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1,2,3-Triazolium Salts as a Versatile New Class of Ionic Liquids

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1. Introduction

Among the various classes of ionic liquids (ILs), those containing *N*-heterocyclic cations are most widely used. Imidazolium salts **1** (Figure 1) represent the most prominent subclass in this area and a number of them are commercially available. Their solvent properties such as melting points, solubility, and viscosity can easily be tuned in a wide range by varying the substituents at the nitrogen atoms as well as by varying the counter-ions. This makes ionic liquids in general, real designer solvents. Even if imidazolium salts have found very wide application in organic synthesis and catalysis, they have some limitations. One important limitation is that, they do not behave as innocent solvents under strongly basic conditions, where they suffer from deprotonation at carbon 2 leading to *N*-heterocyclic carbenes. 1,2,3-Triazolium salts **2** (Figure 1) lack an acidic ring-carbon flanked by two *N*-atoms, consequently they should be advantageous in this aspect. Surprisingly, unlike 1,2,4-triazolium salts, 1,2,3-triazolium salts were neglected as potential ionic liquids until recently. Even though the first examples of 1,2,3-triazolium salts had been known since 1887 (Zincke and Lawson 1887) they were not investigated for their ionic liquid properties. Prior to the first report on stable 1,3,4-trialkyl-1,2,3-triazolium-based ionic liquids 1,2,3-triazolium salts were only interesting when they bear 1-amino groups and contain oxygen-rich anions **3** (Figure 1) and thus can be utilized as highly energetic fuels (Drake, Kaplan et al. 2007). Here, a review is provided on the state of the art in the area of 1,2,3-triazolium salts as ionic liquids and ionic liquid tags for organocatalysts.

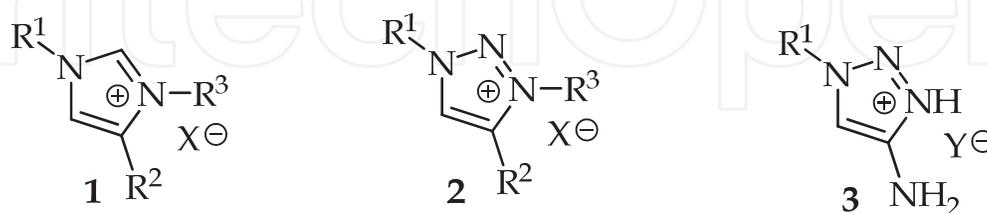


Fig. 1. General structure of common ionic liquids

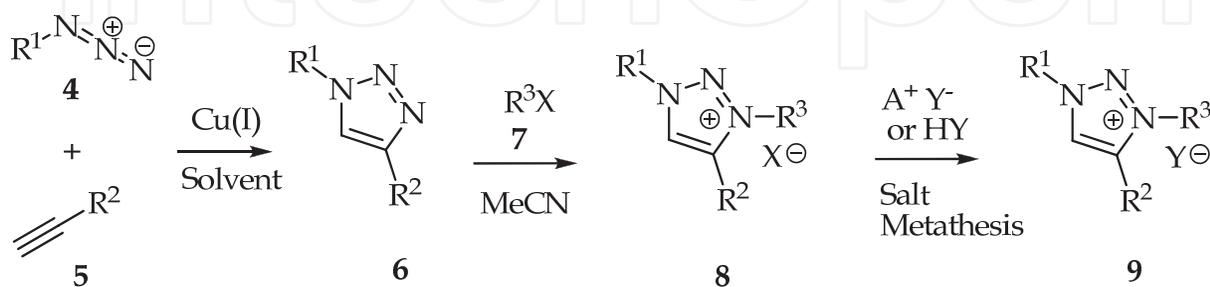
2. Synthesis of 1,2,3-triazolium ionic liquids

The syntheses of 1,2,3-triazolium salts consists of two major steps, which are: construction of the 1,2,3-triazole ring system and then its *N*-alkylation (Scheme 1). While 1-amino-1,2,3-

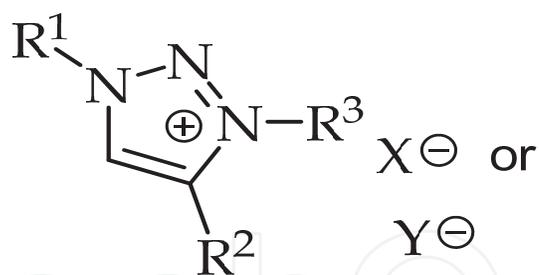
triazoles can be obtained by oxidation of glyoxal bishydrazones (Kaplan, Drake et al. 2005), the 1,4-disubstituted 1,2,3-triazoles are mostly synthesized by [3+2] cycloaddition reactions of azides **4** and terminal alkynes **5**. In the classical manner this reaction was performed as thermal 1,3-dipolar cycloaddition where it suffers from lack of regioselectivity. It gives rise to mixtures of 1,4- and 1,5-disubstituted products (Gompper 1957), which are difficult to separate. Nowadays, cycloaddition of azides and terminal alkynes is realized using metal catalysis with high regioselectivity and improved yields. Most frequently, Cu-catalysis (“Click”-chemistry) is used to synthesise 1,4-disubstituted 1,2,3-triazoles regioselectively. An alternative copper free methodology has also been developed primarily for the crosslinking of biomolecules. This reaction involves the use of strained cyclooctyne ring substituted with an electron-withdrawing group such as fluorine, which can promote a [3 + 2] dipolar cycloaddition with azides (Baskin, Prescher et al. 2007; Bernardin, Cazet et al. 2010; Debets, van Berkel et al. 2010). Regioselectivity of the cycloaddition of azides to alkynes can be changed to the 1,5-disubstituted 1,2,3-triazoles if Ru-catalysis is applied (Johansson, Lincoln et al. 2011; Zhang, Chen et al. 2005).

So far, only 1,4-disubstituted 1,2,3-triazoles were transformed into ionic liquids by further alkylation. Different systems such as Cu(I) salts with triphenylphosphine, with iminopyridine or with mono or polydentate nitrogen ligands, Cu(I) isonitrile complex in water (Liu and Reiser 2011), Cu(0) nanoclusters (Orgueira, Fokas et al. 2005; Pachon, van Maarseveen et al. 2005) and most commonly CuSO₄ with sodium ascorbate (Kolb, Finn et al. 2001) were applied in the click reaction between alkynes and azides to produce 1,4-disubstituted 1,2,3-triazoles regioselectively. Even though this reaction is often termed as “Click-reaction”, it is known for its extended reaction times, which can span from several hours to several days. In order to overcome this limitation it is often assisted by suitable ligands such as tris-(benzyltriazolylmethyl)amine (Chan, Hilgraf et al. 2004), triphenylphosphine or other amines.

The outstanding feature of the Cu-catalyzed cycloaddition of azides to alkynes in producing 1,2,3-triazoles is the fact that many functional groups can be tolerated. Hence, interesting functionalities can be incorporated as substituents of the resulting triazole ring. Additionally the access to 1,4-disubstituted 1,2,3-triazoles can be further facilitated by combing the synthesis of the organic azides (from a halogenated precursors and sodium azide) with the copper catalyzed click reaction in a one pot procedure. In this reaction, the copper catalyst facilitates both the replacement of the halide by the azide, and the subsequent [3+2]



Scheme 1. Synthesis of 1,3,4-trialkylated 1,2,3-triazolium ionic liquids.



R ¹	R ²	R ³	X or Y	Ref
<i>n</i> -Butyl	<i>n</i> -Butyl	Me	CF ₃ ,(MeO)PO ₃ , N(CN) ₂ or BF ₄	1
<i>n</i> -Butyl	<i>n</i> -Decyl	Me	MeSO ₄	1
Benzyl	<i>n</i> -Butyl	Me	I	1, 4
Benzyl	<i>n</i> -Pentyl	Me	TsO	1
Benzyl	CH ₂ OH	Me	I	1
Benzyl	(CH ₂) ₂ OH	Me	I	1
Benzyl		Me	I	1
4-Benzyloxybenzyl	<i>n</i> -Pentyl	Me	I	1
3-Methoxybenzyl	3-Phthalimido propyl	Et	Br	1
3-Methoxybenzyl		<i>n</i> -Pr	I	1
	<i>n</i> -Pentyl	Me	I	1
	Ph or <i>n</i> -Pentyl	Me	I	2
3-Phthalimidopropyl		Me	I	1
Benzyl	H	Me	NTf ₂ , OTf, PF ₆ or BF ₄	3
<i>n</i> -Butyl	H	Me	NTf ₂ , OTf, PF ₆ or BF ₄	3
<i>n</i> -Butyl	H	<i>n</i> -Butyl	NTf ₂ , OTf, PF ₆ or BF ₄	3
Allyl	<i>n</i> -Pentyl	Me	I	4

¹.(Khan, Hanelt et al. 2009), ²(Yacob, Shah et al. 2008) ³.(Jeong and Ryu 2010) ⁴.(Fletcher, Keeney et al. 2010)

Table 1. Some examples of 1,2,3-triazolium ionic liquids **9**

cycloaddition reaction. Remarkably, even iodoarenes which normally are unsuitable substrates for a nucleophilic substitution by azides can be transformed to the corresponding arylazides and further converted to 1-aryl-1,2,3-triazoles under these conditions (Fletcher, Keeney et al. 2010; Yan and Wang 2010).

