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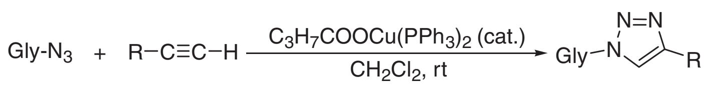
Graphical abstract

Evaluation of bis-triphenylphosphano-copper(I)-butyrate ($C_3H_7COOCu(PPh_3)_2$) as catalyst for the synthesis of 1-glycopyranosyl-4-substituted-1,2,3-triazoles

pp xxx–xxx

Éva Bokor, Csenge Koppány, Zsombor Gonda, Zoltán Novák, László Somsák *



27 examples
yields: 76-99 %

Carbohydrate Research xxx (2012) xxx–xxx

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Note

Evaluation of bis-triphenylphosphano-copper(I)-butyrate ($C_3H_7COOCu(PPh_3)_2$) as catalyst for the synthesis of 1-glycopyranosyl-4-substituted-1,2,3-triazoles

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ABSTRACT

Bis-triphenylphosphano-copper(I)-butyrate ($C_3H_7COOCu(PPh_3)_2$) was applied for the synthesis of O-peracylated 1-glycopyranosyl-4-substituted-1,2,3-triazoles from the corresponding glycosyl azides and alkynes. This catalyst proved superior to the $CuSO_4$/L-ascorbic acid system even with sterically hindered and less reactive glycosyl azides.

1. Introduction

The regioselective formation of 1,4-disubstituted-1,2,3-triazoles by Cu(I) catalysed azide–alkyne cycloaddition (CuAAC) is a reliable and robust transformation characterized by high functional group tolerance and simple work-up.[1] The widespread use of this reaction is, among others, also related to the increasing interest in the 1,2,3-triazole ring as a pharmacophore.[2] The wide variety of conditions used to perform CuAAC include numerous Cu(I) sources such as inorganic salts of copper(I) in the presence of a base and/or a ligand stabilizing the Cu(I) oxidation state, Cu(I) complexes or Cu(II) salts coupled with reducing agents.[1] Development of CuAAC generated remarkable attention in the field of carbohydrate chemistry, as well. Synthesis as well as application of 1,2,3-triazole containing simple glycosides, oligosaccharides, glycomacrocycles, glycoclusters, glycodendrimers, glycopeptides, glycoarrays, glycopolimers and glycosylated biomolecules were surveyed in several reviews.[3–6]

1-Glycosyl-1,2,3-triazole derivatives were obtained from relatively easily available glycosyl azides by using diverse Cu(I) sources. In situ reduction of Cu(II) salts, usually $CuSO_4$ or $Cu(OAc)_2$ by Na-ascorbate or L-ascorbic acid[7–16] as well as by Cu turnings[11,17] is one of the most commonly used possibilities for the catalysis, whereby, with unprotected glycosyl azides, addition of *o*-phenylenediamine[18] proved advantageous. CuI is another often applied catalyst in the presence of either DIPEA or Et_3N with TBTA (*N*,*N*,*N*-tris-[(1-benzyl-1*H*-1,2,3-triazole-4-yl)methy]amine).[19,20] In addition, phosphorous containing copper complexes such as $(EtO)_3P$-CuI[21] and $CuBr(PPh_3)_3$[22,23] proved to be also suitable catalysts for this purpose.

We have reported on the syntheses of three series of 1-(D-glucopyranosyl)-4-substituted-1,2,3-triazoles[24] **4–6** (Table 1) which were tested as inhibitors of glycogen phosphorylase enzyme (GP), a validated molecular target for the treatment of type 2 diabetes. Several β-D-glucopyranosyl derivatives (O-deprotected **4**) proved to be low micromolar inhibitors of GP. Furthermore, their inhibition constants as well as binding modes (revealed by X-ray crystallography) showed a remarkable similarity to those of the corresponding β-D-glucopyranosylamide type inhibitors,[25] thereby providing a new example of the amide-1,2,3-triazole bioisosteric relationship,[26–28] and a new potential biological application of 1-glycosyl-1,2,3-triazoles. Regioselective syntheses of the O-peracylated derivatives **4–6** were carried out in CuAAC reactions of the corresponding D-glucopyranosyl azides **1–3** with terminal alkynes in water in the presence of $CuSO_4$ and L-ascorbic acid (Table 1, conditions *i*). However, under these conditions the desired triazoles could be obtained only in low yields and with incomplete conversions of the starting materials in several cases. Changing the solvent to aqueous CH_3NO_2 or DMSO, and increasing the catalyst load up to 11 mol % did not bring about significant improvements.[24] Recently, bis-triphenylphosphano-copper(I)-butyrate ($C_3H_7COOCu(PPh_3)_2$) was developed as a new, highly active catalyst for the CuAAC reaction. By using this complex, several 1,4-disubstituted-1,2,3-triazoles were synthesised

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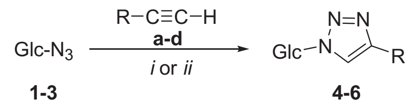
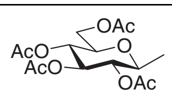
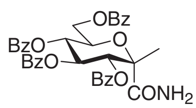
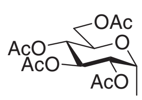
Table 1
Comparison of catalysts in reactions of D-glucopyranosyl azides and alkynes



i[24]) $CuSO_4$, L-ascorbic acid,[a] H_2O, 70 °C, 8 h; *ii*) $C_3H_7COOCu(PPh_3)_2$, CH_2Cl_2, rt

Glc		Alkyne	R	Product	Conditions *i* Yield (%)	Conditions *ii* Catalyst (mol %)	Reaction time[b]	Yield (%)
1		**a**	$-CH_2OH$	**4a**	65	2	1 day	90
		b	$-CH_2OAc$	**4b**	Not investigated	1	1 h	96
		c	$-CO_2Et$	**4c**	89	1	1 h	92
		d	Phenyl	**4d**	58	1	10 min	95
2		**a**	$-CH_2OH$	**5a**	No reaction	5	1 day	89
		b	$-CH_2OAc$	**5b**	Not investigated	1	8 h	97
		c	$-CO_2Et$	**5c**	56[c]	1	4 h	90
		d	Phenyl	**5d**	No reaction	1	4 h	92
3		**a**	$-CH_2OH$	**6a**	36	8	1 day	Traces[d]
		b	$-CH_2OAc$	**6b**	Not investigated	2	5 h	87
		c	$-CO_2Et$	**6c**	72	2	1 day	91
		d	Phenyl	6d	39	5	1 day	76[e]

[a] 1.5 mol % $CuSO_4$, 20 mol % L-ascorbic acid for **4**, 7.5 mol % $CuSO_4$, 20 mol % L-ascorbic acid for **5** and **6** were used.[24]
[b] Necessary for complete consumption of the starting materials **1–3**.
[c] Conversion: 63%.[24]
[d] Reported yield by a different method: 60%.[11]
[e] Reported yield by a different method: 63%.[11]

in excellent yields.[29] In view of the efficiency of this catalyst, the aim of our present work has been to investigate its applicability for the synthesis of the above and other 1-glycosyl-1,2,3-triazoles.

