Carbohydrate Research 379 (2013) 60–67

Contents lists available at SciVerse ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Efficient microwave assisted synthesis of novel 1,2,3-triazole–sucrose derivatives by cycloaddition reaction of sucrose azides and terminal alkynes

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ARTICLE INFO

Article history:
Received 23 May 2013
Received in revised form 19 June 2013
Accepted 20 June 2013
Available online 28 June 2013

Keywords:
1,2,3-Triazoles
Sucrose derived azides
Carbohydrate
Microwave assisted synthesis
'Click' chemistry
1,3-Dipolar cycloaddition

ABSTRACT

Novel 1-(1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-substituted-1,2,3-triazoles were synthesized by microwave assisted copper catalyzed 1,3-dipolar cycloaddition of sucrose derived azides with terminal alkynes in excellent yields and in short reaction times. The compound 1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-azido-6′-deoxy-sucrose was regioselectively synthesized from sucrose by improved procedure and used for the cycloadditions. By combining carbohydrate and 1,2,3-triazole structural motifs, a library of 1,2,3-triazole–sucrose conjugates have been obtained.

1. Introduction

Glycosyl azides are important class of carbohydrate derivatives, which have been used as precursors for the synthesis of glycosyl amines,[1,2] N-glycopeptides,[3] N-glycoproteins,[4] and glycosyl heterocycles, such as 1,2,3-triazoles.[5–7]. In some cases, glycosyl azides have been converted into glycosyl fluorides for their use in the synthesis of oligosaccharides and glycoconjugates.[8] Glycosyl azides have successfully been used in the solid phase preparation of glycopeptides.[9,10] They can also provide chiral templates for the synthesis of glycosyl amino acids.[11–13] Glycosyl azides have been applied as novel substrate for enzymatic transglycosylations.[14]

1,2,3-Triazoles and their derivatives have gained significant amount of attention due to their wide usage in various fields, such as pharmaceutical, agricultural, material science and biology. The combination of both carbohydrate and 1,2,3-triazole structural motifs has led to the flourishing field of conjugates that have proved to possess various biological activities[15–17] Thus, sugar–triazole conjugates were synthesized and tested for glycosidases,[18] transsialidase,[19] glycogen phosphorylase[20] inhibiting activities, antitubercular activity,[21] and as nucleoside mimetics.[22]

The azido sugars are known as versatile starting materials in accessing a number of biologically active compounds, including amino sugars, nucleosides, and many other glycosylated heterocycles.[23–25] The term 'click chemistry' coined by Sharpless and coworkers,[26–28] has opened a new chapter in the area of glycoconjugates and macromolecules bearing the triazolyl moiety by cycloaddition of acetylenic compounds with azides. Copper-catalyzed triazole synthesis was first reported by Tornoe et al.,[29] and this work is getting great applicability nowadays for selective triazole synthesis.

Microwave-enhanced synthesis has been extended to almost all areas of chemistry[30] with the exception of carbohydrate chemistry, which has suffered a certain delay, as it is testified by the limited number of applications.[31,32] In particular, it had previously not been applied to sucrose chemistry, and the general opinion is that the method is hampered by competitive degradation of sucrose because of its thermal instability.[33] Herein, a method to overcome these limitations and to apply highly efficient and fast synthetic protocols for the synthesis of a series of sugar derivatives under microwave irradiation is presented.

The key point to successful synthesis under microwave irradiation is to use proper equipment, especially designed for chemical laboratories. Monomodal microwave equipment has overcome the uncertainties associated with domestic microwave ovens, as it offers much more precise control over conditions of temperature and pressure than any previous technology and the software provides simplified process monitoring and control, which results in accurate and reproducible reaction conditions.[34] In the development of new carbohydrates or in their transformations

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0008-6215/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carres.2013.06.017

there is a need for faster and cleaner methods which can be provided by microwave heating. The microwave assisted protocols presented here, allowed significant reduction of time and energy and potential automatization of tedious multi-step synthesis.

The synthesis of 1,2,3-triazole derived from azido monosaccharide has been extensively investigated, but there are only few reports of 1,2,3-triazoles derived from azido disaccharide.[35] To the best of our knowledge, there is no report on the synthesis of 1,2,3-triazole–sucrose derivatives from 6′-azidosucrose derivatives and alkynes. 1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-azido-6′-deoxy-sucrose **4** was the key intermediate for the synthesis of 1,2,3-triazole–sucrose derivatives and was prepared regioselectively from sucrose in four steps, as shown in Scheme 1.

2. Results and discussion

Initially, 6′-*O*-*tert*-butyldiphenylsilyl-sucrose **1** was prepared by treating sucrose with *tert*-butyldiphenylchlorosilane (TBDPSCl) in pyridine at room temperature, as previously described.[36] Then, all remaining hydroxyl groups of **1** were protected by treating it with acetic anhydride in pyridine at room temperature to afford 6′-*O*-*tert*-butyldiphenylsilyl-1′,2,3,3′,4,4′,6-hepta-*O*-acetylsucrose **2** in excellent yield (90.4%). The product **2** was identical in all aspects as described in the literature.[37] The acetyl groups were chosen because of the advantage of removing them in basic media without affecting the glycosidic bond.

To deprotect the silyloxy group, **2** was treated with tetra-*n*-butylammonium fluoride (TBAF) in THF at room temperature. The reaction afforded the desired 1′,2,3,3′,4,4′,6-hepta-*O*-acetylsucrose **3** in 41.0% yield, along with formation of other undesired products resulting from acyl migration and fluorolysis of acetate groups. In order to obtain alcohol **3** in enhanced yield, other procedures were attempted, such as performing the deprotection reaction using TBAF at lower temperatures or iodine in acetonitrile at 60 °C, but those did not produce **3** with improved yield. When selective deprotection of the silyloxy group of **2** with HF-pyridine in THF at room temperature was tried, it afforded **3** in 81.3% yield as colorless solid. The reaction procedure and work up were easy to perform and gave very clean reaction without any acetyl migration, thus improving the procedures found in the literature.[38,39]

It was then successfully converted into 1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-azido-6′-deoxy-sucrose **4** via two step procedure, as shown in Scheme 1. For this, **3** was treated with methanesulfonyl chloride in CH_2Cl_2 using Et_3N and DMAP at 0 °C to afford 1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-*O*-methanesulfonyl sucrose. Without purifying the mesylate, it was treated with sodium azide in DMF under microwave irradiation at 120 °C (400 W) for 10 min to afford **4** in 89.1% yield as colorless solid.

To establish the reaction conditions for the synthesis of 1,2,3-triazole–sucrose derivatives, a model reaction was carried out between **4** and phenyl acetylene **5a** in the presence of $CuSO_4{\cdot}5H_2O$ (0.2 equiv) and sodium ascorbate (0.4 equiv) in *tert*-BuOH/H_2O (1:1). These conditions have been chosen based on previous experiments. The reaction was carried out at 35, 50, 60, and 70 °C with conventional heating in an oil bath and under microwave irradiation. The best result was obtained at 70 °C, to afford the corresponding product **6a** in 3 h at conventional heating against 5 min under microwave irradiation of 400 W starting power and atmospheric pressure (Scheme 2), in excellent yield (91.0%) under both conditions. Further increase of the temperature beyond 70 °C did not give better results.

The reactions under microwave irradiation were performed using a monomodal microwave reactor MicroSynth Labstation (MileStone, USA)[34] in open flasks equipped with temperature control sensor and magnetic stirring. The energy transfer in a microwave-assisted reaction is very quick, that is why only by programing temperature control the decomposition of the substrates has been avoided and comparatively high yields have been obtained in short reaction times. In this method, as the temperature reaches the input value, the power is reduced so that the reaction mixture does not exceed the set point. It then stays at a lower level in order to maintain the set temperature throughout the entire reaction. Therefore, the reaction conditions are not expressed as a function of the magnetron power, as for most microwave-assisted reactions published, but by the reaction temperature.

