cm^{-1}. MS (EI): m/z (%) = 43 (100), 107 (87), 116 (54), 125 (96), 149 (42), 167 (51), 185 (41), 223 (53), 403 (21), 473 (14) [M]$^+$, 474 (7) [M + 1]$^+$. HRMS (ESI-TOF): m/z calcd. for $C_{23}H_{28}N_3O_8$ [M + H]$^+$ 474.1876; found 474.1866.

4.3.2 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-methylphenyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (13b): This compound was prepared from **7** (93 mg, 0.25 mmol) and (4-methylphenyl)acetylene (35 mg, 0.30 mmol) by **Method A** (112 mg, 92%) or from **2** by **Method B** (98 mg, 80%), as a white solid, m.p. 230.2–230.9 °C. $[\alpha]_D^{25}$ = +99.9 (c = 1.08, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (s, 1 H, triazole H), 7.65 (d, J = 8.1 Hz, 2 H, Ar-H), 7.17 (d, J = 7.9 Hz, 2 H, Ar-H), 5.72 (t, J = 9.8 Hz, 1 H, 2-H), 5.13 (dd, J = 6.2, 3.9 Hz, 1 H, 1-H), 5.10 (dd, J = 4.5, 2.8 Hz, 1 H, 3-H), 5.07 (dd, J = 6.4, 2.9 Hz, 1 H, 6-H), 4.10 (dd, J = 11.6, 4.7 Hz, 1 H, C*H*HOAc), 3.86 (dd, J = 11.6, 3.1 Hz, 1 H, CH*H*OAc), 3.10–2.88 (m, 1 H, 4-H), 2.40–2.32 (m, 1 H, 5-H), 2.31 (s, 3 H, ArCH_3), 2.10–2.02 (m, 1 H, 5-H), 1.98 (s, 3 H, CH_3COO), 1.98 (s, 3 H, CH_3COO), 1.92 (s, 3 H, CH_3COO), 1.87 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.75 (CH$_3$*C*OO), 169.17 (CH$_3$*C*OO), 169.08 (CH$_3$*C*OO), 168.48 (CH$_3$*C*OO), 146.16 (triazole-C$_{quat}$), 137.30 (Ar-C$_{quat}$), 128.59 (Ar-C), 126.29 (Ar-C$_{quat}$), 124.64 (Ar-C), 120.04 (triazole-C), 70.86 (C-3), 70.20 (C-2), 70.18 (C-1), 61.77 (C-6), 55.83 (*C*H$_2$OAc), 34.79 (C-4), 28.31 (C-5), 20.28 (Ar*C*H$_3$), 19.73 (*C*H$_3$COO), 19.63 (*C*H$_3$COO), 19.59 (*C*H$_3$COO), 19.57 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3044, 1733, 1436, 1368, 1264, 1220, 1032, 979, 888, 790 cm^{-1}. MS (EI): m/z (%) = 43 (100), 107 (73), 125 (80), 130 (72), 131 (90), 149 (44), 237 (100), 416 (43), 417 (41), 487 (19) [M]$^+$, 488 (8) [M + 1]$^+$. HRMS (ESI-TOF): m/z calcd. for $C_{24}H_{30}N_3O_8$ [M + H]$^+$ 488.2033; found 488.2021.

4.3.3 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (13c): This compound was prepared from **7** (93 mg, 0.25 mmol) and (4-methoxyphenyl)acetylene (40 mg, 0.30 mmol) by **Method A** (103 mg, 82%) or from **2** by **Method B** (95 mg, 75%), as a white solid, m.p. 195.0–195.3 °C. $[\alpha]_D^{25}$ = +103.2 (c = 1.24, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.8 Hz, 2 H, Ar-H), 7.64 (s, 1 H, triazole H), 6.89 (d, J = 8.9 Hz, 2 H, Ar-H), 5.72 (t, J = 9.8 Hz, 1 H, 2-H), 5.13 (dd, J = 6.7, 3.5 Hz, 1 H, 1-H), 5.09 (dd, J = 4.6, 3.0 Hz, 1 H, 3-H), 5.07 (t, J = 3.1 Hz, 1 H, 6-H), 4.10 (dd, J = 11.6, 4.7 Hz, 1 H, C*H*HOAc), 3.85 (dd, J = 11.6, 3.1 Hz,

1 H, CH*H*OAc), 3.77 (s, 3 H, ArOCH_3), 2.98 (dtt, *J* = 10.5, 7.0, 3.5 Hz, 1 H, 4-H), 2.41–2.24 (m, 1 H, 5-H), 2.11–2.01 (m, 1 H, 5-H), 1.98 (s, 3 H, CH_3COO), 1.98 (s, 3 H, CH_3COO), 1.92 (s, 3 H, CH_3COO), 1.87 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.75 (CH$_3$*C*OO), 169.17 (CH$_3$*C*OO), 169.07 (CH$_3$*C*OO), 168.49 (CH$_3$*C*OO), 158.77 (Ar-C$_{quat}$), 145.94 (triazole-C$_{quat}$), 126.04 (Ar-C), 121.81 (Ar-C$_{quat}$), 119.61 (triazole-C), 113.32 (Ar-C), 70.84 (C-3), 70.22 (C-2), 70.19 (C-1), 61.79 (C-6), 55.82 (*C*H$_2$OAc), 54.32 (ArO*C*H$_3$), 34.80 (C-4), 28.31 (C-5), 19.73 (*C*H$_3$COO), 19.63 (*C*H$_3$COO), 19.60 (*C*H$_3$COO), 19.57 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2960, 1733, 1499, 1369, 1246, 1222, 1032, 980, 810, 788 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 132 (44), 146 (57), 147 (69), 176 (38), 253 (100), 254 (52), 432 (66), 433 (39), 503 (23) $[M]^+$, 504 (9) $[M + 1]^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{24}H_{30}N_3O_9$ $[M + H]^+$ 504.1982; found 504.1988.

4.3.4 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (13d): This compound was prepared from **7** (93 mg, 0.25 mmol) and (4-chlorophenyl)acetylene (41 mg, 0.30 mmol) by **Method A** (113 mg, 89%) or from **2** by **Method B** (92 mg, 72%), as a white solid, m.p. 232.8–234.1 °C. $[\alpha]_D^{25}$ = +93.0 (*c* = 1.34, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (s, 1 H, triazole H), 7.70 (d, *J* = 8.6 Hz, 2 H, Ar-H), 7.33 (d, *J* = 8.6 Hz, 2 H, Ar-H), 5.70 (t, *J* = 10.0 Hz, 1 H, 2-H), 5.14 (dd, *J* = 10.7, 4.6 Hz, 1 H, 1-H), 5.10 (dd, *J* = 4.4, 2.4 Hz, 1 H, 3-H), 5.09 (dd, *J* = 4.7, 2.7 Hz, 1 H, 6-H), 4.10 (dd, *J* = 11.6, 4.7 Hz, 1 H, C*H*HOAc), 3.86 (dd, *J* = 11.6, 3.1 Hz, 1 H, CH*H*OAc), 3.05–2.84 (m, 1 H, 4-H), 2.40–2.30 (m, 1 H, 5-H), 2.14–2.03 (m, 1 H, 5-H), 1.99 (s, 3 H, CH_3COO), 1.98 (s, 3 H, CH_3COO), 1.92 (s, 3 H, CH_3COO), 1.88 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.73 (CH$_3$*C*OO), 169.14 (CH$_3$*C*OO), 169.01 (CH$_3$*C*OO), 168.52 (CH$_3$*C*OO), 145.08 (triazole-C$_{quat}$), 133.15 (Ar-C$_{quat}$), 128.13 (Ar-C), 127.66 (Ar-C$_{quat}$), 125.99 (Ar-C), 120.46 (triazole-C), 70.77 (C-3), 70.15 (C-2), 70.09 (C-1), 61.74 (C-6), 56.05 (*C*H$_2$OAc), 34.81 (C-4), 28.29 (C-5), 19.73 (*C*H$_3$COO), 19.63 (*C*H$_3$COO), 19.59 (*C*H$_3$COO), 19.56 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3045, 1739, 1443, 1380, 1224, 1092, 1063, 1032, 971, 802 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 91 (39), 107 (84), 125 (90), 150 (50), 167 (44), 185 (35), 257 (54), 437 (19), 507 (8) $[M]^+$, 508 (4) $[M + 1]^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{27}ClN_3O_8$ $[M + H]^+$ 508.1487; found 508.1481.