2. Results and discussion

First, the efficiency of $C_3H_7COOCu(PPh_3)_2$ was probed in reactions between peracylated glycopyranosyl azides **1–3** and terminal alkynes **a–d** bearing free hydroxyl, ester, as well as aromatic groups. The experiments were performed according to the literature procedure[29] in dichloromethane at room temperature (Table 1, conditions *ii*). In the reactions with propargyl alcohol (**a**) the copper(I)-butyrate proved to be efficient in 2 and 5 mol % ratio for the syntheses of **4a** and **5a**, respectively, while even 8 mol % of the catalyst was insufficient to obtain **6a**. Alkynes **b–d** with β-D-glucopyranosyl azides **1** and **2** required 1 mol % catalyst load. Generally, syntheses of compounds **5** required longer reaction time as compared to those of derivatives **4**, presumably because of the sterically more crowded environment of the azido group in **2**. However, it has to be noted, that in aqueous medium in the presence of $CuSO_4$/L-ascorbic acid (conditions *i*) transformation of the O-perbenzoylated (β-D-*gluco*-hept-2-ulopyranosylazide)onamide (**2**) occurred only with ethyl propiolate, and under modified reaction conditions in DMSO the conversions were also not complete.[24] Somewhat higher amount of the catalyst and longer reaction time were needed to obtain α-D-glucopyranosyl-1,2,3-triazole derivatives **6b**,**c** (2 mol %) and **6d** (5 mol %) from the less reactive azide[8,11,24] **3**. Yields were around or above 90% in almost each case demonstrating the superior performance of $C_3H_7COOCu(PPh_3)_2$ over the $CuSO_4$/L-ascorbic acid system (compare yields under headings *i* and *ii* in Table 1).

The Cu(I)-butyrate complex was also applied for the syntheses of further O-peracetylated 1-glycopyranosyl-4-substituted-1,2,3-triazoles from the corresponding glycosyl azides **7–13** (Table 2). For the formation of β-D-xylopyranosyl- and 2′-acetamido-2′-deoxy-β-D-glucopyranosyl-1,2,3-triazoles **14** and **15** 1 mol % of the catalyst was as effective as in the β-D-glucopyranosyl series **4**. In a similar manner, reaction of 2-deoxy-2-phtalimido-β-D-glucopyranosyl azide **9** with phenylacetylene worked well in the presence of 1 mol % catalyst to give **16d** in excellent yield, while cycloaddition with the bulky 2-ethynylnaphtalene **e** proceeded only with higher catalyst load (2 mol %). Synthesis of (2′-deoxy-2′-phtalimido-α-D-glucopyranosyl)-4-phenyl-1,2,3-triazole **17d** required higher catalyst concentration and longer reaction time compared to its β counterpart **16d**, similarly to observations with α–β pairs earlier (**4** versus **6**). The observed differences in the reactivity of the anomeric pairs of glycosyl azides are in accord with literature experiences, and may be explained by the higher steric hindrance of the azido group in α-position or by the different dipolar character of the anomeric azides arising from the anomeric effect.[8,11,24]

The behaviour of glycopyranosyl azides **11–13** with an axial substituent in position 4 was different from that of the previously studied 1,2-*trans* glycopyranosyl azides (**1**, **7–9**). Contrary to other β azides, transformation of the β-D-*galacto* configured **11** into the corresponding triazoles **18** needed longer reaction time. The α-L-arabinopyranosyl azide **12** provided similar results, however, 1 mol % catalyst load was sufficient for the synthesis of **19b** and **19d**. Results with the β-L-fucopyranosyl derivatives **20** are similar to experiences in the α-D-glycopyranosyl cases **6**, **17** that is, to achieve total consumption of the starting material **13** the catalyst concentration had to be increased to 2–5 mol %. These observations are in line with literature experiences where β-D-*manno* and β-D-*galacto* configured glycopyranosyl azides with axial substituents gave the 1,2,3-triazoles under longer reaction times and/or in lower yields as compared to the β-D-glucopyranosyl counterparts.[13,17]

3. Conclusion

Application of the $C_3H_7COOCu(PPh_3)_2$ complex as a highly active catalyst in CuAAC reactions with a variety of glycosyl azides gave the corresponding 1,2,3-triazoles in excellent yields. The presence of a free hydroxyl group in the alkyne, increasing steric hindrance or diminished reactivity as well as the presence of an axial substituent in the pyranoid ring of the glycosyl azide required higher catalyst load and/or extended reaction times. Generally, this catalyst has broader applicability with glycosyl azides than the commonly used $CuSO_4$/L-ascorbic acid system.

4. Experimental

4.1. General methods

Melting points were measured in open capillary tubes or on a Kofler hot-stage and are uncorrected. Optical rotations were determined with a Perkin–Elmer 241 polarimeter at rt. NMR spectra were recorded with Bruker 360 (360/90 MHz for $^1H/^{13}C$) spectrometer. Chemical shifts are referenced to Me4Si (^1H), or to the residual solvent signals (^{13}C). TLC was performed on DC-Alurolle Kieselgel 60 F_{254} (Merck), and the plates were visualised under UV light and by gentle heating. For column chromatography Kieselgel 60 (Merck, particle size 0.063–0.200 mm) was used. Dichloromethane was distiled from P_4O_{10} and stored over 4 Å molecular sieves. Propargyl alcohol (**a**), propargyl acetate (**b**), ethyl propiolate (**c**) and phenylacetylene (**d**) were purchased from Aldrich. 2-Ethynylnaphthalene[30] (**e**) and the per-O-acylated glycopyranosyl azides[31–35] **1–3** and **7–13** as well as the complex[29] $C_3H_7COOCu(PPh_3)_2$ were synthesized according to published procedures.

