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ARTICLE

An efficient one-pot synthesis of *N*,*N*′-disubstituted ureas and carbamates from *N*-Acylbenzotriazoles

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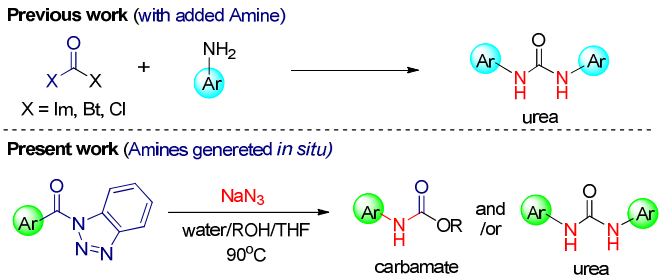
A facile and high-yielding one-pot synthesis of carbamates and *N*,*N*′-disubstituted symmetrical ureas from *N*-acylbenzotriazoles has been devised. It is believed that, the intermediate acyl-azide undergo Curtius rearrangement and in different solvents gives different products *i.e.* carbamates in alcohols and *N*,*N*′-disubstituted symmetrical urea in THF.

Introduction

Functionalized urea and carbamate motifs are essential structural elements of many biologically active compounds.[1] Also, their derivatives play vital role in research of pharmaceuticals and organic chemistry.[2] Generally, synthesis of substituted urea involves reaction of suitable amines with urea,[3] phosgenation[4] and reductive or oxidative carbonylation of amines.[5] But these well-established protocols include some drawbacks, such as, insufficiency for symmetric ureas, involvement of highly toxic reagents and longer reaction time. During past few years, a number of papers have reported synthesis of urea and carbamate derivatives *via* metal catalyst.[6] Katritzky *et al.* have synthesized the symmetric urea's[7a,b] where the benzotriazole moiety acts as a leaving group and was substituted by amines. This methodology has been further explored in a number of ways by many research groups and contributed thousands of pharmaceutical compounds.[8] However, a better yielding, non-toxic, mild and practical approach for synthetic, pharmaceutical as well as industrial significance is still under investigation.

In this manuscript, we have introduced *N*-acylbenzotriazole as a suitable reagent for the preparation of ureas and carbamates *via* Curtius rearrangement.[9] Good leaving tendency of benzotriazole moiety has been used in present work to afford ureas and carbamates without adding amine (**Scheme 1**).

Certainly, an *N*-Acyl azide intermediate is formed, which on hydrolysis generates amines *in situ*. The acyl-azide on heating undergoes Curtius rearrangement which leads to formation of corresponding isocyanates. These isocyanates, on reaction with variety of amines (*in situ* generated by hydrolysis of isocyanates) and/or alcohols, give corresponding ureas and carbamates.



Scheme 1. Comparative illustration of previous and present work

Results and discussion

Our strategy began with the synthesis of core compound *N*-Acyl benzotriazoles by the reaction of corresponding aromatic/aliphatic acids with benzotriazole using $SOCl_2$ reagent in dichloromethane, following the sound known process reported in literature.[10] The one-pot reaction procedure completed within two hours and the crude mass was easily purified by flash column chromatography. The corresponding *N*-acylbenzotriazoles **2a-q** (**Table 1**) were characterized by IR, mass and NMR spectroscopic studies.

The acylated benzotriazole derivatives play a key role in large number of reactions and can be used to synthesize a variety of compounds.[11] Formerly, we have also synthesized amide by the help of acylated benzotriazole derivatives in excellent yields.[12] Our present work is focussed on further exploration of

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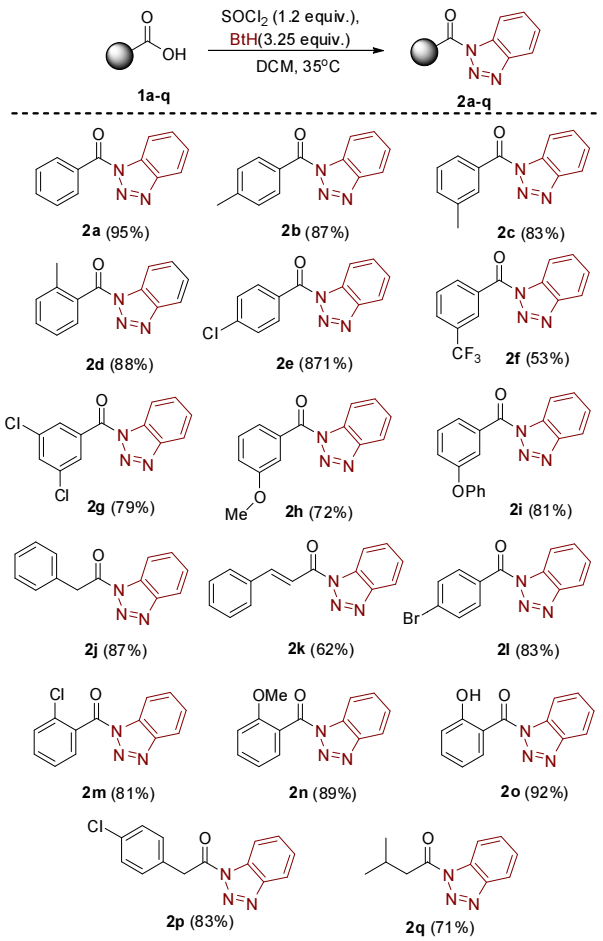
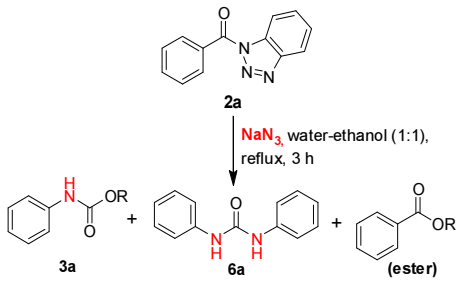
†**Electronic Supplementary Information (ESI) available:** Copies of ^{1}H and ^{13}C NMR for all the developed compounds has been provided. See DOI: DOI:10.1039/ra

Table 1. Synthesis of *N*-acylbenzotriazoles (ArCOBt) **2a-q** from acids



[a]Molar ratios: Carboxylic acids (**1a-q**) (1.0 equiv.), $SOCl_2$ (1.2 equiv), benzotriazole (3.25 equiv). Yields reported after purification by column chromatography (SiO_2).

benzotriazole methodology for Curtius rearrangement, through which synthesis of carbamates and symmetric ureas can be achieved. *N*-acyl benzotriazole, when refluxed with sodium azide in presence of homogeneous medium of water and protic organic solvent, gives carbamates *via* isocyanate intermediate, generated *in situ* when *N*-acylazides were heated. Similar protocol, when applied in water and organic aprotic solvent system, affords symmetric ureas. In our proto-type reaction, a mixture of 1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methanone **2a** (2.0 mmol) & sodium azide (3.0 mmol) was refluxed in water-ethanol (1:1 ratio mixture) for 3 hours (**Scheme 2**).



Scheme 2. Synthesis of carbamate (**3a**) and symmetric ureas (**6a**)

Among the three spots appeared on TLC (10% ethyl acetate/*n*-hexane) of the reaction mass, first spot (R_f = 0.7) was identified as ester, second spot (R_f = 0.5) was characterized as carbamate and the third spot (R_f = 0.4) was symmetric urea. The ratio of the three products i.e. ester, carbamate and urea, was found to be 1.35: 1.61: 1 respectively and these compound have been successfully isolated in pure form after column chromatography (SiO_2) using gradient of EtOAc/*n*-hexane. The formation of carbamate **3a** and urea **6a**, without externally added amines suggests that Curtius rearrangement must be involved here which gives amines by the rearrangement of acyl azides. Further, in search of appropriate solvent system to obtain optimum yield of our products of interest, i.e. urea and carbamate, we performed the reaction in different type of organic solvents with water in different compositions (**table 2**).

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Table 2. Optimization of reaction conditions.

Entry[a]	Solvent system[b]	Ratios	yield of **3a** (%)[c]	yield of **6a** (%)[c]
1	Ethanol/Water	50/50	37	23
2	Ethanol/Water	85/15	64	17
3	Ethanol/Water	90/10	65	7
4	Ethanol/Water	95/05	67	5
5	Ethanol/Water	100/0	20	0
6	Ethanol/Water	15/85	29	20
7	*i*-PrOH/Water	50/50	41	26
8	THF/Water	50/50	0	67
9	THF/Water	15/85	0	18
10	THF/Water	70/30	0	25
11	THF/Water	85/15	0	81
12	t-BuOH/Water	50/50	0	43
13	Toluene/Water	50/50	0	53
14	Benzene/Water	50/50	0	54
15	DCM/Water	50/50	0	Trace
16	Acetone/Water	50/50	0	57
17	Ethyl acetate/Water	50/50	0	55

[a]Molar ratio: 1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methanone **2a** (2.0 mmol) & sodium azide (6.0 mmol). [b]Binary solvents. [c]Yields reported after purification by column chromatography (SiO_2).

