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Glycomacrocycles

Syntheses of *Bis*-Triazole Linked Carbohydrate Based Macrocycles and Their Applications for Accelerating Copper Sulfate Mediated Click Reaction

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Abstract: Macrocyclic compounds play an important role in many research fields including drug discovery and development, bioorganic chemistry, and materials sciences. Carbohydrate-based macrocycles are important compounds with unique structures and many potential applications. In this study, we have designed and synthesized a series of 1,2,3-triazole linked and pyranose embedded macrocycles in short steps through the copper (I) catalyzed azide and alkyne cycloaddition reactions (CuAACs). Eight non-symmetrical glucosamine based and bis-triazole linked macrocycles have been synthesized starting from the readily available *N*-acetyl-D-glucosamine. These triazole-linked glycomacrocycles showed remarkable reaction rate accelerations for $CuSO_4$ mediated azide and alkyne cycloaddition reactions in aqueous mixtures. Several azides including a sugar azide, which react sluggishly with alkynes, have been accelerated with the synthesized macrocycles. The benzoylated macrocycles with three methylene linkage at anomeric positions were the most effective among the eight macrocycles.

Introduction

Macrocyclic frameworks are important structural features in many natural products and pharmaceutics. Natural and synthetic macrocycles often exhibit useful biological activities that allow them to function as drugs or lead compounds for drug discovery.[1–7] They are also important in molecular recognition and materials sciences.[8,9] Among the different types of macrocyclic compounds, carbohydrate-derived macrocycles have attracted great interest due to their unique structures and many applications in biological sciences, materials chemistry, and supramolecular chemistry.[10–13] Selective functionalization of monosaccharides in their furanoid or pyranoid configurations can generate diverse library of sugar-containing macrocyclic compounds. The conformation-restricted nature of sugar ring allows the formation of chiral cavities, which are useful for guest encapsulation and chiral recognition. Because of their unique structures and functions, many synthetic strategies have been developed towards the construction of carbohydrate-based macrocycles.[10,14]

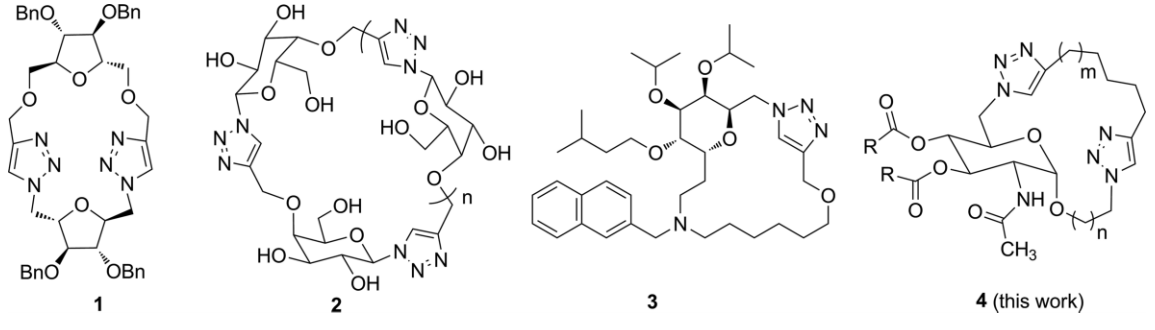

Figure 1. Examples of sugar and triazole based macrocycles with sugar in the backbone of the cycle.

In recent years, copper (I) catalyzed azide alkyne cyclization reaction (CuAAC), or "click chemistry" strategy has shown great applications in many areas.[15] The click chemistry has greatly enabled the syntheses and study of glycoconjugates and shaped carbohydrate research.[14,16–18] The CuAAC products, typically 1,4-disubstituted 1,2,3-triazoles, are useful heterocycles