4.2. General procedure for the synthesis of peracylated 1-glyco pyranosyl-4-substituted-1,2,3-triazoles in the presence of $C_3H_7COOCu(PPh_3)_2$ catalyst

An azide (**1–3** or **7–13**, 0.1 g) and an equimolar amount of an alkyne (**a–e**) were dissolved in anhydrous CH_2Cl_2 (2 mL), $C_3H_7COOCu(PPh_3)_2$ (1–5 mol %, Tables 1 and 2) catalyst was added, the mixture was stirred at rt and monitored by TLC (1:1 EtOAc–hexane). After completion of the reaction (Tables 1 and 2), the solvent was evaporated and the residue was purified by column chromatography.

4.2.1. 4-Hydroxymethyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-gluco pyranosyl)-1,2,3-triazole (4a)

From **1** (0.1 g, 0.27 mmol), propargyl alcohol (16 μL, 0.27 mmol) and $C_3H_7COOCu(PPh_3)_2$ (3.6 mg, 5.4 μmol) according to Section 4.2. Purified by column chromatography (2:1 EtOAc–hexane) to yield 0.10 g (90%) of white solid. ^1H and ^{13}C NMR data correspond to the reported spectra.[8,11]

4.2.2. 4-Acetoxymethyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-gluco pyranosyl)-1,2,3-triazole (4b)

From **1** (0.1 g, 0.27 mmol), propargyl acetate (27 μL, 0.27 mmol) and $C_3H_7COOCu(PPh_3)_2$ (1.8 mg, 2.7 μmol) according to Section 4.2. Purified by column chromatography (1:1 EtOAc–hexane) to yield 0.12 g (96%) of white solid. Mp: 151–153 °C (lit.[8] mp: 143–144 °C); $[\alpha]_D$ −24 (*c* 0.57, $CHCl_3$); ^1H and ^{13}C NMR data correspond to the reported spectra.[8]

4.2.3. Ethyl 1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-1,2,3-triazole-4-carboxylate (4c)

From **1** (0.1 g, 0.27 mmol), ethyl propiolate (28 μL, 0.27 mmol) and $C_3H_7COOCu(PPh_3)_2$ (1.8 mg, 2.7 μmol) according to Section 4.2. Purified by column chromatography (2:3 EtOAc–hexane) to yield 0.12 g (92%) of white solid. ^1H and ^{13}C NMR data correspond to the reported spectra.[24]

4.2.4. 4-Phenyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-1,2,3-triazole (4d)

From **1** (0.1 g, 0.27 mmol), phenylacetylene (29 μL, 0.27 mmol) and $C_3H_7COOCu(PPh_3)_2$ (1.8 mg, 2.7 μmol) according to Section 4.2. Purified by column chromatography (2:3 EtOAc–hexane) to yield 0.12 g (95%) of white solid. ^1H and ^{13}C NMR data correspond to the reported spectra.[7,11,19]

4.2.5. [4-Hydroxymethyl-1-(3′,4′,5′,7′-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)-1,2,3-triazole]onamide (5a)

From **2** (0.1 g, 0.15 mmol), propargyl alcohol (9 μL, 0.15 mmol) and $C_3H_7COOCu(PPh_3)_2$ (5.1 mg, 7.6 μmol) according to Section 4.2. Purified by column chromatography (2:1 EtOAc–hexane) to yield 0.10 g (89%) of white solid. ^1H and ^{13}C NMR data correspond to the reported spectra.[24]

4.2.6. [4-Acetoxymethyl-1-(3′,4′,5′,7′-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)-1,2,3-triazole]onamide (5b)

From **2** (0.1 g, 0.15 mmol), propargyl acetate (15 μL, 0.15 mmol) and $C_3H_7COOCu(PPh_3)_2$ (1.0 mg, 1.5 μmol) according to Section 4.2. Purified by column chromatography (1:1 EtOAc–hexane) to yield 0.11 g (97%) of colourless oil. R_f: 0.51 (5:4 EtOAc–hexane); $[\alpha]_D$ −9 (*c* 0.56, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (ppm) 8.10–7.23 (21H, m, aromatics, triazole CH), 6.97 (1H, s, CONH_2), 6.56 (1H, s, CONH_2), 6.33 (1H, pseudo t, J = 8.0, 8.0 Hz, H-4′ or H-5′), 6.17 (1H, d, J = 8.0 Hz, H-3′), 5.89 (1H, pseudo t, J = 9.2, 8.6 Hz, H-4′ or H-5′), 5.23 (1H, ddd, J = 9.9, 3.7, <1 Hz, H-6′), 5.10 (2H, s, CH_2), 4.89 (1H, dd, J = 12.3, <1 Hz, H-7′a), 4.57 (1H, dd, J = 12.3, 3.7 Hz, H-7′b), 2.00 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$): δ (ppm) 170.5, 166.2, 166.1, 165.0, 164.9, 164.2 (CO), 142.9 (triazole C-4), 133.7–128.2 (aromatics), 122.5 (triazole C-5), 89.4 (C-2′), 73.9, 72.2, 71.0, 68.1 (C-3′–C-6′), 62.3 (C-7′), 57.1 (CH_2), 20.6 (CH_3). Anal. Calcd for $C_{40}H_{34}N_4O_{12}$ (762.74): C, 62.99; H, 4.49; N, 7.35. Found: C, 63.11; H, 4.63; N, 7.24.

4.2.7. [4-Ethoxycarbonyl-1-(3′,4′,5′,7′-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)-1,2,3-triazole]onamide (5c)

From **2** (0.1 g, 0.15 mmol), ethyl propiolate (15 μL, 0.15 mmol) and $C_3H_7COOCu(PPh_3)_2$ (1.0 mg, 1.5 μmol) according to Section 4.2. Purified by column chromatography (2:3 EtOAc–hexane) to yield 0.10 g (90%) of colourless oil. ^1H and ^{13}C NMR data correspond to the reported spectra.[24]

4.2.8. [4-Phenyl-1-(3′,4′,5′,7′-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)-1,2,3-triazole]onamide (5d)

From **2** (0.1 g, 0.15 mmol), phenylacetylene (17 μL, 0.15 mmol) and $C_3H_7COOCu(PPh_3)_2$ (1.0, 1.5 μmol) according to Section 4.2. Purified by column chromatography (2:3 EtOAc–hexane) to yield 0.11 g (92%) of white solid. ^1H and ^{13}C NMR data correspond to the reported spectra.[24]