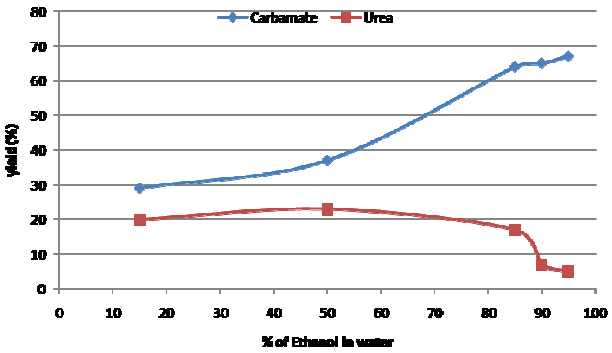
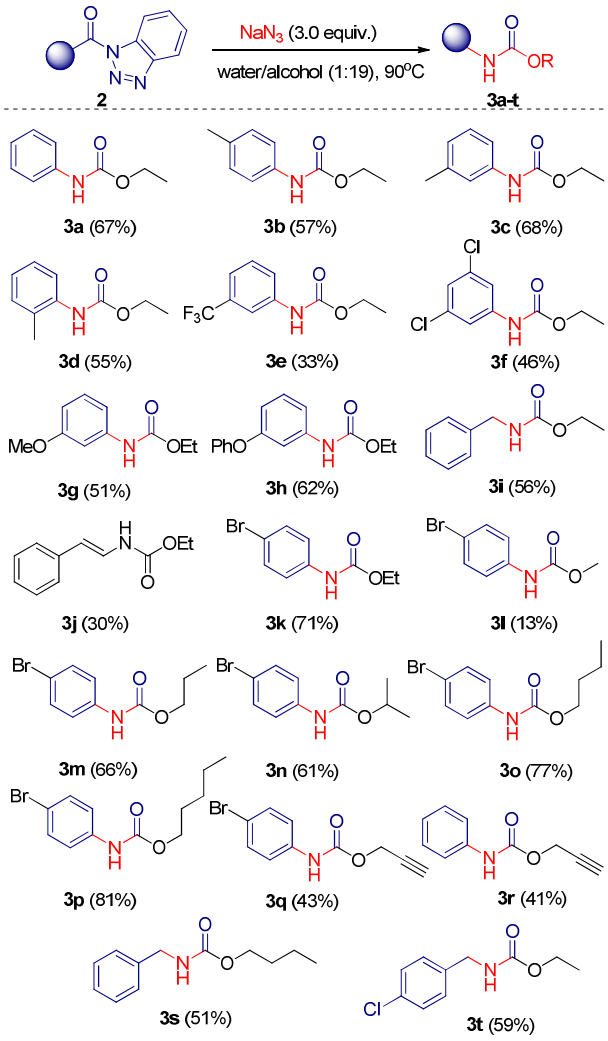


Figure 1. Optimization for carbamate

It was observed that carbamates were formed preferentially when the binary solvent system was a mixture of nucleophilic-protic solvent (generally alcohols) and water (table 2; entry 1-7). Greater composition of nucleophilic alcohols ensures the

capture of intermediate isocyanate leading to formation of carbamate as the major product (table 2; entry 3 & 4). A 19:1 ratio of alcohol and water was found to be most reliable solvent system. However, symmetric urea was the major product, when the binary solvent includes a non-nucleophilic-aprotic organic solvent along with water (table 2; entry 8-17). The carbamate formation was inhibited possibly due to the capture of intermediate isocyanate with aniline in absence of nucleophilic alcohols. The essentiality of water is for the solubility of sodium azide as well as for Curtius rearrangement. Further, to find out optimum ratios of different solvents for the most favourable solvent system to obtain better yields of urea and carbamate separately, the same proto-type reaction was carried out in different solvent ratios as depicted in **table 2** & **figure 1**.

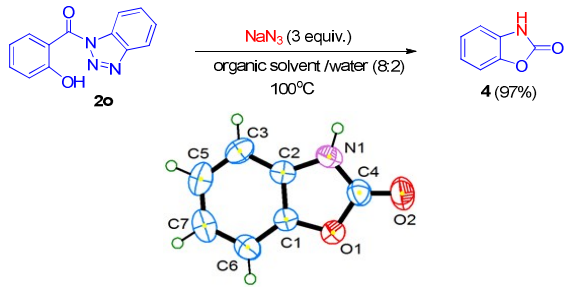
Table 3. Synthesis of carbamates (**3a-t**) from acylbenzotriazoles (ArCOBt) (**2a-q**) by NaN_3 induced Curtius rearrangement.



Molar ratios: acyl benzotriazoles (1.0 equiv.), NaN_3 (3.0 equiv), Alcohols: water (19:1). Yields reported after purification by column chromatography (

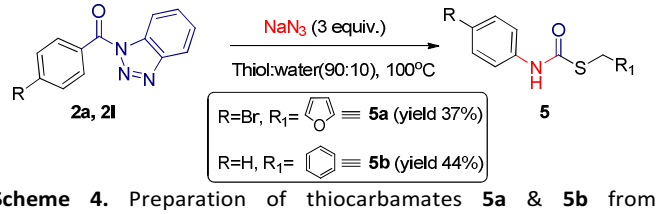
After the optimization of solvent system, we investigated the reaction for generalization by varying the alcohol and acylated benzotriazole derivatives. Experimentally, it was found that primary and secondary alcohols (for example, methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, and isopropyl alcohol) give good yields of carbamates. It was noticed that reaction with tertiary alcohols, lead to the formation of symmetric urea as the major product. For example, reaction of compound **2a** with sodium azide in presence of *t*-butanol/water (in 1:1) ratio gave symmetric urea **6a**. A library of 20 compounds has been prepared which contains both aliphatic (saturated and unsaturated both) and aromatic carbamates in moderate to good yields (**table 3**). The yield of carbamate **3l**, formed with methanol/ water as solvent, is fairly low since methanol undergoes substitution relatively at higher rate than rearrangement. Benzotriazole derivatives of phenyl acetic acid **2j** and **2p** afforded carbamates **3i**, **3s** and **3t** in good yields. Reaction of bezotriazole derivative of isovaleric acid **2q** under similar reaction condition did not produce carbamate product even in trace amount. Compounds have been characterized on the basis of their NMR, mass and IR spectra.

To enhance the generality and utility of this methodology, we further explored the reaction for the synthesis of intramolecular carbamates (**Scheme 3**). The reaction of compound **2o** under above mentioned conditions affords cyclic carbamate **4** via intramolecular cyclization. The intermediate isocyanate formed by Curtius rearrangement must have been captured by hydroxyl at *ortho* to the carbonyl. The structure of compound **4** has been characterized by NMR, mass and IR spectra. Also, the structure of compound **4** was established by single crystal X-ray analysis. The crystallographic and instrumental details for **4** have been summarized in **table 5**.



Scheme 3. Preparation of Carbamate **4** from corresponding acyl benzotriazole (**2o**). Molar ratio: acyl benzotriazole (1.0 equiv.), NaN_3 (3 equiv), Alcohols/THF: water (8:2). Yields reported after purification by column chromatography (SiO_2).

During our investigation, it was found that in intramolecular reaction, single and same product is formed with almost 100% conversion, regardless the solvent system we used. However the results are optimum with aprotic polar solvents. Interestingly, when we used thiols instead of alcohol in the reaction, thiocarbamates were obtained in moderate yields. (**Scheme 4**)



Scheme 4. Preparation of thiocarbamates **5a** & **5b** from corresponding acyl benzotriazole (**2a, 2l**). Yields reported after purification by column chromatography (SiO_2).