4.3.5 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (13e): This compound was prepared from **7** (93 mg, 0.25 mmol) and (4-fluorophenyl)acetylene (36 mg, 0.30 mmol) by **Method A** (110 mg, 90%) or from **2** by **Method B** (90 mg, 73%), as a white solid, m.p. 214.1–215.6 °C. $[\alpha]_D^{25}$ = +101.8 (*c* = 1.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.71 (m, 2 H, Ar-H), 7.71 (s, 1 H, triazole H), 7.12–6.96 (m, 2 H, Ar-H), 5.71 (t, *J* = 9.8 Hz, 1 H, 2-H), 5.14 (dd, *J* = 11.2, 4.1 Hz, 1 H, 1-H), 5.11 (dd, *J* = 9.5, 3.4 Hz, 1 H, 3-H), 5.09 (dd, *J* = 6.3, 3.1 Hz, 1 H, 6-H), 4.10 (dd, *J* = 11.6, 4.7 Hz, 1 H, C*H*HOAc), 3.86 (dd, *J* = 11.6, 3.1 Hz, 1 H, CH*H*OAc), 3.02–2.91 (m, 1 H, 4-H), 2.42–2.27 (m, 1 H, 5-H), 2.08 (ddd, *J* = 15.1, 13.2, 4.4 Hz, 1 H, 5-H), 1.98 (s, 6 H, CH_3COO), 1.92 (s, 3 H, CH_3COO), 1.88 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.73 (CH$_3$*C*OO), 169.14 (CH$_3$*C*OO), 169.01 (CH$_3$*C*OO), 168.53 (CH$_3$*C*OO), 161.77 (d, $^1J_{C,F}$ = 247.6 Hz, Ar-C$_{quat}$), 145.26 (triazole-C$_{quat}$), 126.51 (d, $^3J_{C,F}$ = 8.2 Hz, Ar-C), 125.40 (d, $^4J_{C,F}$ = 3.2 Hz, Ar-C$_{quat}$), 120.20 (triazole-C), 114.92 (d, $^2J_{C,F}$ = 21.8 Hz, Ar-C), 70.79 (C-3), 70.21 (C-2), 70.14 (C-1), 61.79 (C-6), 56.01 (*C*H$_2$OAc), 34.84 (C-4), 28.30 (C-5), 19.72 (*C*H$_3$COO), 19.61 (*C*H$_3$COO), 19.58 (*C*H$_3$COO), 19.55 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3044, 1736, 1444, 1382, 1261, 1225, 1032, 970, 840, 797 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 107 (100), 125 (100), 134 (83), 201 (76), 229 (100), 241 (100), 420 (50), 421 (79), 491 (28) $[M]^+$, 492 (14) $[M + 1]^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{27}FN_3O_8$ $[M + H]^+$ 492.1782; found 492.1778.

4.3.6 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-nitrophenyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (13f): This compound was prepared from **7** (93 mg, 0.25 mmol) and (4-nitrophenyl)acetylene (44 mg, 0.30 mmol) by **Method A** (120 mg, 93%) or from **2** by **Method B** (108 mg, 83%), as a white solid, m.p. 208.5–210.2 °C. $[\alpha]_D^{25}$ = +101.4 (*c* = 0.22, $CHCl_3$). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.90 (s, 1 H, triazole H), 8.34 (d, *J* = 8.9 Hz, 2 H, Ar-H), 8.15 (d, *J* = 8.9 Hz, 2 H, Ar-H), 5.61 (t, *J* = 9.9 Hz, 1 H, 2-H), 5.45 (dd, *J* = 10.5, 5.2 Hz, 1 H, 1-H), 5.27 (dd, *J* = 4.5, 2.8 Hz, 1 H, 3-H), 5.22 (dd, *J* = 10.9, 9.6 Hz, 1 H, 6-H), 4.04 (dd, *J* = 11.3, 5.6 Hz, 1 H, C*H*HOAc), 3.93 (dd, *J* = 11.2, 4.0 Hz, 1 H, CH*H*OAc), 2.93 (qd, *J* = 10.5, 5.1 Hz, 1 H, 4-H), 2.36–2.24 (m, 1 H, 5-H), 2.21 (ddd, *J* = 14.9, 4.9, 2.6 Hz, 1 H, 5-H), 2.03 (s, 3 H, CH_3COO), 2.00 (s, 3 H, CH_3COO), 1.93 (s, 3 H, CH_3COO), 1.88 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 170.70 (CH$_3$*C*OO), 170.16 (CH$_3$*C*OO), 169.87 (CH$_3$*C*OO), 169.80 (CH$_3$*C*OO), 147.19 (triazole-C$_{quat}$), 144.00 (Ar-C$_{quat}$), 137.30 (Ar-C$_{quat}$), 126.51 (Ar-C), 126.47 (triazole-C), 124.90 (Ar-C), 71.96 (C-3), 71.41 (C-2), 70.58 (C-1), 63.93 (C-6), 57.66 (*C*H$_2$OAc), 36.40 (C-4), 28.73 (C-5), 21.00 (*C*H$_3$COO), 20.88 (*C*H$_3$COO), 20.83 (*C*H$_3$COO), 20.71 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3102, 1755, 1732, 1509, 1354, 1255, 1032, 971, 840, 805 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 107 (100), 125 (100), 167 (89), 185 (77), 227 (68), 268 (57), 431 (24), 448 (49), 518 (9) $[M]^+$, 519 (6) $[M + 1]^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{27}N_4O_{10}$ $[M + H]^+$ 519.1727; found 519.1712.

4.3.7 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-(4-butyl-1*H*-1,2,3-triazol-1-yl)cyclohexane-1,2,3-triyl Triacetate (13g): This compound was prepared from **7** (186 mg, 0.50 mmol) and hex-1-yne (49 mg, 0.60 mmol) by **Method A** (202 mg, 89%) or from **2** by **Method B** (188 mg, 83%), as a white solid, m.p. 161.0–161.7 °C. $[\alpha]_D^{25}$ = +103.5 (*c* = 0.51, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (s, 1 H, triazole H), 5.62 (t, *J* = 9.9 Hz, 1 H, 2-H), 5.08 (dd, *J* = 10.4, 5.4 Hz, 1 H, 1-H), 5.07 (dd, *J* = 10.2, 5.0 Hz, 1 H, 3-H), 4.98 (dd, *J* = 7.4, 4.5 Hz, 1 H, 6-H), 4.10 (dd, *J* = 11.6, 4.5 Hz, 1 H, C*H*HOAc), 3.85 (dd, *J* = 11.6, 2.9 Hz, 1 H, CH*H*OAc), 3.11–2.86 (m, 1 H, 4-H), 2.66 (t, *J* = 7.7 Hz, 2 H, CH_2), 2.37–2.23 (m, 1 H, 5-H), 2.08–2.01 (m, 1 H, 5-H), 1.99 (s, 3 H, CH_3COO), 1.98 (s, 3 H, CH_3COO), 1.92 (s, 3 H, CH_3COO), 1.88 (s, 3 H, CH_3COO), 1.67–1.52 (m, 2 H, CH_2), 1.40–1.23 (m, 2 H, CH_2), 0.87 (t, *J* = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.72 (CH$_3$*C*OO), 169.13 (CH$_3$*C*OO), 168.95 (CH$_3$*C*OO), 168.46 (CH$_3$*C*OO), 146.72 (triazole-C$_{quat}$), 121.47 (triazole-C), 70.94 (C-3), 70.24 (C-2), 70.17 (C-1), 61.80 (C-6), 55.40 (*C*H$_2$OAc), 34.83 (C-4), 30.42 (*C*H$_2$), 28.18 (C-5), 24.16 (*C*H$_2$), 21.25 (*C*H$_2$), 19.73 (*C*H$_3$COO), 19.63 (*C*H$_3$COO), 19.57 (*C*H$_3$COO), 19.54 (*C*H$_3$COO), 12.78 (*C*H$_3$) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2961, 2856, 1733, 1437, 1382, 1033, 971, 894, 837, 795 cm^{-1}. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{21}H_{32}N_3O_8$ $[M + H]^+$ 454.2189; found 454.2195.

4.3.8 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-(4-pentyl-1*H*-1,2,3-triazol-1-yl)cyclohexane-1,2,3-triyl Triacetate (13h): This compound was prepared from **7** (193 mg, 0.50 mmol) and hept-1-yne (60 mg, 0.60 mmol) by **Method A** (220 mg, 91%) or from **2** by **Method B** (199 mg, 82%), as a white solid, m.p. 149.1–150.0 °C. $[\alpha]_D^{25}$ = +97.7 (*c* = 0.26, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (s, 1 H, triazole H), 5.62 (t, *J* = 9.9 Hz, 1 H, 2-H), 5.09 (dd, *J* = 10.0, 5.0 Hz, 1 H, 1-H), 5.07 (dd, *J* = 10.4, 5.1 Hz, 1 H, 3-H),

4.98 (dd, J = 7.2, 4.5 Hz, 1 H, 6-H), 4.10 (dd, J = 11.6, 4.5 Hz, 1 H, C*H*HOAc), 3.85 (dd, J = 11.6, 2.9 Hz, 1 H, CH*H*OAc), 3.13–2.84 (m, 1 H, 4-H), 2.65 (t, J = 7.7 Hz, 2 H, CH_2), 2.37–2.20 (m, 1 H, 5-H), 2.11–2.01 (m, 1 H, 5-H), 1.99 (s, 3 H, CH_3COO), 1.98 (s, 3 H, CH_3COO), 1.92 (s, 3 H, CH_3COO), 1.88 (s, 3 H, CH_3COO), 1.69–1.54 (m, 2 H, CH_2), 1.35–1.23 [m, 4 H, (CH_2)$_2$], 0.83 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.72 (CH$_3$*C*OO), 169.13 (CH$_3$*C*OO), 168.95 (CH$_3$*C*OO), 168.45 (CH$_3$*C*OO), 146.78 (triazole-C$_{quat}$), 121.44 (triazole-C), 70.96 (C-3), 70.24 (C-2), 70.17 (C-1), 61.78 (C-6), 55.40 (*C*H$_2$OAc), 34.82 (C-4), 30.39 (*C*H$_2$), 28.20 (C-5), 28.00 (*C*H$_2$), 24.46 (*C*H$_2$), 21.38 (*C*H$_2$), 19.73 (*C*H$_3$COO), 19.63 (*C*H$_3$COO), 19.57 (*C*H$_3$COO), 19.54 (*C*H$_3$COO), 12.98 (*C*H$_3$) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2957, 2928, 1734, 1437, 1382, 1231, 1033, 970, 888, 796 cm^{-1}. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{22}H_{34}N_3O_8$ [M + H]$^+$ 468.2346; found 468.2349.