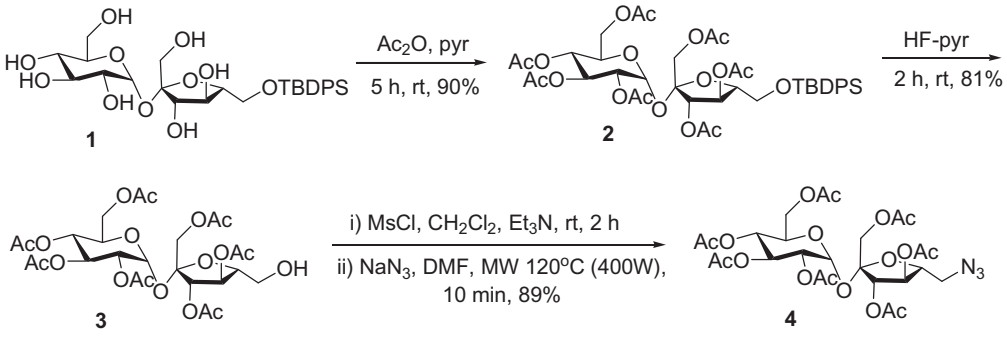
By using these optimized reaction conditions, various alkynes **5a**–**5j** were reacted with 6′-azido sucrose **4** to afford 1-(1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-substituted-1,2,3-triazoles **6a**–**6j** (Fig. 1) in excellent yields and in short reaction time (Table 1).

The bi-functionalized compound 1′,2,3,3′,4,4′-hexa-*O*-acetyl-6,6′-diazido-6,6′-dideoxysucrose **9** has been synthesized as previously described[37] via 6,6′-dibromo-6,6′-dideoxysucrose **7** and 6,6′-diazido-6,6′-dideoxysucrose **8** (Scheme 3).

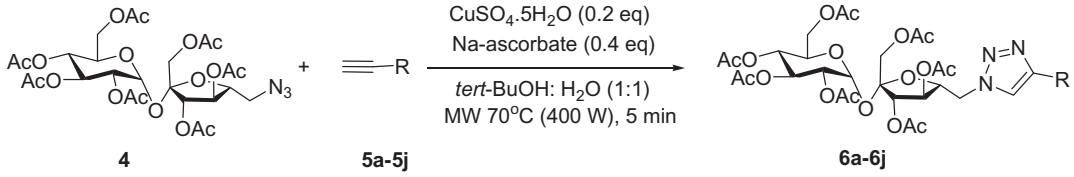
Then, using a similar microwave assisted protocol for the cycloaddition reactions as described above, two 1-(1′,2,3,3′,4,4′-hexa-*O*-acetyl-6,6′-dideoxy-sucros-6,6′-diyl)-bis-4-substituted-1,2,3-triazoles **10a** and **10b** have been obtained (Scheme 4, Fig. 1).

All the products are novel and have been characterized by IR, ^1H NMR, ^{13}C NMR, COSY, HMQC, HMBC, $[\alpha]_D$, melting points, and MALDI TOF MS. This type of sugar–triazole conjugates has proved to possess a large variety of useful biological activities, as shown in numerous reports in the scientific literature.[6,7,15,19–21,40–43] The triazoles **6g** and **6h,** which possess polymerizable moieties, could be polymerized and have potential to produce biodegradable polymers.[44,45]

In conclusion, a convenient protocol for microwave assisted synthesis of 1-(1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-substituted-1,2,3-triazoles and 1-(1′,2,3,3′,4,4′-hexa-*O*-acetyl-6,6′-dideoxy-sucros-6,6′-diyl)-bis-4-substituted-1,2,3-triazoles



Scheme 1. Synthesis of 1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-azido-6′-deoxy-sucrose **4**.



Scheme 2. Synthesis of 1,2,3-triazole–sucrose derivatives.