4.2.9. 4-Acetoxymethyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-gluco pyranosyl)-1,2,3-triazole (6b)

From **3** (0.1 g, 0.27 mmol), propargyl acetate (27 μL, 0.27 mmol) and $C_3H_7COOCu(PPh_3)_2$ (3.6 mg, 5.4 μmol) according to Section 4.2. Purified by column chromatography (1:1 EtOAc–hexane) to yield 0.11 g (87%) of white solid. Mp: 139–141 °C; $[\alpha]_D$ +92 (*c* 0.51, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (ppm) 7.74 (1H, s, triazole CH), 6.37

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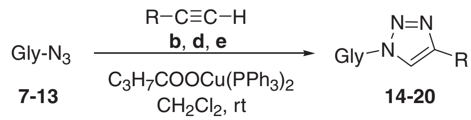
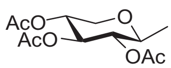
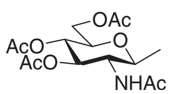
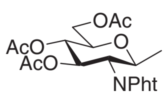
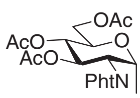
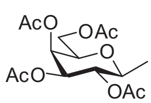
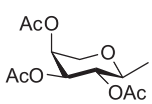
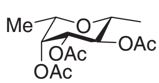
Table 2
Synthesis of 1-glycopyranosyl-4-substituted-1,2,3-triazoles



Gly		Alkyne	R	Conditions			
				Product	Catalyst (mol %)	Reaction time	Yield (%)
7		**b** **d** **e**	–CH_2OAc Phenyl 2-Naphthyl	**14b** **14d** **14e**	1 1 1	2 h 10 min 10 min	96 93 86
8		**b** **d** **e**	–CH_2OAc Phenyl 2-Naphthyl	**15b** **15d** **15e**	1 1 1	1 h 30 min 30 min	88 94[a] 85
9		**d** **e**	Phenyl 2-Naphthyl	**16d** **16e**	1 2	10 min 6 h	99 96
10		**d**	Phenyl	**17d**	5	1 day	98
11		**b** **d**	–CH_2OAc Phenyl	**18b** **18d**	1 2	6 h 8 h	92 90[b]
12		**b** **d**	–CH_2OAc Phenyl	**19b** **19d**	1 1	2 h 5 h	96 98
13		**b** **d**	–CH_2OAc Phenyl	**20b** **20d**	2 5	4 h 2 h	96 97

[a] Reported yield by a different method: 90%.[12]
[b] Reported yield by different methods: 74%;[19] 91%.[16]

(1H, d, J = 6.2 Hz, H-1′), 6.25 (1H, pseudo t, J = 9.9, 9.2 Hz, H-3′ or H-4′), 5.33 (1H, dd, J = 9.9, 6.2 Hz, H-2′), 5.27–5.21 (3H, m, H-3′ or H-4′, CH_2), 4.39 (1H, ddd, J = 10.5, 3.7, <1 Hz, H-5′), 4.27 (1H, dd, J = 12.3, 3.7 Hz, H-6′a), 4.04 (1H, dd, J = 12.3, <1 Hz, H-6′b), 2.10, 2.07 (2), 2.04, 1.88 (5 × 3H, 5s, $OCOCH_3$); ^{13}C NMR ($CDCl_3$): δ (ppm) 170.6, 170.3, 170.0, 169.5 (2) ($COCH_3$), 142.4 (triazole C-4), 125.8 (triazole C-5), 81.3 (C-1′), 71.1, 70.2, 69.6, 67.8 (C-2′–C-5′), 61.1 (C-6′), 57.2 (CH_2), 20.7, 20.5 (3), 20.1 ($COCH_3$). Anal. Calcd for $C_{19}H_{25}N_3O_{11}$ (471.42): C, 48.41; H, 5.35; N, 8.91. Found: C, 48.56; H, 5.44; N, 8.78.

4.2.10. Ethyl 1-(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)-1,2,3-triazole-4-carboxylate (6c)

From **3** (0.1 g, 0.27 mmol), ethyl propiolate (28 μL, 0.27 mmol) and $C_3H_7COOCu(PPh_3)_2$ (3.6 mg, 5.4 μmol) according to Section 4.2. Purified by column chromatography (4:5 EtOAc–hexane) to yield 0.12 g (91%) of white solid. ^1H and ^{13}C NMR data correspond to the reported spectra.[24]

4.2.11. 4-Phenyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)-1,2,3-triazole (6d)

From **3** (0.1 g, 0.27 mmol), phenylacetylene (29 μL, 0.27 mmol) and $C_3H_7COOCu(PPh_3)_2$ (9 mg, 14 μmol) according to Section 4.2. Purified by column chromatography (2:3 EtOAc–hexane) to yield 0.10 g (76%) of white solid. ^1H and ^{13}C NMR data correspond to the reported spectra.[11,24]

4.2.12. 4-Acetoxymethyl-1-(2′,3′,4′-tri-*O*-acetyl-β-D-xylopyranosyl)-1,2,3-triazole (14b)

From **7** (0.1 g, 0.33 mmol), propargyl acetate (33 μL, 0.33 mmol) and $C_3H_7COOCu(PPh_3)_2$ (2.2 mg, 3.3 μmol) according to Section 4.2. Purified by column chromatography (2:3 EtOAc–hexane) to yield 0.13 g (96%) of white solid. Mp: 160–161 °C; $[\alpha]_D$ −55 (c 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (ppm) 7.87 (1H, s, triazole CH), 5.83 (1H, d, J = 8.0 Hz, H-1′), 5.47–5.38 (2H, m, H-2′, H-3′), 5.25–5.14 (3H, m, H-4′, CH_2), 4.31 (1H, dd, J = 11.1, 5.5 Hz, H-5′a), 3.64 (1H, pseudo t, J = 11.1, 11.1 Hz, H-5′b), 2.08 (2), 2.06, 1.89 (4 × 3H, 4s, $OCOCH_3$); ^{13}C NMR ($CDCl_3$): δ (ppm) 170.6, 169.7, 169.6, 168.8 ($OCOCH_3$), 143.5 (triazole C-4), 122.0 (triazole C-5), 86.1 (C-1′), 71.9, 70.4, 68.2 (C-2′–C-4′), 65.4 (C-5′), 57.3 (CH_2), 20.6, 20.5, 20.4, 20.0 ($OCOCH_3$). Anal. Calcd for $C_{16}H_{21}N_3O_9$ (399.35): C, 48.12; H, 5.30; N, 10.52. Found: C, 48.24; H, 5.17; N, 11.02.