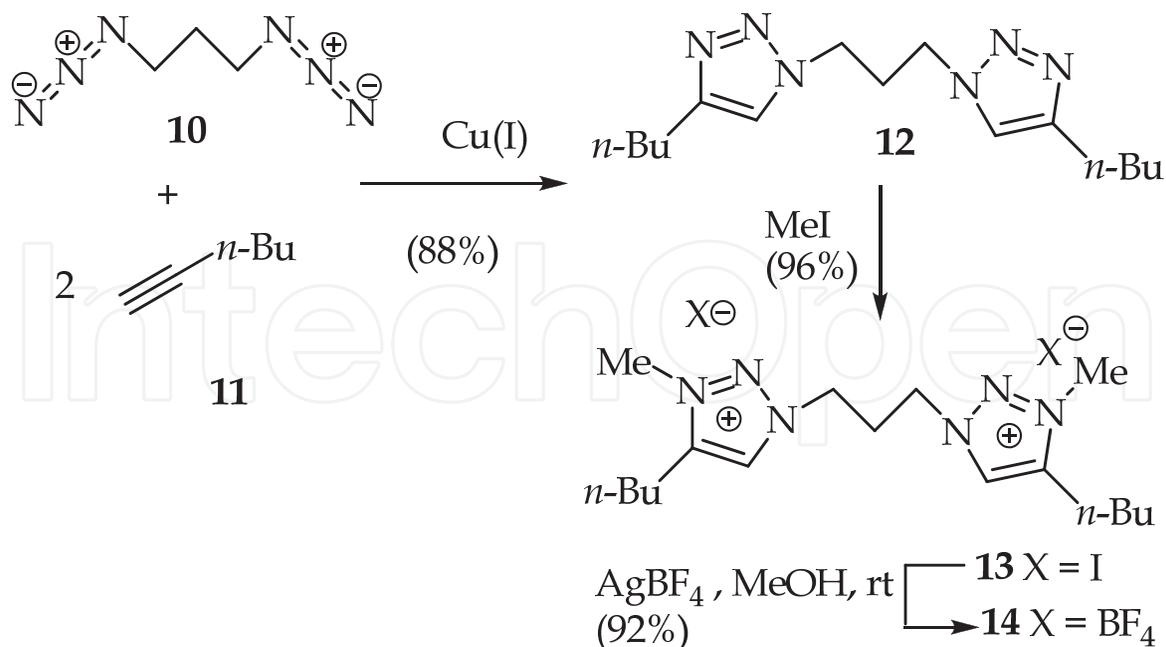
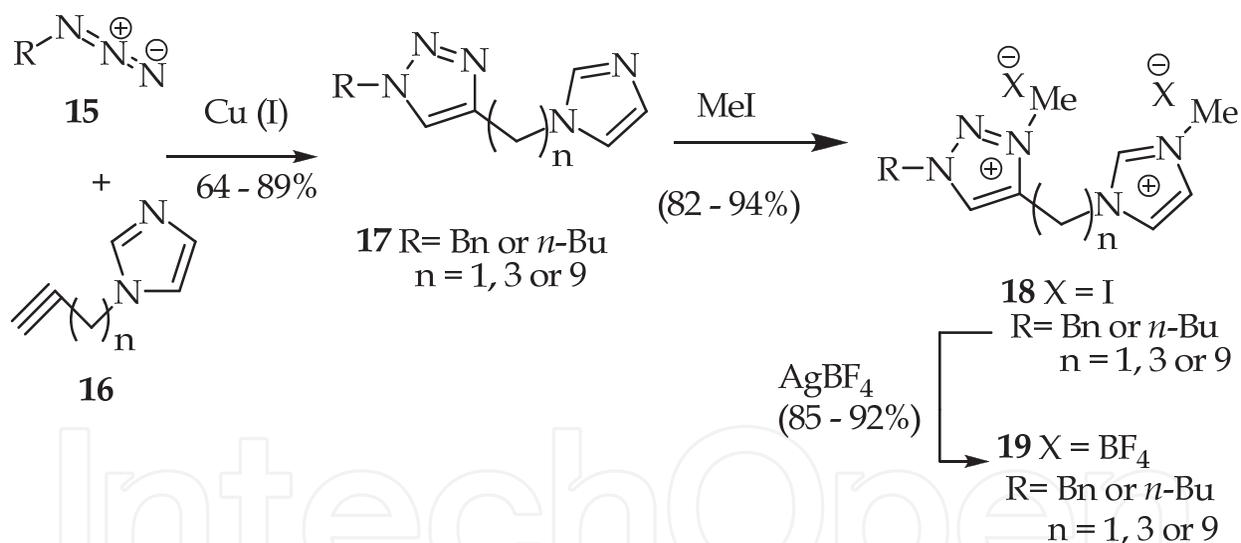
N-Alkylation as the second step in the synthesis of 1,2,3-triazolium salts can produce a 2-alkylated or 3-alkylated 1,4-disubstituted triazolium salt which can present a problem of regioselectivity. However, when 1,4-disubstituted 1,2,3-triazoles are alkylated by soft alkylating reagents **7** (alkyl-, benzyl-, allyl halides, sulphates and sulfonates) only 1,3,4-trisubstituted 1,2,3-triazolium salt products are obtained. Accordingly, both major steps in the synthesis of 1,2,3-triazolium salts can be performed in a highly regioselective manner (Begtrup 1971; Gompper 1957).

Purification of ionic liquids by conventional techniques can be a hideous process. Therefore, obtaining ionic liquids in a pure state from the alkylation reactions is an essential and straightforward alternative. In order to avoid impurities, it is important to start the alkylation reaction with pure 1,2,3-triazoles. Often the alkylation reactions are conducted without solvent. The alkylating agents are used in excess quantities and serve as solvents. The resulting 1,2,3-triazolium salts are obtained in a highly pure state by removal of the excess alkylating agent utilizing high vacuum and/or washing with non-polar solvents (such as diethyl ether or hexane) to remove nonpolar impurities as well. At this stage, when the leaving group of the alkylating reagent is considered as an unsuitable counter ion, it can be exchanged with another anion using salt metathesis (e.g. treatment with AgBF_4 or corresponding acids).

A few 4-amino substituted 1,2,3-triazolium salts **3** (Figure 1) without any alkyl group at the third *N*-atom were obtained by protonation of 1,4-substituted 1,2,3-triazole by an inorganic acid. These salts however may not be interesting as ionic liquid solvents in chemical transformations due to their extremely low stability. They can rather serve as high energetic substances (Drake, Hawkins et al. 2003).

In general, the synthesis of 1,2,3-triazolium-based ionic liquids has a wide scope and numerous functional groups can be introduced as substituents. When 1,2,3-triazolium ionic liquids with only two substituents namely at positions 1 and 3 are required, trimethylsilylethyne (TMS-ethyne) can be used for the click reaction and the TMS-group can be removed from the resulting 1,2,3-triazole by fluoride (Jeong and Ryu 2010; Khan, Shah et al. 2010). Alternatively calcium carbide (CaC_2) was used for the synthesis of 1-mono substituted 1,2,3-triazoles by click chemistry (Jiang, Kuang et al. 2009).

