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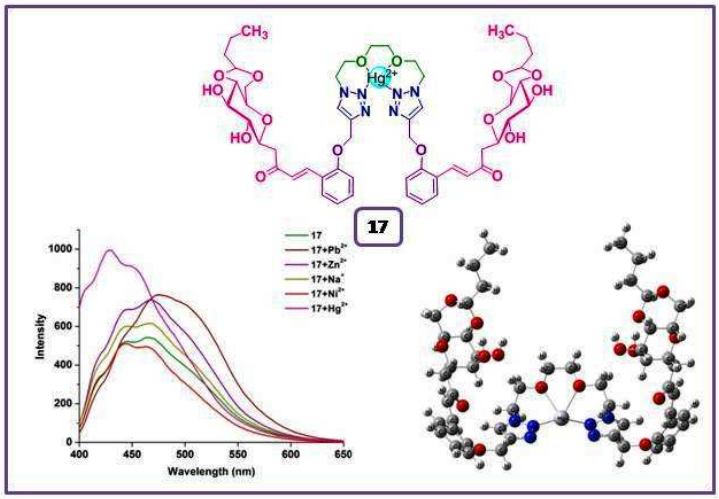
# Graphical Abstract




Ether-linked-bis-triazole derivatives have been synthesized by (CuAAC) "Click" reaction and well characterized by NMR technique, mass and elemental analysis. Application of these materials in the field of sensor has also been demonstrated using various spectroscopic techniques. Interaction of the compound with $Hg^{2+}$ was further confirmed from computational studies.

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ARTICLE TYPE

# Design, synthesis and metal sensing studies of ether-linked bis-triazole derivatives

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**Ether-linked-bis-triazole derivatives have been synthesized by (CuAAC) "Click" reaction and well characterized by NMR technique, mass and elemental analysis. Application of these materials in the field of sensor has also been demonstrated using various spectroscopic techniques. Interaction of the compound with $Hg^{2+}$ was further confirmed from computational studies.**

## Introduction

Mercury is one of the most significant environmental pollutants and its contamination is widespread by various natural sources.[1] The introduction of mercury in to the food chain causes serious hazards to the man kind as well as to the marine lives.[2,3] The accumulation of mercury in the liver, kidney and spleen leads to DNA and nervous system damage. Although a number of chemosensors such as calix[4]arenes and aza-crown ethers has been developed for selective sensor for $Hg^{2+}$ ion, most of them exhibit poor solubility which limits their application as sensor. Moreover, the use of sugar moiety increases the solubility of the reaction.

Molecular recognition of anions and cations is an important subfield within supramolecular chemistry due to the major role that ions play in diverse domains, such as biotechnology, medicine and environmental research.[4-6] Self-assembled monolayers (SAMs) that possess molecular recognition motifs can be used to design chemical sensors,[7] non-linear optical materials,[8] and molecular switches.[9] Incorporation of crown-ether groups into self-assembled monolayers and their use as metal ion sensors were published simultaneously by Moore *et al*.[10] and Flink *et al*.[11]

Fluorescent quenching by heavy metal ions may occur due to spin orbit coupling, energy and electron transfer.[12,13] A facile approach for monitoring $Hg^{2+}$ ions arises due to its propensity to quench fluorescence emission. Among the fluorescent quenching ("turn-off") and enhancement ("turn-on"), the latter is more preferable because it lessens the chance of false positives. Moreover, there are very few literature reports[12] available for the turn-on type fluorescent sensors. Hence designing the fluorescent sensor that provides the turn-on response with $Hg^{2+}$ ion is a challenging target. Recently, there are many reports[14-19] on the sensor materials. In this report, the ether-linked chalcone-based-bis-sugar-triazole derivatives were synthesized and their application in the field of sensor were also realized from the spectroscopic experiments. The designed chemosensor, **17** exhibits a "turn-on" type response and highly selective fluorescence behaviour for $Hg^{2+}$ ions.

## Results and discussion

### Synthesis and characterisation of sugar chalcone derivatives

(4,6-*O*-Butylidene-*β*-**D**-glucopyranosyl)propan-2-one, **1** and 2,3,4,6-tetra-*O*-acetyl-*β*-**D**-glucopyranosyl-propan-2-one, **2** were synthesized by following the literature procedure.[20] The reaction of sugar-*O*-protected-propane-2-one derivatives, **1** & **2** with different aromatic aldehydes using pyrrolidine as catalyst resulted in 65-85% of the corresponding *α*-,*β*-unsaturated compounds, **3-8**. The sugar-chalcone derivatives which possess the free hydroxyl group was propargylated with propargylbromide using potassiumcarbonate as base resulted in the corresponding propargylated derivatives, **9-14**. Ether-linked diazide, **15** was synthesized by adopting the literature procedure.[21] All the synthesized compounds were well characterized using different spectral techniques.

### Ether-linked sugar-triazole derivatives

A series of novel symmetrical ether-linked sugar-chalcone-based-bis-triazole derivatives, **16-20** [**Scheme 1**] were regioselectively synthesized by the copper(I) catalyzed azide alkyne cycloaddion (CuAAC) "Click" reaction of sugar-chalcone-based-propargylated derivatives, **9-14** with ether-linked diazide, **15**. The cycloaddition reaction of triethyleneglycoldiazide with sugar-chalcone based propagylated derivatives was promoted by $CuSO_4$ as catalyst and sodium ascorbate as reducing agent in 1:1 ratio of THF-$H_2O$ mixture. The yield obtained in the reaction was found to be 50-83%. Structures of the synthesized sugar-triazole derivatives were determined by ($^1H$ & $^{13}C$) NMR spectroscopy, mass spectroscopy and elemental analysis.

