Accepted Manuscript

Synthesis of glucose-tagged triazolium ionic liquids and their application as solvent and ligand for copper(I) catalyzed amination

Abadh Kishor Jha, Nidhi Jain

PII:	S0040-4039(13)01090-3
DOI:	http://dx.doi.org/10.1016/j.tetlet.2013.06.114
Reference:	TETL 43167
To appear in:	Tetrahedron Letters
Received Date:	11 May 2013
Revised Date:	18 June 2013
Accepted Date:	22 June 2013



Please cite this article as: Jha, A.K., Jain, N., Synthesis of glucose-tagged triazolium ionic liquids and their application as solvent and ligand for copper(I) catalyzed amination, *Tetrahedron Letters* (2013), doi: http://dx.doi.org/10.1016/j.tetlet.2013.06.114

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Graphical Abstract



Synthesis of glucose-tagged triazolium ionic liquids and their application as solvent and ligand for copper(I) catalyzed amination

Abadh Kishor Jha and Nidhi Jain*

Department of Chemistry, Indian Institute of Technology, New Delhi-110016 E-mail: <u>njain@chemistry.iitd.ac.in</u>

Abstract

Glucose-linked 1,2,3-triazolium ionic liquids have been synthesized as a new class of chiral solvents by copper(I) catalyzed regioselective cycloaddition of a glucose azide with a glucose alkyne followed by quaternization with methyl iodide. The tagging of glucose to triazolium core makes these molecules act as reusable ligand and solvent in copper(I) catalyzed amination of aryl halides with aqueous ammonia. While the free hydroxyl groups of sugar help in stabilizing copper(I) species during the reaction thus acting as a ligand, the triazolium salt which makes it a liquid at room temperature serves as a reusable solvent. These chiral ionic liquids derived from low-cost natural sources can find utility in various transition- metal catalyzed reactions, and can be explored for asymmetric synthesis in future.

Keywords: triazolium cation, glucose, ionic liquids, amination, copper(I) iodide

Ionic liquids (ILs) are low-melting molten salts composed entirely of ions, and many of them are liquid at room temperature.¹ They are versatile solvents suitable for a myriad of applications owing to their unique properties such as wide liquid range, thermal stability, excellent solubility for organic as well as inorganic compounds, attractive recyclability, and negligible vapour pressure.² Most of the research on ionic liquids has been dominated by imidazolium salts with fluorine containing anions.³ Imidazolium salts functionalized with various moieties such as 4-hydroxyproline, TEMPO, ruthenium complexes, carboxylic acid, amine, thiol, hydroxyl, bipyridine etc. have been developed and used as supported reagents and catalysts in a variety of reactions.⁴ Some amount of progress has also taken place over the past few years in the development of chiral ILs derived from naturally occurring chiral precursors such as (-)-ephedrine, (S)-nicotine, (-) menthol, and amino acids.⁵ Glycoside based ILs containing ammonium, pyridinium, sulfonium, and imidazolium cations have also been reported.⁶ However, there are no reports of carbohydrate based ILs tethered to a triazolium core. Compared to the huge advancements made with imidazolium ILs, studies of triazolium ILs are fewer.⁷ So far, the