Ionic liquids in which a 1,2,3-triazolium moiety is linked to other 1,2,3-triazolium or imidazolium units by an alkylene bridge were synthesized (Schemes 2 and 3) utilizing copper catalyzed click reaction between appropriate precursors and final double *N*-alkylation (Khan, Shah et al. 2010). The compounds **14** and **19** were investigated as useful ligands in Pd-catalyzed Suzuki-Miyaura reaction. Here, the imidazolium moiety serves as a precursor of *N*-heterocyclic carbene ligand for Pd as in known cases where simple imidazolium salts were used (Mathews, Smith et al. 2000). Interestingly, the combination of an imidazolium and a 1,2,3-triazolium unit demonstrated a better performance than a single azolium salt or a dicationic salt where two imidazolium or two 1,2,3-triazolium units are found. Aryl chlorides, iodides and triflates turned out to be the best substrates for this new catalytic system.

Scheme 2. Synthesis of di-(1,2,3-triazolium) salts **13**, **14**Scheme 3. Synthesis of mixed imidazolium triazolium ionic liquids **18**, **19**

3. Properties of 1,2,3-triazolium ionic liquids

Most of the 1,2,3-triazolium based ionic liquids are room temperature ionic liquids (RTILs) (Fletcher, Keeney et al. 2010; Khan, Hanelt et al. 2009). So far, not so many physical constants have been reported. Viscosity measurements and differential thermogravimetry (TGA) measurements of some 1,3,4-trisubstituted 1,2,3-triazolium ionic liquids counter-ions (Jeong and Ryu 2010; Khan, Hanelt et al. 2009). These reports indicated good thermal stability up to 355 °C, which is strongly dependent on several variables such as the kind of counter-ion and the nature of substituents on the triazolium ring. One can tune the stability of 1,2,3-

triazolium ionic liquids by the choice of substituents and the anion. The 4-amino-1,2,3-triazolium salts **3** with oxygen-rich anions can be very unstable and possess high explosive nature. Therefore, they need to be handled with caution. In general 1,2,3-triazolium ionic liquids possess weaker thermal stabilities with the onset of decomposition occurring at about 100 °C when the counter-ions are iodide or TfO⁻ while salts with bulky anions such as bis(trifluoromethylsulfonyl)amide, hexafluorophosphate and tetrafluoroborate show much higher stabilities (Jeong and Ryu 2010; Khan, Hanelt et al. 2009).

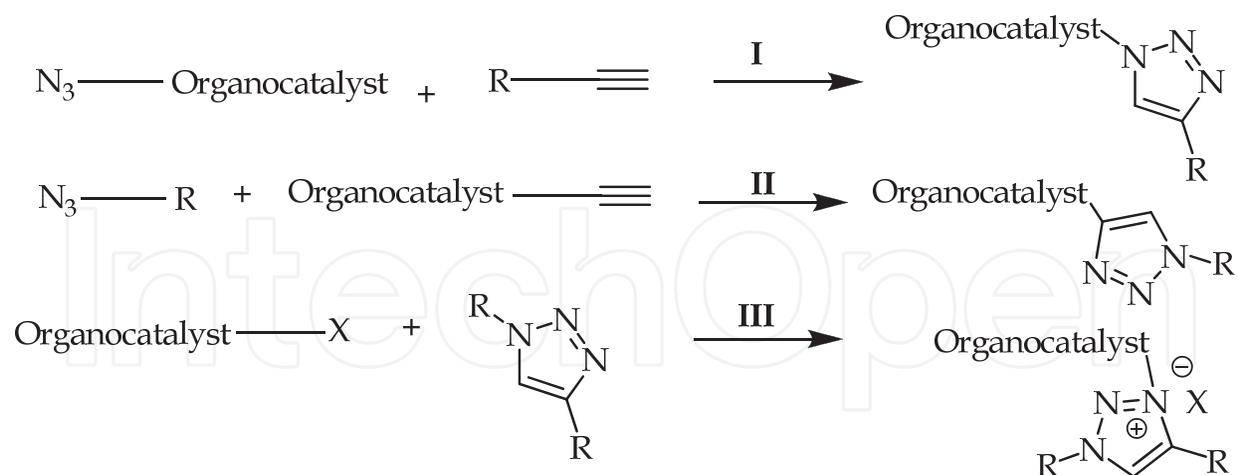
1,2,3-Triazolium salts are chemically relatively stable. However, nucleophilic displacement of the triazole ring by nucleophilic attack at an alkyl group in position 3 can occur in some cases. Furthermore, deprotonation at position 4 or 5 was observed with strong bases or under H-D exchange conditions. Remarkably, the formation of transition metal complexes was found recently wherein the triazolium unit was transformed into an *N*-heterocyclic carbene acting as a ligand for the corresponding metal. However, this deprotonation is much more difficult than in related imidazolium salts (Mathew, Neels et al. 2008, Guisado-Barrios, Bouffard et al. 2010)

4. Applications of 1,2,3-triazolium ionic liquids

Since 1,2,3-triazolium ionic liquids have not been commercially available, their application as mere solvent is rare. 1,3-Dialkyl-1,2,3-triazolium ionic liquids have been developed as stable and recyclable solvents for the Baylis-Hillman reaction. The Baylis-Hillman reaction between *p*-chlorobenzaldehyde and methyl acrylate was conducted in 1,2,3-triazolium ionic liquids at room temperature in the presence of DABCO. Interestingly the reaction furnished improved yields within shorter reaction time in the triazolium ionic liquids as compared to analogous imidazolium ionic liquids (Jeong and Ryu 2010).

4.1 Application of 1,2,3-triazolium ionic liquids in catalyst tagging

So far, the major field of application for 1,2,3-triazolium ionic liquids is in ionic liquid tagging of organocatalysts. In this recent methodology, ionic liquid moieties are covalently bonded to organocatalytic structures affording the so-called ionic liquid tagged organocatalysts (ILTOCs) (Sebesta, Kmentova et al. 2008). This strategy aims to better catalytic performance, better solubility and in particular easier recycling of catalysts. Unlike catalysts fixed on solid supports which are often insoluble in reaction media, ionic liquid tagged organocatalysts can be dissolved in various polar solvents and thus act as homogeneous catalysts. Recycling of the ionic liquid tagged organocatalysts is usually achieved by extracting the products from the reaction mixture using non-polar organic solvents. This leaves behind the ionic liquid tagged organocatalyst, which is eventually dissolved in an appropriate solvent or reagent for the next cycle. 1,2,3-Triazolium ionic liquid tagging is in particular useful because the key step in the synthesis of these catalysts (which is a copper-catalyzed cycloaddition of azides to alkynes) can tolerate many functional groups, amongst them are most of the organocatalytic moieties. Either the alkyne or the azido functionality can be introduced into the organocatalytic moiety enabling it to undergo a copper-catalyzed click reaction to establish the triazole tag. Alternatively, an alkylating function can also be tethered with the organocatalyst, which can later be used to alkylate a triazole thus forming the triazolium tag (Scheme 4).



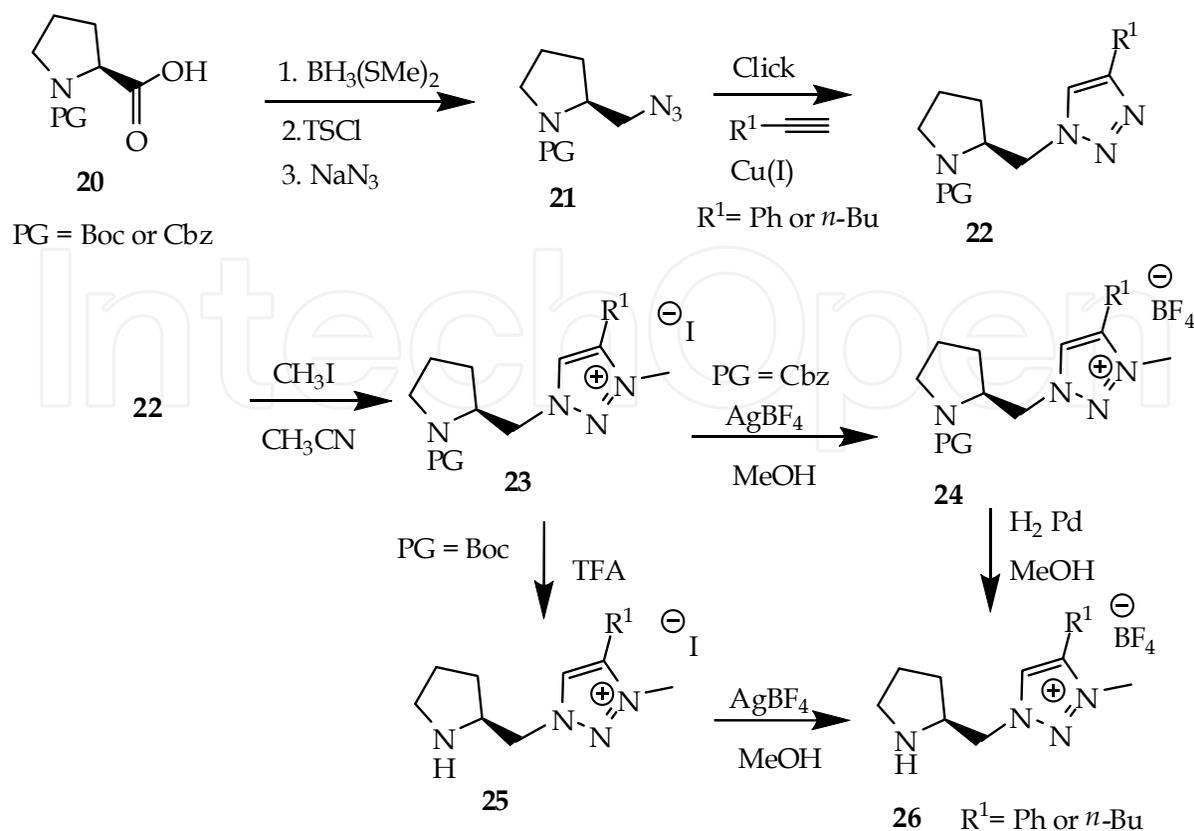
Scheme 4. Various approaches towards 1,2,3-triazolium ionic liquid tagged catalysts