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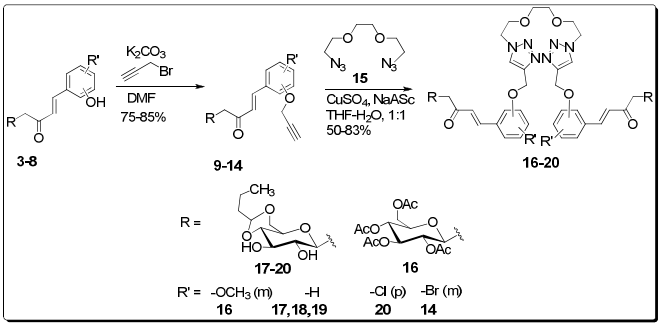


**Scheme 1** Synthesis of ether linked bis-triazole derivatives, **16-20**.

The triazole proton of compound, **16** appeared as a singlet at $\delta$ 7.8 ppm. The appearance of two doublets at $\delta$ 7.79 and 6.64 ppm with $J$ value of ~17 Hz respectively corresponds to the *trans*-alkene protons [**Table 1**]. It also notably exhibited a large coupling constant for the H-1 signal ($^3J_{H1,H2}$ ~ 9.6 Hz), indicating a *trans*-diaxial orientation of H-1 and H-2 as expected for a $\beta$-**D**-configured glucopyranose moiety. The formation of the product, **16** was further confirmed from $^{13}$C NMR spectroscopy where the triazole carbon resonated at $\delta$ 144 and 124 ppm and the $\alpha$-,$\beta$-unsaturated carbonyl signal appeared at $\delta$ 197 ppm. DEPT-135 experiment gave a clear idea for the formation of the sugar-coupled *bis*-triazole product, **16** where eight peaks corresponding to the methylene groups were observed. Formation of the regioisomer of the triazole product was achieved from the Rodius calculation. It is reported in the literature[22] that if the difference between the chemical shift value of C4 and C5 value is greater than 20, it is said to be 1,4-regioisomer and much less value is expected for 1,5-regioisomer. In this case, $\delta$(C4-C5) of the triazole cabon for compound, **16** is found to be 20. Thus, it is very clear from the calculated result that the product is 1,4-regioisomer. Reaction between the compounds, **14** and **15** under Click condition failed to produce the corresponding bis-triazole product and it may be due to the insoluble nature of compound, **14**.

**Table 1** Ether-linked-bis-triazole derivatives, **16-20**

| Compound No. | R' | Time (h) | Yield (%) | NMR data | | | |
|---|---|---|---|---|---|---|---|
| | | | | $\delta$ Ano-H (ppm) | $\delta$ Trz-H (ppm) | $\delta$ Alk-H (ppm) | Alk $J$ ($_{H1,H2}$) Hz |
| **16** | -OCH$_3$ (m) | 24 | 83 | 5.26-5.14[a] | 7.75 | 7.79, 6.64 | 16.5, 16.5 |
| **17** | -H | 24 | 81 | 4.01-3.97 | 7.76 | 7.81,6.69 | 16.5, 16.5 |
| **18** | -Cl (p) | 24 | 50 | 4.56 | 7.87-7.83[b] | 7.87-7.83[b], 6.76 | 16.5 |
| **19** | -H | 48 | 71 | 5.20 | 7.76-7.60[b] | 7.76-7.60[b], 6.87 | 15.6 |
| **20** | -H | 48 | 76 | 5.31 | 8.00 | 7.63-7.59[b], 6.76 | 16.2 |

[a]Peaks overlapped with –OCH$_2$ protons, [b]Peaks overlapped with aromatic protons.

## Fluorescence studies

Fluorescence experiment gives an information about the binding ability of the synthesized *bis*-triazole derivatives with metal ions. Titration experiment was carried out with perchlorate salts of various metal ions including alkali, transition and heavy metal ions using acetonitrile as solvent. The triazole compound, **17** was excited at 330 nm wavelength and the emission was observed around 460 nm. Minimum response was observed with $Na^+$ and $Ni^{2+}$ which clearly depicts that the compound has less affinity towards them whereas excellent response was observed with heavy metal ions such as $Pb^{2+}$, $Zn^{2+}$ and $Hg^{2+}$. The interaction of the compound **17** with all the metal ions except $Ni^{2+}$ ion showed fluorescent enhancement whereas the compound, **17** with $Pb^{2+}$ showed better enhancement along with a slight bathochromic shift. However, the interaction of the compound, **17** with $Hg^{2+}$ gave the highest enhancement with hypsochromic shift of all the metal ions studied. Thus, the result obtained reveals that among the three heavy metal ions studied, $Hg^{2+}$ ions found to have a unique response with the ligand [**Figure 1**]. Similar trend in enhancement of fluorescence was observed upon addition of the metal ion to the receptor.[23] Moreover, upon binding of the target analyte, fluorescent enhancement or quenching can occur by several mechanisms including photo-induced electron transfer and eximer formation.[24] The excellent binding ability of bis-triazole derivatives with $Hg^{2+}$ ion has also been reported in the literature.[25] Similar results was observed with the synthesized compound and it has a unique binding nature with $Hg^{2+}$ ions compared to the other heavy metal ions tested.

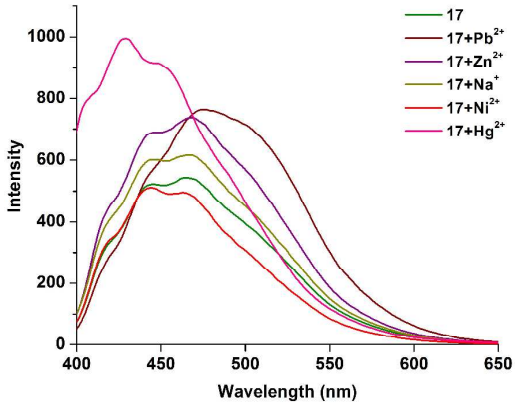


**Figure 1** Fluorescence spectra of compound, **17** (1x10$^{-5}$ M) in $CH_3CN$ with different metal ions (1x10$^{-4}$ M).

## NMR titration experiment

$^1$H NMR titration experiment was carried out to confirm the existence of nature of the interaction of the ether-linked *bis*-triazole compound, **17** with $Hg^{2+}$ ion. **Figure 2** shows the $^1$H NMR spectrum of the ligand, **17** in $CDCl_3$ solvent with different concentration of $Hg^{2+}$ ions in DMSO-$d_6$ solvent. From the titration experiment it has been observed that the triazole protons ($H_{trz}$) were modestly downfield shifted and the peak shapes were significantly broadened and decreased in intensity until almost disappearance upon addition of 1.2 equiv. of $Hg^{2+}$ ions. In addition, the two quartets of ethyleneglycol moiety linked triazole experienced a downfield shift, thereby they join together to form a multiplet. Thus, the downfield shift of the triazole and triethyleneglycol protons