4.3.9 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(phenoxymethyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (13i): This compound was prepared from **7** (186 mg, 0.50 mmol) and propargyl phenyl ether (79 mg, 0.60 mmol) by **Method A** (225 mg, 89%) or from **2** by **Method B** (204 mg, 81%), as a white solid, m.p. 143.5–143.8 °C. $[\alpha]_D^{25}$ = +86.0 (c = 0.40, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1 H, triazole H), 7.22 (dd, J = 8.7, 7.2 Hz, 2 H, Ar-H), 6.90 (t, J = 8.5 Hz, 3 H, Ar-H), 5.62 (t, J = 9.8 Hz, 1 H, 2-H), 5.17 (s, 2 H, CH_2OPh), 5.10 (dd, J = 7.3, 2.1 Hz, 1 H, 1-H), 5.07 (dd, J = 7.3, 2.0 Hz, 1 H, 3-H), 5.02 (dd, J = 7.4, 4.6 Hz, 1 H, 6-H), 4.10 (dd, J = 11.6, 4.7 Hz, 1 H, C*H*HOAc), 3.85 (dd, J = 11.6, 3.0 Hz, 1 H, CH*H*OAc), 3.13–2.86 (m, 1 H, 4-H), 2.39–2.21 (m, 1 H, 5-H), 2.10–1.99 (m, 1 H, 5-H), 1.98 (s, 3 H, CH_3COO), 1.98 (s, 3 H, CH_3COO), 1.91 (s, 3 H, CH_3COO), 1.78 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.69 (CH$_3$*C*OO), 169.10 (CH$_3$*C*OO), 168.95 (CH$_3$*C*OO), 168.43 (CH$_3$*C*OO), 157.08 (Ar-C$_{quat}$), 142.83 (triazole-C$_{quat}$), 128.58 (Ar-C), 123.59 (Ar-C), 120.33 (triazole-C), 113.76 (Ar-C), 70.75 (C-3), 70.16 (C-2), 70.07 (C-1), 61.75 (C-6), 60.87 (*C*H$_2$OPh), 55.88 (*C*H$_2$OAc), 34.83 (C-4), 28.11 (C-5), 19.72 (*C*H$_3$COO), 19.62 (*C*H$_3$COO), 19.55 (*C*H$_3$COO), 19.40 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2962, 2929, 1737, 1598, 1496, 1381, 1232, 1032, 818, 751 cm^{-1}. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{24}H_{29}N_3O_9$ [M + H]$^+$ 503.1904; found 503.1909.

4.3.10 (1*S*,2*S*,3*R*,4*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(methoxycarbonyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (13j): This compound was prepared from **7** (186 mg, 0.50 mmol) and methyl propargylate (50 mg, 0.60 mmol) by **Method A** (196 mg, 86%) or from **2** by **Method B** (172 mg, 76%), as a pink solid, m.p. 175.4–176.4 °C. $[\alpha]_D^{25}$ = +91.5 (c = 0.47, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (s, 1 H, triazole H), 5.55 (t, J = 9.7 Hz, 1 H, 2-H), 5.15 (dd, J = 10.2, 5.1 Hz, 1 H, 1-H), 5.12 (dd, J = 7.1, 3.8 Hz, 1 H, 3-H), 5.08 (d, J = 10.4 Hz, 1 H, 6-H), 4.10 (dd, J = 11.5, 4.6 Hz, 1 H, C*H*HOAc), 3.90 (s, 3 H, OCH_3), 3.86 (dd, J = 11.5, 2.5 Hz, 1 H, CH*H*OAc), 2.98–2.78 (m, 1 H, 4-H), 2.42–2.31 (m, 1 H, 5-H), 2.17–2.04 (m, 1 H, 5-H), 1.99 (s, 6 H, CH_3COO), 1.92 (s, 3 H, CH_3COO), 1.90 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.65 (CH$_3$*C*OO), 169.05 (CH$_3$*C*OO), 168.75 (CH$_3$*C*OO), 168.39 (CH$_3$*C*OO), 159.99 (*C*O$_2$Me), 138.43 (triazole-C$_{quat}$), 128.48 (triazole-C), 70.21 (C-3), 70.01 (C-2), 69.92 (C-1), 61.77 (C-6), 56.61 (*C*H$_2$OAc), 51.25 (O*C*H$_3$), 34.87 (C-4), 27.98 (C-5), 19.71 (*C*H$_3$COO), 19.61 (*C*H$_3$COO), 19.50 (2 C, *C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3133, 2924, 1736, 1548, 1368, 1222, 1034, 981, 839, 777 cm^{-1}. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{19}H_{25}N_3O_{10}$ [M + H]$^+$ 455.1540; found 455.1536.

4.3.11 (1*S*,2*S*,3*R*,6*S*)-4-(Acetoxymethyl)-6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)cyclohex-4-ene-1,2,3-triyl Triacetate (14a): This compound was prepared from **8** (92 mg, 0.25 mmol) and phenylacetylene (31 mg, 0.30 mmol) by **Method A** (108 mg, 92%) or from **2** by **Method B** (101 mg, 86%), as a white solid, m.p. 177.8–178.1 °C. $[\alpha]_D^{25}$ = +198.2 (c = 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (s, 1 H, triazole H), 7.77 (d, J = 7.1 Hz, 2 H, Ar-H), 7.36 (t, J = 7.5 Hz, 2 H, Ar-H), 7.27 (t, J = 7.4 Hz, 1 H, Ar-H), 6.01 (dd, J = 4.8, 0.7 Hz, 1 H, 5-H), 5.74 (t, J = 5.1 Hz, 1 H, 2-H), 5.56–5.39 (m, 2 H, 3-H and 1-H), 5.25 (dd, J = 10.2, 5.5 Hz, 1 H, 6-H), 4.72 (d, J = 13.8 Hz, 1 H, C*H*HOAc), 4.49 (d, J = 13.8 Hz, 1 H, CH*H*OAc), 2.04 (s, 3 H, CH_3COO), 2.02 (s, 3 H, CH_3COO), 1.97 (s, 3 H, CH_3COO), 1.89 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.21 (CH$_3$*C*OO), 169.16 (CH$_3$*C*OO), 168.91 (CH$_3$*C*OO), 168.60 (CH$_3$*C*OO), 146.93 (triazole-C$_{quat}$), 136.89 (C-4), 129.25 (Ar-C$_{quat}$), 127.86 (Ar-C), 127.35 (Ar-C), 124.81 (Ar-C), 120.29 (Ar-C), 118.59 (triazole-C), 69.37 (C-1), 67.32 (C-3), 67.11 (C-2), 61.65 (*C*H$_2$OAc), 54.68 (C-6), 19.71 (*C*H$_3$COO), 19.68 (*C*H$_3$COO), 19.62 (*C*H$_3$COO), 19.53 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 1736, 1432, 1376, 1228, 1164, 1110, 973, 810, 763, 695 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 116 (82), 123 (40), 124 (34), 166 (84), 208 (6), 221 (6), 239 (3), 281 (2), 471 (2) [M]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{26}N_3O_8$ [M + H]$^+$ 472.1720; found 472.1725.

4.3.12 (1*S*,2*S*,3*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-methylphenyl)-1*H*-1,2,3-triazol-1-yl]cyclohex-4-ene-1,2,3-triyl Triacetate (14b): This compound was prepared from **8** (92 mg, 0.25 mmol) and 4-methyl phenylacetylene (35 mg, 0.30 mmol) by **Method A** (113 mg, 93%) or from **1** by **Method B** (103 mg, 85%), as a white solid, m.p. 139.3–140.5 °C. $[\alpha]_D^{25}$ = +211.6 (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 1 H, triazole H), 7.66 (d, J = 8.1 Hz, 2 H, Ar-H), 7.16 (d, J = 8.0 Hz, 2 H, Ar-H), 6.00 (dd, J = 4.9, 1.1 Hz, 1 H, 5-H), 5.73 (t, J = 5.1 Hz, 1 H, 2-H), 5.55–5.41 (m, 2 H, 3-H and 1-H), 5.25 (dd, J = 9.7, 5.4 Hz, 1 H, 6-H), 4.72 (d, J = 13.8 Hz, 1 H, C*H*HOAc), 4.48 (d, J = 13.8 Hz, 1 H, CH*H*OAc), 2.30 (s, 3 H, ArCH_3), 2.04 (s, 3 H, CH_3COO), 2.01 (s, 3 H, CH_3COO), 1.96 (s, 3 H, CH_3COO), 1.89 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.20 (CH$_3$*C*OO), 169.13 (CH$_3$*C*OO), 168.90 (CH$_3$*C*OO), 168.57 (CH$_3$*C*OO), 147.00 (triazole-C$_{quat}$), 137.21 (C-4), 136.75 (Ar-C$_{quat}$), 128.52 (Ar-C), 126.45 (Ar-C$_{quat}$), 124.73 (Ar-C), 120.43 (C-5), 118.23 (triazole-C), 69.26 (C-1), 67.41 (C-3), 67.12 (C-2), 61.67 (*C*H$_2$OAc), 54.65 (C-6), 20.27 (Ar*C*H$_3$), 19.69 (*C*H$_3$COO), 19.67 (*C*H$_3$COO), 19.61 (*C*H$_3$COO), 19.52 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2964, 1732, 1438, 1365, 1264, 1219, 1031, 974, 819, 786 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 123 (100), 130 (100), 165 (69), 166 (100), 208 (34), 235 (40), 253 (25), 295 (15), 485 (14) [M]$^+$, 486 (6) [M + 1]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{24}H_{28}N_3O_8$ [M + H]$^+$ 486.1876; found 486.1881.