major field of application for 1,2,3-triazolium ILs has been in ionic liquid tagging of organocatalysts which enables a better catalytic performance, better solubility, and easy recycling of catalysts. Examples include chiral 1,2,3-triazolium ionic liquid tethered to (S)proline, and TADDOLs⁸ which have been used in asymmetric catalysis, and have been found to give higher yields and stereoselectivities than the bare organocatalyst. As part of our ongoing research on developing ligand-tagged ionic liquids⁹ as stable media for transition metal nanoparticle catalyzed reactions,¹⁰ we initiated the design and synthesis of sugar-tethered triazolium salts as a new class of ionic liquids for metal catalyzed reactions. Copper(I) catalyzed cycloaddition continues to be the most popular method for synthesis of 1,4-disubstituted triazoles.¹¹ Taking the regioselectivity of click chemistry to our advantage, we decided to synthesize 1,4-disubstituted triazolium ILs with sugars occupying the 1,4-position. The obvious advantage of these novel ILs was that they were synthesized starting from low-cost natural sources. Further, owing to the presence of many hydroxyl groups in the sugar, we believed that these ILs might provide high coordination ability to the metal centre that could be tuned by varying the electron density of their oxygens through a proper protecting group pattern. In this paper we report the synthesis of novel glucose-linked triazolium based ionic liquids, and a preliminary study on their application in copper(I) catalyzed amination of aryl halides with aqueous ammonia. A lot of work on amination of aryl halides catalyzed by palladium and copper using direct or indirect amine sources has been carried out in the last decade.¹² While use of palladium offers large substrate scope, its hyper catalytic activity reduces selectivity leading to formation of appreciable amounts of secondary and tertiary amines as by-products.¹³ Copper, on the other hand is much cheaper compared to palladium, and is stabilized with nitrogen and oxygen based donor ligands. However its application in aniline synthesis using aqueous ammonia often requires harsh reaction conditions of high temperature, large excess of ammonia and ligand making the protocol a little less attractive.¹⁴ Hence, the development of a mild catalytic system for selective mono amination still represents a major advance. Our preliminary findings on application of glucose-tethered triazolium ionic liquids for copper catalyzed amination of simple iodo, bromo, and chlorobenzene using aqueous ammonia as amine source gave promising results. On completion of reaction, the ionic liquid could be recovered and reused after extraction of products in organic solvent. The rationale of choosing glucose as the sugar tag was its ready availability and low cost. The synthesis of many more ILs starting from

other monosaccharide or disaccharide molecules can be accomplished by this route. This work can further be extended to a variety of other substrates with different electronic and steric constraints to examine the scope and versatility of the catalytic system.

The synthesis of ionic liquids IL-1, IL-2, and IL-3 (Figure 1) with varied hydroxyl group reactivity was carried out in several steps. The first step involved preparation of the IL precursors: glucose alkyne 3 and glucose azide 6 from commercially available D-glucose (Scheme 1) by reported methods.¹⁵ Compound **3** was synthesized by selectively protecting Dglucose as a diacetonide in the furanose form 2 with a free 3-hydroxy group which on subsequent treatment with propargyl bromide at RT yielded the isopropylidene protected glucose alkyne 3 in 44% overall yield. Compound 6 was prepared by protection of glucose as its pentaacetate derivative 4 followed by selective bromination at anomeric position with HBr to yield 5 which was further transformed to azide on exchange with sodium azide. Final ILs were obtained by copper(I) catalyzed cycloaddition of respective azide with glucose alkyne to yield 1,4disubstituted 1,2,3-triazole¹⁶ followed by guaternization with methyl iodide (Scheme 2). The ILs (IL-1, IL-2, and IL-3) were highly soluble in water and completely insoluble in diethyl ether and methylene chloride. Therefore their purification was achieved by extraction of the impurities in these two organic solvents from the aqueous phase. The methylation of 8 with methyl iodide resulted in addition of two methyl units; one at triazole N-3 and a second methylation at C6primary hydroxy of furanose ring. The dimethylation was evident from an increase of 29 mass units from 8 resulting from loss of a primary hydroxyl proton of OH and addition of two methyl groups leading to the synthesis of **IL-1**. A similar dimethylation at N-3 and primary OH of 10 gave IL-2. The structure of ILs was confirmed by NMR and mass spectroscopic analysis. The molecular ion peak at 660.26 in HRMS corresponded to the molecular mass of glucose linked triazolium cation of **IL-1**. The four acetate groups appeared at (2.14-2.24) ppm in ¹HNMR corresponding to twelve protons, and at 20-21 and 171-174 ppm in the ¹³CNMR spectra for the four methyl and four carbonyl groups respectively. The partial isopropylidene glucose protection was evident from signals at 1.39 and 1.54 ppm revealing six methyl protons of isopropylidene group. Signals at 25-26 ppm and 112.9 ppm in ¹³CNMR could be assigned to the two methyl carbons and one quaternary carbon respectively of isopropylidene group. The quaternization of nitrogen was confirmed by the methyl signal at 4.21 ppm in ¹H NMR and at 38 ppm in ¹³C NMR. An additional methyl signal at 40 ppm pointed out towards the methylation of primary