Chiral 1,2,3-triazolium ionic liquid tethered pyrrolidine catalysts built from (*S*)-proline and its derivatives have been successfully applied in various catalytic reactions (Khan, Shah et al. 2010; Khan, Shah et al. 2010; Maltsev, Kucherenko et al. 2010; Yacob, Shah et al. 2008). The 1,2,3-triazolium ionic liquid-tagged organocatalysts derived from proline and its derivatives are mostly viscous liquids at room temperature and are completely miscible with polar solvents such as methanol, chloroform, acetonitrile, dimethylsulfoxide, dimethylformamide and water. They are insoluble in less-polar solvents such as *n*-hexane and diethyl ether. In some cases, the ionic liquid sub-unit serves not only as a phase tag for efficient recycling but also as an effective chiral amplifier through polar interactions and steric shielding.

1,2,3-Triazolium ionic liquid tethered pyrrolidine organocatalysts **25**, **26**, **30** – **32**, **38**, **44**, **48**–**50**, **58** were synthesised in a simple and versatile way from (*S*)-proline or *trans* 4-hydroxy-(*S*)-proline. The synthesis of these catalysts involves primarily the preparation of the corresponding azide and terminal alkyne derivatives for click cycloaddition reaction. The ionic liquid products were obtained quantitatively with a straightforward two-step procedure by *N*-alkylation of the click reaction products. The protecting groups are finally removed to liberate the target catalyst.

In the first approach (Scheme 5), the carboxyl group of (*S*)-proline was reduced to the corresponding alcohol. The resulting (*S*)-pyrrolidine-2-ylmethanol was transformed into tosylate and was substituted with azide resulting the (*S*)-pyrrolidine-2-ylazide following literature procedures (Luo, Xu et al. 2006). In this case, the (*S*)-proline served as an azide precursor of the click reaction to react with an alkyne. The resulting 1,2,3-triazol-1-yl-methylpyrrolidine **22** was transformed to an ionic liquid tagged catalyst by alkylation with methyl iodide. The exchange of the counter-ion iodide of catalyst **25** to tetrafluoroborate by anion metatheses using AgBF_4 furnished the respective ionic liquid-tagged organocatalysts **26** in quantitative yields (Scheme 5) (Yacob, Shah et al. 2008).

Catalytic application of the triazolium ionic liquid tagged organocatalysts **25** and **26** gave very interesting results in the Michael addition of various unmodified aldehydes and ketones to *trans*- β -nitrostyrenes. 10 mol % phenyl substituted ionic liquid tagged organocatalyst **25** provided excellent yields (>99%), diastereoselectivities (>99:1) and



Scheme 5. Synthesis of (*S*)-proline derived 1,2,3-triazolium ionic liquid tagged organocatalysts **25** and **26**

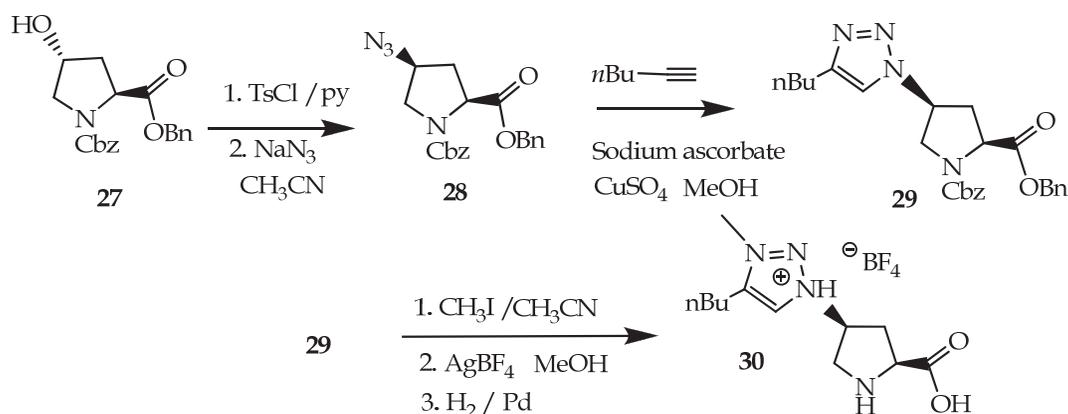
enantioselectivities (ee >99%) for the Michael addition of cyclohexanone to *trans*- β -nitrostyrene. The catalyst was recyclable by extraction of the reaction mixture with diethyl ether and usage of the remainder with a fresh batch of reactants. Recycling provided slightly decreasing yields with rapidly diminishing enantioselectivities and persistently high diastereoselectivities (> 93:7). The yields decreased from 99 % for the first run, to 90 % for the second run, 83 % for the third run and 74 % for the fourth run, but the enantioselectivities rapidly diminished (first run, 99%; second run, 90%; third run, 88 % and fourth run, 58 %) with identical duration of the reaction. Reduction of the amount of catalyst **25** to 5 mol % gave excellent yield (>95%), diastereoselectivity (97:3) and diminished enantioselectivity (ee 82%) after a slightly prolonged reaction duration.

Tetrafluoroborate based catalyst **26** demonstrate improved recyclability than those with iodide counter-ion. The recycling of these catalysts was carried out at least four times without sacrificing the yield or enantioselectivity (Yacob 2010).

The direct application of unmodified aldehydes in catalytic Michael additions can be severely hindered due to the presence of undesirable intermolecular self-aldol reactions (Hagiwara, Komatsubara et al. 2001; Hagiwara, Okabe et al. 2001). Barbas and co-workers achieved the first direct catalytic asymmetric Michael reaction between unmodified aldehydes and nitroolefins. The usage of an (*S*)-2-(morpholinomethyl) pyrrolidine catalyst in 20 % furnished the Michael addition products in 72 % enantioselectivity, 12:1 diastereoselectivity and 78 % yield (Betancort and Barbas 2001; Betancort, Sakthivel et al. 2004; Mosse, Andrey et al. 2006). The utilization of the ionic liquid tagged catalysts **25** and **26** in the Michael reactions of *trans*- β -nitrostyrenes to aldehydes resulted in high yields but

lower enantioselectivities. Isobutyraldehyde provided 95% yield, but the enantiomeric excess was 72%. Isovaleraldehyde resulted in high diastereoselectivity of 95:5 but it gave very low enantioselectivities (<45%). Acetone reacted comparatively faster to give high yield and enantioselectivity of 52%. Comparable results were obtained by Yan et al. with a non ionic trialkyl 1,2,3-triazolylmethylpyrrolidine catalyst (Yan, Niu et al. 2006). The reaction of cyclopentanone with *trans*- β -nitrostyrene gave a good yield of 85% and satisfactory enantioselectivity (ee 82%) but low diastereoselectivity (2:1). Cyclopentanone is known to be a less striking substrate for Michael additions to *trans*- β -nitrostyrene. It often gives enantioselectivity of around 50% and low yield products after prolonged reaction times (Betancort and Barbas 2001; Betancort, Sakthivel et al. 2001).