4.3.13 (1*S*,2*S*,3*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl]cyclohex-4-ene-1,2,3-triyl Triacetate (14c): This compound was prepared from **8** (92 mg, 0.25 mmol) and 4-methoxy phenylacetylene (40 mg, 0.30 mmol) by **Method A** (109 mg, 87%) or from **1** by **Method B** (95 mg, 76%), as colourless needles, m.p. 112.1–113.0 °C. $[\alpha]_D^{25}$ = +221.2 (c = 0.54, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1 H, triazole H), 7.69 (d, J = 8.7 Hz, 2 H, Ar-H), 6.88 (d, J = 8.8 Hz, 2 H, Ar-H), 6.00 (dd, J = 4.9, 1.2 Hz, 1 H, 5-H), 5.72 (t, J = 5.1 Hz, 1 H, 2-H), 5.56–5.42 (m, 2 H, 3-H and 1-H), 5.24 (dd, J = 10.1, 5.5 Hz, 1 H, 6-H), 4.72 (d, J = 13.9 Hz, 1 H, C*H*HOAc), 4.48 (d, J = 13.8 Hz, 1 H, CH*H*OAc), 3.76 (s, 3 H, ArOCH_3), 2.04 (s, 3 H, CH_3COO), 2.01 (s, 3 H, CH_3COO), 1.96 (s, 3 H, CH_3COO), 1.89 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.21 (CH$_3$*C*OO), 169.14 (CH$_3$*C*OO), 168.91 (CH$_3$*C*OO), 168.60 (CH$_3$*C*OO), 158.74 (Ar-C$_{quat}$), 146.77 (triazole-C$_{quat}$), 136.74 (C-4), 126.13 (Ar-C), 121.99 (Ar-C$_{quat}$), 120.45 (C-5), 117.79 (triazole-

C), 113.27 (Ar-C), 69.33 (C-1), 67.40 (C-3), 67.13 (C-2), 61.67 (*C*H$_2$OAc), 54.64 (C-6), 54.31 (ArO*C*H$_3$), 19.70 (*C*H$_3$COO), 19.67 (*C*H$_3$COO), 19.62 (*C*H$_3$COO), 19.53 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3044, 1732, 1499, 1451, 1365, 1244, 1220, 1028, 812, 785 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 123 (87), 146 (100), 147 (71), 166 (65), 258 (92), 269 (46), 311 (29), 354 (35), 501 (12) [M]$^+$, 502 (4) [M + 1]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{24}H_{28}N_3O_9$ [M + H]$^+$ 502.1826; found 502.1827.

4.3.14 (1*S*,2*S*,3*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl]cyclohex-4-ene-1,2,3-triyl Triacetate (14d): This compound was prepared from **8** (92 mg, 0.25 mmol) and (4-chlorophenyl)acetylene (41 mg, 0.30 mmol) by **Method A** (115 mg, 91%) or from **1** by **Method B** (101 mg, 80%), as a white solid, m.p. 180.0–180.7 °C. $[\alpha]_D^{25}$ = +220.5 (*c* = 0.52, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 1 H, triazole H), 7.71 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.32 (d, *J* = 8.6 Hz, 2 H, Ar-H), 6.00 (dd, *J* = 5.0, 0.9 Hz, 1 H, 5-H), 5.74 (t, *J* = 5.1 Hz, 1 H, 2-H), 5.53–5.42 (m, 2 H, 3-H and 1-H), 5.26 (ddd, *J* = 8.4, 6.1, 2.9 Hz, 1 H, 6-H), 4.72 (d, *J* = 13.9 Hz, 1 H, C*H*HOAc), 4.49 (d, *J* = 13.9 Hz, 1 H, CH*H*OAc), 2.04 (s, 3 H, C*H*$_3$COO), 2.02 (s, 3 H, C*H*$_3$COO), 1.97 (s, 3 H, C*H*$_3$COO), 1.89 (s, 3 H, C*H*$_3$COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.19 (2 C, CH_3COO), 168.87 (CH_3COO), 168.64 (CH_3COO), 145.89 (triazole-C_{quat}), 137.14 (C-4), 133.07 (Ar-C_{quat}), 128.05 (Ar-C), 127.84 (Ar-C_{quat}), 126.09 (Ar-C), 120.06 (C-5), 118.73 (triazole-C), 69.63 (C-1), 67.23 (C-3), 67.11 (C-2), 61.63 (*C*H$_2$OAc), 54.78 (C-6), 19.71 (*C*H$_3$COO), 19.67 (*C*H$_3$COO), 19.60 (*C*H$_3$COO), 19.51 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3049, 1743, 1437, 1373, 1222, 1028, 968, 906, 763, 634 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 123 (55), 124 (43), 150 (67), 166 (100), 180 (7), 208 (7), 220 (5), 272 (4), 505 (3) [M]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{25}ClN_3O_8$ [M + H]$^+$ 506.1330; found 506.1330.

4.3.15 (1*S*,2*S*,3*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl]cyclohex-4-ene-1,2,3-triyl Triacetate (14e): This compound was prepared from **8** (92 mg, 0.25 mmol) and (4-fluorophenyl)acetylene (36 mg, 0.30 mmol) by **Method A** (109 mg, 89%) or from **1** by **Method B** (95 mg, 78%), as a white solid, m.p. 155.2–156.8 °C. $[\alpha]_D^{25}$ = +213.5 (*c* = 0.54, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (s, 1 H, triazole H), 7.75 (dd, *J* = 8.6, 5.4 Hz, 2 H, Ar-H), 7.04 (t, *J* = 8.7 Hz, 2 H, Ar-H), 6.01 (d, *J* = 4.9 Hz, 1 H, 5-H), 5.74 (t, *J* = 5.1 Hz, 1 H, 2-H), 5.55–5.40 (m, 2 H, 3-H and 1-H), 5.32–5.18 (m, 1 H, 6-H), 4.72 (d, *J* = 13.8 Hz, 1 H, C*H*HOAc), 4.49 (d, *J* = 13.8 Hz, 1 H, CH*H*OAc), 2.04 (s, 3 H, C*H*$_3$COO), 2.02 (s, 3 H, C*H*$_3$COO), 1.97 (s, 3 H, C*H*$_3$COO), 1.89 (s, 3 H, C*H*$_3$COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.19 (2 C, CH_3COO), 168.88 (CH_3COO), 168.65 (CH_3COO), 161.77 (d, $^1J_{C,F}$ = 247.5 Hz, Ar-C_{quat}), 146.09 (triazole-C_{quat}), 137.09 (C-4), 126.60 (d, $^3J_{C,F}$ = 8.2 Hz, Ar-C), 125.55 (d, $^4J_{C,F}$ = 3.2 Hz, Ar-C_{quat}), 120.14 (C-5), 118.39 (triazole-C), 114.84 (d, $^2J_{C,F}$ = 21.8 Hz, Ar-C), 69.63 (C-1), 67.28 (C-3), 67.14 (C-2), 61.64 (*C*H$_2$OAc), 54.75 (C-6), 19.71 (*C*H$_3$COO), 19.67 (*C*H$_3$COO), 19.60 (*C*H$_3$COO), 19.51 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3141, 1741, 1494, 1439, 1376, 1225, 1029, 908, 840, 798 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 107 (81), 123 (100), 124 (100), 134 (100), 166 (100), 208 (22), 239 (20), 257 (14), 299 (6), 489 (5) [M]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{25}FN_3O_8$ [M + H]$^+$ 490.1626; found 490.1626.

4.3.16 (1*S*,2*S*,3*R*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-nitrophenyl)-1*H*-1,2,3-triazol-1-yl]cyclohex-4-ene-1,2,3-triyl Triacetate (14f): This compound was prepared from **8** (92 mg, 0.25 mmol) and (4-nitrophenyl)acetylene (36 mg, 0.30 mmol) by **Method A** (123 mg, 95%) or from **1** by **Method B** (115 mg, 89%), as a white solid, m.p. 144.8–145.7 °C. $[\alpha]_D^{25}$ = +243.2 (*c* = 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.95 (s, 1 H, triazole H), 8.35 (d, *J* = 8.7 Hz, 2 H, Ar-H), 8.20 (d, *J* = 8.9 Hz, 2 H, Ar-H), 6.23 (dd, *J* = 4.5, 1.0 Hz, 1 H, 5-H), 5.91–5.69 (m, 2 H, 2-H and 3-H), 5.55 (dd, *J* = 10.2, 5.2 Hz, 1 H, 1-H), 5.50 (dd, *J* = 10.2, 6.5 Hz, 1 H, 6-H), 4.79 (d, *J* = 14.1 Hz, 1 H, C*H*HOAc), 4.61 (d, *J* = 13.8 Hz, 1 H, CH*H*OAc), 2.09 (s, 3 H, C*H*$_3$COO), 2.06 (s, 3 H, C*H*$_3$COO), 2.00 (s, 3 H, C*H*$_3$COO), 1.92 (s, 3 H, C*H*$_3$COO) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 170.30 (CH_3COO), 170.26 (CH_3COO), 169.91 (CH_3COO), 169.73 (CH_3COO), 147.20 (triazole-C_{quat}), 144.74 (Ar-C_{quat}), 137.33 (Ar-C_{quat}), 137.03 (C-4), 126.53 (Ar-C), 125.05 (C-5), 124.85 (Ar-C), 122.33 (triazole-C), 69.76 (C-1), 68.98 (C-3), 67.66 (C-2), 62.72 (*C*H$_2$OAc), 56.41 (C-6), 20.93 (*C*H$_3$COO), 20.85 (*C*H$_3$COO), 20.82 (*C*H$_3$COO), 20.76 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3122, 1743, 1604, 1508, 1452, 1367, 1334, 1220, 1032, 847 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 95 (61), 106 (53), 123 (100), 124 (100), 165 (100), 166 (100), 266 (39), 284 (33), 326 (29), 516 (6) [M]$^+$, 517 (4) [M + 1]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{25}N_4O_{10}$ [M + H]$^+$ 517.1571; found 517.1569.