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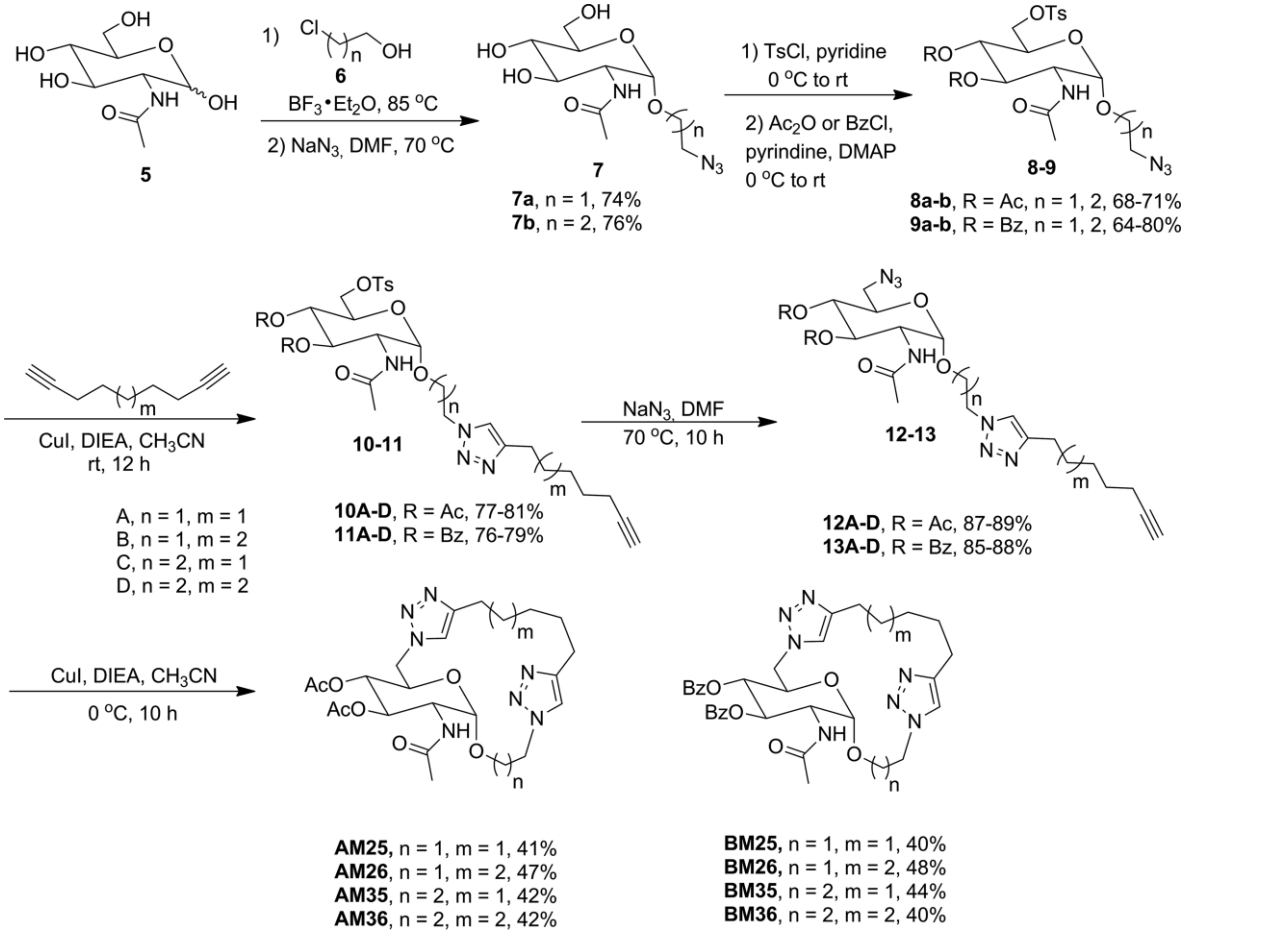
that are not passive linkers, they also have properties leading to biological activities, as ligands in catalysis, sensors for guest recognitions, and in preparation of functional supramolecular assemblies.[19–21] Because of the importance of the reaction, many efforts have been devoted to improve the reaction scopes to include different substrates and optimize reaction conditions for biological applications.[22–24] Many synthetic methods using different copper reagents, ligands and catalysts for the preparation of triazoles by click chemistry have been developed.[25–27] Several organic compounds that can accelerate the copper catalyzed azide alkyne cycloaddition have been reported, including various triazole derivatives as ligands.[28–31] The click chemistry has shown remarkable utility for the construction of sugar based macrocycles typically at the last step of the macrocyclization.[32–42] A few examples of sugar based macrocycles containing the 1,2,3-triazole linkage are shown in Figure 1. *C2*-symmetrical sugar-based macrocycle **1** and cyclodextrin mimics **2** exhibit guest binding and recognition properties.[43,44] And the galactose derived macrocycle **3** was synthesized and identified as an apoptosis inducer in leukemic cells.[45]