Another instance of 1,2,3-triazolium ionic liquid tagged proline was achieved utilizing *trans*-4-hydroxy-(*S*)-proline as the azide precursor for the click reaction (Shah, Khan et al. 2009). A *cis*-4-azido functionalized proline **28** was prepared by tosylating of a doubly protected *trans*-4-hydroxy (*S*)-proline **27** followed by a nucleophilic substitution using sodium azide. The Cu(I) catalyzed click reaction with 1-hexyne produced the *cis*-4-triazoyl substituted proline **29**. Alkylation with methyl iodide and salt metathesis with AgBF₄ resulted the ionic liquid tagged diprotected proline, which was deprotected by palladium catalyzed hydrogenation to give catalyst **30** (Scheme 6).

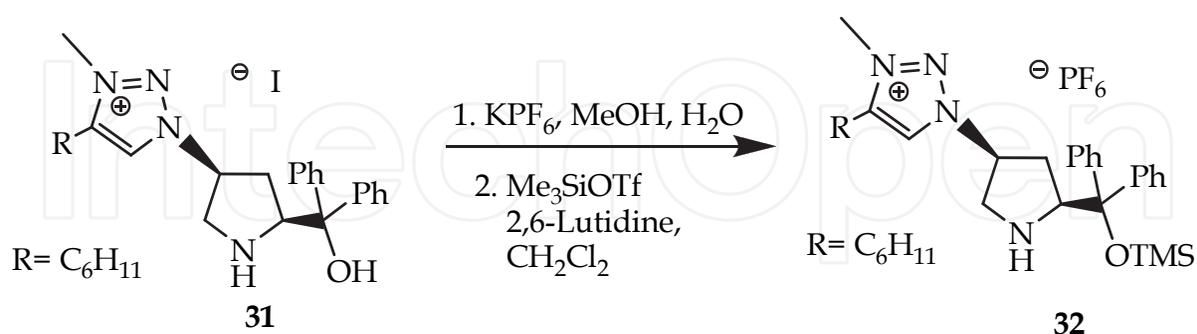


Scheme 6. Synthesis of *trans*-4-hydroxy-(*S*)-proline derived 1,2,3-triazolium ionic liquid tagged organocatalyst **30**

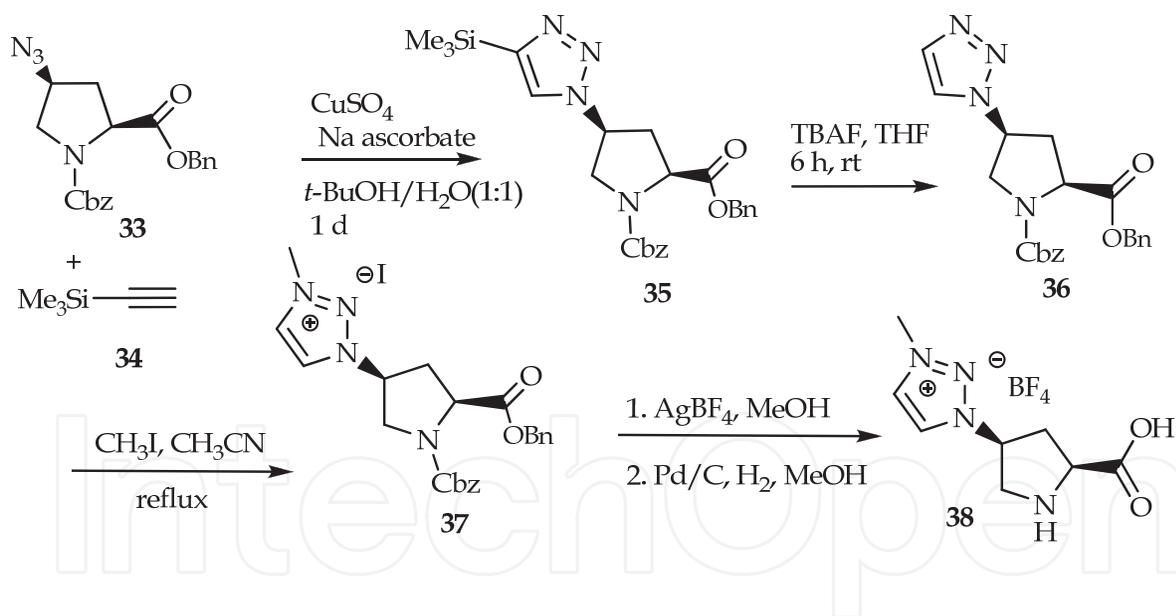
A similar approach was used to prepare α,α -diphenylprolinol derived ionic liquid tagged organocatalysts **31** and **32** (Maltsev, Kucherenko et al. 2010). The synthetic route starts with benzyl protected 4-hydroxydiphenylprolinol and goes through identical reaction conditions as for compound **30** indicated in Scheme 6. The 1,2,3-triazolium ionic liquid tagged catalyst was obtained after final reductive hydrogenation, anion metathesis and treatment with TMS-OTf (Scheme 7). These catalysts were applied in 0.1 equimolar quantities in a domino reaction involving aza-Michael and intramolecular acetalization, between *trans*-cinnamaldehyde and *N*-Cbz protected hydroxyl amines (Maltsev, Kucherenko et al. 2010).

The 4-unsubstituted 1,2,3-triazolium salt **38** was obtained using TMS-ethyne **34** as alkyne component in the reaction with the 4-azidoproline derivative **33** and a consecutive desilylation of the resulting TMS-triazole **35** by fluoride (Scheme 8). Independently of our work this strategy was also used to synthesize 1,3-dialkyl-1,2,3-triazolium salts as ionic liquid solvents useful for Baylis-Hillman reactions (Jeong and Ryu 2010). Catalyst **38**, which

lack a substituent in position 4 of the 1,2,3-triazole ring and thus is less lipophilic performed poorer as compared to catalyst **30**, resulting in 78% ee and 82% yield (Khan, Shah et al. 2011).

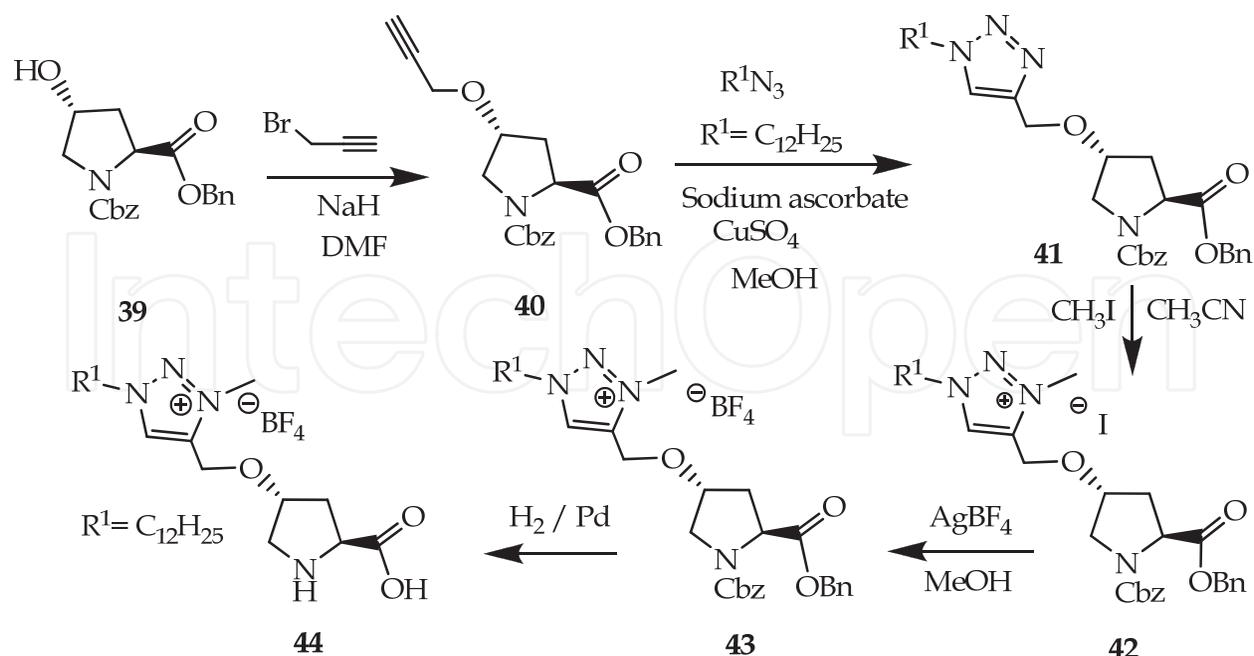


Scheme 7. Synthesis of α,α -diphenylprolinol derived ionic liquid tagged catalyst



Scheme 8. Synthesis of 4-unsubstituted 1,2,3-triazolium ionic liquid tagged (S)proline **38**

In a second approach, the (S)-proline derivative was used as the alkyne precursor in the click reaction. A propargyl subunit was introduced at the 4-hydroxy position of a diprotected *trans*-4-hydroxy proline **39** by means of Williamson ether synthesis. Click reaction with an alkyl azide furnished the triazole **41** in good yield. This product was transformed into the desired 1,2,3-triazolium ionic liquid tagged (S)-proline catalyst **44** by means of an analogous methylation, salt metathesis and a final removal of the protecting groups (Scheme 9) (Shah, Khan et al. 2009).