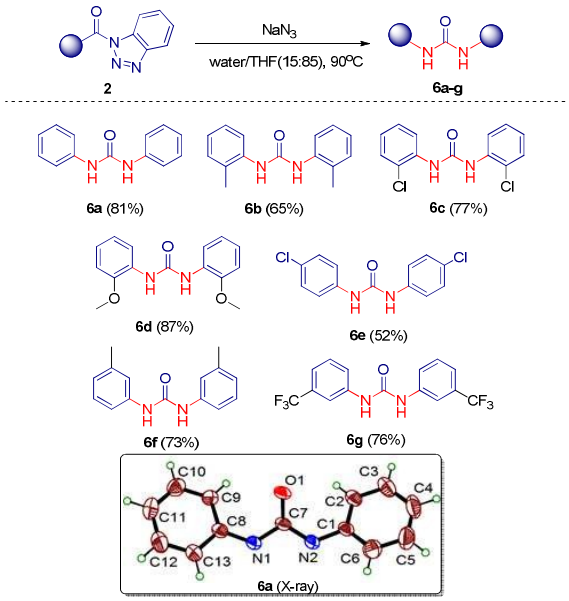
Table 4. Crystallographic refinement data[a] for compound **4**

Property	**4**
Mol. Formula	$C_7 H_5 N O_2$
Formula Weight	135.12
Crystal System	Orthorhombic
Space group	P 21 21 21
a (Å)	4.4436(14)
b (Å)	6.641(2)
c (Å)	20.957(6)
α,β,γ(°)	90,90,90
V (Å^3)	618.5(3)
Z	4
Density (calc)	1.451
F(000)	264
μ (mm^{-1})	0.108
Crystal Size [mm]	0.14 x 0.15 x 0.22
Temperature (K)	293
Radiation (Mo$K\alpha$)	0.71073
θ Min-Max [°]	3.22, 24.94
h, k, l	-5:5; -6:89; -16:27
Tot.,UniqData, R(int)	3269, 1471, 0.0267
Obs. data [I > 2.0 σ(I)]	1322
Nref, Npar	1528, 91
R1, wR2, S	0.0386, 0.0969, 1.061
Min. - Max. resd. dens. [e/ Å^3]	-0.258, 0.133
CCDC	**1482294**

[a]For details, see supporting information file (CIF) enclosed with manuscript.

Contrary to carbamates, urea was preferably formed in aprotic organic solvent-water system and THF/water medium was found the best in this regards. Further optimization of solvent-system composition and temperature for the reaction revealed that THF/water in 85:15 ratios at 90°C gave most significant results. We explored this altered reaction path by changing functionality of *N*-acyl benzotriazole and a series containing seven different symmetric ureas (**table 5**) has been developed.

Table 5: Synthesis of symmetric urea using THF/ water system.

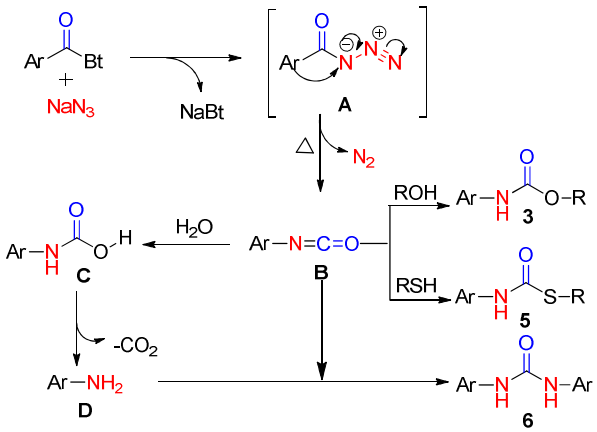


Molar ratios: Acyl benzotriazoles (1.0 equiv.), NaN_3 (3.0 equiv), THF: Water (85:15). Yields reported after purification by column chromatography (SiO_2).

The structures of compounds **6a-g** have been characterized by NMR, mass and IR spectra. Also, the structure of compound **6a** was established by single crystal X-ray analysis (see Supporting Information CIF file for details).

Mechanistic Consideration

A possible mechanistic way to explicate the product formation and rearrangement is given in mechanistic consideration (**Schemes 5**). The mechanism certainly involves Curtius rearrangement as the key step of reaction which gives amines by the rearrangement of acyl azides.



Scheme 5. Plausible mechanism involving Curtius rearrangement

At first, intermediate acyl azide **A**, formed by attack of azide ion on carbonyl carbon to replace the benzotriazole moiety in acyl benzotriazole, undergoes Curtius rearrangement to form isocyanate intermediate **B** with the consequent loss of molecular nitrogen (N_2). Finally, the intermediate isocyanate is immediately captured by nucleophilic alcoholic solvent to afford carbamate product. Alternatively, isocyanate **B** generates aniline *via* carbamic acid, which undergoes decarboxylation to afford anilines. This aniline, on reaction with intermediate isocyanate **B**, generates symmetric urea

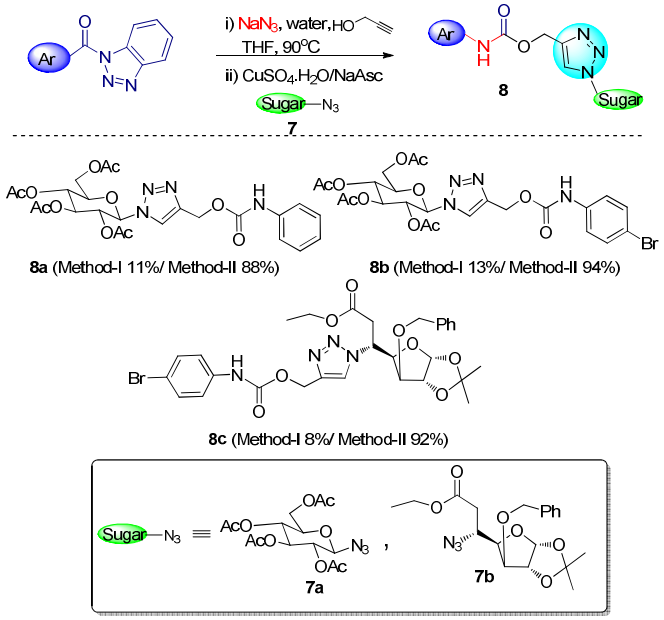
Combination with Click Chemistry

With escalating importance of Click-chemistry[13] as an efficient tool for development of biologically and pharmaceutically relevant compounds, the significance of the methodologies which can easily and effectively afford starting materials for click reaction (i.e. azides and alkynes) has also increased. After successfully employing our methodology in generation of carbamates with a terminal alkyne functionality, we extended this work for cascade synthesis of 1,4-substituted 1,2,3-triazolyl carbohydrate derivatives *via* click chemistry (**Scheme 6**).

The reaction involved heating *N*-acyl benzotriazole with NaN_3 in presence of water and propargyl alcohol (as reactant as well as solvent) followed by removal of excess propargyl alcohol by evaporation and addition of sugar azide along with $CuSO_4$ and sodium ascorbate in ^{t}BuOH-water mixture (8:2). Though the reaction moved in the way we expected, but the desired triazolyl sugar derivatives were formed with very low yields (8-

13%). On the other hand conventional click reaction of developed alkyne-functionalized carbamates (**3q** and **3r**) with sugar azide resulted in excellent yields (88-94%) of triazolyl products. The low yield in cascade approach may be due to some side reactions involved in this process. We are trying to find out the exact causes behind it to improve this reaction for better results.

Scheme 6. Click-inspired synthesis of novel triazoyl glycoconjugate carbamates (**8a-c**)



Molar ratios: acyl benzotriazoles (1.0 equiv.), NaN_3 (6.0 equiv), ^{t}BuOH-water mixture (8:2), Sugar azide (1.1 equiv), $CuSO_4.H_2O$ (0.02 mol%) and NaAsc (0.2 mol%). Method-I: One-pot sequential reaction; Method-II: Successive reaction. Yields reported after purification by column chromatography (SiO_2).

Conclusions

In summary, we have developed a one-pot, low-toxic and efficient method for synthesis of ureas and carbamates from *N*-acyl benzotriazole. Through, this synthetic root we have successfully achieved good yields under mild reaction conditions in aqueous medium without using catalyst and with simple purification methods. Furthermore, we have efficiently utilized this methodology for generation of terminal alkyne armed carbamates which were clicked with sugar azides to afford novel triazolyl sugar derivatives. A cascade approach was also attempted for synthesis of triazolyl sugar derivatives by employing this methodology along with click-chemistry, but results were not very pleasing. Work on improvement of cascade approach is ongoing in our laboratory.

Experimental

General Remarks

All reagents and solvents were of pure analytical grade. Thin-layer chromatography (TLC) was performed on 60 F254 silica gel, pre-coated on aluminium plates and revealed with either a UV lamp (λ max = 254 nm) or a specific colour reagent (*Draggendorff* reagent or iodine vapour) or by spraying with methanolic H_2SO_4 solution and subsequent charring by heating at 100 °C. Solvents were evaporated under reduced pressure at temperature < 50°C. Column chromatography was carried out on silica gel (230-400 mesh, E Merck). Distilled *n*-hexane and ethyl acetate was used for the column chromatography. ^{1}H and ^{13}C NMR were recorded at 300 and 75 MHz, respectively. Chemical shifts given in ppm downfield from internal TMS; *J* values in Hz. Mass spectra recorded using electron spray ionization mass spectrometry (ESI-MS). Elemental analyses were performed on a Perkin-Elmer 2400 C, H, N analyzer and values were found to be within ± 0.5% of the calculated values. Infrared spectra recorded as Nujol mulls in KBr plates.