Results and Discussions

In this research, we designed and synthesized a series of novel macrocycles with the general structure **4**, containing a pyranose ring derived from *N*-acetyl-D-glucosamine in the backbone and linked through two 1,4-disubstituted 1,2,3-triazoles. We have shown that certain sugar triazole derivatives formed functional molecular assemblies and supramolecular gels.[46–48] By incorporating triazole functional groups present in supramolecular gelators into a macrocycle, we can obtain a new class of compounds which may have interesting applications. The resulting macrocycles with unique architectures may lead to interesting biological properties as enzyme inhibitors or they can form molecular assemblies that may function as suitable hosts. The heterocycles in the molecules together with the sugar ring embedded in the macrocycles form unique cavities and binding sites for metals or ligands and can be explored for chiral recognition and catalysis.

Utilizing click chemistry strategy, we can introduce triazole functional groups to the sugar skeleton at the anomeric position and at the 6-hydroxyl group of a pyranose such as glucose or glucosamine. As shown in Scheme 1, glycosylation of *N*-acetyl-D-glucosamine **5** with chloroalkanol **6** using BF_3•Et_2O as the catalyst afforded the α-anomer as the major product. Either the mixture or the pure α-isomer was converted into the azide **7** as pure α-anomer. This was then converted into the tosylated intermediates by a one pot selective tosylation followed by acylation of 3,4-dihydroxyl groups to afford diacetates **8**. Mono click reaction of the intermediate **8a** or **8b** with a bis-terminal



Scheme 1. Synthesis of sugar derived macrocycles via click reaction.

alkyne afforded the intermediates **10A-10D**. The tosyl group was then displaced with an azido group to afford the azido alkynes **12A-12D**, the key precursors used in the cyclization reaction. Compound **12B** (R = Ac, *n* = 1, m = 2) was used as the intermediate for the macrocyclization test reactions, the results are shown in Table 1. When using $CuSO_4$ and sodium ascorbate (NaAsc) as the catalysts, only a small amount of the desired macrocycle was obtained. Using CuI and diisopropyl ethylamine (DIEA) as catalysts has resulted in better yields. The CuI catalyst loading seems to be critical to the cyclization reaction. Through several trials we found that the using 0.2 equiv. of CuI in acetonitrile at normal concentration (15 mM) at 0 °C, clean conversion to the desired product was observed and with acceptable isolated yield of 47 %. This condition was used for the synthesis of several other macrocycles; which are named based on the numbers of hydrocarbons linking the triazoles and the sugar ring: **AM25-AM36**. Besides using acetate as the protective groups, by similar methods from intermediates **9a-b**, we synthesized four other macrocycles: **BM25-BM36**.

Figure 2 shows the structures of the eight macrocycles synthesized in this study. Using Chem3D molecular modeling, we carried out the MM2 energy minimization to obtain the conformation of the macrocycles for the eight macrocycles. The energy-minimized conformations of the benzoylated macrocycles are shown in Figure 3 and the acetylated macrocycles are shown in Supplementary Information (SI) Figure S1. Typically, the distance of the two triazole rings is around 5Å in these macrocycles. The cavities should be flexible and able to bind guest molecules of small size, such as metal ions and amino acid derivatives. For the benzoate derivatives, the cavity seems to be more defined comparing to that of acetate derivatives due to the influence of the aromatic phenyl group. The two benzoate-shielded parts of the macrocycle, this may lead to enhanced binding towards the triazole rings. Due to the flexible linkages, the triazole orientation can change upon binding to guest molecules or metal ions.

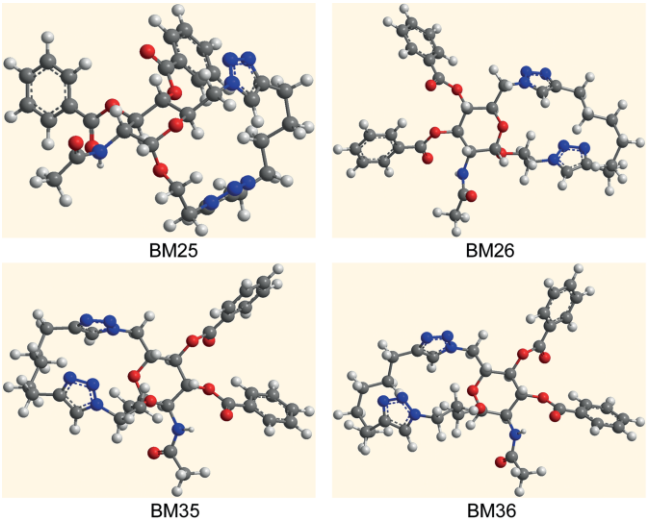


Figure 3. The energy minimized stable conformations of the benzoate protected macrocycles.