4.3.17 (1*S*,2*S*,3*R*,6*S*)-4-(Acetoxymethyl)-6-(4-butyl-1*H*-1,2,3-triazol-1-yl)cyclohex-4-ene-1,2,3-triyl Triacetate (14g): This compound was prepared from **8** (185 mg, 0.50 mmol) and hex-1-yne (49 mg, 0.60 mmol) by **Method A** (189 mg, 84%) or from **1** by **Method B** (163 mg, 72%), as a white solid, m.p. 124.4–124.9 °C. $[\alpha]_D^{25}$ = +144.0 (*c* = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 1 H, triazole H), 5.98 (dd, *J* = 4.8, 1.0 Hz, 1 H, 5-H), 5.67 (t, *J* = 5.1 Hz, 1 H, 2-H), 5.53 (d, *J* = 6.6 Hz, 1 H, 3-H), 5.40 (dd, *J* = 10.1, 6.7 Hz, 1 H, 1-H), 5.20 (dd, *J* = 10.1, 5.4 Hz, 1 H, 6-H), 4.71 (d, *J* = 13.7 Hz, 1 H, C*H*HOAc), 4.47 (d, *J* = 13.7 Hz, 1 H, CH*H*OAc), 2.66 (t, *J* = 7.6 Hz, 2 H, C*H*$_2$), 2.03 (s, 3 H, C*H*$_3$COO), 2.01 (s, 3 H, C*H*$_3$COO), 1.97 (s, 3 H, C*H*$_3$COO), 1.87 (s, 3 H, C*H*$_3$COO), 1.60 (dt, *J* = 15.3, 7.6 Hz, 2 H, C*H*$_2$), 1.38–1.26 (m, 2 H, C*H*$_2$), 0.87 (t, *J* = 7.4 Hz, 3 H, C*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.18 (CH_3COO), 169.04 (CH_3COO), 168.79 (CH_3COO), 168.59 (CH_3COO), 147.57 (triazole-C_{quat}), 136.35 (C-4), 120.83 (C-5), 119.48 (triazole-C), 68.97 (C-1), 67.51 (C-3), 67.15 (C-2), 61.70 (*C*H$_2$OAc), 54.37 (C-6), 30.43 (*C*H$_2$), 24.36 (*C*H$_2$), 21.26 (*C*H$_2$), 19.67 (2 C, *C*H$_3$COO), 19.63 (*C*H$_3$COO), 19.47 (*C*H$_3$COO), 12.78 (*C*H$_3$) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2961, 2855, 1735, 1436, 1228, 1112, 1028, 972, 912, 796 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 95 (52), 123 (100), 124 (63), 165 (100), 166 (78), 207 (13), 452 (2) [M + 1]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{21}H_{30}N_3O_8$ [M + H]$^+$ 452.2033; found 452.2036.

4.3.18 (1*S*,2*S*,3*R*,6*S*)-4-(Acetoxymethyl)-6-(4-pentyl-1*H*-1,2,3-triazol-1-yl)cyclohex-4-ene-1,2,3-triyl Triacetate (14h): This compound was prepared from **8** (185 mg, 0.50 mmol) and hept-1-yne (58 mg, 0.60 mmol) by **Method A** (201 mg, 86%) or from **1** by **Method B** (178 mg, 76%), as a white solid, m.p. 106.0–106.7 °C. $[\alpha]_D^{25}$ = +128.0 (*c* = 0.40, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 1 H, triazole H), 5.98 (dd, *J* = 4.9, 1.3 Hz, 1 H, 5-H), 5.67 (t, *J* = 5.1 Hz, 1 H, 2-H), 5.53 (d, *J* = 6.6 Hz, 1 H, 3-H), 5.40 (dd, *J* = 10.1, 6.7 Hz, 1 H, 1-H), 5.20 (dd, *J* = 10.1, 5.4 Hz, 1 H, 6-H), 4.71 (d, *J* = 13.6 Hz, 1 H), 4.47 (d, *J* = 13.7 Hz, 1 H), 2.65 (t, *J* = 7.6 Hz, 2 H), 2.03 (s, 3 H), 2.01 (s, 3 H), 1.97 (s, 3 H), 1.87 (s, 3 H), 1.61 (dd, *J* = 9.9, 5.1 Hz, 2 H), 1.35–1.20 (m, 4 H), 0.83 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.18 (CH_3COO), 169.04 (CH_3COO), 168.79 (CH_3COO), 168.57 (CH_3COO), 147.61 (triazole-C_{quat}), 136.37 (C-4), 120.81 (C-5), 119.47 (triazole-C), 69.00 (C-1), 67.51 (C-3), 67.15 (C-2), 61.70 (*C*H$_2$OAc), 54.37 (C-6), 30.38 (*C*H$_2$), 28.02 (*C*H$_2$), 24.65 (*C*H$_2$), 21.37 (*C*H$_2$), 19.66 (2 C, *C*H$_3$COO), 19.63 (*C*H$_3$COO), 19.47 (*C*H$_3$COO), 12.98 (*C*H$_3$) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2961, 2857,

1735, 1446, 1376, 1227, 1027, 972, 911, 799 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 95 (51), 123 (100), 124 (56), 165 (100), 166 (79), 207 (18), 216 (8), 327 (3), 466 (3) [M + 1]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{22}H_{32}N_3O_8$ [M + H]$^+$ 466.2189; found 466.2188.

4.3.19 (1*S*,2*S*,3*R*,6*S*)-4-(Acetoxymethyl)-6-(4-{[4-(*tert*-butyl)-phenoxy]methyl}-1*H*-1,2,3-triazol-1-yl)cyclohex-4-ene-1,2,3-triyl Triacetate (14i): This compound was prepared from **8** (185 mg, 0.50 mmol) and propargyl [4-(*tert*-butyl)]phenyl ether (113 mg, 0.60 mmol) by **Method A** (206 mg, 85%) or from **1** by **Method B** (182 mg, 75%), as a pink solid, m.p. 82.2–82.7 °C. $[\alpha]_D^{25}$ = +109.3 (*c* = 0.30, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1 H, triazole H), 7.23 (d, *J* = 8.8 Hz, 2 H, Ar-H), 6.85 (d, *J* = 8.8 Hz, 2 H, Ar-H), 5.97 (dd, *J* = 4.8, 1.2 Hz, 1 H, 5-H), 5.69 (t, *J* = 4.9 Hz, 1 H, 2-H), 5.54 (d, *J* = 6.4 Hz, 1 H, 3-H), 5.41 (dd, *J* = 9.9, 6.5 Hz, 1 H, 1-H), 5.21 (dd, *J* = 9.9, 5.4 Hz, 1 H, 6-H), 5.13 (s, 2 H, Ar-OC*H*$_2$), 4.70 (d, *J* = 13.8 Hz, 1 H, C*H*HOAc), 4.46 (d, *J* = 13.8 Hz, 1 H, CH*H*OAc), 2.02 (s, 3 H, *C*H$_3$COO), 2.00 (s, 3 H, C*H*$_3$COO), 1.97 (s, 3 H, C*H*$_3$COO), 1.80 (s, 3 H, C*H*$_3$COO), 1.22 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.16 (CH$_3$*C*OO), 169.01 (CH$_3$*C*OO), 168.76 (CH$_3$*C*OO), 168.47 (CH$_3$*C*OO), 154.93 (Ar-C$_{quat}$), 143.66 (Ar-C$_{quat}$), 142.99 (triazole-C$_{quat}$), 136.66 (C-4), 125.32 (Ar-C), 121.79 (C-5), 120.44 (triazole-C), 113.25 (Ar-C), 68.65 (C-1), 67.45 (C-3), 67.03 (C-2), 61.67 (*C*H$_2$OAc), 61.05 (ArO*C*H$_2$), 54.69 (C-6), 33.07 [*C*(CH$_3$)$_3$], 30.48 [C(*C*H$_3$)$_3$], 19.66 (*C*H$_3$COO), 19.64 (*C*H$_3$COO), 19.62 (*C*H$_3$COO), 19.37 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2961, 2870, 1742, 1512, 1368, 1216, 1030, 907, 866, 729 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 95 (52), 123 (93), 135 (87), 165 (69), 176 (29), 218 (12), 320 (10), 557 (1) [M]$^+$, 558 (1) [M + 1]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{28}H_{36}N_3O_9$ [M + H]$^+$ 558.2452; found 558.2448.

4.3.20 (1*S*,2*R*,3*S*,4*S*,6*S*)-4-(Acetoxymethyl)-4-hydroxy-6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)cyclohexane-1,2,3-triyl Triacetate (15a): This compound was prepared from **9** (97 mg, 0.25 mmol) and phenylacetylene (31 mg, 0.30 mmol) by **Method A** (108 mg, 88%) or from **3** by **Method B** (92 mg, 75%), as a white solid, m.p. 216.7–218.2 °C. $[\alpha]_D^{25}$ = +62.6 (*c* = 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1 H, triazole H), 7.73–7.63 (m, 2 H, Ar-H), 7.38–7.29 (m, 2 H, Ar-H), 7.29–7.22 (m, 1 H, Ar-H), 5.74 (t, *J* = 10.2 Hz, 1 H, 2-H), 5.51 (s, 1 H, O*H*), 5.32 (td, *J* = 6.0, 2.4 Hz, 1 H, 6-H), 5.20 (dd, *J* = 10.2, 5.3 Hz, 1 H, 1-H), 5.19 (d, *J* = 9.9 Hz, 1 H, 3-H), 4.12 (d, *J* = 11.4 Hz, 1 H, C*H*HOAc), 3.77 (d, *J* = 11.4 Hz, 1 H, CH*H*OAc), 2.53 (dd, *J* = 16.1, 2.4 Hz, 1 H, 5-H), 2.45 (dd, *J* = 16.1, 6.1 Hz, 1 H, 5-H), 2.02 (s, 3 H, C*H*$_3$COO), 2.01 (s, 3 H, C*H*$_3$COO), 1.93 (s, 3 H, C*H*$_3$COO), 1.84 (s, 3 H, C*H*$_3$COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.33 (CH$_3$*C*OO), 168.96 (CH$_3$*C*OO), 168.89 (CH$_3$*C*OO), 168.40 (CH$_3$*C*OO), 146.62 (triazole-C$_{quat}$), 128.80 (Ar-C$_{quat}$), 127.92 (Ar-C), 127.49 (Ar-C$_{quat}$), 124.74 (Ar-C), 120.83 (triazole-C), 70.76 (C-4), 70.64 (C-3), 69.96 (C-2), 67.13 (C-1), 64.89 (*C*H$_2$OAc), 55.63 (C-6), 32.95 (C-5), 19.78 (*C*H$_3$COO), 19.53 (*C*H$_3$COO), 19.49 (*C*H$_3$COO), 19.47 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 1735, 1425, 1383, 1230, 1035, 974, 819, 765, 696, 626 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 123 (100), 146 (62), 179 (92), 183 (58), 226 (23), 239 (30), 328 (23), 370 (29), 419 (23), 489 (23) [M]$^+$, 490 (11) [M + 1]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{28}N_3O_9$ [M + H]$^+$ 490.1826; found 490.1823.