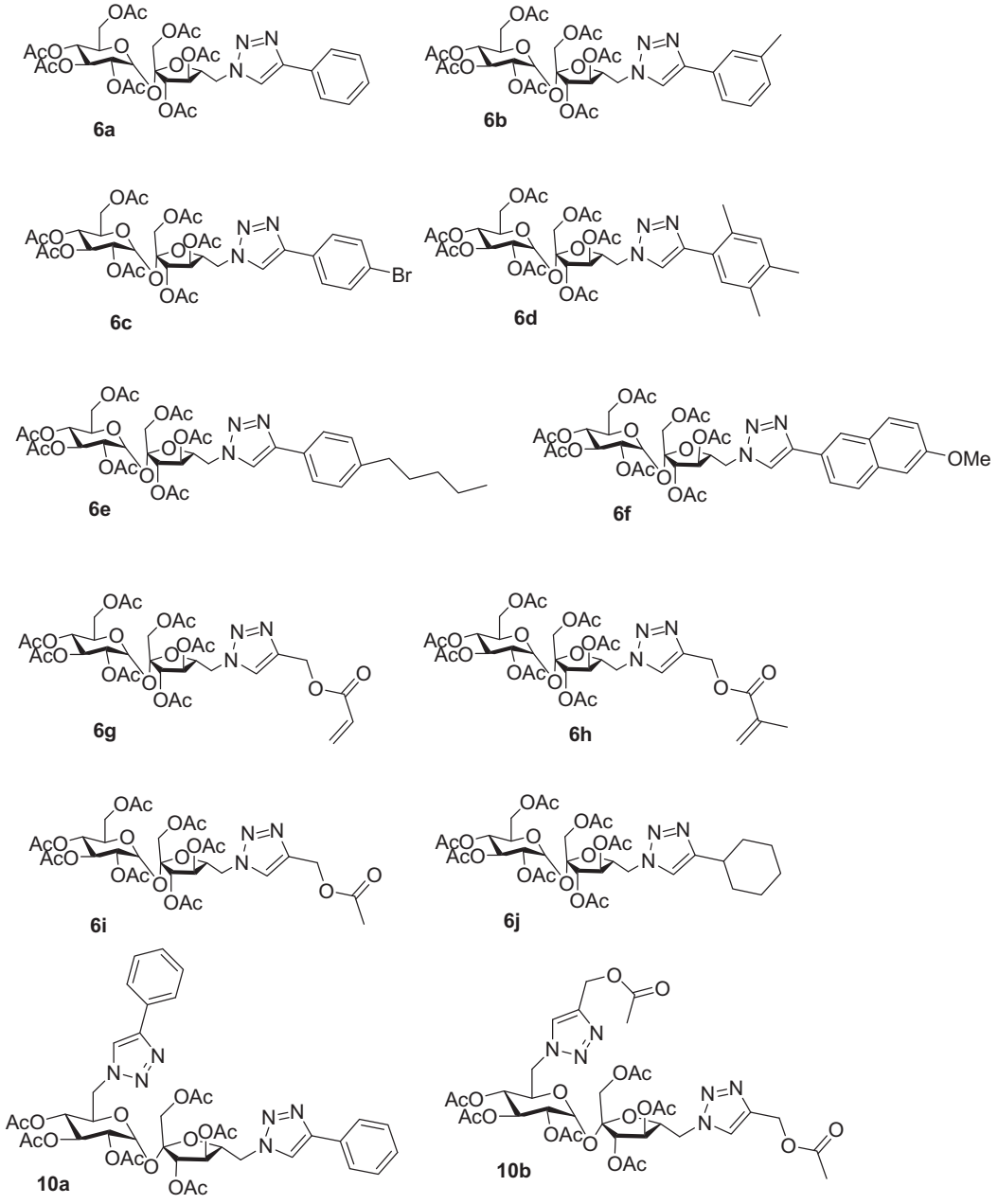


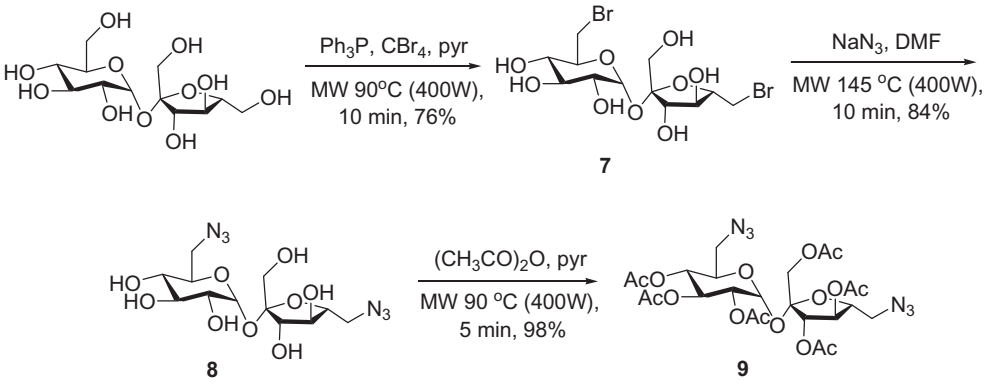
Fig. 1. Library of 1,2,3-triazole–sucrose derivatives synthesized under microwave irradiation.

is here reported for the first time. All new compounds have been characterized by IR, ^{1}H NMR, ^{13}C NMR, COSY, HMQC, HMBC, $[\alpha]_D$, melting points, and MALDI TOF MS. The reaction conditions reported here can be applied to a large number of alkynes, thus expanding further the presented library of derivatives. The utilization of microwave irradiation as a more efficient mode of heating leading to shorter reaction periods was evaluated. It has been shown that microwave irradiation efficiently promoted the reactions and allowed a great reduction in reaction times, at the same time affording high yields (82–94%). In the case of sucrose functionalization the elimination of solvent was not recommended as it led to significantly lower yields because of overheating.

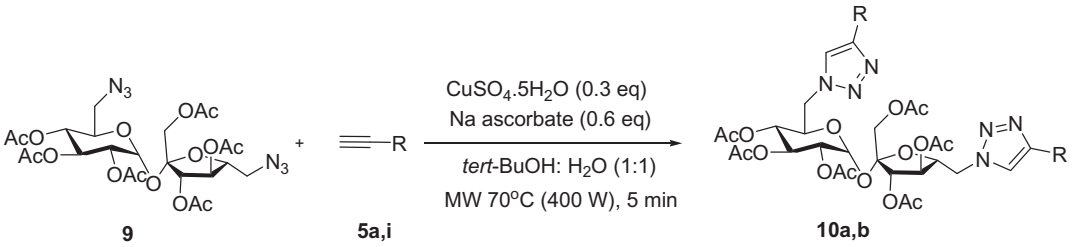
Table 1
Microwave assisted synthesis of 1,2,3-triazole–sucrose derivatives, 70 °C (400 W), 1 atm, 5 min

Entry	Alkyne **5**	R- (see Scheme 2)	Product (see Fig. 1)	Yield[a] (%)	Mp (°C)
1	Phenyl acetylene **5a**	Phenyl	**6a**	91.0	60–61
2	3-Ethynyltoluene **5b**	*m*-Tolyl	**6b**	88.6	60–61
3	1-Ethynyl-4-bromobenzene **5c**	4-Bromophenyl	**6c**	86.2	57–58
4	1-Ethynyl-2,4,5-trimethylbenzene **5d**	2,4,5-Trimethylphenyl	**6d**	85.5	64–65
5	1-Ethynyl-4-(*n*-pentyl)benzene **5e**	4-(*n*-Pentyl)phenyl	**6e**	94.6	54–55
6	2-Ethynyl-6-methoxynaphthalene **5f**	6-Methoxynaphthalen-2-yl	**6f**	93.5	87–88
7	Propargyl acrylate **5g**	Acryloxymethyl	**6g**	90.7	58–59
8	Propargyl methacrylate **5h**	Methacryloxymethyl	**6h**	82.3	47–48
9	Propargyl acetate **5i**	Acetoxymethyl	**6i**	85.6	53–54
10	Cyclohexylacetylene **5j**	Cyclohexyl	**6j**	85.9	53–54
11	Phenyl acetylene **5a**	Phenyl	**10a**	89.3	88–89
12	Propargyl acetate **5i**	Acetoxymethyl	**10b**	91.2	59–60

[a] Isolated yields after column chromatography.



Scheme 3. Synthesis of 1′,2,3,3′,4,4′-hexa-*O*-acetyl-6,6′-diazido-6,6′-dideoxysucrose **9**.



Scheme 4. Synthesis of 1-(1′,2,3,3′,4,4′-hexa-*O*-acetyl-6,6′-dideoxy-sucros-6,6′-diyl)-bis-4-substituted-1,2,3-triazoles **10a** and **10b**.

3. Experimental part

3.1. General

Reagents and solvents were purified by standard procedures.[46] NMR spectra were recorded at 400 MHz in $CDCl_3$, with chemical shift values (δ) in ppm downfield from TMS (0 ppm) as internal standard. Optical rotations were measured at 25 °C on an AA-1000 polarimeter (0.5 dm cell) at 589 nm. The concentrations (*c*) are expressed in g/100 mL. Melting points were determined with a capillary apparatus with heating plate *Electrothermal* type, in open capillary on Buchi melting Point B-540 apparatus. FTIR spectra were recorded on Perkin-Elmer Spectrum BX apparatus. Mass Spectra were recorded on GC-TOF-MS (Gas Chromatography-Time Of Flight-Mass Spectrometer) Micromass, model GCT. The reactions under microwave irradiation were performed using a monomodal microwave reactor MicroSynth Labstation (MileStone, USA)[34] in open flasks equipped with temperature control sensor and magnetic stirring.

3.2. 6′-*O*-*tert*-Butyldiphenylsilyl-1′,2,3,3′,4,4′,6-hepta-*O*-acetylsucrose (2)

To a cooled solution of 6′-*O*-*tert*-butyldiphenylsilyl-sucrose **1** (prepared as described)[36] (2 g, 3.44 mmol) in pyridine (30 mL) at 0 °C was added acetic anhydride (3.25 mL, 34.40 mmol) dropwise over 5 min. After completion of addition of acetic anhydride, ice-water bath was removed and reaction was left stirred at room temperature for 5 h. The reaction progress was monitored by TLC. After completion, pyridine was distilled off under reduced pressure and the residue was purified by flash column chromatography (eluent Et_2O:hexane, 1:1) to afford 6′-*O*-*tert*-butyldiphenylsilyl-1′,2,3,3′,4,4′,6-hepta-*O*-acetylsucrose **2** in 90.4% (2.72 g) as colorless solid.

Mp 50–52 °C; lit.[37] 52–54 °C.