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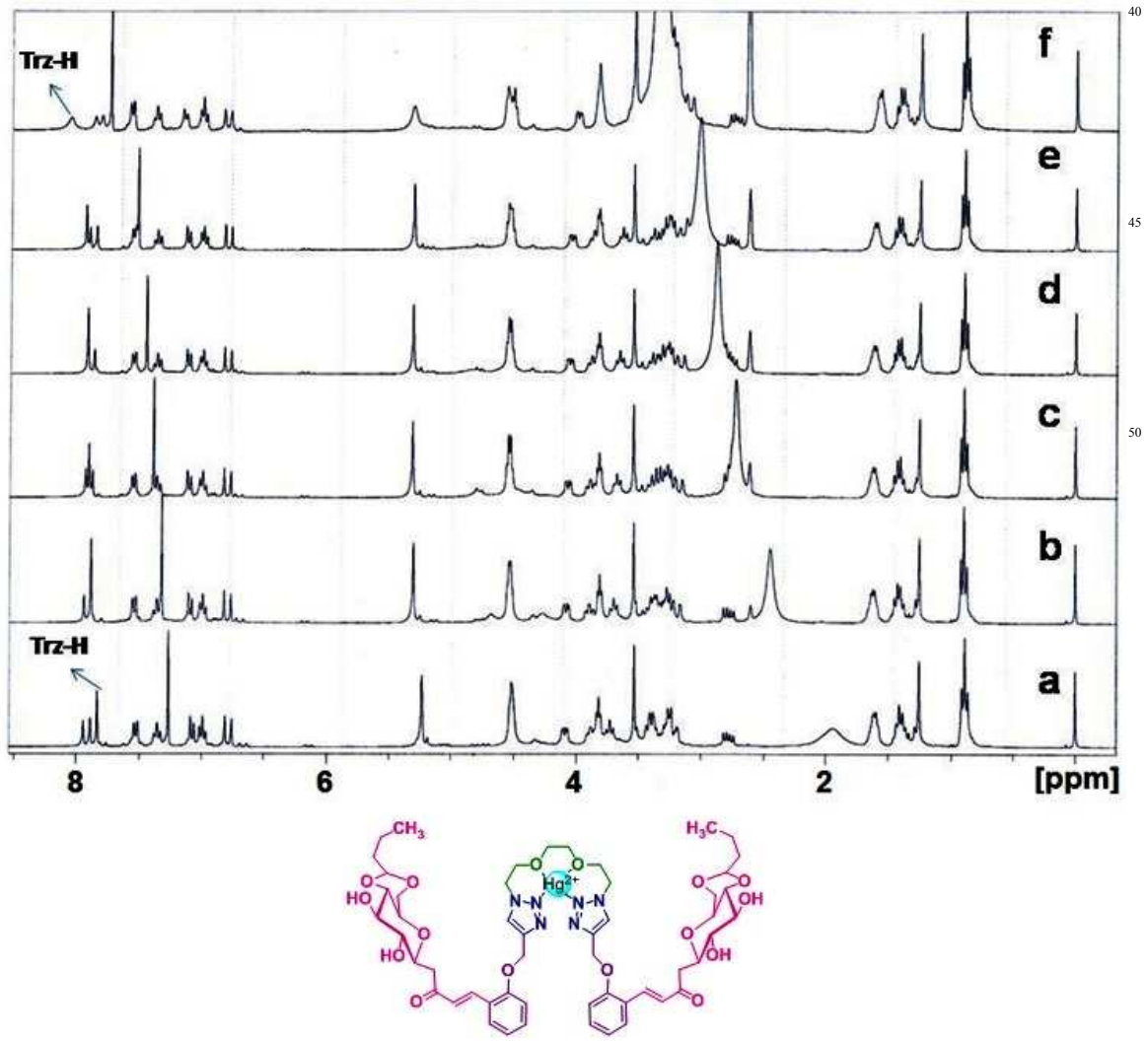


**Figure 2** $^1$H NMR titration spectrum of compound, **17** in $CDCl_3$ upon addition of $Hg^{2+}$: (a), **17** alone; (b), 0.2 equiv.; (c), 0.4 equiv.; (d), 0.6 equiv.; (e), 0.8 equiv. and (f), 1.2 equiv.

confirmed the co-ordination site of $Hg^{2+}$ ion with the two oxygen atoms of the ether-linked moiety and the nitrogen atom of the triazole system. Since negligible shift only has been observed with benzyl ether moieties, it is well clear that the ligand is found to have only one co-ordination site. It implies the existence of only one binding mode and it is confirmed from the titration experiment that even after the addition of more than one equivalent of $Hg(ClO_4)$, there is no prominent shift in the triazole protons. In addition, out of the three nitrogens of the 1,2,3-triazole moiety, though the $Hg^{2+}$ can bind through either the N-2 or N-3, due to the chelation effect only the N-2 of the triazole moieties is capable of co-ordinating with $Hg^{2+}$ ion.[26] It is also revealed that the two triazoles should be faced each other inwards for the greater co-ordinating ability with the metal ion. The possible representation for the binding nature of the ether linked *bis*-triazole with $Hg^{2+}$ ion is shown in **Figure 2**.

**Fluorescence titration experiment**

To investigate the interaction between sensor, **17** and $Hg^{2+}$ ion further, fluorescence titration experiment was performed. When the compound, **17** was excited at 330 nm, a broad emission band is observed at 440 nm. As shown in **Figure 3** on addition of $Hg^{2+}$ ions to the sensor, **17** the intensity of the peak increased with significant hypsochromic shift. However, upon continuous addition of $Hg^{2+}$, the intensity of the peak gradually increased with increase in concentration of $Hg^{2+}$ ion. This clearly depicts the binding of $Hg^{2+}$ ion with the compound, **17**.

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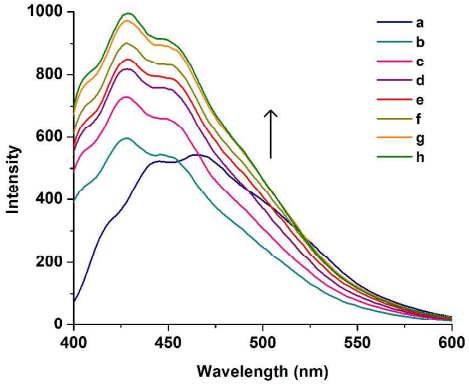


**Figure 3** Fluorescence titration spectra of compound, **17** [5 x $10^{-2}$ M] upon titration with $Hg(ClO)_4$ in acetonitrile+water mixture at 25°C [1X$10^{-5}$ M], (a), 0 equiv. $Hg^{2+}$; (b), 0.2 equiv. $Hg^{2+}$; (c), 0.4 equiv. $Hg^{2+}$; (d), 0.6 equiv. $Hg^{2+}$; (e), 0.8 equiv. $Hg^{2+}$; (f), 1 equiv. $Hg^{2+}$; (g), 1.2 equiv. $Hg^{2+}$; (h), 1.4 equiv. $Hg^{2+}$; The arrow mark shows the change in the intensity upon addition of $Hg^{2+}$ ion.