sugar hydroxyl under the employed reaction conditions. The assignments were further confirmed by 2D NMR (¹H-¹³C HMQC) spectroscopy (Supplementary). ¹H NMR of **IL-2** was similar to that of **IL-1** except that it showed the disappearance of all acetate proton signals in the range 2.0-2.2 ppm, and the carbon signals from carbonyl and methyl in ¹³CNMR spectrum. Unlike **IL-1** and **IL-2**, the methylation of **12** occurred with addition of two methyl groups at *N*-1 and *N*-3 nitrogen of triazole ring and not at C-6 hydroxyl of sugar giving **IL-3**. This was evident from the lack of N-H stretching frequency peak in the IR spectra (Supplementary). The quaternary C-atom in position 4 of the 1,2,3-triazole ring shifted upfield from (144-145) ppm to 139.5 ppm when triazole was transformed to the corresponding 1,2,3-triazolium salt in all the three ILs. Likewise, as expected a downfield shift of 6-10 ppm was observed in tertiary C-atom in position 5 on transforming triazole to triazolium IL.

In an attempt to find new applications of these novel ILs in synthesis, preliminary study involving amination of iodo-, bromo-, and chlorobenzene with aqueous ammonia catalyzed by copper(I) iodide in ionic liquids IL-1, IL-2, and IL-3 using different co-solvents was explored. It was observed that in the absence of ionic liquid, amination did not occur at all in THF alone indicating that IL was indispensible for the reaction (Table 1, entry 4). Further of the three ILs, IL-2 showed maximum efficiency in promoting amination compared to IL-1 and IL-3 (Table 1, entries 1, 10, 11). The higher efficiency of IL-2 may be attributed to the free hydroxyl groups of pyranose sugar that help in stabilizing copper(I) intermediate by forming a stable chelate. Ability of sugars and amino sugars to act as ligands for copper catalyzed aniline synthesis has recently been reported.^{6a,17} Further, it was found that amination of iodobenzene in THF at 60 °C, THF at 90 °C and THF-H₂O at 90 °C with CuI (20 mol%) and glucose added externally (20 mol%) as a ligand gave aniline in only 5%, 10%, and 15% yields respectively (Table 1, entry 5, 6, 7). This clearly demonstrates that tethering of glucose to triazolium core facilitates a homogeneous catalytic reaction by bringing the substrate, reagent and catalyst in the same phase. Initially, the intention of adding a co-solvent to IL was simply to reduce the viscosity of the reaction media, and allow a more efficient stirring of the reactants. However, the nature of co-solvent played a considerable role in controlling the reaction yield. The yield of aminated product based on cosolvent followed the order THF \approx DMSO > EtOH-H₂O (1:1) > CH₃CN > H₂O (Table 1, entries 1, 14, 15, 16, 17). Of all the solvents tested, THF was the co-solvent of choice since it could be

easily removed during work-up leaving behind the amine in IL which could be easily extracted using IL immiscible organic solvent such as hexane-ethyl acetate mixture. In contrast, DMSO which also gave the aminated product in similar yield as THF was avoided since water miscible ILs could not be recovered and reused after aqueous work-up with DMSO. As expected, reactivity of halides for amination followed the order iodo- > bromo- > chloro- (Table 2, entry 1, 12, 13). Further studies exploring the scope and versatility of this system for amination with different substrates are underway.

After completion of reaction, the products were extracted with diethyl ether leaving behind catalyst in IL. The immobilized copper in IL, however, was found to be inactive when used as such for the next batch of amination. The obvious logic therefore was to recover and reuse IL. To accomplish the same, recovered CuI-IL system was diluted with methanol, and inactive copper catalyst was removed by centrifugation. Removal of methanol under reduced pressure yielded back the IL whose reusability for amination was tested by addition of a fresh lot of CuI to the reaction mixture. The yield of amine after first and second recycle was found to be 70 and 64% respectively (Table 1, entry 1).

1,2,3-triazolium ionic liquids with sugar at 1,4-position have been synthesized using click chemistry. These compounds are the first example of low cost carbohydrate based ILs containing a triazolium cation. Screening of these ILs for Cu(I) catalyzed amination reveals that they act as reusable coordinating solvents and ligands that help in promoting amination of simple iodo, bromo, and chloro benzene under mild conditions in the order IL-2 > IL-1 > IL-3. The higher activity of IL-2 towards amination may be due to the free hydroxyl groups on pyranose sugar responsible for imparting high stability to Cu(I) species during the reaction. Since these ILs contain chiral sugar unit, their application in asymmetric reactions is in progress.

Acknowledgments

This work has been financially supported by the Department of Science and Technology, India under the project RP02555. A. S. thanks the Council of Scientific and Industrial Research, India for graduate fellowship.