IR ($CHCl_3$): ν_{max} 3014, 2958, 2859, 1751, 1428, 1369, 1224, 1039 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ ppm 1.06 (s, 9H, $-C(CH_3)_3$), 1.97 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.09

(s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 3.84–3.86 (m, 2H, H-6′), 3.96 (d, $J_{1',1'}$ = 12.0 Hz, 1H, H-1′), 4.09–4.22 (m, 5H, 1H of H-1′, 2H of H-6, H-4 & H-5′) 4.83 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.4 Hz, 1H, H-2), 5.03 (t, $J_{4,5} = J_{5,6}$ = 10.0 Hz, 1H, H-5), 5.37–5.42 (m, 2H, H-3′ & H-3), 5.52 (t, $J_{3',4'} = J_{4',5'}$ = 5.6 Hz, 1H, H-4′), 5.64 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-2), 7.36–7.44 (m, 6H, ArH), 7.64–7.68 (m, 4H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 19.1 (–*C*(CH_3)$_3$), 20.5 (*C*H_3), 20.7 (*C*H_3), 26.7 (–C(*C*H_3)$_3$), 61.5 (C-1′), 62.9 (C-6), 63.8 (C-6′), 68.0 (C-5), 68.2 (C-4), 69.7 (C-3), 70.1 (C-2), 75.0 (C-4′), 76.1 (C-3′), 81.3 (C-5′), 89.6 (C-1), 103.6 (C-2′), 127.7, 129.8, 132.9, 135.5 (Ar), 169.4, 169.7, 169.9, 170.0, 170.1, 170.5 (CO).

MALDI-TOF MS: Calcd for $C_{42}H_{54}O_{18}Si$ ([M+Na]$^+$): 897.2977, found 897.3809.

3.3. 1′,2,3,3′,4,4′,6-Hepta-*O*-acetylsucrose (3)

To a solution of 6′-*O*-*tert*-butyldiphenylsilyl-1′,2,3,3′,4,4′,6-hepta-*O*-acetylsucrose **2** (1 g, 1.14 mmol) in dry THF (15 mL) in plastic vial was added HF-Pyridine (70%, 1.71 mL) dropwise and reaction mixture was stirred at room temperature for 2 h. After completion of reaction as indicated by appearance of new polar spot on TLC and complete disappearance of the starting material, the reaction mixture was poured to water (50 mL), neutralized using solid $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford crude, which was further purified by flash column chromatography (eluent EtOAc:hexane, 3:2) to afford the desired 1′,2,3,3′,4,4′,6-hepta-*O*-acetylsucrose **3** (590 mg, 81.3%) as colorless solid.

Mp 158–160 °C; lit.[38] 158–160 °C.

IR ($CHCl_3$): ν_{max} 3491 (br), 2962, 2859, 1748, 1370, 1226, 1040 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.02 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.11 (s, 9H, 3 × CH_3), 2.12 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.75 (s, 1H, OH), 3.64–3.70 (m, 1H, H-6′), 3.84 (d, $J_{6',6'}$ = 12.0 Hz, 1H, H-6′), 4.07–4.10 (m, 2H, H-1′ & H-5′), 4.16–4.19 (m, 2H, H-1′ & H-6), 4.26–4.28 (m, 2H, H-4 & H-6), 4.88 (dd, $J_{1,2}$ = 2.4 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H-2), 5.09 (t, $J_{4,5} = J_{5,6}$ = 9.6 Hz, 1H, H-5), 5.41–5.47 (m, 3H, H-3, H-3′ & H-4′), 5.68 (d, $J_{1,2}$ = 2.4 Hz, 1H, H-1).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 20.6 (*C*H_3), 61.1 (C-6′), 61.4 (C-6), 63.9 (C-1′), 67.9 (C-5), 68.7 (C-4), 69.3 (C-3), 70.2 (C-2), 73.6 (C-3′), 76.1 (C-4′), 81.6 (C-5′), 90.0 (C-1), 103.2 (C-2′), 169.4, 169.9, 170.5, 170.6 (CO).

MALDI-TOF MS: Calcd for $C_{26}H_{36}O_{18}$ ([M+Na]$^+$): 659.18, found 659.70.

3.4. 1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-azido-6′-deoxy-sucrose (4)

To a solution of 1′,2,3,3′,4,4′,6-hepta-*O*-acetylsucrose **3** (1 g, 1.57 mmol) in CH_2Cl_2 (25 mL) was added Et_3N (0.24 mL, 1.72 mmol) followed by catalytic amount of 4-dimethylamino pyridine (DMAP). The reaction mixture was cooled to 0 °C in ice-water bath. To this cooled reaction mixture was added methane sulfonyl chloride (0.13 mL, 1.64 mmol) dropwise and reaction mixture was stirred for 30 min at 0 °C followed by stirring at rt for 2 h. After completion of reaction, as indicated by disappearance of the starting material and appearance of non-polar spot on TCL, reaction was quenched with satd solution of NH_4Cl and extracted with CH_2Cl_2 (2 × 20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give crude 1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-*O*-methanesulfonyl sucrose (1.42 g), which was used without further purification.

The obtained crude 1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-*O*-methanesulfonylsucrose (1.42 g) was dissolved in DMF (25 mL), followed by addition of NaN_3 (520 mg, 7.85 mmol) and the reaction was subjected to microwave irradiation of max 400 W at constant temperature 120 °C for 10 min. After completion of reaction, DMF was evaporated under reduced pressure. The residue was dissolved in EtOAc (25 mL) and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford crude, which was further purified by flash column chromatography (eluent EtOAc:hexane, 2:3) to afford 1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-azido-6′-deoxy-sucrose **4** (925 mg, 89.1%) as colorless solid.

Mp 143–145 °C; lit[47] 136–141 °C.

IR ($CHCl_3$): ν_{max} 2961, 2103 (N_3), 1748 (CO), 1433, 1370, 1223, 1039, 772 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.02 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.11 (s, 12H, 4 × CH_3), 2.17 (s, 3H, CH_3), 3.51 (dd, $J_{5',6'}$ = 4.0 - Hz, $J_{6',6'}$ = 13.0 Hz,1H, H-6′), 3.69–3.74 (m, 1H, H-6′), 4.12–4.31 (m, 6H, H-5, H-5′, H-1 & H-6), 4.90 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.4 Hz, 1H, H-2), 5.06 (t, $J_{3,4} = J_{4,5}$ = 9.8 Hz, 1H, H-4), 5.31 (t, $J_{3',4'} = J_{4',5'}$ = 6.1 Hz, 1H, H-4′), 5.45–5.50 (m, 2H, H-3 & H-3′), 5.64 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 20.4, 20.5 (*C*H_3), 52.8 (C-6′), 61.9 (C-6), 62.7 (C-1′), 68.2 (C-4), 68.5 (C-5), 69.4 (C-3), 70.2 (C-2), 75.7 (C-3′ & C-4′), 80.1 (C-5′), 90.3 (C-1), 103.8 (C-2′), 169.5, 169.6, 169.9, 170.0, 170.6 (CO).

MALDI-TOF MS: Calcd for $C_{26}H_{35}N_3O_{17}$ ([M+Na]$^+$): 684.1864, found 684.6854.

3.5. General procedure for microwave assisted synthesis of 1,2,3-triazole–sucrose derivatives

To a well-stirred solution of sugar monoazide **4** (1 eq) and alkyne **5a-j** (1.5 eq) in *tert*-BuOH and H_2O (1:1, 2.50 mmol/mL), was added aqueous suspension (0.5 mL H_2O) of $CuSO_4{\cdot}5H_2O$ (0.2 equiv) and sodium ascorbate (0.4 equiv). The mixture was then subjected to microwave irradiation of max 400 W at constant temperature 70 °C for 5 min. After completion, the resulting mixture was diluted with H_2O (10 mL) and extracted with EtOAC (3 × 10 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give crude residue. The crude residue was purified by flash column chromatography.

3.6. 1-(1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-phenyl-1,2,3-triazole (6a)

Compound **6a** (132 mg, 91.0%) has been obtained from **4** (125 mg, 0.19 mmol) and phenyl acetylene **5a** (32 μL, 0.28 mmol) by the general procedure.

Colorless solid; mp 60–61 °C.