## Absorption studies

Absorption studies were carried out with different equiv. of $Hg^{2+}$ in acetonitrile solvent in order to find the ligand-metal binding ratio. The variation in the absorption peak of the chemosensor, **17** was monitored upon addition of $Hg^{2+}$ ion using UV-vis spectroscopy. The absorbance for the compound was observed around 284 and 330 nm. Upon addition of 0.5 equiv. of $Hg^{2+}$ ion, a new peak was observed around 230 nm. On further addition of 0.5 equiv. results in the decrease in the absorbance band around 284 and 330 nm with an increase in the absorption band around 230 nm. This clearly confirms the interaction of $Hg^{2+}$ ion with the chemosensor. Furthermore, due to the presence of one isobestic point, it clearly confirmed the ratio of binding of the ligand with metal as 1:1.

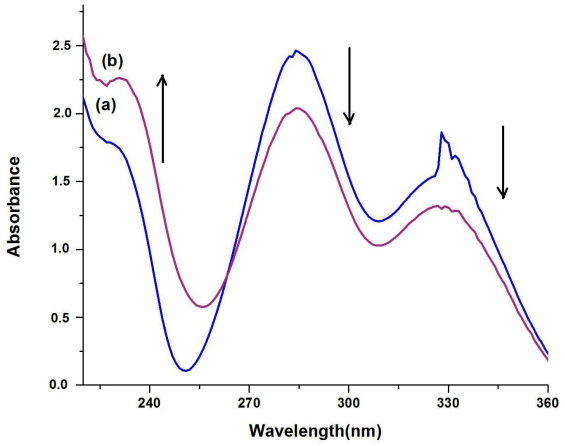


**Figure 4** Absorption spectra of compound, **17** [5 x $10^{-4}$ M] with $Hg^{2+}$ ion [1 x $10^{-2}$ M] in acetonitrile+water mixture at 25°C (a), 0.5 equiv. $Hg^{2+}$; (b), 1 equiv. $Hg^{2+}$. The arrow mark shows the change in the absorbance intensity upon addition of $Hg^{2+}$ ion.

## Computational Studies

The geometry of complex was optimized using density functional theory (DFT) with Becke's three parameter hybrid exchange functional and the Leee Yange Parr correlation functional (B3LYP)[27-29] and 6-31+G** basis set was used. The relativistic effects for mercury ion were added with the help of Stuttgart Dresden effective core potentials. The geometry optimization was carried out without any geometrical constraints. To ensure that the optimized geometries correspond to true minima on the potential energy surface, vibrational frequencies were computed using DFT (B3LYP/6-31+G**. All these calculations were carried out using Gaussian 09 package.[30] The optimized geometry is shown in **figure 5**. From the figure, it can be seen that the mercury ion coordinated to the four groups (two N-2 nitrogens of the five member rings and two oxygens from ethers). The four coordinated bond lengths are 2.105Å (Hg-N), 2.105Å (Hg-N), 2.478Å (Hg-O) and 2.478Å (Hg-O), respectively. Square planar complex has not been observed for four co-ordinated Hg metal. The calculated bond angles are measured as N-Hg-N (153.40˚), N-Hg-O (79.42˚), O-Hg-O (68.04˚) and O-Hg-N (79.42˚). Two coordinated nitrogens are not exactly linear and two triazole rings are not in same plane. The dihedral angle between the two planes of triazole rings is 107.3˚. From these results, it is confirmed that the proposed geometry in the experimental part was correct. The Cartesian coordinates of the optimized geometry is given in supporting information.

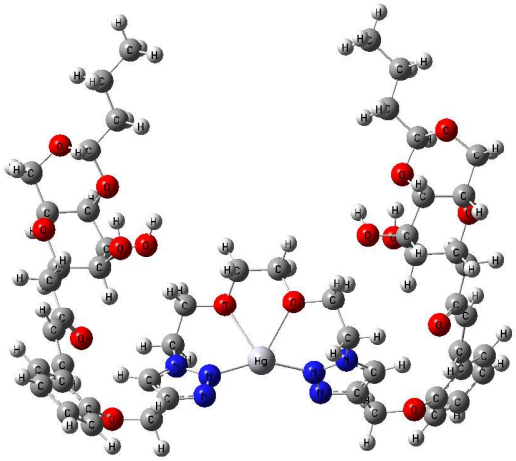

**Figure 5** Optimized geometry of ether-linked-bis-triazole derivative, **17** with $Hg^{2+}$ion.

## Conclusion

Several symmetrical ether-linked-*bis*-sugar-triazole derivatives, **16-20** have been synthesized and characterized using various spectral techniques. In acetonitrile solution, of the 5 metal ions screened, chemosensor, **17** responded selectively to $Hg^{2+}$ ion. It showed selective fluorescence enhancement with hypsochromic shift only towards $Hg^{2+}$. The shift of the triazole protons towards downfield in the $^1H$ NMR titration in the ether-linked bis-triazole derivatives reveals the interaction of compound with $Hg^{2+}$ ion. Also, the metal to ligand ratio was found to be 1:1 from the proton NMR titration experiment and absorption studies. Hence, the synthesized ether-linked bis-triazole compounds may act as a potential sensor for the environmental or biological detection of $Hg^{2+}$.

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## Experimental section

### General methods

D-Glucose, triethyleneglycol, sodiumazide and propargylbromide, were purchased from Sigma-Aldrich Chemicals Pvt. Ltd., USA and were of high purity. Butyraldehyde, pyrrolidine and p-toluenesulphonylchloride were purchased from SRL, India. Other reagents, such as hydrochloricacid, sodiumhydrogencarbonate and solvents (AR grade) were obtained from Sd-fine, India, in high purity and were used without any purification. Acetylacetone, coppersulphate and sodiumascorbate were obtained from Loba-Chemie, India. Aceticanhydride was purchased from Fischer Chemicals Pvt. Ltd., India. The solvents were purified according to standard methods. Column chromatography was performed on silica gel (100 – 200 mesh). NMR spectra were recorded on a Bruker DRX 300 MHz instrument in either $CDCl_3$ or DMSO-d6. Chemical shifts were referenced to internal TMS. Absorption studies were recorded on 1800 Shimadzu UV spectrophotometer in the range 190-800 nm. Fluorescence titration studies were carried out using a Perkin Elmer LS 45 fluorescence spectrometer. Electrospray ionization (ESI) mass spectra were recorded on a WATERS-Q-TOF Premier-HAB213 instrument. Elemental analysis was performed using Perkin-Elmer 2400 series CHNS/O analyzer.

**General procedure for the synthesis of triethyleneglycoldiazide (15):**

Triethyleneglycolditosylate (1 equiv.) was treated with sodium azide (2.5 equiv.) under stirring and then heated for 3 hours. After completion of the reaction, work up was done using ethylacetate followed by the evaporation of the solvent resulted in the product, **15**.