4.3.21 (1*S*,2*R*,3*S*,4*S*,6*S*)-4-(Acetoxymethyl)-4-hydroxy-6-[4-(4-methylphenyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (15b): This compound was prepared from **9** (97 mg, 0.25 mmol) and 4-methyl phenylacetylene (35 mg, 0.30 mmol) by **Method A** (106 mg, 84%) or from **3** by **Method B** (98 mg, 78%), as a white solid, m.p. 220.5–221.7 °C. $[\alpha]_D^{25}$ = +54.2 (*c* = 1.12, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1 H, triazole H), 7.57 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.12 (d, *J* = 7.9 Hz, 1 H, Ar-H), 5.73 (t, *J* = 10.2 Hz, 1 H, 2-H), 5.62 (s, 1 H, O*H*), 5.30 (td, *J* = 5.9, 2.5 Hz, 1 H, 6-H), 5.18 (d, *J* = 9.9 Hz, 1 H, 3-H), 5.18 (dd, *J* = 10.9, 5.3 Hz, 1 H, 1-H), 4.12 (d, *J* = 11.4 Hz, 1 H, C*H*HOAc), 3.76 (d, *J* = 11.4 Hz, 1 H, CH*H*OAc), 2.52 (dd, *J* = 16.1, 2.5 Hz, 1 H, 5-H), 2.45 (dd, *J* = 16.2, 6.0 Hz, 1 H, 5-H), 2.29 (s, 3 H, ArC*H*$_3$), 2.02 (s, 3 H, C*H*$_3$COO), 2.01 (s, 3 H, C*H*$_3$COO), 1.93 (s, 2 H, C*H*$_3$COO), 1.83 (s, 3 H, C*H*$_3$COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.31 (CH$_3$*C*OO), 168.99 (CH$_3$*C*OO), 168.91 (CH$_3$*C*OO), 168.36 (CH$_3$*C*OO), 146.70 (triazole-C$_{quat}$), 137.40 (Ar-C$_{quat}$), 128.57 (Ar-C), 125.95 (Ar-C$_{quat}$), 124.64 (Ar-C), 120.51 (triazole-C), 70.67 (C-4), 70.64 (C-3), 70.03 (C-2), 67.15 (C-1), 64.88 (*C*H$_2$OAc), 55.56 (C-6), 32.95 (C-5), 20.27 (Ar*C*H$_3$), 19.78 (*C*H$_3$COO), 19.54 (*C*H$_3$COO), 19.49 (*C*H$_3$COO), 19.47 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 1742, 1430, 1374, 1226, 1068, 1031, 971, 901, 814, 640 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 123 (97), 132 (62), 160 (57), 183 (52), 240 (30), 253 (28), 433 (30), 503 (39) [M]$^+$, 504 (17) [M + 1]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{24}H_{30}N_3O_9$ [M + H]$^+$ 504.1982; found 504.1978.

4.3.22 (1*S*,2*R*,3*S*,4*S*,6*S*)-4-(Acetoxymethyl)-4-hydroxy-6-[4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (15c): This compound was prepared from **9** (97 mg, 0.25 mmol) and 4-methoxy phenylacetylene (40 mg, 0.30 mmol) by **Method A** (107 mg, 82%) or from **3** by **Method B** (93 mg, 72%), as a white solid, m.p. 160.3–161.2 °C. $[\alpha]_D^{25}$ = +48.9 (*c* = 1.36, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 1 H, triazole H), 7.59 (d, *J* = 8.7 Hz, 2 H, Ar-H), 6.84 (d, *J* = 8.7 Hz, 2 H, Ar-H), 5.74 (t, *J* = 10.2 Hz, 1 H, 2-H), 5.68 (s, 1 H, O*H*), 5.30 (td, *J* = 5.9, 2.3 Hz, 1 H, 6-H), 5.18 (d, *J* = 9.9 Hz, 1 H, 3-H), 5.18 (dd, *J* = 10.5, 5.8 Hz, 1 H, 1-H), 4.12 (d, *J* = 11.4 Hz, 1 H, C*H*HOAc), 3.77 (d, *J* = 11.1 Hz, 1 H, CH*H*OAc), 3.75 (s, 3 H, ArOC*H*$_3$), 2.53 (dd, *J* = 16.1, 2.2 Hz, 1 H, 5-H), 2.45 (dd, *J* = 16.2, 6.1 Hz, 1 H, 5-H), 2.02 (s, 3 H, C*H*$_3$COO), 2.01 (s, 3 H, C*H*$_3$COO), 1.93 (s, 3 H, C*H*$_3$COO), 1.84 (s, 3 H, C*H*$_3$COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.32 (CH$_3$*C*OO), 169.00 (CH$_3$*C*OO), 168.91 (CH$_3$*C*OO), 168.39 (CH$_3$*C*OO), 158.82 (Ar-C$_{quat}$), 146.45 (triazole-C$_{quat}$), 126.05 (Ar-C), 121.42 (Ar-C$_{quat}$), 120.07 (triazole-C), 113.31 (Ar-C), 70.69 (C-4), 70.65 (C-3), 70.02 (C-2), 67.18 (C-1), 64.87 (*C*H$_2$OAc), 55.58 (C-6), 54.31 (ArO*C*H$_3$), 32.99 (C-5), 19.78 (*C*H$_3$COO), 19.54 (*C*H$_3$COO), 19.50 (*C*H$_3$COO), 19.48 (*C*H$_3$COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3173, 2920, 1750, 1369, 1248, 1221, 1204, 1033, 817, 681 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 147 (82), 176 (58), 256 (57), 269 (43), 448 (37), 449 (25), 491 (18), 519 (43) [M]$^+$, 520 (17) [M + 1]$^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{24}H_{30}N_3O_{10}$ [M + H]$^+$ 520.1931; found 520.1925.

4.3.23 (1*S*,2*R*,3*S*,4*S*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl]-4-hydroxycyclohexane-1,2,3-triyl Triacetate (15d): This compound was prepared from **9** (97 mg, 0.25 mmol) and (4-chlorophenyl)acetylene (41 mg, 0.30 mmol) by **Method A** (106 mg, 81%) or from **3** by **Method B** (96 mg, 73%), as a white solid, m.p. 242.7–244.5 °C. $[\alpha]_D^{25}$ = +62.5 (*c* = 0.92, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1 H, triazole H), 7.59 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.28 (d, *J* = 8.3 Hz, 2 H, Ar-H), 5.76 (t, *J* = 10.2 Hz, 1 H, 2-H), 5.35 (td, *J* = 6.1, 1.6 Hz, 1 H, 6-H), 5.27 (s, 1 H, O*H*), 5.21 (dd, *J* = 11.1, 7.8 Hz, 1 H, 1-H), 5.19 (d, *J* = 9.5 Hz, 1 H, 3-H), 4.12 (d, *J* = 11.4 Hz, 1 H, C*H*HOAc), 3.78 (d, *J* = 11.4 Hz, 1 H, CH*H*OAc), 2.57 (dd, *J* = 16.0, 1.5 Hz, 1 H, 5-H), 2.44 (dd, *J* = 16.1, 6.2 Hz, 1 H, 5-H), 2.04 (s, 3 H, C*H*$_3$COO), 2.02 (s, 3 H, C*H*$_3$COO), 1.95 (s, 3 H, C*H*$_3$COO), 1.84 (s, 3 H, C*H*$_3$COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.32 (CH$_3$*C*OO), 168.88 (CH$_3$*C*OO), 168.81 (CH$_3$*C*OO), 168.50 (CH$_3$*C*OO), 145.49 (triazole-C$_{quat}$), 133.24 (Ar-C$_{quat}$), 128.09 (Ar-

C), 127.28 (Ar-C_{quat}), 125.88 (Ar-C), 120.73 (triazole-C), 70.92 (C-4), 70.62 (C-3), 69.81 (C-2), 67.15 (C-1), 64.90 (CH_2OAc), 55.76 (C-6), 33.03 (C-5), 19.76 (CH_3COO), 19.53 (CH_3COO), 19.50 (CH_3COO), 19.46 (CH_3COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3044, 1742, 1431, 1376, 1222, 1069, 1029, 974, 816, 631 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 123 (100), 141 (54), 150 (45), 152 (49), 180 (45), 183 (52), 273 (29), 404 (17), 453 (17), 523 (22) $[M]^+$, 525 (9) [M + 2]. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{27}N_3O_9$ $[M + H]^+$ 524.1436; found 524.1440.