Single-crystal X-ray data of compound **6a** were collected on Xcalibur Eos (Oxford) CCD-Diffractometer using graphite monochromated Mo*K*α radiation (λ = 0.71073 Å). The data integration and reduction were processed with CrysAlis Pro software.[14] Data of compound **4** was collected on Bruker SMART CCD-Diffractometer using graphite monochromated Mo*K*α radiation (λ = 0.71073 Å). The structures were solved by the direct method and then refined on F^2 by the full matrix least-squares technique with the SHELX-97 set of software[15] using the WinGX (version 1.80.05) program package.[16] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have drawn using ORTEP software.Further information on the crystal structure (excluding structure factors) has been given CIF file, Table S1 & S2 and figure S1 & S2 (Electronic Supporting Information)and also deposited in the Cambridge Crystallographic Data Centre as supplementary publications numbers 1482293 (**6a**) and 1482294 (**4**). Copies of the data can be obtained free of charge upon application to CCDC, 12 Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

Procedure for crystallization of compound 6a and 4

For crystallization a mixture of ethyl acetate and hexane (2:8) has been used and kept in dark place at temperature 25 °C. The single crystal appeared after three days was isolated in its initial state of growth.

Typical experimental procedure for synthesis of *N*-acylbenzotriazoles

Compound **1** (1.0 g, 7.34 mmol) was added to a RB flask containing dichloromethane (15.0 mL) equipped with freshly prepared $CaCl_2$ guard tube and temperature was maintained 0-5 °C.Thionyl chloride (0.6 mL, 8.27 mmol) was added dropwise with vigorous stirring and constant cooling. The reaction mixture was allowed to stir for 15 min then added 1*H*-1,2,3-benzotriazole (3.06g, 25.69mmol) in fraction after complete addition stirred the reaction mixture 2-3 hour at room temperature. After completion of reaction (monitored by TLC), the excess $SOCl_2$ was quenched with ice maintaining the

temperature at 0°C. Extracted with CH_2Cl_2, washed with 10% Na_2CO_3, water, and brine solution, the organic layer wasdried over anhydrous Na_2SO_4, concentrated till dry under reduced pressure. Further, purification using flash column chromatography using gradient mixtures of ethyl acetate and *n*-hexane afforded product **2a-q** in pure.

Physical data of developed compounds (2a-q)

(1*H*-1,2,3-Benzotriazole-1-yl)-phenyl-methanone (2a).[17] White crystalline Solid, 1.73g, yield 95%; R_f = 0.6 (10% ethyl acetate/n-hexane); m.p.=112-113 °C (lit. m.p.=112 °C) ; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.1 Hz, 1H), 8.23-8.16 (m, 3H), 7.73-7.67 (m, 2H), 7.61-7.53 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 145.7, 133.6, 132.3, 131.7, 131.6, 131.4, 130.3, 128.4, 126.3, 120.1 and 114.7 ppm; MS: *m/z* 224 $[M+H]^+$; Anal. Calcd for $C_{13}H_9N_3O$: C, 69.95; H, 4.06; N, 18.82. Found: C, 69.78; H, 4.09; N, 18.7

(1*H*-benzo[d][1,2,3]triazol-1-yl)(*p*-tolyl)methanone(2b).[17] white crystalline Solid,1.5g, yield 87%; R_f = 0.7 (10% ethyl acetate/*n*-hexane); m.p.=123-124 °C (lit. m.p.=123 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.1Hz, 1H), 8.17-8.12 (m, 3H), 7.69 (t, *J* = 7.5Hz, 1H), 7.53 (t, *J* = 7.5Hz, 1H), 7.38 (d, *J* = 7.2Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 145.6, 144.8, 131.8, 130.2, 129.1, 128.5, 126.1, 120.0, 114.7 and 21.7 ppm; MS: *m/z* 238 $[M+H]^+$; Anal. Calcd for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.63; H, 4.78; N, 17.89.

(1*H*-benzo[d][1,2,3]triazol-1-yl)(*m*-tolyl)methanone (2c).[18] White crystalline Solid, 1.4g, yield 83%; R_f=0.8 (10% ethyl acetate/*n*-hexane); m.p.=207-209°C (lit. m.p.=205 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, *J*=8.1Hz, 1H), 8.16 (d, *J* = 8.4Hz, 1H), 7.99 (bs, 2H), 7.69 (t, *J* = 7.5Hz, 1H), 7.56-7.43 (m, 3H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8, 145.7, 138.2, 134.4, 132.3, 132.0, 131.3, 130.2, 128.8, 128.2, 126.2, 120.1, 114.7 and 21.3 ppm; MS: *m/z* 238 $[M+H]^+$; Anal. Calcd for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.53; H, 4.71; N, 17.95.

(1*H*-benzo[d][1,2,3]triazol-1-yl)(*o*-tolyl)methanone (2d).White crystalline Solid, 1.5g, yield 88%; R_f=0.8 (10% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.1Hz, 1H), 8.15 (d, *J* = 8.4Hz, 1H), 7.72-7.61 (m, 2H), 7.56-7.47 (m, 2H), 7.34 (t, *J* = 8.1Hz, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 146.0, 137.8, 132.2, 131.7, 131.6, 130.9, 130.3, 129.9, 126.3, 125.3, 120.1, 114.5 and 19.9 ppm; MS: *m/z* 238 $[M+H]^+$.

(1*H*-benzo[d][1,2,3]triazol-1-yl)(4-chlorophenyl)methanone (2e).[19] White crystalline Solid,1.2g, yield 71%; R_f=0.5 (10% ethyl acetate/*n*-hexane); m.p.=137-138°C (lit. m.p.=138 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.1Hz, 1H), 8.25–8.16 (m, 3H), 7.72 (t, *J* = 7.5Hz, 1H), 7.60–7.55 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.6, 145.7, 140.4, 133.1, 130.5, 129.7, 128.8, 126.4, 120.2 and 114.8 ppm; MS: *m/z* 258 $[M+H]^+$.

(1*H*-benzo[d][1,2,3]triazol-1-yl)(3-(trifluoromethyl) phenyl)methanone (2f). White crystalline solid, 0.817g, yield 53%; R_f = 0.7 (10% ethyl acetate/n-hexane); m.p.=52-53°C; IR (KBr): ν_{max}(cm^{-1}) 3230, 2920, 1699, 1594, 1485, 1452, 1390, 1330, 1302, 1265, 1071, 958, 946, 802, 759, 749, 693, 677; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.42 (d, *J* = 7.5Hz, 1H), 8.35 (d, *J* = 8.1Hz, 1H), 8.15 (d, *J* = 8.4, 1H), 7.92 (d, *J* = 7.5Hz, 1H), 7.74-7.68 (m, 2H), 7.55 (t, *J* = 7.5Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2, 145.7, 134.8, 132.2, 132.0 130.6, 130.0, 129.9, 129.0, 128.5, 128.4, 126.5, 120.2 and 114.6 ppm; MS: *m/z* 292 $[M+H]^+$; Anal. Calcd for $C_{14}H_8F_3N_3O$: C, 57.74; H, 2.77; N, 14.43. Found: C, 57.91; H, 2.87; N, 14.29.

(1*H*-benzo[d][1,2,3]triazol-1-yl)(3,5-dichlorophenyl)methanone (2g). White crystalline solid, 1.2 g, yield 79%; R_f = 0.7 (10% ethyl acetate/*n*-hexane x 2); m.p.=148-152°C; IR (KBr): ν_{max} (cm^{-1}) 3068, 2333, 1708, 1564, 1484, 1452, 1420, 1379, 1322, 1291, 1240, 1155, 969, 877, 773, 664; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.4Hz, 1H), 8.18 (d, *J* = 8.1Hz, 1H), 8.11 (s, 2H), 7.73 (t, *J* = 7.5Hz, 1H), 7.66 (d, *J* = 1.8Hz, 1H), 7.57 (t, *J* = 7.5Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1, 145.7, 135.3, 134.0, 133.4, 132.0, 130.8, 129.9, 126.8, 120.4 and 114.7 ppm; MS: *m/z* 292 $[M+H]^+$; Anal. Calcd for $C_{13}H_7Cl_2N_3O$: C, 53.45; H, 2.42; N, 14.38. Found: C, 53.71; H, 2.31; N, 14.27.

(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(3-methoxyphenyl)methanone (2h). White crystalline solid, 1.2 g, yield 72%; R_f = 0.7 (10% ethyl acetate/*n*-hexane); m.p.=80-84°C; IR (KBr):ν_{max} (cm^{-1}) 3105, 3087, 3019, 2963, 2837, 1943, 1704, 1585, 1486, 1449, 1367, 951, 746 cm^{-1}; MS: *m/z* 254 [M + H]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.1Hz, 1H), 8.13 (d, *J* = 8.1Hz, 1H), 7.79 (d, *J* = 7.5Hz, 1H), 7.64-7.70 (m, 2H), 7.54-7.43 (m, 2H), 7.21 (d, *J* = 6.3Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 159.2, 145.5, 132.4, 132.2, 130.2, 129.3, 126.1, 124.1, 119.9, 116.0, 114.6, 114.5 and 55.4 ppm.