Since 1,2,3-triazoles have been used as ligands for CuAACs, as a proof of principle studies, we explored the applications of these macrocycles as ligands for copper sulfate- mediated azide alkyne cycloaddition reactions (AACs). We had carried out click reactions using 1-azido-1-deoxy-β-D-glucopyranoside tetraacetate (Ac-Glc-N_3) and 2-acetamido-2-deoxy-β-D-glucopyranosyl azide 3,4,6-triacetate **14** with a series of alkynes previously.[47,48] These reactions typically required 12–24 h and sometimes elevated temperatures to achieve desirable products in good yields, and phenylacetylene reacts much slower than aliphatic alkynes. The glucosamine derivative **14** typically reacts slower

Table 1. Conditions and yields for the macrocyclization of **12B** through click chemistry for the synthesis of **AM26**.

Entry	Catalyst and additives	Solvent, temperature	Concentration mM	Conversion % estimated by NMR	Yield% isolated
1	$CuSO_4$ 0.2, NaAsc 0.4	DCM/H_2O (5:1), room temp. to 50 °C	2.8	50 %	15 %
2	CuI 2.0, DIEA 3.0	THF, room temp.	2.3	100 %, mixture	30 %
3	CuI 1.2, DIEA 3.0	THF, reflux	2.3	polymerization	0 %
4	CuI 1.0, DIEA 3.0	THF, room temp.	2.3	100 %, mixture	28 %
5	CuI 0.5, DIEA 5.0	THF, room temp.	4.5	100 %	44 %
6	**CuI 0.2, DIEA 5.0**	**CH_3CN, 0 °C**	**15**	**100 %**	**47 %**

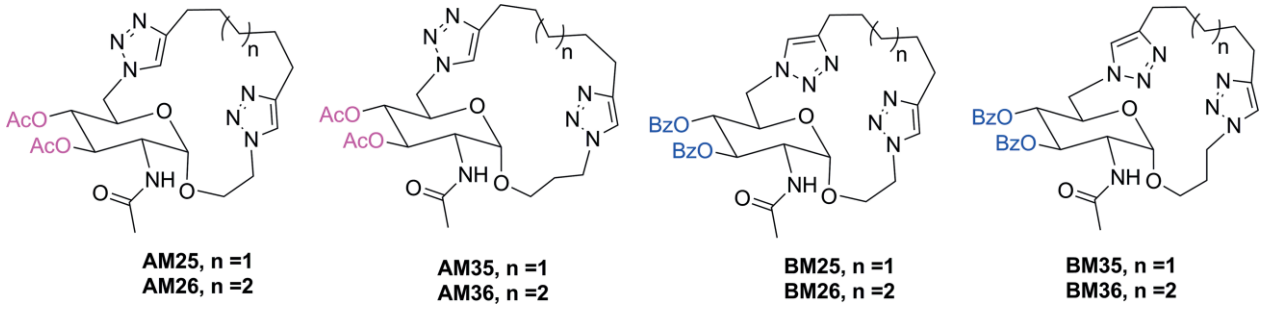
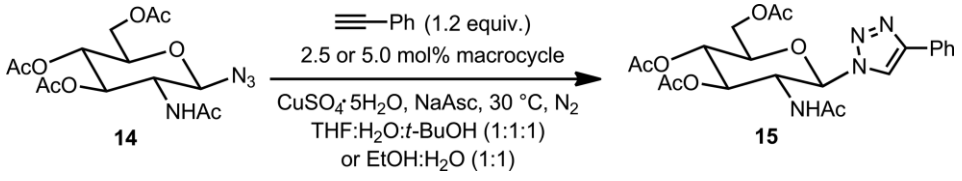


Figure 2. Structures of the eight macrocycles synthesized.