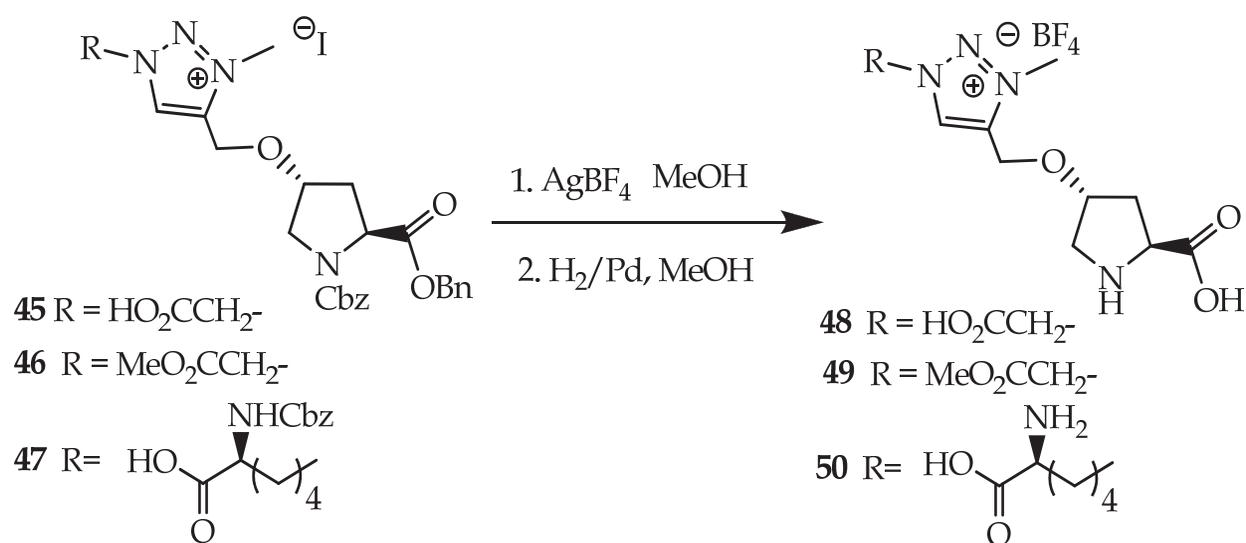


Scheme 9. Synthesis of *trans*-4-hydroxy (*S*)-proline derived 1,2,3-triazolium ionic liquid-tagged organocatalyst **44**

The application of 20 mol% *trans*-4-hydroxy-(*S*)-proline derived triazolium tagged catalysts **30** and **44** in a direct aldol reaction of aromatic aldehydes with acetone, cyclohexanone, or cyclopentanone resulted excellent diastereoselectivities and enantioselectivities (> 90%) (Shah, Khan et al. 2009). Cyclopentanone gave lower diastereoselectivities and enantioselectivities as compared with cyclohexanone. The application of catalyst **44** in the Michael addition of cyclohexanone to *trans*- β -nitrostyrene did not provide satisfactory results. The enantioselectivities found were low (<54 %) even if the reaction proceeded with high yields and good diastereoselectivities. The recycling experiments for the aldol reaction of cyclohexanone with 4-bromobenzaldehyde in the presence of excess cyclohexanone as solvent and 20 mol% of the catalyst were performed by extraction of the reaction mixture with diethyl ether or cyclohexane. The triazolium tagged organocatalyst remained in the reaction flask as an oil, which was combined with fresh reactants for the next cycle (Shah, Khan et al. 2009). High yields (> 80%) were achieved until the 5th cycle and the diastereoselectivity remained excellent. However, the enantioselectivity diminished with recycling, finally reaching 44% ee. Extraction with less polar cyclohexane gave better results in recycling experiments. Under these conditions, 88% yield with 68% ee and a diastereomeric ratio of 97:3 could be achieved in the 5th cycle. Unlike other reported recycling efforts in organocatalysis, there was still a drop in yields and enantioselectivities.

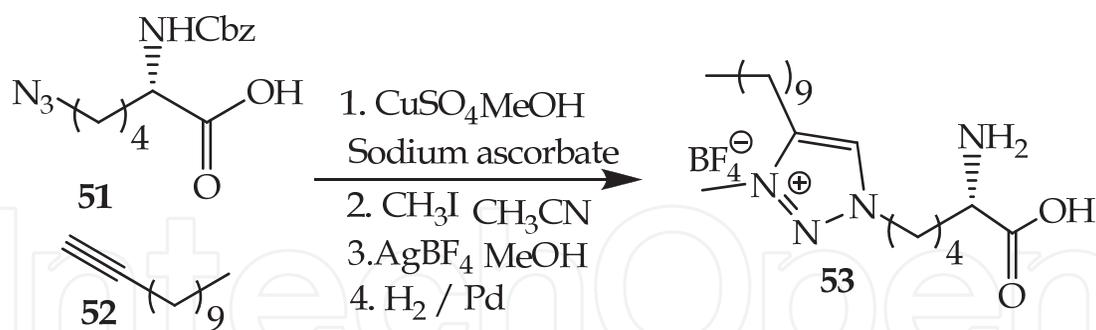
The aldol reactions were also performed in ionic liquid solvents namely *N,N*-diethyl-*N'*-hexyl-*N'*-methyl-*N''*,*N''*-dipropylguanidinium iodide and the commercially available 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] (Shah, Khan et al. 2009). Equimolar ratios of cyclohexanone and 4-bromobenzaldehyde were used and the reaction mixture was extracted with diethyl ether. The guanidinium salt gave improved results than the neat reaction. Application of the commercially available [bmim][BF₄] resulted in a rapidly diminishing enantioselectivity for the recycling.

The influence of other functional groups (such as a carboxyl moiety or an acyclic amino acid) on the performance of the ionic liquid tagged catalysts was investigated by introducing these functional groups as appendages on the 1,2,3-triazolium ionic liquid tags. Click reaction of diprotected *trans*-4-propargyloxyproline **40** with either azidoacetic acid, azidoacetic acid methylester or a lysine-derived azide give access to the 1,2,3-triazolium ionic liquid tagged catalyst precursors **48** - **50** with additional functional groups. The synthesis involved similar steps as the one indicated in Scheme 9. A final anion metathesis using silver tetrafluoroborate and palladium catalyzed hydrogenative deprotection furnished the required triazolium tetrafluoroborates **48** - **50** as oils. The Cbz-protective group of the side chain in the triazolium iodide **47** was also removed during the final reduction step providing the product **50** which has two unprotected α -amino acids (Scheme 10).