(1*H*-benzo[d][1,2,3]triazol-1-yl)(3-phenoxyphenyl) methanone (2i). White crystalline solid, 1.19 g, yield 81%; R_f= 0.6 (13% ethyl acetate/*n*-hexane); m.p.=52-53°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d,*J*=8.1Hz, 1H), 8.12 (d, *J* = 8.4Hz, 1H), 7.91 (d, *J* = 7.5Hz, 1H), 7.81 (s, 1H), 7.67-7.62 (m, 1H), 7.52 (t, *J* = 7.8Hz, 2H), 7.37-7.29 (m, 3H), 7.14-7.05 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8, 157.2, 156.1, 145.5, 132.8, 132.0, 130.2, 129.8, 129.6, 126.2, 126.1, 123.9, 123.5, 121.1, 120.0, 119.1 and 114.5 ppm; MS: *m/z* 316 $[M+H]^+$; Anal. Calcd for $C_{19}H_{13}N_3O_2$: C, 72.37; H, 4.16; N, 13.33. Found: C, 72.67; H, 4.09; N, 13.23.

1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylethanone(2j).[17] White solid, 1.5 g, yield 87%; R_f = 0.7 (5% ethyl acetate/*n*-hexane); m.p.=63-64°C (lit. m.p.=65-66 °C); MS: *m/z* 238 [M + H]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.1Hz, 1H), 8.11 (d, *J* = 8.4Hz, 1H), 7.61 (t, *J* = 7.5Hz, 1H), 7.50-7.44 (m,

3H), 7.38-7.29 (m, 3H), 4.72 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 146.2, 132.4, 131.1, 130.4 (2C), 129.7 (2C), 128.7, 127.5, 126.2, 120.1, 114.4 and 41.9 ppm.

(*E*)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-3-phenylprop-2-en-1-one (2k). White solid, 1.0g, yield 62 %; R_f=0.7 (5% ethyl acetate/*n*-hexane); m.p.=114-118°C; MS: *m/z* 250 $[M + H]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.1Hz, 1H), 8.11 (bs, 3H), 7.70-7.61 (m, 3H), 7.51- 7.43 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.7, 148.5, 146.2, 133.9, 131.3, 130.1, 128.9, 128.8, 126.0, 120.0, 115.9 and 114.6 ppm.

(1*H*-benzo[d][1,2,3]triazol-1-yl)(4-bromophenyl)methanone. (2l).[20] Pale yellow solid, 1.2 g, yield 83%; R_f=0.5 (10% ethyl acetate/n-hexane); m.p.=140-142°C (lit. m.p.=142-143 °C); IR (KBr):ν_{max} (cm^{-1}) 3117, 3092, 1706, 1588, 1482, 1449, 1377, 1226, 943, 888, 750; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.4Hz, 1H), 8.17-8.09 (m, 3H), 7.72-7.67 (m, 3H), 7.54 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.6, 145.6, 133.1, 132.1, 131.7, 130.5, 130.1, 129.0, 126.4, 120.2 and 114.7 ppm; MS: m/z 302 $[M+H]^+$.

(1*H*-benzo[d][1,2,3]triazol-1-yl)(2-chlorophenyl)methanone (2m).[21] White crystalline solid,1.3 g, yield 81%; R_f = 0.5 (10% ethyl acetate/*n*-hexane); m.p.=81-83°C; IR (KBr):ν_{max} (cm^{-1}) 3112, 3062, 1723, 1588, 1484, 1449, 1361, 936, 738; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, *J* = 7.8Hz, 1H), 8.13 (d, *J* = 7.5Hz, 1H), 7.72-7.63 (m, 2H), 7.56-7.51 (m, 2H), 7.43 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.6, 146.1, 132.7, 132.4, 132.1, 131.1, 130.5, 130.0, 126.5, 120.2 and 114.3 ppm; MS: m/z 258 $[M+H]^+$.

(1H-benzo[d][1,2,3]triazol-1-yl)(2-methoxyphenyl)methanone(2n).[22] Colourless solid, 1.48g, yield 89%; R_f = 0.6 (10% ethyl acetate/*n*-hexane); m.p. = 95-96°C (lit. m.p.= 97 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.1Hz, 1H), 8.09 (d, *J* = 8.1Hz, 1H), 7.67-7.59 (m, 2H), 7.56-7.45 (m, 2H), 7.11-7.01 (m, 2H), 3.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9, 157.8, 146.0, 133.5, 131.4, 130.3, 130.2, 126.2, 122.7, 120.4, 120.0, 114.4, 111.7 and 55.8 ppm; MS: m/z 254 $[M+H]^+$.

(1*H*-benzo[d][1,2,3]triazol-1-yl)(2-hydroxyphenyl) methanone (2o).[23] Pale yellow solid, 1.6 g, yield 92%; R_f=0.7 (15% ethyl acetate/*n*-hexane); m.p.=115-116°C (lit. m.p.=116 °C); ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (d, *J* = 8.1Hz, 1H), 8.33 (d, *J* = 8.1Hz,1H), 8.19 (d, *J* = 8.1Hz, 1H), 7.92-7.89 (m, 1H), 7.72 (t, *J* = 7.5Hz, 1H), 7.69-7.46 (m, 2H), 7.15-7.01 (m, 2H) ;^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 163.4, 145.2, 136.9, 133.6, 132.2, 130.4, 126.3, 120.1, 119.4, 118.2 and 114.7 ppm; MS: *m/z* 240 $[M+H]^+$.

1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-chlorophenyl)ethanone (2p). White solid, yield 83%; 1.65g, R_f = 0.7 (5% ethyl acetate/n-hexane); m.p. = 80-82°C; MS: *m/z* 272 $[M + H]^+$; IR (KBr):ν_{max} cm^{-1} 2926, 1732, 1688, 1483, 1453, 1400, 1325, 1121, 1089, 1074, 980, 806, 772, 751; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.64 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.50 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.69 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 146.3, 133.7, 131.2 (2C), 131.1, 130.9, 130.6, 129.0 (2C), 126.4, 120.2, 114.4 and 41.3 ppm.

1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-methylbutan-1-one (2q). Oil, yield 71%; R_f = 0.6 (15% ethyl acetate/*n*-hexane); MS: *m/z* 204 $[M + H]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, *J* = 7.2 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 3.30 (d, *J* = 6.9 Hz, 2H), 2.49-2.40 (m,1H), 1.11 (d, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 145.8, 130.8, 129.9, 125.7, 119.7, 114.1, 43.8, 25.3 and 22.2 (2C) ppm.

Typical experimental procedure for the synthesis of Carbamates (3a-t)

To a stirring solution of compound **2** (1.0 equiv) in mixture of alcohol/water (19:1) was added sodium azide (3.0 equiv) in portions. The reaction was stirred under heating at 90-100°C for 4 hours. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated in vacuo. The crude reaction mixture was purified directly using flash column chromatography to afford carbamate derivative (**3a-t**). Purified compounds were recrystalised using $CHCl_3$/*n*-hexane.

Physical data of developed compounds (3a-t)

Ethylphenylcarbamate (3a).[24] White crystalline solid, 0.49 g, yield 67%; R_f = 0.6 (15% ethyl acetate/*n*-hexane); m.p.=50-51°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.8Hz, 2H), 7.19 (t, *J* = 6.9Hz, 2H), 6.95 (t, *J* = 7.2Hz, 1H), 6.78 (bs, 1H), 4.13 (q, *J* = 6.9Hz, 2H), 1.20 (t, *J* = 6.9Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 138.0, 129.0, 123.3, 118.8, 61.2 and 14.5 ppm; MS: *m/z* 166 $[M+H]^+$; Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.27; H, 6.88; N, 8.46.

Ethyl *p*-tolylcarbamate (3b).[25] Oil, 0.43g, yield 57%; R_f=0.6, (15% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.1Hz, 2H), 6.99 (d, *J* = 8.1Hz, 2H), 6.65 (bs, 1H), 4.12 (q, *J* = 6.9Hz, 2H), 2.20 (s, 3H), 1.20 (t, *J* = 6.9Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.7, 135.3, 132.7, 129.4, 118.8, 61.0, 20.6 and14.4 ppm; MS: *m/z* 180 $[M+H]^+$.