4.2.13. 4-Phenyl-1-(2′,3′,4′-tri-*O*-acetyl-β-D-xylopyranosyl)-1,2,3-triazole (14d)

From **7** (0.2 g, 0.66 mmol), phenylacetylene (73 μL, 0.66 mmol) and $C_3H_7COOCu(PPh_3)_2$ (4.5 mg, 6.6 μmol) according to Section 4.2. Purified by recrystallisation from EtOH to yield 0.25 g (93%) of white solid. Mp: 271–272 °C; $[\alpha]_D$ −104 (*c* 0.50, DMSO); ^{1}H NMR (DMSO-d_6): δ (ppm) 8.95 (1H, s, triazole CH), 7.84–7.34 (5H, m, aromatics), 6.29 (1H, d, *J* = 8.6 Hz, H-1′), 5.64, 5.56 (2 × 1H, 2 pseudo t, *J* = 9.2, 9.2 Hz in each, H-2′, H-3′), 5.12 (1H, ddd, *J* = 10.5, 9.2, 5.5 Hz, H-4′), 4.13 (1H, dd, *J* = 11.1, 5.5 Hz, H-5′a), 3.90 (1H, pseudo t, *J* = 11.1, 10.5 Hz, H-5′b), 2.03, 2.01, 1.81 (3 × 3H, 3s, OCOCH_3); ^{13}C NMR (DMSO-d_6): δ (ppm) 169.5 (2), 168.6 (OCOCH$_3$), 146.8 (triazole C-4), 130.1, 129.0 (2), 128.2, 125.1 (2) (aromatics), 120.2 (triazole C-5), 84.7 (C-1′), 71.7, 70.4, 68.0 (C-2′–C-4′), 64.0 (C-5′), 20.4, 20.3, 19.9 (OCOCH_3). Anal. Calcd for $C_{19}H_{21}N_3O_7$ (403.39): C, 56.57; H, 5.25; N, 10.42. Found: C, 56.44; H, 5.37; N, 10.30.

4.2.14. 4-(2-Naphthyl)-1-(2′,3′,4′-tri-*O*-acetyl-β-D-xylopyranosyl)-1,2,3-triazole (14e)

From **7** (0.1 g, 0.33 mmol), 2-ethynylnaphthalene (0.05 g, 0.33 mmol) and $C_3H_7COOCu(PPh_3)_2$ (2.2 mg, 3.3 µmol) according to Section 4.2. Purified by recrystallisation from EtOH to yield 0.13 g (86%) of white solid. Mp: 285–286 °C; ^{1}H NMR (DMSO-d_6): δ (ppm) 9.08 (1H, s, triazole CH), 8.41–7.54 (7H, m, aromatics), 6.33 (1H, d, *J* = 8.6 Hz, H-1′), 5.67, 5.58 (2 × 1H, 2 pseudo t, *J* = 9.2, 9.2 Hz in each, H-2′, H-3′), 5.14 (1H, ddd, *J* = 10.5, 9.2, 4.9 Hz, H-4′), 4.15 (1H, dd, *J* = 11.1, 4.9 Hz, H-5′a), 3.92 (1H, pseudo t, *J* = 11.1, 10.5 Hz, H-5′b), 2.05, 2.02, 1.83 (3 × 3H, 3s, OCOCH_3); ^{13}C NMR (DMSO-d_6): δ (ppm) 169.5 (2), 168.6 (OCOCH$_3$), 146.8 (triazole C-4), 132.9, 132.6, 128.6, 127.9, 127.6, 127.5, 126.6, 126.2, 123.6, 123.4 (aromatics), 120.5 (triazole C-5), 84.7 (C-1′), 71.7, 70.4, 67.9 (C-2′–C-4′), 64.0 (C-5′), 20.4, 20.2, 19.8 (OCOCH_3). Anal. Calcd for $C_{23}H_{23}N_3O_7$ (453.44): C, 60.92; H, 5.11; N, 9.27. Found: C, 61.01; H, 5.25; N, 9.18.

4.2.15. 1-(2′-Acetamido-2′-deoxy-3′,4′,6′-tri-*O*-acetyl-β-D-glucopyranosyl)-4-acetoxy-methyl-1,2,3-triazole (15b)

From **8** (0.2 g, 0.54 mmol), propargyl acetate (53 µL, 0.54 mmol) and $C_3H_7COOCu(PPh_3)_2$ (3.6 mg, 5.4 µmol) according to Section 4.2. Purified by column chromatography (4:1 EtOAc–hexane, then EtOAc) to yield 0.22 g (88%) of white solid. Mp: 240–241 °C; $[\alpha]_D$ −30 (*c* 0.51, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ (ppm) 7.98 (1H, s, triazole CH), 6.75 (1H, d, *J* = 8.8 Hz, *NH*Ac), 6.15 (1H, d, *J* = 9.6 Hz, H-1′), 5.55 (1H, pseudo t, *J* = 9.6, 9.6 Hz, H-3′or H-4′), 5.27–5.22 (3H, m, H-3′or H-4′, CH$_2$) 4.61 (1H, ddd, *J* = 9.6, 9.6, 8.7 Hz H-2′), 4.30 (1H, dd, *J* = 12.3, 4.4 Hz, H-6′a), 4.16 (1H, dd, *J* = 12.3, <1 Hz, H-6′b), 4.09 (1H, ddd, *J* = 8.8, 4.4, <1 Hz, H-5′), 2.07 (12H, s, 4 × OCOCH_3), 1.77 (3H, s, NHCOCH_3); ^{13}C NMR (CDCl$_3$): δ (ppm) 170.6 (4), 169.3, (*C*OCH$_3$), 143.2 (triazole C-4), 123.0 (triazole C-5), 85.7 (C-1′), 74.8, 72.1, 68.0 (C-3′–C-5′), 61.7 (C-6′), 57.3 (CH$_2$), 53.3 (C-2′), 22.7, 20.8, 20.6, 20.5 (2) (COCH_3). Anal. Calcd for $C_{19}H_{26}N_4O_{10}$ (470.43): C, 48.51; H, 5.57; N, 11.91. Found: C, 48.66; H, 5.65; N, 11.74.