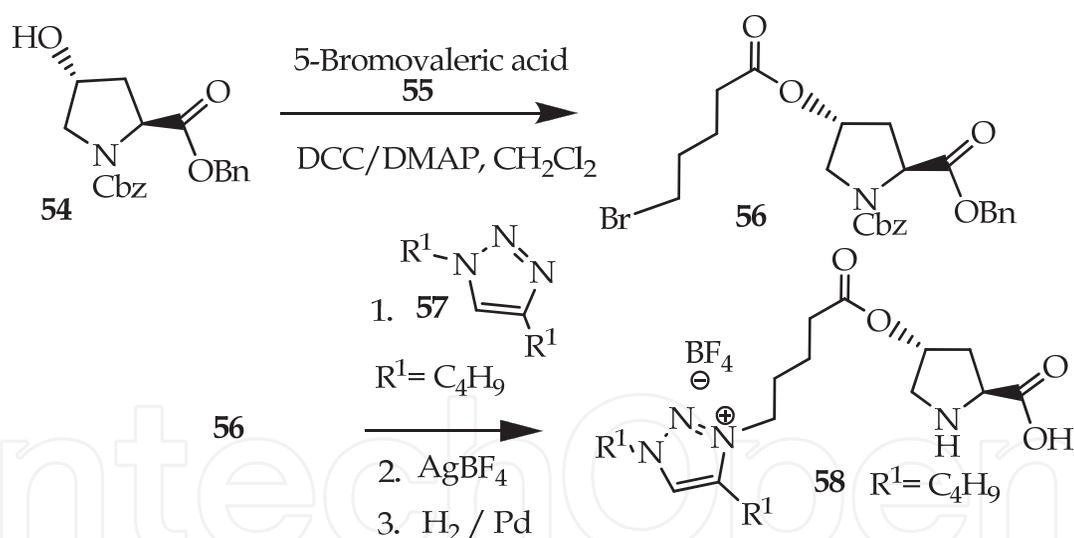
Scheme 10. Synthesis of *trans*-4-hydroxy(*S*)-proline derived functionalized 1,2,3-triazolium ionic liquid tagged catalysts.

In the α -aminoxylation of cyclohexanone with nitrosobenzene using [bmim][BF₄] as an ionic liquid solvent at room temperature, the lipophilic dodecyl 1,2,3-triazolium ionic liquid tagged catalyst **44** gave a high enantioselectivity 96%. However, the short chain carboxylate containing catalyst **49** gave 8% enantioselectivity and the carboxylic acid containing catalyst **48** provided 10% enantioselectivity. Placing an additional α -amino acid moiety in the side chain of the 1,2,3-triazolium salt **50** had a disadvantageous effect resulting in only 52% ee. By means of an analogous reaction sequence an acyclic 1,2,3-triazolium tetrafluoroborate tagged catalyst **53** was synthesised starting from lysine derivative **51** and 1-dodecyne **52** (Scheme 11). The product was obtained as a colourless solid (mp 91 °C). A similar Cu-catalyzed cycloaddition was reported for the synthesis and biochemical application of a lower homologue of **53** (Gajewski, Seaver et al. 2007). Unexpectedly, the triazolium ionic liquid tagged catalyst **53** wherein a noncyclic α -amino acid unit was found instead of proline failed to give any enantioselectivity. However, this catalyst gave good results in aldol reactions (Khan, Shah et al. 2010).



Scheme 11. Synthesis of (*S*)-lysine derived 1,2,3-triazolium ionic liquid tagged catalyst **53**

1,2,3-Triazolium ionic liquid tagged proline in which, the ionic liquid tag is several carbon atoms away from the pyrrolidine sub-unit was realized by transforming the diprotected proline into an alkylating agent **56**. The esterification of the 4-hydroxy group of a diprotected *trans*-4-hydroxy (*S*)-proline **54** with 5-bromovaleric acid **55** resulted in the bromo substituted ester **56**. This molecule was used in the alkylation of 1,4-dibutyl-1,2,3-triazole **57** to obtain the required ionic liquid tagged diprotected proline. Salt metathesis with AgBF_4 and hydrogenative deprotection of the triazolium bromide lead to the triazolium tagged proline organocatalyst **58** (Scheme 12).



Scheme 12. Synthesis of (*S*)-proline derived 1,2,3-triazolium ionic liquid tagged catalyst **58**

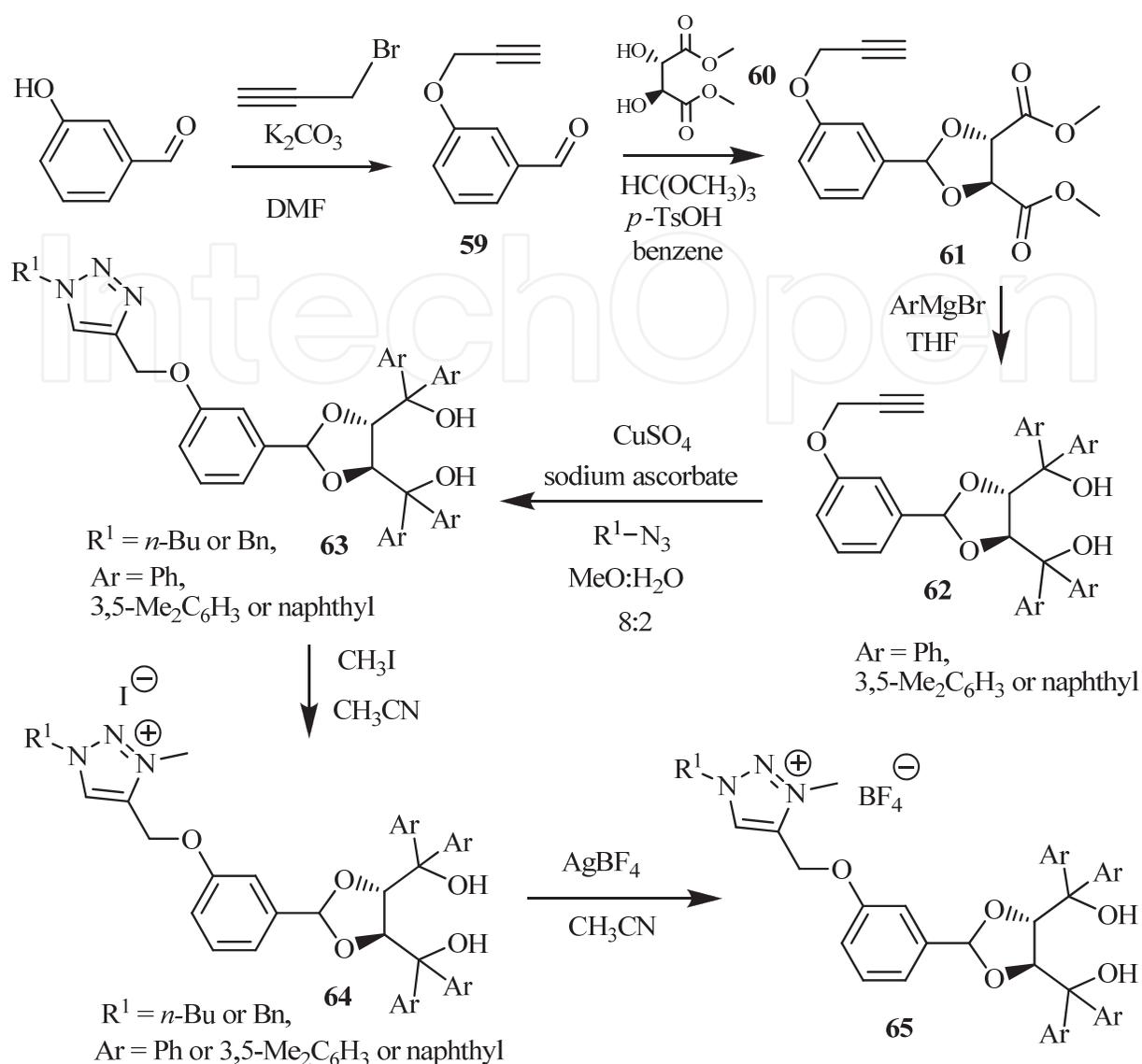
The deprotection of the Cbz-protecting group from some of the ionic liquid tagged catalyst precursors by reductive hydrogenation using palladium was found to be problematic. In cases where iodide was the counter ion it showed no selectivity between benzyloxycarbonyl protecting groups and benzyl substituents eventually found at the 1,2,3-triazolium rings. The reduction reaction was unsuccessful when iodide is found as counter-ion probably due to poisoning of the palladium surface. In these cases exchange of iodide by tetrafluoroborate was essential for the palladium-catalyzed reductive deprotection to take place. Thus anion metathesis is used not only to vary the physical properties of the ionic liquid such as viscosity and melting points but also to facilitate the deprotection reaction.