Supporting Information

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tetlet.2013.02.022

References and notes

- a) Petkovic, M.; Seddon, K. R.; Rebelo, L. P. N.; Pereira, C. S. *Chem. Soc. Rev.* 2011, 40, 1383; b) Davis, J. H. Jr. *Chem. Lett.* 2004, 33, 1072; c) Jain, N.; Kumar A.; Chauhan S.; Chauhan S. M. S. *Tetrahedron* 2005, 61, 1015; d) Hallett, J. P.; Welton, T. *Chem. Rev.* 2011, 111, 3508; e) Sheldon, R. *Chem. Commun.* 2001, 2399.
- a) De Maria, P. D. Angew. Chem. Int. Ed. 2008, 47, 6960; b) Ohno, H.; Fukumoto, K. Acc. Chem. Res. 2007, 40, 1122; c) Plechkova, N. V.; Seddon, K. R. Chem. Soc. Rev. 2008, 37, 123; d) Parvulescu, V. I.; Hardacre, C. Chem. Rev. 2007, 107, 2615.
- a) Ahrens, S.; Peritz, A.; Strassner, T. Angew. Chem. Int. Ed. 2009, 48, 7908; b) Wulf, A.; Fumino, K.; Ludwig, R. Angew. Chem. Int. Ed. 2010, 49, 449; c) Forsyth, S. A.; Frohlich, U.; Goodrich, P.; Gunaratne, H. Q. N.; Hardacre, C.; McKeown, A.; Seddon, K. R. New J. Chem. 2010, 34, 723; d) Ma, Q.; Sun, S.; Meng, X.-B.; Li, Q.; Li, S.-C.; Li, Z.-J. J. Org. Chem. 2011, 76, 5652.
- 4. a) Miao, W.; Chan, T. H. Acc. Chem. Res. 2006, 39, 897; b) Mehnert, C. P. Chem. Eur. J. 2005, 11, 50; c) Miao, C.-X.; He, L.-N.; Wang J.-Q. Adv. Synth. Catal. 2009, 351, 2209; d) Miao, W.; Chan, T. H. Adv. Synth. Catal. 2006, 348, 1711; e) Yao, Q.; Sheets, M. J. Organomet. Chem. 2005, 690, 3577; f) Leger, B.; Denicourt-Nowicki, A.; Olivier-Bourbigou, H.; Roucoux, A. Tetrahedron Lett. 2009, 50, 6531; g) Itoh, H.; Naka, K.; Chujo, Y. J. Am. Chem. Soc. 2004, 126, 3026.
- a) Gausepohl, R.; Buskens, P.; Kleinen, J.; Bruckmann, A.; Lehmann, C. W.; Klankermayer, J.; Leitner, W. Angew. Chem. Int. Ed. 2006, 45, 3689; b) Malhotra, S. V.; Wang, Y. *Tetrahedron: Asymmetry*, 2006, 17, 1032; c) Ding, J.; Desikan, V.; Han, X.; Xiao, T. L.; Ding, R.; Jenks, W. S.; Armstrong, D. W. Org. Lett. 2005, 7, 335; d) Baudequin, C.; Bregeon, D.; Levillain, J.; Guillen, F.; Plaquevent, J.-C.; Gaumont, A.-C. *Tetrahedron: Asymmetry* 2005, 16, 3921; e) Luo, S. Z.; Mi, X. L.; Zhang, L.; Liu, S.; Xu, H.; Cheng, J. P. Angew. Chem. Int. Ed. 2006, 45, 3093.

6. a) Thakur, K. G.; Srinivas, K. S.; Chiranjeevi, K.; Sekar, G. *Green Chem.* 2011, *13*, 2326;
b) Poletti, L.; Chiappe, C.; Lay, L.; Pieraccini, D.; Polito L.; Russo, G. *Green Chem.* 2007, *9*, 337; c) Kumar, V.; Olsen, C. E.; Schäffer, S. J. C.; Parmar, V. S.; Malhotra, S. V. *Org. Lett.* 2007, *9*, 3905; d) Van Buu, O. N.; Aupoix, A.; Vo-Thanh, G. *Tetrahedron* 2009, *65*, 2260; e) Thomas, M.; Rothman, L.; Hatcher, J.; Agarkar, P.; Ramkirath, R.; Lall-Ramnarine, S.; Engel,

R. *Synthesis* **2009**, *9*, 1437; f) Plaza, P. G. J.; Bhongade, B. A.; Singh, G. *Synlett* **2008**, 2973; g) Engel, R. In Ionic Liquids-Classes and Properties; Handy, S., Ed.; InTech, Available from: http://www.intechopen.com/books/ionic-liquids-classes-and-properties/glycoside-based-ionic-liquids, **2011**, pp 65-80.