Ethyl *m*-tolylcarbamate(3c).[26] Oil, 0.51g, yield 68%; R_f=0.6, (15% ethyl acetate/*n*-hexane); IR (KBr):ν_{max} (cm^{-1}) 3320, 2980, 2928, 1735, 1717, 1614, 1596, 1542, 1492, 1445, 1227, 1070, 778, 690; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22-7.10 (m, 3H), 6.98 (bs, 1H), 6.83 (d, *J* = 6.9Hz, 1H), 4.20 (q, *J* = 6.9, 2H), 2.27 (s, 3H), 1.26 (t, *J* = 6.9, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.7, 138.5, 137.9, 128.5, 123.7, 119.2, 115.7, 60.7, 21.0 and 14.1 ppm; MS: *m/z* 180 $[M+H]^+$.

Ethyl *o*-tolylcarbamate (3d).[27] Oil, 0.41g, yield 55%; R_f= 0.5, (10% ethyl acetate/*n*-hexane); IR (KBr):ν_{max} (cm^{-1}) 3328, 3025, 2977, 2933, 2868, 1736, 1719, 1591, 1542, 1459, 1302, 1218,

1063, 753; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, *J* = 5.7Hz, 1H), 7.24-7.13 (m, 2H), 7.10 (t, *J* = 7.5Hz), 6.54 (bs, 1H), 4.22 (q, *J* = 6.9, 2H), 2.24 (s, 3H), 1.30 (t, *J* = 6.9Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.9, 135.7, 130.1, 127.9, 126.5, 123.9, 121.4, 60.9, 17.3 and 14.3 ppm; MS: *m/z* 180 $[M+H]^+$.

Ethyl(3-(trifluoromethyl)phenyl)carbamate (3e). Oil, 0.26g, yield 33%; R_f=0.45, (10% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (s, 1H),7.55 (d, *J*=8.1Hz, 1H), 7.43-7.38 (m, 1H), 7.32-7.26 (m, 1H), 6.75 (bs, 1H), 4.24 (q, *J* = 6.9Hz, 2H), 1.37 (t, *J* = 6.9, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.2, 151.9, 146.5, 138.6, 138.5, 129.4, 121.4, 119.8, 115.2, 61.4 and 14.3 ppm; MS: *m/z* 234 $[M+H]^+$; Anal. Calcd for $C_{10}H_{10}NO_2F_3$: C, 51.51; H, 4.32; N, 6.01. Found: C, 51.32; H, 4.48; N, 5.97.

Ethyl (3,5-dichlorophenyl)carbamate (3f). Oil, 0.39g, yield 46%; R_f = 0.5, (15% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (s, 2H), 7.06 (s, 1H), 6.67 (bs, 1H), 4.25(q, *J* = 6.9Hz, 2H), 1.33 (t, *J* = 6.9Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.0, 139.9, 135.3, 123.2, 116.7, 61.7 and 14.4 ppm; MS: *m/z* 234 $[M+H]^+$; Anal. Calcd for $C_9H_9NO_2Cl_2$: C, 46.18; H, 3.88; N, 5.98. Found: C, 45.97; H, 3.91; N, 5.89.

Ethyl (3-methoxyphenyl)carbamate (3g)[28]. Oil, 0.39g, yield 51 %; R_f=0.5 (15% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16-7.12 (m, 3H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 8.1Hz, 1H), 4.20 (q, *J*=6.9 Hz, 2H), 3.73 (s, 3H), 1.26 (t, *J* = 6.9Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0, 153.6, 139.2, 129.4, 110.8, 108.9, 104.3, 61.1, 55.0 and 14.3 ppm; MS: *m/z* 196 $[M+H]^+$.

Ethyl (3-phenoxyphenyl)carbamate (3h). Oil, 0.50g yield 62%; R_f = 0.6, (15% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (t, *J* = 7.8Hz, 2H), 7.12-7.06 (m, 1H), 7.00-6.96 (m, 3H), 6.90-6.84 (m, 3H), 6.56 (d, *J* = 7.5Hz, 1H), 4.06 (q, *J* = 7.2Hz, 2H), 1.14 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.8, 156.8, 153.4, 139.4, 129.8, 129.6, 123.2, 118.9, 113.3, 109.2, 61.1 and 14.3 ppm; MS: *m/z* 258 $[M+H]^+$; Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.27; H, 6.01; N, 5.41.

Ethyl benzylcarbamate (3i).[29] Oil, 0.42g, yield 56 %; R_f=0.5, (15 % ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.26 (m, 5H), 4.98 (bs, 1H), 4.35 (d, *J* = 4.8Hz, 2H), 4.14 (q, *J*=7.2Hz, 2H), 1.24 (t, *J*=7.2Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.6, 138.5, 128.6, 127.4, 120.0, 60.9, 44.9 and 14.6 ppm; MS: *m/z* 180 $[M+H]^+$.

(E)-Ethyl styrylcarbamate(3j).[30] Oil, 0.23g; yield 30%; R_f= 0.5, (20 % ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26-7.15 (m, 6H), 6.81 (s, 1H), 5.95 (d, *J* = 14.4Hz, 1H), 4.21-4.19 (m, 2H), 1.28 (bs, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.7, 136.3, 128.5, 126.1, 125.2, 124.1, 110.5, 61.5 and 14.4 ppm; MS: *m/z* 192 $[M+H]^+$.

Ethyl (4-bromophenyl)carbamate (3k).[31] White solid, 0.57g yield 71%; R_f=0.5, (20% ethyl acetate/*n*-hexane); m.p.=58-62°C (lit. m.p.=85°C);;^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, *J* = 9.0Hz, 2H), 7.27 (d, *J* = 9.0Hz, 2H), 6.67 (bs, 1H), 4.21 (q, *J* = 6.9Hz, 2H), 1.30 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.4, 137.0, 131.9, 131.5, 120.1, 115.7, 61.4 and 14.4 ppm; MS: *m/z* 244 $[M+H]^+$.

Methyl (4-bromophenyl)carbamate (3l).[25] White solid, 0.09g, yield 13%; R_f = 0.45 (15% ethyl acetate/*n*-hexane); m.p.=94-96°C; IR (KBr):ν_{max}(cm^{-1}) 3345, 2948, 1704, 1600, 1547, 1488, 1397, 1312, 1240, 1075, 825;^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.7Hz, 2H), 7.27 (d, *J* = 8.4Hz, 2H), 6.74 (bs, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 136.9, 131.9, 120.2, 115.9 and 52.4 ppm; MS: *m/z* 230 $[M+H]^+$.

Propyl (4-bromophenyl)carbamate (3m). White solid, 0.56g yield 66%; R_f=0.5, (15% ethyl acetate/*n*-hexane);m.p.=62-64°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, *J* = 9.0Hz, 2H), 7.27 (d, *J* = 9.3Hz, 2H), 6.62 (bs, 1H), 4.12 (t, *J* = 6.6Hz, 2H), 1.69 (q, *J* = 7.2Hz, 2H), 0.97 (t, *J* = 7.5Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.4, 137.1, 131.9, 120.1, 115.8, 67.0, 22.2 and 10.3 ppm; MS: *m/z* 258 $[M+H]^+$;Anal. Calcd for $C_{10}H_{12}NO_2Br$: C, 46.53; H, 4.69; N, 5.43. Found: C, 46.37; H, 4.76; N, 5.35.

Isopropyl (4-bromophenyl)carbamate (3n).[32] White crystalalline solid, 0.52g, yield 61%; R_f = 0.5 (20% ethyl acetate/n-hexane); m.p.=107-108°C (lit. m.p.=105°C);^{1}H; IR (KBr):ν_{max} (cm^{-1}) 3353, 2978, 2933, 1692, 1590, 1530, 1399, 1236, 1110, 826, 774;^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.7Hz, 2H), 7.27 (d, *J* = 8.7Hz, 2H), 6.64 (bs, 1H), 5.04-4.96 (m, 1H), 1.34-1.27 (*m*, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.0, 137.2, 131.8, 120.1, 115.6, 69.0 and 22.0 ppm; MS: *m/z* 258 $[M+H]^+$.

Butyl (4-bromophenyl)carbamate (3o).[32] White crystalline solid, 0.69g yield 77%; R_f = 0.5 (10% ethyl acetate/*n*-hexane);m.p.=56-58°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.7Hz, 2H), 7.28 (d, *J* = 8.7Hz, 2H), 6.71 (bs, 1H), 4.15 (t, *J* = 6.6Hz, 2H), 1.64 (t, *J* = 7.5Hz, 2H), 1.40 (q, *J* = 7.5Hz, 2H), 0.94 (t, *J* = 7.5Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5, 137.1, 131.9, 120.1, 115.7, 65.3, 30.8, 19.0 and 13.6 ppm; MS: *m/z* 272 $[M+H]^+$.