The α -aminoxylations of carbonyl compounds with nitrosobenzene was also investigated using catalyst **30** and analogous 4-hydroxy-(*S*)-proline derived catalyst (where the counter-anion is triflate) resulting from alkylation with MeOTf and lysine derived 1,2,3-triazolium tagged catalysts. All the ionic liquid tagged catalysts were screened in the α -aminoxylation of cyclohexanone with nitrosobenzene using [bmim][BF₄] as ionic liquid solvent at room temperature. The 1,2,3-triazolium tagged proline tetrafluoroborate **32** gave superior enantioselectivity (>99%) and yield (91%). These results are better than reported in cases where simple (*S*)-proline was used (Sunden, Dahlin et al. 2005). Exchanging the anion with triflate resulted in a somewhat lower enantioselectivity (92%). A less lipophilic triazolium-tagged proline lacking a substituent at carbon 4 of the 1,2,3-triazole ring surprisingly demonstrated lower performance of 78% enantioselectivity and 82% yield after prolonged reaction time. Another 4-hydroxy-(*S*)-proline derived catalyst with three ionic liquid-tags provided only 50% ee (Khan, Shah et al. 2011).

Another interesting types of catalysts, which can be tethered with 1,2,3-triazolium based ionic liquids are TADDOLs ($\alpha,\alpha',\alpha',\alpha'$ -tetraaryl-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol). TADDOLs are among the most prominent chiral scaffolds used as metal ligands in chiral Lewis acid catalysis and as organocatalysts in hydrogen bonding catalysis. In the latter case TADDOLs can activate carbonyl compounds and imines by decreasing the LUMO energy through hydrogen-bonding interaction with the carbonyl oxygen atom or imine nitrogen atom, respectively. The activated carbonyl compounds or imines can undergo highly enantiofacial addition of carbon nucleophiles to furnish the corresponding alcohols and amines with excellent stereoselectivities (Huang and Rawal 2002).

The synthesis of hitherto unknown 1,2,3-triazolium core ionic liquid tagged TADDOL catalysts was achieved using commercially available *L*-(+)-tartaric acid dimethyl ester and relevant carbonyl compounds (Scheme 13) (Yacob 2010). The synthesis starts with the reaction between *L*-(+)-tartaric acid dimethyl ester and a carbonyl compound to furnish the dioxolane ring. This step is crucial in binding the two chiral centres of the TADDOL which render it the ability to induce chirality. The resulting ester is then treated with aryl Grignard reagents to furnish the tetraaryl dimethanol.

As a common practice, TADDOLs are often tethered through position 2 of the dioxolane ring. This keeps the tethered entry far from the two active tetraaryl dimethanol units. The functional groups necessary for the tethering can be introduced relatively easily and at earlier stages of the synthesis. Other sites on TADDOL can influence the catalytic activity by either steric congestion or permanently altering its stereochemistry (Seebach, Beck et al. 2001). Thus the synthesis of 1,2,3-triazolium ionic liquid tagged TADDOL organocatalysts **64** – **65** was achieved starting from 3-hydroxybenzaldehyde (Yacob 2010). Treatment of 3-hydroxybenzaldehyde with propargyl bromide in the suspension of potassium carbonate gave the 3-propargyloxybenzaldehyde **59**. Reaction of **59** with *L*-(+)-tartaric acid dimethyl ester **60** in the presence of excess trimethylorthoformate catalyzed by a small quantity of *p*-toluenesulfonic acid furnished the intended dioxolane **61** (Scheme 13). Grignard reaction was employed to introduce the necessary aromatic sub-units with moderate yields. The Cu (I) catalyzed click reaction of **62** with butyl or benzyl azide furnished the triazole compounds **63** in good yields. The 1,2,3-triazolium ionic liquid tags were finally prepared from these triazolyl tethered TADDOLs **63** by a straight forward alkylation and salt metathesis using methyl iodide and silver tetrafluoroborate, respectively. Investigations of the application of the new ionic liquid tagged TADDOLs **65** are currently underway.



Scheme 13. Synthesis of 1,2,3-triazolium ionic liquid tagged TADDOL catalysts

Although in general the performance of 1,2,3-triazolium tagged organocatalysts in asymmetric syntheses was often excellent their behaviour in recycling experiments still needs some improvement because yields and enantioselectivities decreased after several runs. Leaching of the ionic liquid tagged organocatalysts can cause this effect. In cases of enamine activation by proline-derived ionic liquid tagged organocatalysts also trapping by oxazolidine formation (Khan, Shah et al. 2011) and in the light of recent findings of Maltsev et al. on the deactivation of ionic liquid tagged Jørgensen-Hayashi-type catalysts in asymmetric Michael reactions an oxidation of oxazoline or enamine intermediates can be responsible for the deactivation of the catalyst. While this phenomenon does not give a great effect in a single organocatalyzed reaction, it becomes crucial when the organocatalyst is repeatedly used after recycling. As shown by the same group oxidative poisoning of the ionic liquid tagged organocatalysts could be circumvented by working under oxygen free conditions (Maltsev, Chizhov et al. 2011). It seems to be worthy to examine the applications of 1,2,3-triazolium-based ionic liquid tagged organocatalysts in organocatalyzed reaction

running via intermediate enamines under oxygen free conditions because a better performance can be expected after recycling.

Very recently, transition metal complexes were reported where 1,2,3-triazolium salts served as precursors for 1,2,3-triazolylidene ligands (Mathew, Neels et al. 2008). However, application of these carbene complexes as catalysts in organic synthesis has not been reported so far. We tried to apply an in situ procedure in Suzuki reaction using $\text{Pd}_2(\text{dba})_3$, 1,2,3-triazolium salts and CsCO_3 as base expecting formation of corresponding palladium-triazolydene complexes as catalytic species. However, the outcome of these reactions was not satisfactory neither when ligand precursors were used wherein two triazolium units were tethered to each other. However, the combination of a 1,2,3-triazolium- and a imidazolium unit **18** and **19** (Scheme 3) provided good results in Suzuki reactions. It can be assumed that the imidazolium unit is deprotonated in this case rather than the triazole moiety thus giving imidazolydene ligands for the Pd. Remarkably, the combination of one 1,2,3-triazolium with one imidazolium salt performed much better than two imidazolium units in one compound showing the synergistic effect exerted by the triazolium moiety (Khan, Hanelt et al. 2009).

5. Miscellaneous

In a very unique approach cyano substituted triazolate based ionic liquids were prepared by exchanging the anions in common ionic liquids such as [emim][I], [empyrr][I] or [epy][I] with silver 4,5-dicyano-triazolate in water. Here the triazolate ring serves as a counter-anion with delocalized negative charge, and results in a diminished cation-anion interaction due to its decreased charge density. Hence, there is a decrease in the viscosity of the resulting ionic liquids as compared to those with iodide counter-ions (Kitaoka, Nobuoka et al. 2010).

6. Summary

1,2,3-Triazolium salts as a new class of ionic liquid can be prepared with a wide scope by Cu(I)-catalyzed cycloaddition of terminal alkynes and azides followed by *N*-alkylation and eventual salt metathesis. This synthesis tolerates many functional groups and is therefore in particular important for developing functionalized ionic liquids. In this area already a number of successful applications in asymmetric catalysis were reported wherein organocatalysts with 1,2,3-triazolium tags gave higher yields and stereoselectivities than the bare organocatalyst. Recycling and re-usage of ionic liquid tagged organocatalysts was possible by extraction of reaction products with nonpolar solvents. The catalytic performance was found to be reproducible for a number of cycles.

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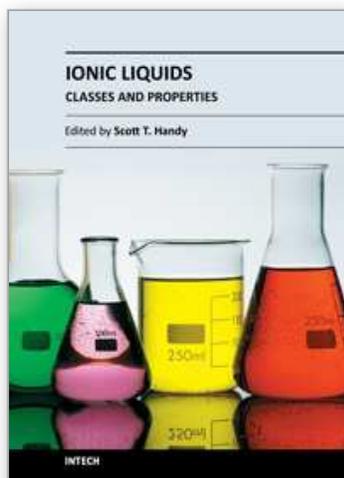
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Ionic Liquids - Classes and Properties

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Room temperature ionic liquids (RTILs) are an interesting and valuable family of compounds. Although they are all salts, their components can vary considerably, including imidazolium, pyridinium, ammonium, phosphonium, thiazolium, and triazolium cations. In general, these cations have been combined with weakly coordinating anions. Common examples include tetrafluoroborate, hexafluorophosphate, triflate, triflimide, and dicyanamide. The list of possible anionic components continues to grow at a rapid rate. Besides exploring new anionic and cation components, another active and important area of research is the determination and prediction of their physical properties, particularly since their unusual and tunable properties are so often mentioned as being one of the key advantages of RTILs over conventional solvents. Despite impressive progress, much work remains before the true power of RTILs as designer solvents (i.e. predictable selection of a particular RTIL for any given application) can be effectively harnessed.

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