than Ac-Glc-N_3 for the same alkynes. Therefore, we choose compound **14** as the main substrate to test whether the synthesized macrocycles can catalyze the cycloaddition reactions. We were pleased to find that these macrocycles were effective ligands in accelerating $CuSO_4$ catalyzed AACs. As shown in Table 2, the sugar azide **14** and phenylacetylene were used as the substrates. With 5.0 mol-% macrocycle loading in 2 h all eight compounds were effective to accelerate the reaction to quantitative conversion without byproducts, the products were obtained in 97 % isolated yield. Without the added macrocycle ligands, the click reaction product was only obtained in 23 % conversion at 2 h. Next, we screened the reactions with different amount of macrocycle (**BM35**) and copper sulfate, different solvents, the results are shown in SI Table S1 and Figures S3-S4. Using 5.0 mol-% macrocycle, and 5.0 mol-% $CuSO_4$, the reaction proceeded with 100 % conversion in 4 h, further reduction of copper amount was not effective under these conditions. Using 20 mol-% $CuSO_4$, the **BM35** loading can be reduced to 2.5 % without affecting reaction rate much. Further reduction of macrocycle however was not effective. Therefore, next we screened all macrocycle ligand loading at 2.5 mol-% using EtOH/H_2O (1:1) as the solvent. Interestingly all eight macrocycles showed similar catalytic effects (Table 2, **Condition A**), all reactions achieved 100 % conversion at 5 h. The control reaction without the ligand had 21 % conversion at 5 h.

Using compound **BM35** as the ligand, we screened reaction conditions of **14** with 1-octyne, the results are shown in SI Table S2 and Figure S7. There was not much difference using *t*BuOH/THF/H_2O, or *t*BuOH/H_2O, or EtOH/H_2O mixtures as the solvents. When 20 % copper sulfate and 2.0–2.5 mol-% macrocycle (as

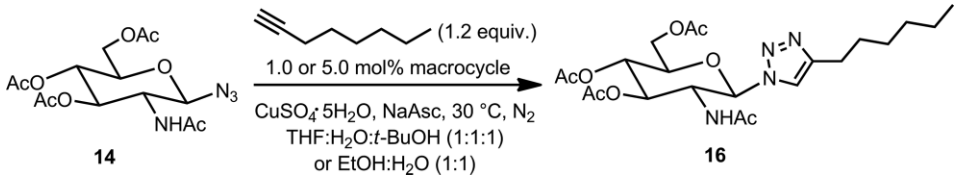
Table 2. Effect of the macrocycle on catalyzing the click chemistry using phenyl acetylene.[a]



Entry	Macrocycle	Condition A (2.5 mol-%) Conversion (%) at 2 h	Conversion (%) at 5 h	Condition B (5.0 mol-%) Conversion (%) at 2 h	Isolated yield (%)
1	none	15	21	23	N/A
2	**AM25**	55	100	100	97
3	**AM26**	53	100	100	98
4	**AM35**	55	100	100	98
5	**AM36**	57	100	100	98
6	**BM25**	61	100	100	98
7	**BM26**	64	100	100	98
8	**BM35**	67	100	100	97
9	**BM36**	66	100	100	97

[a] For both conditions: Sugar azide (1 equiv.), $CuSO_4$·$5H_2O$ (0.2 equiv.), phenylacetylene (1.2 equiv.), NaAsc (0.4 equiv.). **Condition A**: 2.5 mol-% macrocycle in EtOH/H_2O (1:1); **Condition B**: 5.0 mol-% macrocycle in *t*BuOH/THF/H_2O (1: 1: 1). All solvent ratios are volume ratios.

Table 3. Effect of the macrocycles on copper mediated click reaction of azide **14** with 1-octyne.[a]



Entry	Macrocycle	Condition A (1.0 mol-%) Conversion (%) at 2 h	Conversion (%) at 6 h	Condition B (5.0 mol-%) Conversion (%) at 1 h	Isolated yield (%)
1	none	25	28	19	N/A
2	**AM25**	33	38	91, (100, 2 h)	94
3	**AM26**	43	50	100	91
4	**AM35**	31	36	86, (100, 2 h)	94
5	**AM36**	59	62	100	94
6	**BM25**	49	68	100	91
7	**BM26**	85	89	100	91
8	**BM35**	100		100	91
9	**BM36**	100		100	91