Pentyl (4-bromophenyl)carbamate (3p). White solid, 0.76g yield 81%; R_f=0.4, (10% ethyl acetate/*n*-hexane); m.p.=58-60°C;^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.7Hz, 2H), 7.27 (d, *J* = 8.7Hz, 2H), 6.94 (bs, 1H), 4.13 (t, *J* = 6.6Hz, 2H), 1.64 (t, *J* = 6.6Hz, 2H), 1.32 (m, 4H), 0.90 (t, *J* = 6.6Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.6, 137.1, 131.7, 120.2, 115.6, 65.5, 28.4, 27.8, 22.2 and 13.8 ppm; MS: *m/z* 286 $[M+H]^+$;Anal. Calcd for $C_{12}H_{16}NO_2Br$: C, 50.37; H, 5.64; N, 4.89. Found: C, 50.54; H, 5.47; N, 4.73.

Prop-2-yn-1-yl (4-bromophenyl)carbamate (3q).[33] White crystalline solid, 0.36g yield 43%; R_f=0.5, (10% ethyl acetate/n-hexane);m.p.=142-143°C (lit. m.p.=143-144°C);^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.7Hz, 2H), 7.28 (d, *J* = 8.7Hz, 2H), 6.71 (bs, 1H), 4.77 (s, 2H), 2.51 (s,1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.2, 136.5, 132.0, 120.3, 116.4, 77.4, 75.2 and 52.9 ppm; MS: *m/z* 254 $[M+H]^+$.

Prop-2-yn-1-yl phenylcarbamate (3r).[34] White crystalline solid, 0.33g yield 41%; R_f=0.6, (15% ethyl acetate/*n*-hexane); m.p.=59-61°C (lit. m.p.= 62-63 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.24 (m, 5H), 7.07 (t, *J* = 7.5Hz, 1H), 6.78 (m, 1H), 4.78 (s, 2H), 2.50 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.4, 137.3, 129.0, 123.7, 118.8, 77.8, 75.0 and 52.7 ppm; MS: *m/z* 176 $[M+H]^+$.

butyl benzylcarbamate (3s).[35] oil, .45g yield 51%; R_f=0.5, (10% ethyl acetate/n-hexane);MS: *m/z* 208 $[M+H]^+$;^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24-7.17 (m, 5H), 5.05 (bs, 1H), 4.26 (d, *J* = 5.5Hz, 2H), 4.00-3.98 (m, 2H), 1.50-1.47 (m, 2H) 1.29-1.26 (m, 2H), .83 (t, *J* = 7.5Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7, 138.5, 128.5, 127.4, 127.2, 64.7, 44.8, 30.9, 18.9 and 13.6 ppm.

Ethyl (4-Chlorobenzyl)carbamate (3t). white solid, 0.46g yield 59%; R_f = 0.4, (10% ethyl acetate/n-hexane); m.p.=55-58°C (lit. m.p.=62°C); MS: *m/z* 214 $[M+H]^+$;^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.5Hz, 2H), 7.21 (d, *J* = 8.0Hz, 2H), 5.06 (bs, 1H), 4.31 (d, *J* = 5.5Hz, 2H), 4.16-4.11 (m, 2H), 1.25-1.23 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.6, 137.1, 133.1, 128.7, 61.0, 44.2 and 14.5 ppm.

Benzo[d]oxazol-2(3*H*)-one (4). Crystalline solid, 0.54g yield 97%; R_f = 0.5, (15% ethyl acetate/*n*-hexane); m.p.=134-138°C (lit. m.p.=138°C); ^{1}H NMR (300 MHz, DMSO-d^6): δ 9.86 (bs, 1H), 7.18-7.04 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d^6): δ 156.3, 143.8, 129.4, 124.1, 122.6, 110.2 and 110.1 ppm; MS: *m/z* 136 $[M+H]^+$;Anal. Calcd for $C_7H_5NO_2$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.45; H, 5.26; N, 10.11.

Typical experimental procedure for the synthesis of thiocarbamates (5a & 5l)

To a stirring solution of compound **2a** & **2l** (1.0 equiv) in mixture of thiol/ water (9:1) was added sodium azide (3.0 equiv) in portions. The reaction was stirred at 100°C for 4 hours. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated in vacuo. The crude reaction mixture was purified directly using flash column chromatography to afford thiocarbamate derivative (**5a** & **5b**).

***S*-Furfuryl *N*-(4-bromophenyl)thiocarbamate (5a).** brown oil, 0.38g yield 37%; R_f=0.5, (10% ethyl acetate/n-hexane); MS: *m/z* 312 $[M+H]^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 9.0Hz, 2H), 7.28 (s, 1H), 7.24 (d, *J* = 9Hz, 2H), 6.96 (bs, 1H), 6.22 (d, *J* = 14Hz, 2H), 4.18 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.6, 150.5, 142.3, 136.5, 132.1, 131.9, 128.7, 121.2, 110.6, 108.1 and 27.0 ppm.

***S*-Benzyl *N*-phenylthiocarbamate (5b).**[36] brown solid, 0.48g yield 44%; R_f=0.5, (10% ethyl acetate/n-hexane);m.p.=88-90°C (lit. m.p.=94.5°C); MS: *m/z* 244 $[M+H]^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.16 (m, 9H), 7.06-7.03 (m, 1H), 6.97 (bs, 1H), 4.16 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1, 137.9, 137.4, 129.1, 128.9, 128.8, 128.6, 127.3, 124.5, 119.7 and 34.4 ppm.

Typical experimental procedure for the synthesis of symmetric urea

To a stirring solution of compound **2** (1 equiv) in mixture of THF/ water (85:15) of was added sodium azide (3.0 equiv.) in portions. The reaction mixture was stirred under heating at 90-100°Cfor 4 hours. After, completion of the reaction (monitored by TLC), the reaction mixture was concentrated in vacuo. The crude reaction mixture was purified directly using flash column chromatography to afford carbamates derivative (**6a-g**). Purified compounds were recrystallized using ethyl acetate/ *n*-hexane.

1,3-Diphenylurea (6a).[25] White crystalline solid, 0.43g yield 81%; R_f=0.7, (25% ethyl acetate/*n*-hexane);m.p. = 240-242°C (lit. m.p.=238°C); IR (KBr):ν_{max}3328, 3034, 1646, 1594, 1543, 1497, 1440, 1314, 1231cm^{-1}:^{1}H NMR (300 MHz, DMSO-d^6): δ 8.64 (bs, 2H), 7.46 (d, *J* = 7.8Hz, 4H), 7.26 (t, *J* = 6.9Hz, 4H), 6.95 (t, *J* = 6.9Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d^6): δ 152.5, 139.7, 128.7, 121.8 and 118.2 ppm; MS: *m/z* 213 $[M+H]^+$.

1,3-Di-*o*-tolylurea (6b).[25] White crystalline solid, 0.33g yield 65%; R_f=0.6, (25% ethyl acetate/*n*-hexane);m.p.=235-236°C (lit. m.p.=245-247°C);^{1}H NMR (300 MHz, DMSO-d^6): δ 8.20 (bs, 2H), 7.78 (bs, 2H), 7.14 (bs, 4H), 6.94 (bs, 2H), 2.24 (m, 6H); ^{13}C NMR (75 MHz, DMSO-d^6): δ 154.3, 141.4, 130.1, 127.7, 126.0, 121.5, 119.4 and 17.9 ppm; MS: *m/z* 241 $[M+H]^+$.

1,3-Bis(2-chlorophenyl)urea (6c).[25] White solid, 0.42g yield 77%; R_f=0.4, (10% ethyl acetate/*n*-hexane);m.p.=242-244°C (lit. m.p.=240-241°C);^{1}H NMR (300 MHz, DMSO-d^6): δ 8.97 (bs, 2H), 8.10 (d, *J* = 7.8Hz, 2H) 7.38 (bs, 2H), 7.25 (bs, 2H), 7.01 (bs, 2H); ^{13}C NMR (75 MHz, DMSO-d^6): δ 148.4, 135.6, 128.9, 126.9, 122.6 and 122.1 ppm; MS: *m/z* 281 $[M+H]^+$.

1,3-Bis(2-methoxyphenyl)urea (6d).[25] White solid, 0.47g, yield 87%; R_f=0.4, (15% ethyl acetate/*n*-hexane);m.p.=180-184°C (lit. m.p.=185-186°C);^{1}H NMR (300 MHz, DMSO-d^6): δ 8.13-8.10 (m, 2H), 7.19 (bs, 2H), 7.02-6.88 (m, 4H), 6.86 (d, *J* = 7.2Hz, 2H), 3.85 (bs, 6H); ^{13}C NMR (75 MHz, DMSO-d^6): δ 152.4, 148.1, 128.1, 122.8, 121.1, 119.6, 110.0 and 55.6 ppm; MS: *m/z* 273 $[M+H]^+$.