4.2.16. 1-(2′-Acetamido-2′-deoxy-3′,4′,6′-tri-*O*-acetyl-β-D-glucopyranosyl)-4-phenyl-1,2,3-triazole (15d)

From **8** (0.1 g, 0.27 mmol), phenylacetylene (29 µL, 0.27 mmol) and $C_3H_7COOCu(PPh_3)_2$ (1.8 mg, 2.7 µmol) according to Section 4.2. Purified by column chromatography (7:3 EtOAc–hexane, then MeOH) to yield 0.12 g (94%) of white solid. Mp: 282–284 °C; $[\alpha]_D$ −71 (*c* 0.58, DMSO); ^{1}H and ^{13}C NMR data correspond to the reported spectra.[12]

4.2.17. 1-(2′-Acetamido-2′-deoxy-3′,4′,6′-tri-*O*-acetyl-β-D-glucopyranosyl)-4-(2-naphthyl)-1,2,3-triazole (15e)

From **8** (0.2 g, 0.54 mmol), 2-ethynylnaphthalene (0.08 g, 0.54 mmol) and $C_3H_7COOCu(PPh_3)_2$ (3.6 mg, 5.4 µmol) according to Section 4.2. Purified by column chromatography (7:3 EtOAc–hexane, then MeOH) to yield 0.24 g (85%) of white solid. Mp: 298–300 °C; $[\alpha]_D$ −70 (*c* 0.51, DMSO); ^{1}H NMR (DMSO-d_6): δ (ppm) 9.00 (1H, s, triazole CH), 8.42 (1H, s, aromatic), 8.17–7.54 (7H, m, aromatics, *NH*Ac), 6.19 (1H, d, *J* = 9.6 Hz, H-1′), 5.42, 5.14 (2 × 1H, 2 pseudo t, *J* = 9.6 Hz in each, H-3′, H-4′), 4.69 (1H, ddd, *J* = 9.6, 9.6, 8.8 Hz, H-2′), 4.31 (1H, ddd, *J* = 8.8, 4.4, <1 Hz, H-5′), 4.20 (1H, dd, *J* = 12.3, 4.4 Hz, H-6′a), 4.10 (1H, dd, *J* = 12.3, <1 Hz, H-6′b), 2.03, 2.01, 1.97 (3 × 3H, 3s, OCOCH_3), 1.60 (3H, s, NHCOCH_3); ^{13}C NMR (DMSO-d_6): δ (ppm) 170.0, 169.6 169.5, 169.4, (*C*OCH$_3$), 146.5 (triazole C-4), 133.0, 132.6, 128.6, 128.0, 127.7, 127.6, 126.7, 126.3, 123.6, 123.4 (aromatics), 120.6 (triazole C-5), 84.9 (C-1′), 73.3, 72.2, 68.0 (C-3′–C-5′), 61.7 (C-6′), 52.3 (C-2′), 22.3, 20.5, 20.4, 20.3 (COCH_3). Anal. Calcd for $C_{26}H_{28}N_4O_8$ (524.52): C, 59.54; H, 5.38; N, 10.68. Found: C, 59.70; H, 5.29; N, 10.81.

4.2.18. 1-(2′-Deoxy-2′-phtalimido-3′,4′,6′-tri-*O*-acetyl-β-D-glucopyranosyl)-4-phenyl-1,2,3-triazole (16d)

From **9** (0.3 g, 0.65 mmol), phenylacetylene (71 µL, 0.65 mmol) and $C_3H_7COOCu(PPh_3)_2$ (4.4 mg, 6.5 µmol) according to Section 4.2. Purified by column chromatography (2:3 EtOAc–hexane) to yield 0.37 g (99%) of white solid. Mp: 194–196 °C; $[\alpha]_D$ −107 (*c* 0.55, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ (ppm) 8.05 (1H, s, triazole CH), 7.83–7.28 (9H, m, aromatics, Pht), 6.85 (1H, d, *J* = 10.5 Hz, H-1′), 6.06 (1H, *J* = 10.5, 9.2 Hz), 5.39 (1H, *J* = 9.9, 9.2 Hz), 4.94 (1H, *J* = 10.5, 9.9 Hz) (3 pseudo t, H-2′, H-3′, H-4′), 4.40 (1H, dd, *J* = 12.3, 4.3 Hz, H-6′a), 4.24–4.20 (2H, m, H-5′, H-6′b), 2.12, 2.09, 1.89 (3 × 3H, 3s, OCOCH_3); ^{13}C NMR (CDCl$_3$): δ (ppm) 170.5, 169.8, 169.3 (*C*OCH$_3$), 167.5, 166.4 (NPht*C*O), 148.2 (triazole C-4), 134.6, 134.4, 131.0, 130.5, 129.7, 128.7, 128.4, 125.7, 123.8 (aromatics, Pht), 117.7 (triazole C-5), 83.0 (C-1′), 75.0, 70.4, 68.1 (C-3′–C-5′), 61.6 (C-6′), 53.9 (C-2′), 20.6, 20.5, 20.3 (COCH_3). Anal. Calcd for $C_{28}H_{26}N_4O_9$ (562.53): C, 59.78; H, 4.66; N, 9.96. Found: C, 59.89; H, 4.81; N, 9.90.

4.2.19. 1-(2′-Deoxy-2′-phtalimido-3′,4′,6′-tri-*O*-acetyl-β-D-glucopyranosyl)-4-(2-naphthyl)-1,2,3-triazole (16e)

From **9** (0.3 g, 0.65 mmol), 2-ethynylnaphthalene (0.1 g, 0.65 mmol) and $C_3H_7COOCu(PPh_3)_2$ (8.8 mg, 6.5 µmol) according to Section 4.2. Purified by column chromatography (2:3 EtOAc–hexane) to yield 0.38 g (96%) of white solid. Mp: 194–196 °C; $[\alpha]_D$ −164 (*c* 0.54, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ (ppm) 8.30–7.45 (12H, m, aromatics, Pht, triazole CH), 6.88 (1H, d, *J* = 10.5 Hz, H-1′), 6.08 (1H, *J* = 10.5, 9.2 Hz), 5.40 (1H, *J* = 9.9, 9.2 Hz), 4.97 (1H, *J* = 10.5, 9.9 Hz) (3 pseudo t, H-2′, H-3′, H-4′), 4.42 (1H, dd, *J* = 12.3, 4.9 Hz, H-6′a), 4.26–4.21 (2H, m, H-5′, H-6′b), 2.13, 2.10, 1.90 (3 × 3H, 3s, OCOCH_3); ^{13}C NMR (CDCl$_3$): δ (ppm) 170.5, 169.9, 169.4 (*C*OCH$_3$), 167.6, 166.5 (NPht*C*O), 148.3 (triazole C-4), 134.6–123.8 (aromatics, Pht), 118.0 (triazole C-5), 83.1 (C-1′), 75.1, 70.4, 68.2 (C-3′–C-5′), 61.6 (C-6′), 54.0 (C-2′), 20.7, 20.6, 20.3 (COCH_3). Anal. Calcd for $C_{32}H_{28}N_4O_9$ (612.59): C, 62.74; H, 4.61; N, 9.15. Found: C, 62.60; H, 4.70; N, 9.04.