[a] For both conditions: Sugar azide (1 equiv.), $CuSO_4$·$5H_2O$ (0.1 equiv.), 1-octyne (1.2 equiv.), NaAsc (0.2 equiv.). **Condition A**: 1.0 mol-% macrocycle in EtOH/H_2O (1:1); **Condition B**: 5.0 mol-% macrocycle in *t*BuOH/THF/H_2O (1: 1: 1). All solvent ratios are volume ratios.

the ligand) were used, all reactions showed 100 % conversion to the product **16** within one hour. When the macrocycle loading was reduced to 1.0 mol-%, either using 0.1 or 0.2 equivalents of copper sulfate, the reaction completed within two hours. But further reduction of the macrocycle loading to 0.5 mol-% led to slower reaction rates with only 50 % conversion observed at 1 h. Based on the screening results using **BM35**, we used 10 mol-% $CuSO_4$ and tested all eight macrocycles, as shown in Table 3 At 5.0 mol-% macrocycle loading, all but two reactions were completed in less than 1 h, the reactions using **AM35** and **AM25** were completed in 2 h. In all these reactions the desired product was obtained as the only product and the triazole **16** was isolated in excellent yields. The control reaction without macrocycles only proceeded with 19 % conversion at 1 h. When we reduced the loading of the macrocycle ligands to 1.0 mol-%, **BM35** and **BM36** were the most efficient at accelerating the reactions, with 100 % conversion to products in 2 h, but the others were not as effective.

Based on the screening results in Table 2 and Table 3, the benzoylated macrocycles (**BM** series) worked better than the corresponding acetylated derivatives (**AM** series) with the same ring sizes. This suggests that the peripheral modifications of the macrocycles made a difference in guest binding. The modeling studies indicated that the benzoate phenyl ring contributed to aryl π-π stacking interactions forcing the macrocycle to adopt a different conformation. As for ring sizes and positions of triazoles, typically the 6-methylene spacer linked macrocycles are slightly more effective than the corresponding 5-carbon linked systems. The alkyl spacer at the anomeric position played an important role, the three carbon linked compounds were more effective than the corresponding two carbon linked systems. The position of triazoles affected the conformation of the macrocycle, which also affected binding with metal ions. Binding to Cu^{2+} will likely require rotation or conformational change of the two triazoles, **BM35** and **BM36** were able to adopt a more favorable conformation due to the more flexible three-methylene linkage at the anomeric center.

Besides the sugar azide, we also screened a few other azides and found that two azido derivatives participated in the cycloaddition reaction rather slowly when using $CuSO_4$ and sodium ascorbate as the catalyst; these include the tetraethylene glycol derived mono azide **17** and the *meta* acetyl phenyl azide **19** (Figure 4). We found that the macrocycle **BM35** was very effective in accelerating the cycloaddition reactions. The click reaction of the aliphatic azide **17** with phenyl acetylene had only 25 % conversion at 1 h and 56 % conversion at 12 h. However, in the presence of 2.0 mol-% of **BM35**, the reaction was completed in 1 h with 100 % conversion to the desired product. For the phenyl azide **19**, the reaction had only 15 % conversion at 2 h and 21 % conversion at 4 h; but with the macrocycle ligand, the reaction was completed in 4 h with 2.5 mol-% **BM35** and with 5.0 mol-% **BM35**, the reaction had 100 % conversion within 2 h.

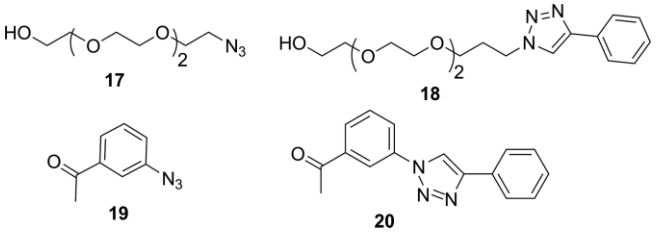


Figure 4. The azides and click reaction products that were catalyzed using **BM35**.