1,3-Bis(4-chlorophenyl)urea (6e).[25] White solid, 0.28g, yield 52%; R_f=0.5, (20% ethyl acetate/*n*-hexane);m.p.=306-308°C (lit. m.p.=306-307°C); IR (KBr):ν_{max}(cm^{-1}) 3296, 2923, 2852, 1633, 1590, 1560, 1491, 1395, 1298, 1237, 822, 639, 508; ^{1}H NMR (300 MHz, DMSO-d^6): δ 8.34 (s, 2H), 7.35 (d, *J*=9.0Hz, 4H), 7.15 (d, *J*=8.7Hz, 4H); ^{13}C NMR (75 MHz, DMSO-d^6): δ 150.5 , 137.7, 128.1, 126.2, 124.8 and 119.3 ppm; MS: *m/z* 281 $[M+H]^+$.

1,3-Di-*m*-tolylurea (6f).[25] White solid, 0.36g, yield 73%; R_f=0.5, (25 % ethyl acetate/*n*-hexane);m.p.=224-228°C (lit. m.p.=217°C);^{1}H NMR (300 MHz, DMSO-d^6): δ 8.55 (s, 2H), 7.30 (s, 2H), 7.23-7.12 (m, 4H), 6.78 (d, *J* = 6.9Hz, 2H), 2.27 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d^6): δ 152.4, 139.6, 137.9, 128.5, 122.4, 118.6, 115.2 and 21.2 ppm; MS: *m/z* 241 $[M+H]^+$.

1,3-Bis(3-(trifluoromethyl)phenyl)urea (6g). White solid, 0.45g yield 76%; R_f=0.5, (30% ethyl acetate/*n*-hexane);m.p.=198-200°C (lit. m.p.=194-196°C);^{1}H NMR (300 MHz, DMSO-d^6): δ 8.93 (sbr, 2H), 7.97 (s, 2H), 7.56 (d, *J* = 7.8Hz, 2H), 7.43 (t, *J* = 7.8Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d^6): δ 152.2, 139.9, 130.1, 129.6, 129.0, 125.5, 121.9, 121.4, 118.0, 117.9 and 114.4 ppm; MS: *m/z* 349 $[M+H]^+$;Anal. Calcd for $C_{15}H_{10}F_6N_2O$: C, 51.73; H, 2.89; N, 8.04. Found: C, 52.02; H, 2.95; N, 7.89.

Typical experimental procedure for the synthesis of triazolyl sugar derivatives

Method I. To a solution of compound **2** (1.0 equiv.) in mixture of propargyl alcohol/ water (9:1) was added sodium azide (1.2 equiv.) and allow to stir for 10 hours at 90-100°C. After completion of the reaction (monitored by TLC), then propargyl alcohol was removed and added ^{t}BuOH-water (8:2) and allow to stir. sugar azide (1.1 equiv.) was added in portions followed by addition of $CuSO_4.H_2O$ (0.02 mol%) and NaAsc (0.2 mol%) and stirred for 4 hours at rt. After completion of reaction the reaction mixture was concentrated in vacuum. The crude reaction mixture was purified directly using flash column chromatography to afford triazolyl derivatives of carbamate (**8a-c**).

Method II. A solution of compound **3** (1.0 equiv.) in a R.B. flask containing a mixture of ^{t}BuOH/ water (8:2) was added sugar azide (1.1 equiv.), $CuSO_4.H_2O$ (0.02 mol%) and NaAsc (0.2 mol%) and stirred for 4 hours at rt. After completion of reaction the reaction mixture was concentrated in vacuum. The crude reaction mixture was purified directly using flash column chromatography to afford triazolyl derivatives of carbamate (**8a-c**).

1'-(4-(((Phenylcarbamoyl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)-2,3,4,6-tetra-*O*-acetyl-α-d-glucopyranose (8a). Oil, yield = Method I-302 mg (11%), Method II-2.75g (88%); R_f=0.5, (60% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.40 (d, *J* = 7.8Hz, 2H), 7.30 (t, *J* = 7.2Hz, 2H), 7.27 (bs, 1H), 7.08-7.06 (m, 1H) 5.87 (d, *J* = 9.0Hz, 1H), 5.55 (t, *J* = 9.9Hz, 2H), 5.23-5.38 (m, 3H), 4.25- 4.13 (m, 3H), 2.22 (s, 3H), 2.02-2.00(m, 6H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 169.9, 169.7, 168.9, 153.1, 143.6, 137.6, 128.9, 123.5, 122.5, 118.8, 86.1, 76.5, 73.9, 70.6, 67.8, 66.8, 61.1, 57.6, 20.6, 20.5, 20.3 and 20.1 ppm; MS: *m/z* 549 $[M+H]^+$.

1'-(4-((((4-bromophenyl)carbamoyl)oxy)methyl)-1H-1,2,3-triazol-1-yl)-2,3,4,6-tetra-*O*-acetyl-α-d-glucopyranose (8b). oil, yield= Method I-304 mg (13%), Method II-2.34g (94%); R_f = 0.5, (50% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.41 (d, *J* = 8.7Hz, 2H), 7.32-7.29 (m, 2H), 7.18 (bs, 1H), 5.85 (d, *J* = 9.0 Hz, 1H), 5.57-5.50 (m, 2H), 5.38-5.24 (m, 3H), 4.24-4.14 (m, 3H), 2.22 (s, 3H), 2.06-2.01 (m, 6H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 169.9, 169.7, 169.0, 152.9, 143.4, 136.8, 131.9, 122.5, 120.3, 86.2, 76.5, 74.0, 70.6, 67.8, 66.7, 61.1, 57.8, 20.6, 20.5. 20.3 and 20.1 ppm; MS: *m/z* 627 $[M+H]^+$.

Ethyl 1',2'-isopropylidine-3'-*O*-benzyl-5'-(4-((((4-bromophenyl)carbamoyl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)-5'-deoxy-α-D-*xylo*-heptofuranuronoate (8c). Oil, yield = Method I- 186 mg (8%), Method II- 2.33g (92%); R_f = 0.5, (60% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.45 (s, 1H), 7.38-7.32 (m, 9H), 5.88 (d, *J* = 3.0 Hz, 1H), 5.28-5.19 (m, 2H), 5.14-5.08 (m, 1H), 4.59-4.56 (m, 1H), 4.76-4.67 (m, 2H), 4.44 (d, *J* = 11.7Hz, 1H), 4.00-3.95 (m, 3H), 3.16 (dd, *J* = 10.5, 6.0Hz, 1H), 2.43 (d, *J* = 15.0Hz, 1H), 1.45 (s, 3H), 1.25 (s, 3H), 1.10 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 153.1, 141.6, 137.1, 136.2, 131.7, 128.6, 128.4, 128.1, 126.0, 120.2, 112.2, 104.8, 81.5, 80.6, 80.5, 71.6, 60.9, 60.3, 58.0, 57.3, 34.8, 29.6, 26.6, 26.1 and 13.8 ppm; MS: *m/z* 645 $[M+H]^+$.

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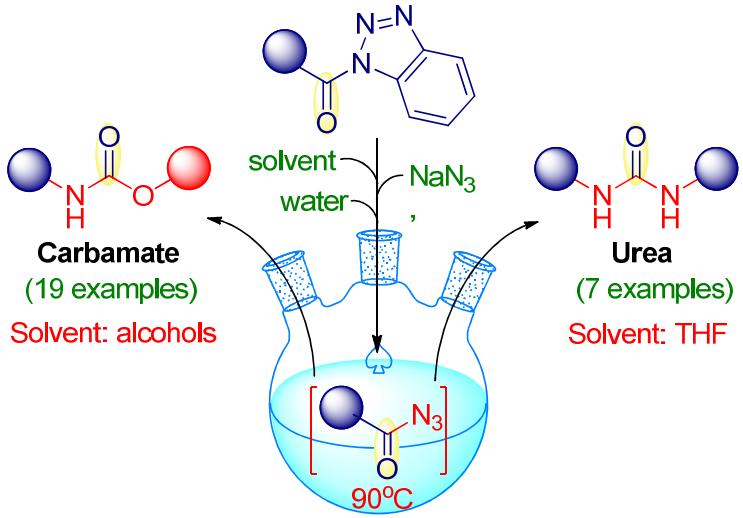
An efficient one-pot synthesis of *N*,*N*′-disubstituted ureas and carbamates from *N*-Acylbenzotriazoles

Graphical Abstract:



A facile and high-yielding one-pot synthesis of carbamates and *N*,*N'*-disubstituted symmetrical ureas from *N*-acylbenzotriazoles has been devised. It is believed that, the intermediate acyl-azide undergo Curtius rearrangement and under different solvent gives different products, the carbamates in alcohols and *N*,*N'*-disubstituted symmetrical urea in THF. The products were characterized by IR, MS, ^{1}H, and ^{13}C NMR spectroscopic studies.