4.3.24 (1*S*,2*R*,3*S*,4*S*,6*S*)-4-(Acetoxymethyl)-6-[4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl]-4-hydroxycyclohexane-1,2,3-triyl Triacetate (15e): This compound was prepared from **9** (97 mg, 0.25 mmol) and (4-fluorophenyl)acetylene (36 mg, 0.30 mmol) by **Method A** (108 mg, 85%) or from **3** by **Method B** (94 mg, 74%), as a white solid, m.p. 228.5–229.2 °C. $[\alpha]_D^{25}$ = +59.2 (*c* = 1.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1 H, triazole H), 7.69–7.57 (m, 2 H, Ar-H), 7.07–6.93 (m, 2 H, Ar-H), 5.76 (t, *J* = 10.2 Hz, 1 H, 2-H), 5.38 (s, 1 H, O*H*), 5.34 (td, *J* = 6.0, 2.2 Hz, 1 H, 6-H), 5.21 (dd, *J* = 10.4, 6.0 Hz, 1 H, 1-H), 5.20 (dd, *J* = 8.0, 1.9 Hz, 1 H, 3-H), 4.12 (d, *J* = 11.4 Hz, 1 H, C*H*HOAc), 3.78 (d, *J* = 11.4 Hz, 1 H, CH*H*OAc), 2.57 (dd, *J* = 16.1, 2.2 Hz, 1 H, 5-H), 2.45 (dd, *J* = 16.1, 6.2 Hz, 1 H, 5-H), 2.03 (s, 3 H, CH_3COO), 2.01 (s, 3 H, CH_3COO), 1.94 (s, 3 H, CH_3COO), 1.84 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.34 (CH_3*C*OO), 168.91 (CH_3*C*OO), 168.83 (CH_3*C*OO), 168.49 (CH_3*C*OO), 161.79 (d, $^1J_{C,F}$ = 247.9 Hz, Ar-C_{quat}), 145.68 (triazole-C_{quat}), 126.48 (d, $^3J_{C,F}$ = 8.2 Hz, Ar-C), 125.06 (d, $^4J_{C,F}$ = 3.3 Hz, Ar-C_{quat}), 120.51 (triazole-C), 114.90 (d, $^2J_{C,F}$ = 21.8 Hz, Ar-C), 70.90 (C-4), 70.66 (C-3), 69.87 (C-2), 67.18 (C-1), 64.92 (CH_2OAc), 55.74 (C-6), 33.03 (C-5), 19.75 (CH_3COO), 19.52 (CH_3COO), 19.49 (CH_3COO), 19.45 (CH_3COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 3045, 1738, 1494, 1428, 1382, 1230, 1068, 974, 809, 647 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 123 (100), 134 (87), 164 (78), 183 (62), 257 (51), 346 (22), 388 (27), 437 (35), 507 (34) $[M]^+$, 508 (16) $[M + 1]^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{27}FN_3O_9$ $[M + H]^+$ 508.1731; found 508.1730.

4.3.25 (1*S*,2*R*,3*S*,4*S*,6*S*)-4-(Acetoxymethyl)-4-hydroxy-6-[4-(4-nitrophenyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (15f): This compound was prepared from **9** (97 mg, 0.25 mmol) and (4-nitrophenyl)acetylene (44 mg, 0.30 mmol) by **Method A** (122 mg, 91%) or from **3** by **Method B** (111 mg, 83%), as a white solid, m.p. 238.5–239.4 °C. $[\alpha]_D^{25}$ = +90.2 (*c* = 0.58, $CHCl_3$). ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 9.11 (s, 1 H, triazole H), 8.38 (d, *J* = 8.7 Hz, 2 H, Ar-H), 8.18 (d, *J* = 9.0 Hz, 2 H, Ar-H), 5.84 (s, 1 H, O*H*), 5.71 (t, *J* = 9.1 Hz, 1 H, 2-H), 5.53 (t, *J* = 4.6 Hz, 1 H, 6-H), 5.48 (dd, *J* = 10.4, 6.0 Hz, 1 H, 1-H), 5.28 (d, *J* = 9.0 Hz, 1 H, 3-H), 4.08 (d, *J* = 11.2 Hz, 1 H, C*H*HOAc), 3.84 (d, *J* = 11.2 Hz, 1 H, CH*H*OAc), 2.61 (dd, *J* = 15.4, 5.4 Hz, 1 H, 5-H), 2.43 (dd, *J* = 15.4, 2.7 Hz, 1 H, 5-H), 2.09 (s, 3 H, CH_3COO), 2.08 (s, 3 H, CH_3COO), 2.04 (s, 3 H, CH_3COO), 1.91 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, [D_6]DMSO): δ = 170.46 (CH_3*C*OO), 169.98 (CH_3*C*OO), 169.76 (CH_3*C*OO), 169.67 (CH_3*C*OO), 147.14 (triazole-C_{quat}), 144.62 (Ar-C_{quat}), 137.43 (Ar-C_{quat}), 126.42 (Ar-C), 124.94 (Ar-C), 124.65 (triazole-C), 71.98 (C-4), 71.70 (C-3), 69.98 (C-2), 68.82 (C-1), 66.43 (CH_2OAc), 57.13 (C-6), 33.74 (C-5), 21.05 (CH_3COO), 20.86 (CH_3COO), 20.77 (CH_3COO), 20.70 (CH_3COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 1740, 1602, 1517, 1429, 1379, 1346, 1216, 1070, 1029, 822 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 123 (100), 141 (54), 183 (48), 191 (63), 284 (50), 415 (33), 447 (16), 464 (17), 534 (20) $[M]^+$, 535 (9) $[M + 1]^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{23}H_{27}N_4O_{11}$ $[M + H]^+$ 535.1676; found 535.1676.

4.3.26 (1*S*,2*R*,3*S*,4*S*,6*S*)-4-(Acetoxymethyl)-6-(4-butyl-1*H*-1,2,3-triazol-1-yl)-4-hydroxycyclohexane-1,2,3-triyl Triacetate (15g): This compound was prepared from **9** (194 mg, 0.50 mmol) and hex-1-yne (49 mg, 0.60 mmol) by **Method A** (212 mg, 91%) or from **3** by **Method B** (188 mg, 80%), as a white solid, m.p. 143.3–143.5 °C. $[\alpha]_D^{25}$ = +41.5 (*c* = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 1 H, triazole H), 6.13 (s, 1 H, O*H*), 5.64 (t, *J* = 10.2 Hz, 1 H, 2-H), 5.16 (dd, *J* = 9.1, 5.0 Hz, 1 H, 6-H), 5.16 (d, *J* = 10.1 Hz, 1 H, 1-H), 5.10 (dd, *J* = 10.3, 5.8 Hz, 1 H, 3-H), 4.13 (d, *J* = 11.4 Hz, 1 H, C*H*HOAc), 3.72 (d, *J* = 11.4 Hz, 1 H, CH*H*OAc), 2.65 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.47 (dd, *J* = 16.1, 6.0 Hz, 1 H, 5-H), 2.40 (dd, *J* = 16.1, 2.2 Hz, 1 H, 5-H), 2.04 (s, 3 H, CH_3COO), 2.03 (s, 3 H, CH_3COO), 1.92 (s, 3 H, CH_3COO), 1.86 (s, 3 H, CH_3COO), 1.64–1.49 (m, 2 H, CH_2), 1.30 (dt, *J* = 14.6, 7.4 Hz, 2 H, CH_2), 0.87 (t, *J* = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.26 (CH_3*C*OO), 169.05 (CH_3*C*OO), 168.84 (CH_3*C*OO), 168.22 (CH_3*C*OO), 147.32 (triazole-C_{quat}), 122.16 (triazole-C), 70.64 (C-4), 70.34 (2 C, C-3 and C-2), 67.08 (C-1), 64.81 (CH_2OAc), 55.26 (6-H), 32.92 (5-H), 30.40 (CH_2), 24.11 (CH_2), 21.18 (CH_2), 19.80 (CH_3COO), 19.57 (CH_3COO), 19.49 (CH_3COO), 19.42 (CH_3COO), 12.74 (CH_3) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2926, 2854, 1736, 1428, 1382, 1231, 973, 946, 904, 802 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 123 (41), 126 (25), 152 (17), 183 (14), 206 (12), 308 (10), 322 (8), 350 (11), 470 (2) $[M + 1]^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{21}H_{32}N_3O_9$ $[M + H]^+$ 470.2139; found 470.2141.