**Spectral data of triethyleneglycoldiazide (15)[16]:**

Azidation of the compound triethyleneglycolditosylate with $NaN_3$ gave **15** as a yellow liquid.

Nature:Liquid; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.71-3.68 (m, 8H, $-CH_2$), 3.39 (t, J = 5.0 Hz, 4H, $-CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 70.7, 70.1, 50.7.

**General procedure for the synthesis of *O*-propargylated sugar-chalcone derivatives (9-14):**

The hydroxy sugar-chalcone derivative (1 equiv.) in DMF was added the $K_2CO_3$ (5 equiv.) and stirred for 10 minutes. To the solution was added propargyl bromide (1.2 equiv.) and then the mixture was allowed stir for 24 hrs. Once after the completion of the reaction, work up was done using chloroform and the product was isolated by the evaporation of the organic layer.

**Spectral data of (*E*)-1-(2,3,4,6-tetra-*O*-acetyl-$\beta$-D-glucopyranosyl)-4-(3-methoxy-4-prop-2-ynyloxyphenyl)-but-3-en-2-one (9):**

*O*-Propargylation of compound, **3** (0.52 g, 1 mmol) with propargyl bromide (0.09 ml, 1.2 mmol) using $K_2CO_3$ (0.69 g, 5 mmol) as base gave **9** as a yellow liquid.

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.05 (d, J = 16.8 Hz, 1H, Alk-H), 7.21 (d, J = 7.8 Hz, 1H, Ar-H), 7.11 (t, J = 8.0 Hz, 1H, Ar-H), 6.98 (d, J = 8.1 Hz, 1H, Ar-H), 6.73 (d, J = 16.5 Hz, 1H, Alk-H), 5.24 (t, J = 9.5 Hz, 1H, Sac-H), 5.08 (t, J = 9.6 Hz, 1H, Sac-H), 5.00 (t, J = 9.6 Hz, 1H, Sac-H), 4.78 (d, J = 2.1 Hz, 2H, $-OCH_2$), 4.27 (dd, J = 4.8 Hz, J = 12.5 Hz, 1H, Sac-H), 4.21-4.13 (m, 1H, Sac-H), 4.10 (t, J = 7.2 Hz, 1H, Sac-H), 4.01 (d, J = 11.7 Hz, 1H, Sac-H), 3.88 (s, 3H, $-OCH_3$), 3.76-3.71 (m, 1H, Sac-H), 3.11 (dd, J = 8.4 Hz, J = 16.5 Hz, 1H, $-CH_2$), 2.73 (dd, J = 3.0 Hz, J = 16.4 Hz, 1H, $-CH_2$), 2.62 (t, J = 2.3 Hz, 1H, -C≡CH), 2.03-2.01 (m, 12H, $-COCH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 196.5, 170.5, 170.1, 169.8, 169.4, 162.5, 152.9, 146.2, 139.1, 129.3, 127.4, 124.8, 118.7, 114.2, 79.0, 76.4, 75.6, 74.2, 74.1, 71.7, 68.5, 62.0, 60.6, 55.8, 41.8, 36.4, 20.6, 20.5 (2C), 14.1.

**Spectral data of (*E*)-1-(4,6-*O*-butylidene-$\beta$-D-glucopyranosyl)-4-(2-prop-2-ynyloxyphenyl)-but-3-en-2-one (10):**

*O*-propargylation of compound, **4** (0.38 g, 1 mmol) with propargylbromide (0.09 ml, 1.2 mmol) using $K_2CO_3$ (0.69 g, 5 mmol) as base resulted in compound, **10** as a colourless solid.

Mp: 107-108 $^o$C; Yield: 0.29 g (69%); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, J = 16.5 Hz, 1H, Alk-H), 7.57 (d, J = 7.5 Hz, 1H, Ar-H), 7.39 (t, J = 8.0 Hz, 1H, Ar-H), 7.07-7.00 (m, 2H, Ar-H), 6.82 (d, J = 16.5 Hz, 1H, Alk-H), 4.79 (d, J = 2.4 Hz, 2H, $-OCH_2$), 4.53 (t, J = 5.1 Hz, 1H, Sac-H), 4.14 (dd, J = 4.2 Hz, J = 9.6 Hz, 1H, Sac-H), 3.98-3.91 (m, 1H, Sac-H), 3.73 (t, J = 8.9 Hz, 1H, Sac-H), 3.46-3.31 (m, 3H, Sac-H), 3.25 (t, J = 8.9 Hz, 1H, Sac-H), 3.25 (t, J = 8.9 Hz, 1H, Sac-H), 3.14 (dd, J = 4.2 Hz, J = 16.4 Hz, 1H, $-CH_2$), 3.00 (dd, J = 7.2 Hz, J = 16.1 Hz, 1H, $-CH_2$), 2.55 (t, J = 2.4 Hz, 1H, -C≡CH), 1.62-1.60 (m, 2H,$-CH_2$), 1.42 (q, J = 7.8 Hz, 2H, $-CH_2$), 0.92 (t, J = 7.4 Hz, 3H, $-CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 198.7, 156.4, 138.8, 131.8, 128.7, 127.3, 124.0, 121.8, 112.8, 102.5, 80.5, 78.1, 76.2, 75.4, 74.6, 70.6, 68.3, 56.2, 43.2, 36.2, 17.5, 13.9; Elemental analysis Anal. Calc. for $C_{23}H_{28}O_7$: C, 66.33; H, 6.78%. Found: C, 66.36; H, 6.81.

**Spectral data of (*E*)-1-(4,6-*O*-butylidene-$\beta$-D-glucopyranosyl)-4-(5-chloro-2-prop-2-ynyloxyphenyl)-but-3-en-2-one (11):**

*O*-Propargylation of compound, **5** (0.41 g, 1 mmol) with propargylbromide (0.09 ml, 1.2 mmol) using $K_2CO_3$ (0.69 g, 5 mmol) as a base furnished compound **11** as a colourless solid.