$[\alpha]_D^{25}$ +41.84 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3023, 2959, 2855, 1749, 1485, 1465, 1437, 1370, 1224, 1041 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 2.04 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 3.97 (d, $J_{1',1'}$ = 12.1 Hz, 1H, H-1′), 4.14–4.18 (m, 2H, H-1′ & H-6), 4.28–4.35 (m, 2H, H-4 & H-6), 4.50–4.55 (m, 1H, H-5′), 4.73–4.78 (m, 1H, H-6′), 4.86–4.90 (m, 1H, H-6′), 4.96 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.4 Hz, 1H, H-2), 5.08 (t, $J_{4,5} = J_{5,6}$ = 9.8 Hz, 1H, H-5), 5.45–5.57 (m, 3H, H-3, H-3′ & H-4′), 5.67 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 7.32–7.36 (t, $J_{Ar3,4} = J_{Ar4,3}$ = 7.3 Hz, 1H, ArH_4), 7.42–7.46 (t, $J_{Ar2,3} = J_{Ar3,4}$ = 7.3 Hz, 2H, ArH_3), 7.86 (d, $J_{Ar2,3}$ = 7.5 Hz, 2H, ArH_2), 7.95 (s, 1H, ArH triazole ring).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 20.4 (*C*H_3), 20.5 (*C*H_3), 20.5 (*C*H_3), 20.6 (*C*H_3), 52.7 (C-6′), 62.1 (C-6), 62.7 (C-1′), 68.3 (C-5), 69.0 (C-4), 69.2, 70.0 (C-2), 74.9, 75.4 (C-3), 79.2 (C-5′), 90.0 (C-1), 103.7 (C-2′), 121.1 (C triazole), 125.7 (Ar*C*), 128.2 (Ar*C*), 128.8 (Ar*C*), 130.3 (ArC quart), 147.8 (Cquat triazole ring), 169.5 (CO), 169.73 (CO), 169.9 (CO), 170.0 (CO), 170.2 (CO), 170.3 (CO), 170.5 (CO).

MALDI TOF MS calcd $C_{34}H_{42}N_3O_{17}$: [M+H]$^+$ 764.2514; found 764.2439.

3.7. 1-(1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-(*m*-tolyl)-1,2,3-triazole (6b)

Compound **6b** has been obtained (310 mg, 88.6%) from **4** (300 mg, 0.45 mmol) and 3-ethynyltoluene **5b** (90 μL, 0.68 mmol) by the general procedure.

Colorless solid; mp 60–61 °C.

$[\alpha]_D^{25}$ +54.8 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3018, 2965, 2864, 1751, 1451, 1433, 1370, 1229, 1043 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 2.04 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.08 (s, 6H, 2 × CH_3), 2.12 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.42 (s, 3H, $ArCH_3$), 3.96 (d, $J_{1′,1′}$ = 12.1 -Hz, 1H, H-1′), 4.14–4.19 (m, 2H, H-1′ & H-6), 4.28–4.36 (m, 2H, H-5 & H-6), 4.50–4.54 (m, 1H, H-5′), 4.72–4.78 (m, 1H, H-6′), 4.88 (dd, $J_{5′,6}$ = 3.3 Hz, $J_{6′,6′}$ = 14.3 Hz, 1H, H-6′), 4.96 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.4 Hz, 1H, H-2), 5.08 (t, $J_{3,4} = J_{4,5}$ = 9.8 Hz, 1H, H-4), 5.45–5.57 (m, 3H, H-4′, H-3, H-3′), 5.67 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 7.16 (d, $J_{Ar4,5}$ = 7.5 Hz, 1H, ArH_4), 7.32 (t, $J_{Ar4,5} = J_{Ar5,6}$ = 7.6 Hz, 1H, ArH_5), 7.63 (d, $J_{Ar5,6}$ = 7.7 Hz, 1H, ArH_6), 7.72 (s, 1H, ArH_2), 7.93 (s, 1H, triazole H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 20.4 (*C*H_3), 20.5 (*C*H_3), 20.6 (*C*H_3), 21.4 (Ar*C*H_3), 52.8 (C-6′), 62.1 (C-6), 62.7 (C-1′), 68.2 (C-4), 69.0 (C-5), 69.2 (C-3), 70.0 (C-2), 74.9 (C-3′), 75.3 (C-4′), 79.2 (C-5′), 90.0 (C-1), 103.6 (C-2′), 121.1 (*C*H of triazole), 122.9 (ArH), 126.4 (ArH), 128.7 (ArH), 129.0 (ArH), 130.0 (Ar*C*quat), 138.5 (Ar*C*-quat), 147.9 (Cquat triazole), 169.4, 169.7, 169.9, 170.0, 170.2, 170.3, 170.4 (CO).

MALDI TOF MS calcd for $C_{35}H_{44}N_3O_{17}$: $[M+H]^+$ 778.2671; found 778.2543.

3.8. 1-(1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-(4-bromophenyl)-1,2,3-triazole (6c)

Compound **6c** (167 mg, 86.2%) has been obtained from **4** (150 mg, 0.23 mmol) and 1-ethynyl-4-bromobenzene **5c** (62 mg, 0.34 mmol) by the general procedure.

Colorless solid; mp 57.58.

$[\alpha]_D^{25}$ +70.4 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3023, 2961, 1753, 1550, 1482, 1456, 1432, 1370, 1226, 1225, 1041 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 2.04 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.96 (d, $J_{1′,1′}$ = 12.1 Hz, 1H, H-1′), 4.11–4.17 (m, 2H, H-1′, H-6), 4.29–4.35 (m, 2H, H-5, H-6), 4.48–4.53 (m, 1H, H-5′), 4.72–4.78 (m, 1H, H-6′), 4.88 (dd, $J_{5′,6′}$ = 3.6 Hz, $J_{6′,6′}$ = 14.1 Hz, 1H, H-6′), 4.95 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-2), 5.07 (t, $J_{3,4} = J_{4,5}$ = 10.1 Hz, 1H, H-4), 5.43–5.57 (m, 3H, H-4′, H-3, H-3′), 5.65 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 7.57 (d, $J_{Ar2,3}$ = 8.4 Hz, 1H, Ar-H_3), 7.75 (d, $J_{Ar2,3}$ = 8.4 Hz, 1H, Ar-H_2), 9.96 (s, 1H, triazole H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 20.4 (*C*H_3), 20.5 (*C*H_3), 20.6 (*C*H_3), 52.8 (C-6′), 62.0 (C-6), 62.6 (C-1′), 68.3 (C-4), 69.0 (C-5), 69.1 (C-3), 70.1 (C-2), 74.8 (C-3′), 75.3 (C-4′), 79.2 (C-5′), 90.0 (C-1), 103.7 (C-2′), 121.3 (*C*H of triazole), 122.1 (Ar*C*quat), 127.3 (ArH), 129.2 (Ar*C*quat), 132.0 (ArH), 146.8 (Cquat triazole), 169.4, 169.7, 169.9, 170.0, 170.3, 170.5 (CO).

MALDI TOF MS calcd for $C_{34}H_{41}BrN_3O_{17}$: $[M+H]^+$ 842.1619; found 842.1614.

3.9. 1-(1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-[(2,4,5-trimethyl)phenyl]-1,2,3-triazole (6d)

Compound **6d** (310 mg, 85.5%) has been obtained from **4** (300 mg, 0.45 mmol) and 1-ethynyl-2,4,5-trimethylbenzene **5d** (98 mg, 0.68 mmol) by the general procedure.

Colorless solid; mp 64–65 °C.

$[\alpha]_D^{25}$ +45.6 (*c* 0.75, $CHCl_3$).