4.3.27 (1*S*,2*R*,3*S*,4*S*,6*S*)-4-(Acetoxymethyl)-4-hydroxy-6-[4-(phenoxymethyl)-1*H*-1,2,3-triazol-1-yl]cyclohexane-1,2,3-triyl Triacetate (15h): This compound was prepared from **9** (194 mg, 0.50 mmol) and (prop-2-ynyloxy)benzene (79 mg, 0.60 mmol) by **Method A** (220 mg, 85%) or from **3** by **Method B** (203 mg, 78%), as a white solid, m.p. 176.4–177.3 °C. $[\alpha]_D^{25}$ = +47.5 (*c* = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (s, 1 H, triazole H), 7.20 (t, *J* = 7.9 Hz, 2 H, Ar-H), 6.87 (dd, *J* = 10.8, 3.7 Hz, 3 H, Ar-H), 5.64 (t, *J* = 10.1 Hz, 1 H, 2-H), 5.61 (s, 1 H, O*H*), 5.25 (dd, *J* = 9.9, 4.3 Hz, 1 H, 6-H), 5.17 (d, *J* = 10.1 Hz, 1 H, 1-H), 5.15 (dd, *J* = 10.6, 5.6 Hz, 1 H, 3-H), 5.10 (s, 2 H, ArOCH_2), 4.10 (d, *J* = 11.4 Hz, 1 H, C*H*HOAc), 3.74 (d, *J* = 11.4 Hz, 1 H, CH*H*OAc), 2.45 (d, *J* = 4.0 Hz, 2 H, 5-H), 2.02 (s, 3 H, CH_3COO), 2.00 (s, 3 H, CH_3COO), 1.91 (s, 3 H, CH_3COO), 1.74 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.29 (CH_3*C*OO), 168.94 (CH_3*C*OO), 168.80 (CH_3*C*OO), 168.27 (CH_3*C*OO), 156.98 (Ar-C_{quat}), 143.33 (triazole-C_{quat}), 128.59 (Ar-C), 124.09 (Ar-C), 120.37 (triazole-C), 113.75 (Ar-C), 70.61 (C-4), 70.58 (C-3), 69.88 (C-2), 67.02 (C-1), 64.87 (CH_2OAc), 60.64 (ArOCH_2), 55.63 (6-H), 32.78 (5-H), 19.77 (CH_3COO), 19.53 (CH_3COO), 19.47 (CH_3COO), 19.27 (CH_3COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2962, 2926, 1738, 1596, 1496, 1377, 1034, 976, 821, 754 cm^{-1}. MS (EI): *m*/*z* (%) = 43 (100), 94 (33), 123 (38), 176 (73), 194 (21), 236 (29), 356 (25), 398 (12), 426 (7), 520 (4) $[M + 1]^+$. HRMS (ESI-TOF): *m*/*z* calcd. for $C_{24}H_{30}N_3O_{10}$ $[M + H]^+$ 520.1931; found 520.1926.

4.3.28 (1*R*,2*S*,3*R*,4*S*,5*R*,6*R*)-1-(Acetoxymethyl)-5-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-7-oxabicyclo[4.1.0]heptane-2,3,4-triyl Triacetate (16a): This compound was prepared from **11** (193 mg, 0.50 mmol) and phenylacetylene (61 mg, 0.60 mmol) by **Method A** (225 mg, 92%), as a white solid, m.p. 227.2–227.8 °C. $[\alpha]_D^{25}$ = +151.0 (*c* = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1 H, triazole H), 7.87–7.75 (m, 2 H, Ar-H), 7.37 (t, *J* = 7.5 Hz, 2 H, Ar-H), 7.32–7.24 (m, 1 H, Ar-H), 5.82 (dd, *J* = 7.5, 4.2 Hz, 1 H, 6-H), 5.59 (d, *J* = 7.8 Hz, 1 H, 3-H), 5.42 (dd, *J* = 10.5, 7.8 Hz, 1 H, 2-H), 5.17 (dd, *J* = 10.4, 7.5 Hz, 1 H, 1-H), 4.39 (d, *J* = 12.4 Hz, 1 H, C*H*HOAc), 3.97 (d, *J* = 12.4 Hz, 1 H, CH*H*OAc), 3.72 (d, *J* = 4.2 Hz, 1 H, 5-H), 2.10 (s, 3 H, CH_3COO), 2.03 (s, 3 H, CH_3COO), 1.95 (s, 3 H, CH_3COO), 1.74 (s, 3 H, CH_3COO) ppm. ^{13}C NMR

(101 MHz, $CDCl_3$): δ = 168.97 (CH_3COO), 168.71 (CH_3COO), 168.35 (CH_3COO), 168.28 (CH_3COO), 147.43 (triazole-C_{quat}), 129.23 (Ar-C_{quat}), 127.86 (Ar-C), 127.38 (Ar-C), 124.84 (Ar-C), 119.14 (triazole-C), 67.95 (C-2), 66.80 (C-3), 66.49 (CH_2OAc), 60.49 (C-1), 60.18 (C-4), 55.85 (C-6), 53.93 (C-5), 19.54 (CH_3COO), 19.47 (2 C, CH_3COO), 19.05 (CH_3COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 1740, 1381, 1234, 1096, 1079, 1033, 1029, 974, 938, 801, 716 cm^{-1}. MS (EI): *m/z* (%) = 43 (100), 116 (88), 123 (66), 165 (91), 207 (11), 237 (7), 255 (6), 417 (3), 487 (6) $[M]^+$, 488 (7) $[M + 1]^+$. HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{26}N_3O_9$ $[M + H]^+$ 488.1669; found 488.1673.

4.3.29 (1*R*,2*S*,3*R*,4*S*,5*R*,6*R*)-1-(Acetoxymethyl)-5-[4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl]-7-oxabicyclo[4.1.0]heptane-2,3,4-triyl Triacetate (16b): This compound was prepared from **11** (193 mg, 0.50 mmol) and (4-chlorophenyl)acetylene (82 mg, 0.60 mmol) by **Method A** (246 mg, 94%), as a white solid, m.p. 246.2–247.0 °C. $[a]_D^{25}$ = +146.5 (*c* = 0.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1 H, triazole H), 7.75 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.35 (d, *J* = 8.5 Hz, 2 H, Ar-H), 5.82 (dd, *J* = 7.5, 4.2 Hz, 1 H, 6-H), 5.58 (d, *J* = 7.9 Hz, 1 H, 3-H), 5.41 (dd, *J* = 10.6, 7.9 Hz, 1 H, 2-H), 5.15 (dd, *J* = 10.6, 7.5 Hz, 1 H, 1-H), 4.39 (d, *J* = 12.4 Hz, 1 H, C*H*HOAc), 3.95 (d, *J* = 12.4 Hz, 1 H, CH*H*OAc), 3.70 (d, *J* = 4.3 Hz, 1 H, 5-H), 2.10 (s, 3 H, CH_3COO), 2.04 (s, 3 H, CH_3COO), 1.96 (s, 3 H, CH_3COO), 1.75 (s, 3 H, CH_3COO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.96 (CH_3COO), 168.68 (CH_3COO), 168.33 (CH_3COO), 168.30 (CH_3COO), 146.43 (triazole-C_{quat}), 133.17 (Ar-C_{quat}), 128.07 (Ar-C), 127.74 (Ar-C_{quat}), 126.10 (Ar-C), 119.18 (triazole-C), 67.90 (C-2), 66.71 (C-3), 66.44 (CH_2OAc), 60.42 (C-1), 60.28 (C-4), 55.82 (C-6), 53.98 (C-5), 19.53 (CH_3COO), 19.47 (CH_3COO), 19.46 (CH_3COO), 19.05 (CH_3COO) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 1744, 1375, 1225, 1092, 1032, 970, 937, 908, 815, 740, 710 cm^{-1}. MS (EI): *m/z* (%) = 43 (100), 111 (21), 123 (64), 139 (26), 150 (31), 165 (48), 207 (5), 451 (2), 521 (1) $[M]^+$, 522 (5) $[M + 1]^+$. HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{25}ClN_3O_9$ $[M + H]^+$ 522.1279; found 522.1275.

4.3.30 (1*R*,2*S*,3*R*,4*S*,5*R*,6*R*)-1-(Acetoxymethyl)-5-(4-butyl-1*H*-1,2,3-triazol-1-yl)-7-oxabicyclo[4.1.0]heptane-2,3,4-triyl Triacetate (16c): This compound was prepared from **11** (193 mg, 0.50 mmol) and hex-1-yne (49 mg, 0.60 mmol) by **Method A** (216 mg, 92%), as a white solid, m.p. 170.9–171.3 °C. $[a]_D^{25}$ = +94.5 (*c* = 0.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70 (s, 1 H, triazole H), 5.74 (dd, *J* = 7.5, 4.2 Hz, 1 H, 6-H), 5.56 (d, *J* = 7.8 Hz, 1 H, 3-H), 5.36 (dd, *J* = 10.4, 7.8 Hz, 1 H, 2-H), 5.11 (dd, *J* = 10.4, 7.5 Hz, 1 H, 1-H), 4.37 (d, *J* = 12.3 Hz, 1 H), 3.93 (d, *J* = 12.3 Hz, 1 H), 3.66 (d, *J* = 4.2 Hz, 1 H, 5-H), 2.67 (t, *J* = 7.5 Hz, 2 H, CH_2), 2.09 (s, 3 H, CH_3COO), 2.03 (s, 3 H, CH_3COO), 1.95 (s, 3 H, CH_3COO), 1.71 (s, 3 H, CH_3COO), 1.61 (dt, *J* = 13.1, 7.5 Hz, 2 H, CH_2), 1.39–1.24 (m, 2 H, CH_2), 0.87 (t, *J* = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.97 (CH_3COO), 168.71 (CH_3COO), 168.32 (CH_3COO), 168.28 (CH_3COO), 148.10 (triazole-C_{quat}), 120.20 (triazole-C), 67.99 (C-2), 66.89 (C-3), 66.59 (CH_2OAc), 60.59 (C-1), 60.01 (C-4), 55.97 (C-6), 53.64 (C-5), 30.44 (CH_2), 24.38 (CH_2), 21.24 (CH_2), 19.54 (CH_3COO), 19.50 (CH_3COO), 19.46 (CH_3COO), 18.96 (CH_3COO), 12.78 (CH_3) ppm. FT-IR (neat): $\tilde{\nu}_{max}$ = 2962, 2928, 1739, 1431, 1378, 1233, 1083, 1032, 973, 937, 804 cm^{-1}. MS (EI): *m/z* (%) = 43 (100), 96 (13), 111 (22), 123 (17), 139 (10), 153 (8), 166 (5), 192 (6), 217 (4), 354 (3), 468 (1) $[M]^+$. HRMS (ESI-TOF): *m/z* calcd. for $C_{21}H_{30}N_3O_9$ $[M + H]^+$ 468.1982; found 468.1980.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra of compounds **7**, **8**, **9**, **11**, **13a**–**j**, **14a**–**i**, **15a**–**h**, **16a**–**c** and ^1H-^1H NOESY, HMBC and HSQC spectra of compound **15a**.

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