Mp: 124-125 $^o$C; Yield: 0.34 g (76%); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.82 (d, J = 16.2 Hz, 1H, Alk-H), 7.51 (s, 1H, Ar-H), 7.31 (dd, J = 2.4 Hz, J = 8.9 Hz, 1H, Ar-H), 6.98 (d, J = 9.0 Hz, 1H, Ar-H), 6.77 (d, J = 16.5 Hz, 1H, Alk-H), 4.76 (d, J = 2.1 Hz, 2H, $-OCH_2$), 4.53 (t, J = 5.0 Hz, 1H, Sac-H), 4.15-4.10 (m, 1H, Sac-H), 3.97-3.90 (m, 1H, Sac-H), 3.73 (t, J = 8.9 Hz, 1H, Sac-H), 3.44-3.22 (m, 4H, Sac-H, $-CH_2$), 3.14 (dd, J = 3.6 Hz, J = 16.1 Hz, 1H, $-CH_2$), 2.58 (t, J = 2.4 Hz, 1H, -C≡CH), 1.64-1.60 (m, 2H, $-CH_2$), 1.43 (q, J = 7.2 Hz, 2H, $-CH_2$), 0.91 (t, J = 7.4 Hz, 3H, $-CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 198.3, 154.8, 137.0, 131.1, 128.1, 128.0, 127.0, 125.6, 114.3, 102.5, 80.5, 77.7, 76.2, 75.3, 74.5, 70.6, 68.3, 56.6, 43.4, 36.2, 17.5, 13.9; Elemental analysis Anal. Calc. for $C_{23}H_{27}ClO_7$: C, 61.26; H, 6.04%. Found: C, 61.29; H, 6.08.

**Spectral data of (*E*)-1-(4,6-*O*-butylidene-$\beta$-D-**

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**glucopyranosyl)-4-(3-prop-2-ynyloxyphenyl)-but-3-en-2-one (12):**

*O*-Propargylation of compound, **6** (0.38 g, 1 mmol) with propargyl bromide (0.09 ml, 1.2 mmol) using $K_2CO_3$ (0.69 g, 5 mmol) as base gave **12** as a colourless solid.

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.55 (d, J = 16.2 Hz, 1H, Alk-H), 7.34 (t, J = 8.0 Hz, 1H, Ar-H), 7.20-7.15 (m, 2H, Ar-H), 7.03 (d, J = 8.1 Hz, 1H, Ar-H), 6.75 (d, J = 16.2 Hz, 1H, Alk-H), 4.73 (d, J = 2.4 Hz, 2H, -$OCH_2$), 4.53 (t, J = 5.1 Hz, 1H, Sac-H), 4.13 (dd, J = 4.2 Hz, J = 9.6 Hz, 1H, Sac-H), 3.96-3.91 (m, 1H, Sac-H), 3.11 (t, J = 8.7 Hz, 1H,. Sac-H), 3.46-3.30 (m, 3H, Sac-H), 3.24 (t, J = 8.9 Hz, 1H, Sac-H), 3.13 (dd, J = 3.9 Hz, J = 16.1 Hz, 1H, Sac-H), 2.95 (dd, J = 7.5 Hz, J = 16.2 Hz, 1H, Sac-H), 2.55 (t, J = 2.3 Hz, 1H, -C≡CH), 1.65-1.56 (m, 2H, -$CH_2$), 1.42 (q, J = 7.8 Hz, 2H, -$CH_2$), 0.92 (t, J = 7.4 Hz, 3H, -$CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 198.0, 157.9, 143.4, 135.8, 130.0, 126.8, 122.0, 117.4, 114.4, 102.5, 80.4, 78.2, 75.4, 74.5, 70.6, 68.3, 55.9, 43.5, 36.2, 17.5, 13.9.

**Spectral data of (*E*)-1-(4,6-*O*-butylidene-*β*-D-glucopyranosyl)-4-(4-prop-2-ynyloxyphenyl)-but-3-en-2-one (13):**

*O*-Propargylation of compound, **7** (0.38 g, 1 mmol) with propargylbromide (0.09 ml, 1.2 mmol) using $K_2CO_3$ (0.69 g, 5 mmol) as a base resulted in compound, **13** as a colourless solid.

Mp: 178-180 $^o$C; Yield : 0.26 g (62%); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.44-8.39 (m, 3H, Ar-H, Alk-H), 7.88 (d, J = 8.7 Hz, 2H, Ar-H), 7.56 (d, J = 16.2 Hz, 2H, Alk-H), 5.63 (d, J = 2.4 Hz, 2H, -$OCH_2$), 5.43 (t, J = 5.0 Hz, 1H, Sac-H), 5.35 (d, J = 3.6 Hz, 1H, Sac-OH), 5.06 (s, 1H, Sac-OH), 4.99 (dd, J = 3.6 Hz, J = 9.6 Hz, 1H, Sac-H), 4.80 (t, J = 8.4 Hz, 1H, Sac-H), 4.56 (t, J = 8.4 Hz, 1H, Sac-H), 4.30 (t, J = 9.8 Hz, 1H, Sac-H), 4.24-4.11 (m, 3H, Sac-H), 4.03 (dd, J = 2.4 Hz, J = 14.4 Hz, 1H, -$CH_2$), 3.73 (dd, J = 8.7 Hz, J = 15.9 Hz, 1H, -$CH_2$), 3.49 (t, J = 2.3 Hz, 1H, -C≡CH), 2.55-2.49 (m, 2H, -$CH_2$), 2.32 (q, J = 7.5 Hz, 2H, -$CH_2$), 1.80 (t, J = 7.4 Hz, 3H, -$CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 192.5, 154.2, 137.3, 124.7, 122.7, 119.5, 110.1, 97.1, 75.3, 72.7, 72.1, 71.3, 70.8, 69.9, 69.6, 65.3, 63.1, 50.6, 38.1, 31.0, 12.1, 8.6; Elemental analysis Anal. Calc. for $C_{20}H_{26}O_7$: C, 63.48; H, 6.93%. Found: C, 66.53; H, 6.97.

**Spectral data of (*E*)-1-(4,6-*O*-butylidene-*β*-D-glucopyranosyl)-4-(3-bromo-2-prop-2-ynyloxyphenyl)-but-3-en-2-one (14):**

*O*-Propargylation of compound, **8** (0.46 g, 1 mmol) with propargyl bromide (0.09 ml, 1.2 mmol) using $K_2CO_3$ (0.69 g, 5 mmol) as a base gave a colourless solid, **14**.

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.83 (d, J = 16.2 Hz, 1H, Alk-H), 7.67 (s, 1H, Ar-H), 7.46 (dd, J = 2.4 Hz, J = 8.7 Hz, 1H, Ar-H), 6.95 (d, J = 9.0 Hz, 1H, Ar-H), 6.77 (d, J = 16.5 Hz, 1H, Alk-H), 4.77 (d, J = 2.4Hz, 2H, -$OCH_2$), 4.53 (t, J = 5.1 Hz, 1H, Ace-H), 4.14 (dd, J = 4.2 Hz, J = 9.6 Hz, 1H, Sac-H), 3.97-3.90 (m, 1H, Sac-H), 3.72 (t, J = 8.9 Hz, 1H, Sac-H), 3.46-3.30 (m, 3H, Sac-H), 3.24 (t, J = 9.0 Hz, 1H, Sac-H), 3.13 (dd, J = 3.9 Hz, J = 16.2 Hz, 1H, -$CH_2$), 2.96 (dd, J = 7.2 Hz, J = 16.2 Hz, 1H, -$CH_2$), 2.56 (t, J = 2.4 Hz, 1H, -C≡CH), 1.65-1.60 (m, 2H, -$CH_2$), 1.42 (q, J = 7.8 Hz, 2H, -$CH_2$), 0.92 (t, J = 7.4 Hz, 3H, -$CH_3$); $^{13}$C NMR(75 MHz, $CDCl_3$): $\delta$ 195.0, 137.0, 134.1, 130.9, 128.0, 114.6, 102.5, 80.4, 76.0, 75.4, 74.5, 74.0, 70.6, 68.3, 56.4, 43.4, 36.2, 17.5, 13.9.