IR ($CHCl_3$): 3014, 2957, 2864, 2097, 1751, 1556, 1496, 1465, 1307, 1223, 1041 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 2.03 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.27 (s, 3H, $ArCH_3$), 2.28 (s, 3H, $ArCH_3$), 2.40 (s, 3H, $ArCH_3$), 3.97 (d, $J_{1′,1′}$ = 12.1 Hz, 1H, H-1′), 4.13–4.18 (m, 2H, H-1′ & H-6), 4.26–4.35 (m, 2H, H-5 & H-6), 4.54–4.59 (m, 1H, H-5′), 4.73–4.78 (m, 1H, H-6′), 4.87–4.95 (m, 2H, H-2 & H-6′), 5.07 (t, $J_{3,4} = J_{4,5}$ = 9.8 Hz, 1H, H-4), 5.45–5.58 (m, 3H, H-4′, H-3, H-3′), 5.64 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1), 7.05 (s, 1H, ArH_3), 7.60 (s, 1H, ArH_6), 7.83 (s, 1H, triazole H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 19.1, 19.3, 20.4, 20.5, 20.6, 52.7 (C-6′), 62.1 (C-6), 62.7 (C-1′), 68.3 (C-4), 69.0 (C-5), 69.2 (C-3), 70.0 (C-2), 75.2 (C-3′), 75.6 (C-4′), 79.3 (C-5′), 90.1 (C-1), 103.7 (C-2′), 123.1 (*C*H of triazole), 126.9 (Ar*C*quat), 129.9 (ArH), 132.2 (ArH), 132.5 (Ar*C*quat), 134.2 (Ar*C*quat), 136.7 (Ar*C*quat), 147.0 (Cquat triazole), 169.4, 169.7, 169.9, 170.0, 170.1, 170.2, 170.4 (CO).

MALDI TOF MS calcd $C_{37}H_{48}N_3O_{17}$: $[M+H]^+$ 806.2984; found 806.2952.

3.10. 1-(1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-(4-pentylphenyl)-1,2,3-triazole (6e)

Compound **6e** (355 mg, 94.6%) has been obtained from **4** (300 mg, 0.45 mmol) and 1-ethynyl-4-pentylbenzene **5e** (130 μL, 0.68 mmol) by the general procedure.

Colorless solid; mp 54–55 °C.

$[\alpha]_D^{25}$ +54.4 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3022, 2929, 2855, 1749, 1496, 1453, 1433, 1370, 1225, 1043 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 0.89 (t, $J_{CH3-CH2}$ = 6.9 Hz, 3H, *C*H_3CH$_2$–), 1.32–1.35 (m, 4H, CH_3*C*H_2*C*H_2–), 1.60–1.67 (m, 2H, CH_3CH $_2CH$ *C*H_2–), 2.04 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.63 (t, $J_{CH2-CH2}$ = 7.8 Hz, 2H, Ar*C*H_2CH$_2$–), 3.96 (d, $J_{1′,1′}$ = 12.1 Hz, 1H, H-1′), 4.13–4.18 (m, 2H, H-1′ & H-6), 4.27–4.35 (m, 2H, H-5 & H-6), 4.49–4.54 (m, 1H, H-5′), 4.72–4.77 (m, 1H, H-6′), 4.87 (dd, $J_{5′,6′}$ = 3.7 Hz, $J_{6′,6′}$ = 14.2 Hz, 1H, H-6′), 4.96 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.4 Hz, 1H, H-2), 5.07 (t, $J_{3,4} = J_{4,5}$ = 9.8 Hz, 1H, H-4), 5.44–5.57 (m, 3H, H-4′, H-3 & H-3′), 5.66 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1), 7.25 (d, $J_{Ar2,3}$ = 8.1 Hz, 2H, ArH_3), 7.77 (d, $J_{Ar2,3}$ = 8.1 Hz, 2H, ArH_2), 7.91 (s, 1H, thrizole H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 14.0 (*C*H_3CH$_2$), 20.4 (COCH_3), 20.5 (COCH_3), 20.5 (COCH_3), 20.6 (COCH_3), 22.5 (*C*H_2), 31.0 (*C*H_2), 31.4 (*C*H_2), 35.6 (Ar*C*H_2), 52.7 (C-6′), 62.1 (C-6), 62.7 (C-1′), 68.3 (C-4), 69.0 (C-5), 69.2 (C-3), 70.0 (C-2), 74.9 (C-3′), 75.3 (C-4′), 79.2 (C-5′), 90.0 (C-1), 103.6 (C-2′), 120.8 (*C*H of triazole), 125.7 (ArH), 127.6 (Ar*C*quat), 128.9 (ArH), 143.2 (Ar*C*quat), 147.9 (Cquat triazole), 169.5, 169.7, 169.9, 170.0, 170.2, 170.3, 170.5 (CO).

MALDI TOF MS calcd $C_{39}H_{52}N_3O_{17}$: $[M+H]^+$ 834.3297; found 834.3619.

3.11. 1-(1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-(6-methoxynaphthalen-2-yl)-1,2,3-triazole (6f)

Compound **6f** (355 mg, 93.5%) has been obtained from **4** (300 mg, 0.45 mmol) and 2-ethynyl-6-methoxynaphthalene **5f** (125 mg, 0.68 mmol) by the general procedure.

Colorless solid; mp 87–88 °C.

$[\alpha]_D^{25}$ +47.6 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3022, 2957, 2855, 1749, 1613, 1552, 1506, 1482, 1455, 1435, 1366, 1221, 1043 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 2.04 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.08 (s, 6H, 2 × CH_3), 2.12 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 3.94 (s, 3H, OCH_3), 3.98 (d, $J_{1',1'}$ = 12.1 Hz, 1H, H-1′), 4.11–4.20 (m, 2H, H-1′ & H-6), 4.30–4.38 (m, 2H, H-5 & H-6), 4.52–4.56 (m, 1H, H-5′), 4.76–4.82 (m, 1H, H-6′), 4.92 (d, $J_{6',6'}$ = 14.1 Hz, 1H, H-6′), 4.98 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-2), 5.09 (t, $J_{3,4} = J_{4,5}$ = 9.8 Hz, 1H, H-4), 5.47–5.58 (m, 3H, H-4′, H-3, H-3′), 5.69 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1), 7.15–7.19 (m, 2H, $ArH_{5,7}$), 7.79–7.82 (m, 2H, $ArH_{3,4}$), 7.92 (d, $J_{Ar7,8}$ = 8.4 Hz, 1H, ArH), 8.04 (s, 1H, triazole H), 8.32 (s, 1H, ArH_1).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 20.4 (*C*H_3), 20.5 (*C*H_3), 20.6 (*C*H_3), 52.9 (C-6′), 55.3 (OCH_3), 62.2 (C-6), 62.7 (C-1′), 68.3 (C-4), 69.0 (C-5), 69.2 (C-3), 70.0 (C-2), 74.9 (C-3′), 75.3 (C-4′), 79.2 (C-5′), 90.0 (C-1), 103.7 (C-2′), 105.7 (ArH) 119.3 (ArH), 121.1 (*C*H of triazole), 124.3 (ArH). 124.5 (ArH), 125.30 (ArCquat), 127.4 (ArH), 128.9 (ArCquat), 129.7 (ArH), 134.4 (ArCquat), 147.9 (*C*quat triazole), 158.0 (ArCquat), 169.5, 169.7, 169.9, 170.0, 170.2, 170.3, 170.5 (CO).

MALDI TOF MS calcd for $C_{39}H_{45}N_3O_{18}Na$: $[M+Na]^+$ 866.2596; found 866.2590.

3.12. 1-(1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-(acryloxymethyl)-1,2,3-triazole (6g)

Compound **6g** (315 mg, 90.7%) has been obtained from **4** (300 mg, 0.45 mmol) and propargyl acrylate **5g** (75 μL, 0.68 mmol) by the general procedure.

Colorless solid; mp 58–59 °C.