Conclusions

In summary, using CuAAC as the key cyclization step we have synthesized a series of eight *N*-acetyl-D-glucosamine based 18–20 membered ring macrocycles in synthetically useful yields and quantities. The method to construct large glycomacrocycles from readily available starting materials can be extended to the synthesis of other sugar-based macrocycles. The macrocycles synthesized have shown significant rate acceleration for the $CuSO_4$ mediated AACs of 2-acetamido-2-deoxy-β-D-glucopyranosyl azide 3,4,6-triacetate **14** with alkynes in aqueous mixtures. The benzoate protected macrocycles were more efficient than the acetate protected compounds. For the click reaction of sugar azide with 1-octyne, the **BM35** and **BM36** were much more efficient than the other macrocycles. Similar catalytic effects using **BM35** were observed for two other azides, which indicated the scope of the substrates was not limited to sugar azide. These results clearly indicated that the macrocycles obtained in this study are effective ligands to accelerate the copper sulfate mediated azide and alkyne cycloaddition reactions. The structure and activity correlation can lead to more efficient ligand design for other copper catalyzed reactions. Besides being useful for catalysis, these sugar-embedded macrocycles are expected to exhibit interesting properties as natural product analogs and they may be useful for chiral recognition, etc. We are continuing with the study of these macrocycles for other applications and the results will be reported in due course.

Experimental Section

The detailed synthetic procedures and characterizations for all intermediates **7a-13D**, the eight macrocycles, and compounds **18** and **20** are included in the Supporting Information (SI). The experimental conditions and ^1H NMR spectra used for reaction monitoring for all tables and macrocycles **AM25-BM36**, copies of ^1H and ^{13}C NMR spectra for all intermediates, 2D-COSY and HSQC NMR spectra for macrocycles are also provided in SI. One example of the synthesis for **AM25** is given below.

General procedure for the synthesis of macrocycles.

To a 50 mL round-bottomed flask, macrocycle precursor (1 equiv.), CuI (0.2 equiv.) and DIEA (5 equiv.) were mixed with CH_3CN as solvent (starting material/solvent = ca. 0.015 mmol/mL). The reaction mixture was stirred for 10 hours at 0 °C. Solvent was removed by a rotavap to afford the crude, which was purified by column chromatography using eluent from pure DCM to 5 % MeOH/DCM to afford desired macrocycles. Amount of all chemicals, yield, R_f value and characterization of the macrocycle are listed respectively.

Synthesis of compound AM25. Compound **12A** (54 mg, 0.104 mmol, 1 equiv.), CuI (3.8 mg, 0.021 mmol, 0.2 equiv.), DIEA (0.09 mL, 0.520 mmol, 5 equiv.), CH_3CN (7 mL). Off-white solid

(22 mg, 41 %) was obtained as the desired product (R_f = 0.2 in 5 % MeOH/DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1 H, *H*C=C-), 7.31 (s, 1 H, *H*C=C-), 5.77 (d, J = 9.4 Hz, 1 H, -N*H*), 5.25 (dd, J = 10.7, 9.4 Hz, 1 H, H-3), 5.06 (t, J = 9.4 Hz, 1 H, H-4), 4.81 (d, J = 3.7 Hz, 1 H, H-1), 4.72–4.63 (m, 1 H, -O-CH_2-C*H*$_a$-N), 4.52–4.22 (m, 5 H, H-6$_a$, H-2, -O-CH_2-C*H*$_b$-N, H-6$_b$, H-5), 3.53–3.44 (m, 1 H, -O-C*H*$_a$-CH_2-N), 3.40–3.32 (m, 1 H, -O-C*H*$_b$-CH_2-N), 2.92–2.73 (m, 3 H), 2.68–2.57 (m, 1 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.00 (s, 3 H), 1.86–1.65 (m, 3 H), 1.65–1.51 (m, 1 H), 1.32–1.19 (m, 1 H), 1.15–1.01 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.0, 169.8, 96.5 (C-1), 70.8 (C-3), 70.0 (C-4), 68.9 (C-5), 65.9 (-O-CH_2-CH_2-N), 51.7 (C-2), 51.3 (C-6), 48.5 (-O-CH_2-CH_2-N), 27.1, 26.7, 25.6, 24.6, 24.0, 23.1, 20.6. HRMS (ESI$^+$) ([M + Na]$^+$) m/z calcd. for $C_{23}H_{33}N_7O_7Na$, 542.2334, found 542.2330.

Acknowledgments

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Keywords: Glycomacrocycle · N-acetyl-D-glucosamine · Macrocycle synthesis · Click chemistry · Copper catalysis

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