**General procedure for the synthesis of ether-linked-bis-triazole derivatives (16-20):**

To a solution of acetylenic compound, **9-14** (2 equiv.) in a 1:1 (V/V) mixture of THF:$H_2O$ were added ether-linked-diazide, **15** (1 equiv.), $CuSO_4.5H_2O$ (0.2 equiv.), sodiumascorbate (0.4 equiv.). The mixture was stirred at room temperature for 24 hrs. The reaction mixture was extracted with chloroform and washed with saturated $NH_4Cl$, water & brine solution. Organic layer was collected, dried over anhydrous $Na_2SO_4$ and concentrated to dryness under vaccum. The crude mixture was further purified by column chromatographic technique.

**Spectral data of 1,8-bis-(4-hydroxy-methylene-triazolo-4-(E)-1-2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosyl-4-phenyl-but-3-en-2-one)-3,6-dioxadecane (16):**

Compound, **16** was obtained by the (CuAAC) "Click" reaction of sugar-propargyl derivative, **9** (0.56 g, 2 mmol) and triethyleneglycoldiazide, 15 (0.1 g, 1 mmol) as a yellow solid.

Mp 78-80 °C; Yield:1.10 g (83%); $^1$H NMR (300 MHz, CDCl3): δ 7.79 (d, J = 16.5 Hz, 2H, Alk-H), 7.75 (s, 2H, Trz-H), 7.13 (d, J = 7.8 Hz, 2H, Ar-H), 7.08 (t, J = 8.0 Hz, 2H, Ar-H), 6.98 (d, J = 7.7 Hz, 2H, Ar-H), 6.64 (d, J = 16.5 Hz, 2H, Alk-H), 5.26-5.14 (m, 6H, -$OCH_2$, Sac-H), 5.08 (t, J = 9.6 Hz, 2H, Sac-H), 4.99 (t, J = 9.6 Hz, 2H, Sac-H), 4.53 (t, J = 5.1 Hz, 4H, -$OCH_2$), 4.24 (dd, J = 4.8 Hz, J = 12.3 Hz, 2H, Sac-H), 4.16-4.09 (m, 2H, Sac-H), 4.02 (d, J = 12.3 Hz, 2H, Sac-H), 3.88 (s, 6H, -$OCH_3$), 3.83 (t, J = 5.1 Hz, 4H, -$OCH_2$), 3.76-3.70 (m, 2H, Sac-H), 3.56 (s, 4H, -$OCH_2$), 2.98 (dd, J = 8.1 Hz, J = 16.5 Hz, 2H, -$CH_2$), 2.73 (dd, J = 3.3 Hz, J = 16.5 Hz, 2H, -$CH_2$), 2.03 (s, 12H, -$COCH_3$), 2.01 (s, 12H, -$COCH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 196.5, 170.7, 170.3, 169.9, 169.6, 153.1, 146.8, 143.7, 138.6, 129.0, 127.3, 124.7, 124.2, 118.8, 114.3, 75.7, 74.4, 74.1, 71.7, 70.4, 69.4, 68.5, 66.6, 62.1, 60.4, 55.9, 50.1, 42.2, 29.7, 20.7 (2C), 20.6 (2C); ESI-MS: Calc. for $C_{62}H_{76}N_6O_{26}$, 1320.48; m/z found, 1343.47 $[M+Na]^+$; Elemental analysis Anal. Calc. for $C_{62}H_{76}N_6O_{26}$: C, 56.36; H, 5.80; N, 6.36%. Found: C, 56.39; H, 5.83; N, 6.39.

**Spectral data of 1,8-bis-(4-hydroxy-methylene-triazolo-2-(*E*)-1-4,6-*O*-butylidene-*β*-D-glucopyranosyl-4-phenyl-but-3-en-2-one)-3,6-dioxadecane (17):**

Compound, **17** was obtained by the (CuAAC) "Click" reaction of sugar-propargyl derivative, **10** (0.42 g, 2 mmol) and triethyleneglycoldiazide, **15** (0.10 g, 1 mmol) as a yellow liquid.

Mp:92-94 $^o$C; Yield :0.83 g (81%); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 16.5 Hz, 2H, Alk-H), 7.76 (s, 2H, Trz-H), 7.42 (d, J = 6.6 Hz, 2H, Ar-H), 7.25 (t, J = 7.7 Hz, 2H, Ar-H), 6.98 (d, J = 8.1 Hz, 2H, Ar-H), 6.88 (t, J = 7.4 Hz, 2H, Ar-H), 6.69 (d, J = 16.5 Hz, 2H, Alk-H), 5.14 (s, 4H, -$OCH_2$), 4.43 (bs, 6H, Sac-H), 4.01-3.97 (m, 2H, Sac-H), 3.83-3.77 (m, 2H, Sac-H), 3.73 (t, J = 4.7 Hz, 4H, -$OCH_2$), 3.64 (t, J = 8.6 Hz, 2H, Sac-H), 3.44 (bs, 4H, Sac-H), 3.30 (t, J = 8.7 Hz, 4H, -$OCH_2$), 3.20-3.07 (m, 6H, -$OCH_2$, -$CH_2$), 2.78 (dd, J = 8.1 Hz, J = 15.8 Hz, 2H, -$CH_2$), 1.53-1.49 (m, 4H, -$CH_2$), 1.32 (q, J = 6.0 Hz, 4H, -$CH_2$), 0.80 (t, J = 7.2 Hz, 6H, -$CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 198.7, 157.1, 143.4, 138.4, 132.0, 128.6, 126.8, 124.2, 123.8, 121.7, 113.2, 102.4, 80.5, 76.8,

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75.0, 74.7, 70.6, 70.4, 69.3, 68.3, 62.6, 50.4, 43.6, 36.2, 29.7, 17.5, 13.9; ESI-MS: Calc. for $C_{52}H_{68}N_6O_{16}$, 1032.47; m/z found, 1033.48 $[M+H]^+$; Elemental analysisAnal. Calc. for $C_{52}H_{68}N_6O_{16}$: C, 60.45; H, 6.63; N, 8.13%. Found: C, 60.48; H, 6.66; N, 8.16.