$[\alpha]_D^{25}$ +53.2 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3014, 2961, 2851, 2125, 1749, 1409, 1378, 1225, 1043 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 2.03 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.08 (s, 6H, 2 × CH_3), 2.11 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.95 (d, $J_{1',1'}$ = 12.1 Hz, 1H, H-1′), 4.11–4.16 (m, 2H, H-1′ & H-6), 4.24–4.33 (m, 2H, H-5 & H-6), 4.45–4.50 (m, 1H, H-5′), 4.69–4.75 (m, 1H, H-6′), 4.85 (dd, $J_{5',6'}$ = 3.8 Hz, $J_{6',6'}$ = 14.2 Hz, 1H, H-6′), 4.94 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-2), 5.06 (t, $J_{3,4} = J_{4,5}$ = 9.8 Hz, 1H, H-4), 5.32 (d, *J* = 2.3, 2H, triazole-CH_2O), 5.40–5.55 (m, 3H, H-4′, H-3, H-3′), 5.61 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1), 5.86 (dd, $J_{CH\text{-}CH2}$ = 1.3 Hz, J_{H-C-H} = 17.40 Hz, 1H, CH_2=), 6.11–6.18 (m, 1H, –CH=), 6.44 (dd, $J_{CH\text{-}CH2}$ = 1.32 Hz, J_{H-C-H} = 17.40 Hz, 1H, CH_2=), 7.80 (s, 1H, triazole H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 20.4 (*C*H_3), 20.5 (*C*H_3), 20.6 (*C*H_3), 52.8 (C-6′), 57.4 (*C*H_2), 62.2 (C-6), 62.6 (C-1′), 68.2 (C-4), 69.0 (C-5), 69.1 (C-3), 70.0 (C-2), 74.9 (C-3′), 75.5 (C-4′), 79.3 (C-5′), 90.1 (C-1), 103.7 (C-2′), 125.3 (*C*H of triazole), 127.9 (*C*H_2=), 131.5 (–*C*H=), 142.6 (Cquat triazole), 165.8 (CO), 169.5 (CO), 169.7 (CO), 169.9 (CO), 170.0 (CO), 170.1 (CO), 170.2 (CO), 170.4 (CO).

MALDI TOF MS calcd $C_{32}H_{41}N_3O_{19}Na$: $[M+Na]^+$ 794.2232; found 794.2226.

3.13. 1-(1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-(methacryloxymethyl)-1,2,3-triazole (6h)

Compound **6h** (291 mg, 82.3%) has been obtained from **4** (300 mg, 0.45 mmol) and propargyl acrylate **5h** (84 mg, 0.68 mmol) by the general procedure.

Colorless solid; mp 47–48 °C.

$[\alpha]_D^{25}$ +79.2 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3022, 2961, 1751, 1435, 1316, 1291, 1225, 1041 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 1.94 (s, 3H, CH_3 methacryl), 2.04 (s, 6H, 2 × CH_3), 2.08 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.97 (d, $J_{1',1'}$ = 12.1 Hz, 1H, H-1′), 4.11–4.17 (m, 2H, H-1′ & H-6), 4.24–4.34 (m, 2H, H-6 & H-5), 4.46–4.51 (m, 1H, H-5′), 4.70–4.75 (m, 1H, H-6′), 4.85 (dd, $J_{5',6'}$ = 4.0 Hz, $J_{6',6'}$ = 14.3 Hz, 1H, H-6′), 4.94 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.4 Hz, 1H, H-2), 5.06 (t, $J_{3,4} = J_{4,5}$ = 9.9 Hz, 1H, H-4), 5.31 (d, *J* = 3.0, 2H, triazole-*C*H_2O), 5.40–5.55 (m, 3H, H-4′, H-3, H-3′), 5.40 (t, $J_{CH2\text{-}O}$ = 1.5 Hz, 1H, *C*H_2=), 5.62 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 6.13 (s, 1H, *C*H_2=), 7.80 (s, 1H, triazole H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 18.4 (–C(*C*H_3)=), 20.3 (–CO*C*H_3), 20.4 (–CO*C*H_3), 20.5 (–CO*C*H_3), 52.6 (C-6′), 57.6 (triazole-*C*H_2O), 61.1 (C-6), 62.5 (C-1′), 68.1 (C-4), 68.9 (C-5), 69.1 (C-3), 69.9 (C-2), 74.9 (C-3′), 75.4 (C-4′), 79.2 (C-5′), 90.0 (C-1), 103.6 (C-2′), 125.2 (*C*H of triazole), 126.1 (*C*H_2=C-CH_3), 135.8 (–*C*(CH$_3$)=, 142.8 (Cquat triazole), 166.9 (CO), 169.4 (CO), 169.6 (CO), 169.8 (CO), 169.9, 170.0 (CO), 170.1 (CO), 170.3 (CO).

MALDI TOF MS calcd for $C_{33}H_{44}N_3O_{19}$: $[M+H]^+$ 786.2569; found 786.2564.

3.14. 1-(1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-(acetoxymethyl)-1,2,3-triazole (6i)

Compound **6i** (195 mg, 85.6%) has been obtained from **4** (200 mg, 0.30 mmol) and propargyl acetate **5i** (75 μL, 0.76 mmol) by the general procedure at 50 °C. The propargyl acetate was added in two portions.

Colorless solid; mp 53–54 °C.

$[\alpha]_D^{25}$ +72.8 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3018, 2965, 1745, 1455, 1433, 1368, 1225, 1039 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 2.04 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.09 (s, 9H, 3 × CH_3), 2.12 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.96 (d, $J_{1',1'}$ = 12.1 Hz, 1H, H-1′), 4.11–4.16 (m, 2H, H-1′ & H-6), 4.25–4.33 (m, 2H, H-5 & H-6), 4.45–4.49 (m, 1H, H-5′), 4.70–4.75 (m, 1H, H-6′), 4.84 (dd, $J_{5',6'}$ = 3.8 Hz, $J_{6',6'}$ = 14.1 Hz, 1H, H-6′), 4.94 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.7 Hz, 1H, H-2), 5.06 (t, $J_{3,4} = J_{4,5}$ = 9.9 Hz, 1H, H-4), 5.23 (d, J_{H-C-H} = 3.9, 2H, –*C*H_2O), 5.39–5.55 (m, 3H, H-4′, H-3, H-3′), 5.61 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 7.77 (s, 1H, triazole H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 20.4 (*C*H_3), 20.5 (*C*H_3), 20.8 (*C*H_3), 52.8 (C-6′), 57.3 (–*C*H_2O), 62.1 (C-6), 62.5 (C-1′), 68.2 (C-4), 69.0 (C-5), 69.1 (C-3), 70.1 (C-2), 74.9 (C-3′), 75.4 (C-4′), 79.3 (C-5′), 90.1 (C-1), 103.7 (C-2′), 125.2 (*C*H of triazole), 142.7 (*C*quat triazole), 169.4, 169.7, 169.9, 170.0, 170.1, 170.2, 170.5, 170.7 (CO).

MALDI TOF MS calcd for $C_{31}H_{41}N_3O_{19}Na$: $[M+Na]^+$ 782.2232; found 782.2226.

3.15. 1-(1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-deoxy-sucros-6′-yl)-4-(cyclohexyl)-1,2,3-triazole (6j)

Compound **6j** (152 mg, 85.9%) has been obtained from **4** (150 mg, 0.23 mmol) and cyclohexylacetylene **5j** (45 μL, 0.34 mmol) by the general procedure.

Colorless solid; mp 53–54 °C.