4.2.20. 1-(2′-Deoxy-2′-phtalimido-3′,4′,6′-tri-*O*-acetyl-α-D-glucopyranosyl)-4-phenyl-1,2,3-triazole (17d)

From **10** (0.1 g, 0.22 mmol), phenylacetylene (24 µL, 0.22 mmol) and $C_3H_7COOCu(PPh_3)_2$ (7.3 mg, 11 µmol) according to Section 4.2. Purified by column chromatography (4:5 EtOAc–hexane) to yield 0.12 g (98%) of white solid. Mp: 161–163 °C; $[\alpha]_D$ +182 (*c* 0.54, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ (ppm) 7.91 (1H, s, triazole CH), 7.79–7.29 (9H, m, aromatics, Pht), 7.17 (1H, pseudo t, *J* = 10.5, 10.5 Hz, H-3′), 6.44 (1H, d, *J* = 5.5 Hz, H-1′), 5.30 (1H, pseudo t, *J* = 9.9, 9.2 Hz, H-4′), 5.07 (1H, dd, *J* = 10.5, 5.5 Hz, H-2′), 4.70 (1H, ddd, *J* = 10.5, 3.1, <1 Hz, H-5′), 4.37 (1H, dd, *J* = 12.3, 3.1 Hz, H-6′a), 4.12 (1H, dd, *J* = 12.3, <1 Hz, H-6′b), 2.10, 1.90 (9H, 2s, 3 × OCOCH_3); ^{13}C NMR (CDCl$_3$): δ (ppm) 170.4, 170.1, 168.9 (*C*OCH$_3$), 166.8 (2) (NPht*C*O), 147.3 (triazole C-4), 134.5 (2), 130.7 (2), 129.6, 128.7 (2), 128.4, 125.8 (2), 123.7 (2) (aromatics, Pht), 121.0 (triazole C-5), 82.8 (C-1′), 71.9, 69.6, 67.2 (C-3′–C-5′), 61.4 (C-6′), 53.3 (C-2′), 20.6 (3) ($COCH_3$). Anal. Calcd for $C_{28}H_{26}N_4O_9$ (562.53): C, 59.78; H, 4.66; N, 9.96. Found: C, 59.68; H, 4.77; N, 10.05.

4.2.21. 4-Acetoxymethyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl)-1,2,3-triazole (18b)

From **11** (0.1 g, 0.27 mmol), propargyl acetate (27 μL, 0.27 mmol) and $C_3H_7COOCu(PPh_3)_2$ (1.8 mg, 2.7 μmol) according to Section 4.2. Purified by column chromatography (1:1 EtOAc–hexane) to yield 0.12 g (92%) of white solid. Mp: 110–112 °C; $[\alpha]_D$ −7 (*c* 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (ppm) 7.93 (1H, s, triazole CH), 5.92 (1H, d, *J* = 9.2 Hz, H-1′), 5.57–5.52 (2H, m, H-2′, H-4′), 5.33–5.19 (3H, m, H-3′, CH_2), 4.32 (1H, pseudo t, *J* = 6.2, 6.2, H-5′), 4.25–4.13 (2H, m, H-6′a, H-6′b), 2.24, 2.10, 2.05, 2.02, 1.89 (5 × 3H, 5s, $OCOCH_3$); ^{13}C NMR ($CDCl_3$): δ (ppm) 170.6, 170.1, 169.8, 169.6, 168.8 ($OCOCH_3$), 143.3 (triazole C-4), 122.1 (triazole C-5), 85.9 (C-1′), 73.8, 70.5, 67.7, 66.7 (C-2′–C-5′), 61.1 (C-6′), 57.2 (CH_2), 20.6, 20.4 (2), 20.3, 20.0 ($OCOCH_3$). Anal. Calcd for $C_{19}H_{25}N_3O_{11}$ (471.42): C, 48.41; H, 5.35; N, 8.91. Found: C, 48.52; H, 5.26; N, 8.78.

4.2.22. 4-Phenyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl)-1,2,3-triazole (18d)

From **11** (0.1 g, 0.27 mmol), phenylacetylene (29 μL, 0.27 mmol) and $C_3H_7COOCu(PPh_3)_2$ (3.6 mg, 5.4 μmol) according to Section 4.2. Purified by column chromatography (4:5 EtOAc–hexane) to yield 0.12 g (90%) of white solid. Mp: 197–199 °C (lit.[19] mp: 197–199 °C); $[\alpha]_D$ −44 (*c* 0.50, $CHCl_3$); ^1H and ^{13}C NMR data correspond to the reported spectra.[19]

4.2.23. 4-Acetoxymethyl-1-(2′,3′,4′-tri-*O*-acetyl-α-L-arabinopyranosyl)-1,2,3-triazole (19b)

From **12** (0.1 g, 0.33 mmol), propargyl acetate (33 μL, 0.33 mmol) and $C_3H_7COOCu(PPh_3)_2$ (2.2 mg, 3.3 μmol) according to Section 4.2. Purified by column chromatography (1:1 EtOAc–hexane) to yield 0.13 g (96%) of white solid. Mp: 183–184 °C; $[\alpha]_D$ +2 (*c* 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (ppm) 7.93 (1H, s, triazole CH), 5.81 (1H, d, *J* = 9.2 Hz, H-1′), 5.58 (1H, pseudo t, *J* = 9.9, 9.2 Hz, H-2′), 5.45 (1H, br s, H-4′), 5.29 (1H, dd, *J* = 9.9, 3.1 Hz, H-3′), 5.21, 5.19 (2 × 1H, 2d, *J* = 12.9 Hz in each, CH_2a, CH_2b), 4.20(1H, d, *J* = 13.6 Hz, H-5′a), 4.00 (1H, d, *J* = 13.6 Hz, H-5′b), 2.23, 2.09, 2.04, 1.90 (4 × 3H, 4s, $OCOCH_3$); ^{13}C NMR ($CDCl_3$): δ (ppm) 170.6, 169.9, 169.6, 168.8 ($OCOCH_3$), 143.3 (triazole C-4), 122.1 (triazole C-5), 86.4 (C-1′), 70.2, 68.0, 67.5 (C-2′–C-4′), 67.1 (C-5′), 57.2 (CH_2), 20.7, 20.6, 20.3, 20.0 ($OCOCH_3$). Anal. Calcd for $C_{16}H_{21}N_3O_9$ (399.35): C, 48.12; H, 5.30; N, 10.52. Found: C, 48.17; H, 5.46; N, 10.41.