- Yacob, Z.; Liebscher, J. In Ionic Liquids-Classes and Properties; Handy, S., Ed.; InTech, Available from: <u>http://www.intechopen.com/books/ionic-liquids-classes-and-properties/1-2-3-</u> triazolium-salts-as-a-versatile-new-class-of-ionic-liquids, 2011, pp 1-22.
- a) Meyer, D.; Strassner, T. J. Org. Chem. 2011, 76, 305; b) Tseng, M.-C.; Cheng, H.-T.; Shen, M.-J.; Chu, Y.-H. Org. Lett. 2011, 13, 4434; c) Wang, C.; Cui, G.; Luo, X.; Xu, Y.; Li, H.; Dai, S. J. Am. Chem. Soc. 2011, 133, 11916; d) Nulwala, H. B.; Tang, C. N.; Kail, B. W.; Damodaran, K.; Kaur, P.; Wickramanayake, S.; Shi, W.; Luebke, D. R. Green Chem., 2011, 13, 3345; (e) Khan, S. S.; Shah, J.; Liebscher, J. Tetrahedron 2011, 67, 1812.
- 9. a) Fei, Z.; Geldbach, T. J.; Zhao, D.; Dyson, P. J. Chem. Eur. J. 2006, 12, 2122; b) Bates, E. D.; Mayton, D.; Ntai, I.; Davis, J. H. J. Am. Chem. Soc. 2002, 124, 926; c) Wang, L.; Li, H.; Li, P. Tetrahedron 2009, 65, 364.
- a) Wasserscheid, P.; Keim, W. Angew. Chem. Int. Ed. 2000, 39, 3772; b) Dupont, J.; Scholten, J. D. Chem. Soc. Rev. 2010, 39, 1780; c) Vollmer, C.; Janiak C. Coor. Chem. Rev. 2011, 255, 2039; d) Dupont, J. Acc. Chem. Res. 2011, 44, 1223; e) Astruc, D.; Lu, F.; Aranzaes, J. R. Angew. Chem. Int. Ed. 2005, 44, 7852.
- 11. a) Meldal, M.; TornØe, C. W. *Chem. Rev.* 2008, *108*, 2952; b) Chattopadhyay, B.; Vera, C. I.
 R.; Chuprakov, S.; Gevorgyan, V. *Org. Lett.* 2010, *12*, 2166; c) Ackermann, L.; Potukuchi,
 H. K.; Landsberg, D.; Vicente, R. *Org. Lett.* 2008, *10*, 3081; d) Demko, Z. P.; Sharpless, K.
 B. *Angew. Chem. Int. Ed.* 2002, *41*, 2110.
- a) Shen, Q.; Hartwig, J. F. J. Am. Chem. Soc. 2006, 128, 10028; b) Lundgren, R. J.; Sappong-Kumankumah, A.; Stradiotto, M. Chem. Eur. J. 2010, 16, 1983; c) Yang, C.; Fu, Y.; Huang, Y.; Yi; Huang, J.; Guo, Q.; Liu, L. Angew. Chem. Int. Ed. 2009, 48, 7398; d) Wu, X.; Darcel, C. Eur. J. Org. Chem. 2009, 4753; e) Maejima, T.; Shimoda, Y.; Nozaki, K.; Mori, S.; Sawama, Y.; Monguchi, Y.; Sajiki, H. Tetrahedron 2012, 68, 1712.
- 13. a) Vo, G. D.; Hartwig, J. F. J. Am. Chem. Soc. 2009, 131, 11049; b) Surry, D. S.; Buchwald, S. L. J. Am. Chem. Soc. 2007, 129, 10354; c) Schulz, T.; Torbog, C.; Enthaler, S.; Schaffner, B.; Dumrath, A.; Spannenberg, A.; Neumann, H.; Borner, A.; Beller M. Chem. Eur. J. 2009,

15, 4528; d) Lundgren, R. J.; Peters, B. D; Alsaben, P. G.; Stradiotto, M. Angew. Chem. Int. Ed. 2010, 49, 4071.