$[\alpha]_D^{25}$ +80.8 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3022, 2933, 2855, 1749, 1497, 1433, 1372, 1223, 1043 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 1.24–1.82 (m, 10H, –CH_2), 2.04 (s, 6H, 2 × CH_3), 2.08 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.74–2.79 (m, 1H, CH, cyclohexane*CH*), 3.98 (d, $J_{1',1'}$ = 12.1 Hz, 1H, H-1′), 4.11–4.18 (m, 2H, H-1′ & H-6), 4.22–4.33 (m, 2H, H-6, H-5), 4.46–4.50 (m, 1H, H-5′), 4.63–4.69 (m, 1H, H-6′), 4.78 (dd, $J_{5,6}$ = 3.9 Hz, $J_{6,6}$ = 14.1 Hz, 1H, H-6′), 4.95 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.6 Hz, 1H, H-2), 5.06 (t, $J_{3,4} = J_{4,5}$ = 9.8 Hz, 1H, H-4), 5.41–5.54 (m, 3H, H-4′, H-3 & H-3′), 5.62 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 7.40 (s, 1H, triazole H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 20.4 (*C*H_3), 20.5 (*C*H_3), 20.6 (*C*H_3), 25.9 (cyclohexane*C*H_2), 26.0 (cyclohexane*C*H_2), 32.8 (cyclo-

hexaneCH_2), 32.9 (cyclohexaneCH_2), 35.1 (cyclohexane*C*H), 52.5 (C-6′), 62.1 (C-6), 62.6 (C-1′), 68.2 (C-4), 68.9 (C-5), 69.1 (C-3), 70.0 (C-2), 75.0 (C-3′), 75.3 (C-4′), 79.3 (C-5′), 89.9 (C-1), 103.6 (C-2′), 120.7 (*C*H of triazole), 153.6 (*C*quat triazole), 169.4, 169.6, 169.9, 170.1, 170.4 (CO).

MALDI TOF MS calcd for $C_{34}H_{48}N_3O_{17}$: $[M+H]^+$ 770.2984; found 770.2978.

3.16. 1-(1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6,6′-dideoxy-sucros-6,6′-diyl)-bis-4-phenyl-1,2,3-triazole (10a)

Compound **10a** (144 mg, 89.3%) has been obtained from **9** (122 mg, 0.19 mmol) and phenyl acetylene **5a** (64 μL, 0.57 mmol) by the general procedure.

Colorless solid; mp 88–89 °C.

IR ($CHCl_3$): 3136, 3026, 2965, 1751, 1484, 1464, 1436, 1367, 1221, 1041 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 1.97 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.14 (s, 6H, 2 × CH_3), 3.96 (d, $J_{1′,1′}$ = 12.1 Hz, 1H, H-1′), 4.08 (d, $J_{1′,1′}$ = 12.0 Hz, 1H, H-1′), 4.25 (m, 1H, H-5′), 4.39–4.51 (m, 2H, 2xH-6), 4.56–4.64 (m, 2H, H-5 & H-6′), 4.67–4.71 (m, 1H, H-6′), 4.80 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.4 Hz, 1H, H-2), 4.94 (t, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, 1H, H-4), 5.30 (t, $J_{3′,4′}$ = $J_{4′,5′}$ = 6.7 Hz, 1H, H-4′), 5.38 (d, $J_{3′,4′}$ = 6.9 Hz, 1H, H-3′), 5.51 (t, $J_{2,3}$ = $J_{3,4}$ = 9.9 Hz, 1H, H-3), 5.65 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 7.27–7.44 (m, 6H, $ArH_{3,4}$), 7.79 (d, $J_{Ar2,3}$ = 7.5 Hz, 2H, ArH_2), 7.87 (d, $J_{Ar2,3}$ = 7.5 Hz, 2H, ArH_2), 7.92 (s, 1H, ArH triazole ring), 7.97 (s, 1H, ArH triazole ring).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 20.4 (*C*H_3), 20.5 (*C*H_3), 20.6 (*C*H_3), 20.7 (*C*H_3), 50.7 (C-6′), 51.7 (C-6), 61.5 (C-1′), 68.9 (C-5), 69.2 (C-4), 69.7, 70.2 (C-2), 75.1, 75.6 (C-3), 79.8 (C-5′), 90.1 (C-1), 104.5 (C-2′), 121.1, 121.6 (C triazole), 125.6, 125.8 (Ar*C*), 128.2, 128.3 (Ar*C*), 128.8, 128.9 (Ar*C*), 130.0, 130.3 (ArC quart), 147.8 (Cquat triazole ring), 169.4 (CO), 169.8 (CO), 170.0 (CO), 170.2 (CO).

MALDI TOF MS calcd $C_{40}H_{44}N_6O_{15}$: $[M]^+$ 849.2898; found 849.4776.

3.17. 1-(1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6,6′-dideoxy-sucros-6,6′-diyl)-4-(acetoxymethyl)-1,2,3-triazole (10b)

Compound **10b** (345 mg, 91.2%) has been obtained from **9** (292 mg, 0.45 mmol) and propargyl acetate **5i** (150 μL, 1.36 mmol) by the general procedure.

Colorless solid; mp 59–60 °C.

IR ($CHCl_3$): 3144, 3014, 2970, 1749, 1434, 1373, 1225, 1043 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ ppm 2.04 (s, 3H, CH_3), 2.06 (s, 6H, 2 × CH_3), 2.08 (s, 6H, 2 × CH_3), 2.10 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.93 (d, $J_{1′,1′}$ = 12.1 Hz, 1H, H-1′), 4.01 (d, $J_{1′,1′}$ = 12.1 Hz, 1H, H-1′), 4.07–4.12 (m, 1H, H-6), 4.18–4.20 (m, 1H, H-5′), 4.35–4.42 (m, 2H, H-6,6′), 4.46–4.52 (m, 1H, H-5′), 4.58–4.63 (m, 2H, H-6,6′), 4.73 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H-2), 4.87 (t, $J_{3,4}$ = $J_{4,5}$ = 9.9 Hz, 1H, H-4), 5.14 (s, 2H, triazole-CH_{2a}-O), 5.20 (s, 1H, triazole-CH_{2b}O), 5.22 (s, 1H, triazole-CH_{2b}O), 5.27 (t, $J_{3′,4′}$ = $J_{4′,5′}$ = 6.8 Hz, 1H, H-4′), 5.32 (d, $J_{3′,4′}$ = 6.9 Hz, 1H, H-3′), 5.44 (t, $J_{2,3}$ = $J_{3,4}$ = 9.9 Hz, 1H, H-3), 5.57 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 7.69 (s, 1H, triazole H), 7.80 (s, 1H, triazole H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 20.3 (*C*H_3), 20.4 (*C*H_3), 20.5 (*C*H_3), 20.6 (*C*H_3), 20.7 (*C*H_3), 20.8 (*C*H_3), 50.6 (C-6′), 51.6 (C-6), 57.4, 57.4 (CH_2), 60.9 (C-1′), 68.6 (C-4), 69.1 (C-5), 69.5 (C-3), 70.2 (C-2), 75.1 (C-3′), 75.9 (C-4′), 80.1 (C-5′), 90.1 (C-1), 104.7 (C-2′), 125.2, 125.6 (*C*H of triazole), 142.7, 142.9 (Cquat triazole), 169.2 (CO), 169.7 (CO), 169.8 (CO), 169.8 (CO), 169.9 (CO), 170.2 (CO), 170.7 (CO), 170.8 (CO).

MALDI TOF MS calcd $C_{34}H_{44}N_6O_{19}Na$: $[M]^+$ 841.2695; found 841.3643.

Acknowledgements

This work has been supported by Fundação para a Ciência e a Tecnologia through Grant No. PEst-C/EQB/LA0006/2011. T. M. Potewar is grateful to Fundação para a Ciência e a Tecnologia for the pos-doctoral Grant No. SFRH/BPD/65173/2009.

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