4.2.24. 4-Phenyl-1-(2′,3′,4′-tri-*O*-acetyl-α-L-arabinopyranosyl)-1,2,3-triazole (19d)

From **12** (0.1 g, 0.33 mmol), phenylacetylene (37 μL, 0.33 mmol) and $C_3H_7COOCu(PPh_3)_2$ (2.2 mg, 3.3 μmol) according to Section 4.2. Purified by column chromatography (2:3 EtOAc–hexane) to yield 0.13 g (98%) of white solid. Mp: 217–219 °C; $[\alpha]_D$ −55 (*c* 0.51, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (ppm) 8.07 (1H, s, triazole CH), 7.87–7.33 (5H, m, aromatics), 5.83 (1H, d, *J* = 9.2 Hz, H-1′), 5.68 (1H, pseudo t, *J* = 9.9, 9.2 Hz, H-2′), 5.47 (1H, br s, H-4′), 5.29 (1H, dd, *J* = 9.9, 2.5 Hz, H-3′), 4.20 (1H, d, *J* = 13.6 Hz, H-5′a), 3.99 (1H, d, *J* = 13.6 Hz, H-5′b), 2.24, 2.04, 1.90 (3 × 3H, 3s, $OCOCH_3$); ^{13}C NMR ($CDCl_3$): δ (ppm) 170.0, 169.8, 169.1 ($OCOCH_3$), 148.2 (triazole C-4), 130.0, 128.8 (2), 128.4, 125.8 (2) (aromatics), 117.7 (triazole C-5), 86.6 (C-1′), 70.5, 68.0, 67.7 (C-2′–C-4′), 67.2 (C-5′), 20.9, 20.5, 20.2 ($OCOCH_3$). Anal. Calcd for $C_{19}H_{21}N_3O_7$ (403.39): C, 56.57; H, 5.25; N, 10.42. Found: C, 56.64; H, 5.11; N, 10.27.

4.2.25. 4-Acetoxymethyl-1-(2′,3′,4′-tri-*O*-acetyl-β-L-fucopyranosyl)-1,2,3-triazole (20b)

From **13** (0.1 g, 0.32 mmol), propargyl acetate (32 μL, 0.32 mmol) and $C_3H_7COOCu(PPh_3)_2$ (4.3 mg, 6.4 μmol) according to Section 4.2. Purified by column chromatography (1:1 EtOAc–hexane) to yield 0.13 g (96%) of colourless oil. R_f: 0.37 (1:1 EtOAc–hexane); $[\alpha]_D$ +13 (*c* 0.52, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (ppm) 7.94 (1H, s, triazole CH), 5.89 (1H, d, *J* = 9.2 Hz, H-1′), 5.52 (1H, pseudo t, *J* = 9.9, 9.9 Hz, H-2′), 5.42 (1H, d, *J* = 2.5 Hz, H-4′), 5.32 (1H, dd, *J* = 9.9, 2.5 Hz, H-3′), 5.25, 5.20 (2 × 1H, 2d, *J* = 12.9 Hz in each, CH_2a, CH_2b), 4.20 (1H, q, *J* = 6.2 Hz, H-5′), 2.26, 2.09, 2.02, 1.89 (4 × 3H, 4s, $OCOCH_3$), 1.28 (3H, d, *J* = 6.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ (ppm) 170.4, 170.1, 169.5, 168.8 ($OCOCH_3$), 143.0 (triazole C-4), 122.0 (triazole C-5), 85.9 (C-1′), 72.3, 70.8, 69.6, 67.8 (C-2′–C-5′), 57.1 (CH_2), 20.5, 20.3, 20.2, 19.9 ($OCOCH_3$), 15.7 (CH_3). Anal. Calcd for $C_{17}H_{23}N_3O_9$ (413.38): C, 49.39; H, 5.61; N, 10.17. Found: C, 49.32; H, 5.75; N, 10.11.

4.2.26. 4-Phenyl-1-(2′,3′,4′-tri-*O*-acetyl-β-L-fucopyranosyl)-1,2,3-triazole (20d)

From **13** (0.1 g, 0.32 mmol), phenylacetylene (35 μL, 0.32 mmol) and $C_3H_7COOCu(PPh_3)_2$ (10.7 mg, 16 μmol) according to Section 4.2. Purified by column chromatography (2:3 EtOAc–hexane) to yield 0.13 g (97%) of white solid. Mp: 237–239 °C; $[\alpha]_D$ +67 (*c* 0.51, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (ppm) 8.08 (1H, s, triazole CH), 7.87–7.29 (5H, m, aromatics), 5.89 (1H, d, *J* = 9.2 Hz, H-1′), 5.62 (1H, pseudo t, *J* = 9.9, 9.9 Hz, H-2′), 5.42 (1H, d, *J* = 2.5 Hz, H-4′), 5.29 (1H, dd, *J* = 9.9, 2.5 Hz, H-3′), 4.16 (1H, q, *J* = 6.2 Hz, H-5′), 2.26, 2.02, 1.89 (3 × 3H, 3s, $OCOCH_3$), 1.28 (3H, d, *J* = 6.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ (ppm) 170.2, 169.7, 169.1 ($OCOCH_3$), 148.1 (triazole C-4), 130.0, 128.7 (2), 128.3, 125.8 (2) (aromatics), 117.7 (triazole C-5), 86.2 (C-1′), 72.6, 71.1, 69.8, 67.8 (C-2′–C-5′), 20.6, 20.4, 20.2 ($OCOCH_3$), 15.9 (CH_3). Anal. Calcd for $C_{20}H_{23}N_3O_7$ (417.41): C, 57.55; H, 5.55; N, 10.07. Found: C, 57.64; H, 5.69; N, 9.98.

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