- 14. a) Wang, D.; Cai, Q.; Ding, K. Adv. Synth. Catal. 2009, 351, 1722; b) Meng, F.; Zhu, X.; Li, Y.; Xie, J.; Wang, B.; Yao, J.; Wan, Y. Eur. J. Org. Chem. 2010, 6149; c) Kim, J.; Chang, S. Chem. Commun. 2008, 3052; (d) Xia, N.; Taillefer, M. Angew.Chem. Int. Ed. 2009, 48, 337; e) Xu, H.; Wolf, C. Chem. Commun. 2009, 3035; f) Jiang, L.; Lu, X.; Zhang, H., Jiang, Y., Ma, D. J. Org. Chem. 2009, 74, 4542.
- a) Gomez, A. M.; Company, M. D.; Valverde, S.; Lopez, J. C. Org. Lett. 2002, 4, 383; b)
 Cui, J.; Liu, A.; Guan, Y.; Zheng, J.; Shen, Z.; Wan, X. Langmuir 2010, 26, 3615; c) Lin, Y.
 A.; Chalker, J. M.; Davis, B. G. J. Am. Chem. Soc. 2010, 132, 16805; d) Kumar, R.; Maulik,
 P. R.; Misra, A. K. Glycoconj. J. 2008, 25, 595; e) Xu, H.-J.; Liang, Y.-F.; Cai, Z.-Y.; Qi, H.-X.; Yang, C.-Y.; Feng, Y.-S. J. Org. Chem. 2011, 76, 2296.
- 16. Hotha, S.; Kashyap, S. J. Org. Chem. 2006, 71, 364.
- 17. Thakur, K. G.; Ganapathy, D.; Sekar, G. Chem. Commun. 2011, 47, 5076.

Table 1

Influence of reaction conditions on amination.^a



] -	Solvent, aq. NH ₃ s K ₂ CO ₃ , IL1-IL3 ,	<u>90 °C</u> 20 h	
X=CI,	Br, I			
Entry	Х	Solvent	ΙL	Yield(%) ^b
1	Ι	THF	IL-2	$82 (70)^i (64)^j$
2	Ι	THF	IL-2	$30^{k}(80)^{l}(50)^{m}$
3	Ι	THF	IL-2	$70^{n}(80)^{o}$
4 ^c	Ι	THF	-	0
5 ^d	Ι	THF	-	5
6 ^e	Ι	THF	-	10
$7^{\rm f}$	Ι	THF-H ₂ O (1:1)	-	15
8 ^g	Ι	EtOH:H ₂ O (1:1)	-	5
$9^{\rm h}$	Ι	-	IL-2	50
10	Ι	THF	IL-1	45
11	Ι	THF	IL-3	5
12	Br	THF	IL-2	70
13	Cl	THF	IL-2	20
14	Ι	DMSO	IL-2	80
15	Ι	CH ₃ CN	IL-2	20
16	Ι	H_2O	IL-2	10
17	Ι	EtOH:H ₂ O (1:1)	IL-2	25

^aReaction Conditions: Aryl halide (0.5 mmol), Commercial 20% aq. NH₃ (0.75 mmol), CuI (0.1 mmol, 20 mol%), K₂CO₃ (1.5 mmol), IL (0.1 mmol, 20 mol%), 90 °C, 20 h, ^bIsolated yield, ^cNo IL, No Glucose, ^dNo IL, Glucose (20 mol%), Temperature (60 °C), ^eNo IL, Glucose (20 mol%), Temperature (90 °C), ^fNo IL, Glucose (20 mol%), 90 °C, ^gNo IL, Glucose (20 mol%), 90 °C, ^hNo Co-Solvent, ⁱYield after Ist recycle, ^jYield after 2nd recycle, ^kAt RT, ¹At 120 °C, ^mIL (0.05 mmol, 10 mol%), ⁿK₂CO₃ (1.0 mmol), ^oK₂CO₃ (2.0 mmol)

Legends:

Figure 1. Glucose-linked triazolium ionic liquids.

Scheme 1. Synthesis of (a) sugar alkyne and (b) sugar azide.

Scheme 2. Synthesis of glucose-linked triazolium ionic liquids.



Scheme 2.

Graphical Abstract