**Spectral data of 1,8-bis-(4-hydroxy-methylene-triazolo-5-chloro-2-(*E*)-1-4,6-O-butylidene-*β*-D-glucopyranosyl-4-phenyl-but-3-en-2-one)-3,6-dioxadecane (18):**

Compound, **18** was obtained by the (CuAAC) "Click" reaction of sugar-propargyl derivative, **11** (0.45 g, 2 mmol) and triethyleneglycoldiazide, **15** (0.10 g, 1 mmol) as a yellow liquid.

Yield :0.55 g (50%); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.87-7.83 (m, 4H, Trz-H, Alk-H), 7.50 (s, 2H, Ar-H), 7.32 (d, J = 8.7 Hz, 2H, Ar-H), 7.07 (d, J = 9.0 Hz, 2H, Ar-H), 6.76 (d, J = 16.5 Hz, 2H, Alk-H), 5.26 (d, J = 1.5 Hz, 4H, -$OCH_2$), 4.56 (t, J = 5.0 Hz, 2H, Sac-H), 4.53 (t, J = 5.0 Hz, 2H, Sac-H), 4.12 (t, J = 6.8 Hz, 2H, Sac-H), 3.90 (t, J = 5.0 Hz, 2H, Sac-H), 3.65-3.61 (m, 8H, -$OCH_2$, Sac-H), 3.38-3.35 (m, 6H, -$OCH_2$, Sac-H), 3.29-3.22 (m, 6H, -$OCH_2$, Sac-H), 2.91-2.77 (m, 4H,-$CH_2$), 1.63-1.61 (m, 4H, -$CH_2$), 1.46-1.38 (m, 4H, -$CH_2$), 0.88 (t, J= 7.2 Hz, 6H, -$CH_3$); $^{13}$C NMR(75 MHz, $CDCl_3$): $\delta$ 196.4, 168.6, 135.4, 129.5, 126.2, 124.7, 123.9, 100.6, 78.6, 73.5, 68.8, 68.2, 67.6, 66.5, 64.0, 48.8, 46.9, 15.6, 12.1; Elemental analysis Anal. Calc. for $C_{52}H_{66}N_6O_{16}$: C, 56.67; H, 6.04; N, 7.63%. Found: C, 56.71; H, 7.66; N, 7.67.

**Spectral data of 1,8-bis-(4-hydroxy-methylene-triazolo-3-(*E*)-1-4,6-*O*-butylidene-*β*-D-glucopyranosyl-4-phenyl-but-3-en-2-one)-3,6-dioxadecane (19):**

Compound, **19** was obtained by the (CuAAC) "Click" reaction of sugar-propargyl derivative, **12** (0.42 g, 2 mmol) and triethyleneglycoldiazide, **15** (0.10 g, 1 mmol) as a yellow liquid.

Yield :0.73 g (71%); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.76-7.60 (m, 4H, Trz-H, Alk-H), 7.36-7.02 (m, 8H, Ar-H), 6.87 (d, J = 15.6 Hz, 2H, Alk-H), 5.20 (bs, 2H, Ace-H), 4.73 (bs, 6H, -Sac-H), 4.49 (t, J = 5.4 Hz, 4H, -$OCH_2$), 4.15-4.08 (m, 2H, Sac-H), 3.76-3.67 (m, 6H, -$OCH_2$, Sac-H), 3.49-3.44 (m, 6H, -$OCH_2$, Sac-H), 3.26-3.16 (m, 6H, -$OCH_2$, Sac-H), 2.71-2.55 (m, 4H, -$CH_2$), 1.61-1.59 (m, 4H, -$CH_2$), 1.43-1.37 (m, 4H, -$CH_2$), 0.90 (t, J = 6.9 Hz, 6H, -$CH_3$); $^{13}$C NMR(75 MHz, $CDCl_3$): $\delta$ 198.4, 157.9, 143.4, 135.9, 130.0, 125.5, 122.0, 117.3, 114.6, 102.5, 82.7, 80.3, 78.8, 78.2, 75.9, 75.1, 72.9, 70.8, 69.7, 68.2, 55.9, 50.8, 36.2, 29.6, 17.4, 13.9; Elemental analysis Anal. Calc. for $C_{52}H_{68}N_6O_{16}$: C, 60.45; H, 6.63; N, 8.13%. Found: C, 60.48; H, 6.67; N, 8.17.

**Spectral data of 1,8-bis-(4-hydroxy-methylene-triazolo-4-(*E*)-1-4,6-*O*-butylidene-*β*-D-glucopyranosyl-4-phenyl-but-3-en-2-one)-3,6-dioxadecane (20):**

Compound, **20** was obtained by the (CuAAC) "Click" reaction of sugar-propargyl derivative, **13** (0.42 g, 2 mmol) and triethyleneglycoldiazide, **15** (0.10 g, 1 mmol) as a yellow liquid.

Mp :152-154 $^o$C; Yield :0.78 g (76%); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.00 (s, 2H, Trz-H), 7.63-7.59 (m, 6H, Ar-H, Alk-H), 7.11 (d, J = 8.4 Hz, 4H, Ar-H), 6.76 (d, J = 16.2 Hz, 2H, Alk-H), 5.31 (bs, 4H, -$OCH_2$), 4.87 (bs, 2H, Ace-H), 4.64 (bs, 4H, Sac-H), 4.17-4.14 (m, 2H, Sac-H), 4.01-3.93 (m, 6H, -$OCH_2$, Sac-H), 3.71-3.65 (m, 4H, Sac-H), 3.64 (bs, 4H, -$OCH_2$), 3.25-3.20 (m, 6H, -$OCH_2$, Sac-H), 2.96-2.88 (m, 4H, -$CH_2$), 1.72-1.71 (m, 4H, -$CH_2$), 1.52 (q, J = 6.9 Hz, 4H, -$CH_2$), 1.01 (t, J = 7.2 Hz, 6H, -$CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 202.6, 165.0, 147.3, 134.8, 134.7, 132.3, 129.4, 120.1, 106.9, 85.4, 81.6, 79.6, 79.4, 75.4, 74.9, 73.9, 73.1, 66.5, 54.9, 48.1, 41.0, 22.1, 18.7; Elemental analysis Anal. Calc. for $C_{52}H_{68}N_6O_{16}$: C, 60.45; H, 6.63; N, 8.13%. Found: C, 60.47; H, 6.68; N, 8.17.

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