

Chapter 4

Use of Ionic Liquids and DES for Synthesis of Medicinally Important 1,2,3-Triazole Scaffolds

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ABSTRACT

Cu catalysed azide alkyne cycloaddition reactions, known as click reactions, result in the regioselective formation of 1,4 disubstituted 1,2,3-triazoles. 1,2,3-triazoles are five membered nitrogen containing heterocycles that have gained much importance in recent times due to their various applications such as anti-cancer, anti- TB etc.

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Several greener approaches have been developed by different researchers to prepare 1,2,3-triazoles using benign methodologies. Greener solvents like Deep Eutectic Solvents (DES) and Ionic Liquids (IL) can serve as good alternative for volatile organic solvents used during azide alkyne cycloaddition reactions

INTRODUCTION TO GREEN SOLVENTS

Green solvents are environmentally friendly, sustainable solvents that minimize the hazard of using conventional organic solvents that are harmful to human health and the environment. Conventional solvents are found to be volatile, flammable, carcinogenic and toxic. (Khandelwal, Tailor, & Kumar, 2016) Green solvents are prime alternatives to volatile organic solvents and almost practically reduce chemical waste. Ionic Liquids (ILs) and Deep Eutectic Solvents (DES) are examples of such solvents that are considered 'Green'. Extensive research works have been on going on such green solvents for the past few decades.

ILs are green solvents made up of a discrete (Abbott, Capper, Davies, & Rasheed, 2004) bigger organic cation and a smaller organic or inorganic anion that stay liquid at ambient temperature and cannot form a lattice. They can be designed and tuned to meet the necessity of a reaction, and hence, they are called designer solvents or task-specific solvents. Changing anion-cation combinations of ionic liquids also changes their physicochemical properties. (Clarke, Tu, Levers, Brohl, & Hallett, 2018) ILs are ion conducting, viscous, non-volatile and non-flammable. Hence their application has been seen in various fields such as solar industry, catalysis, separation medium and elements of electrochemical devices. (Abbott, Capper, Davies, & Rasheed, 2004) The low vapour pressure of the ILs infer the electrostatic interaction between the oppositely charged ions. ILs have great chemical stability and low volatility. Hence, they are found to be of very little environmental concern. Most common ILs are made up of quaternary ammonium cations such as of pyridinium, imidazolium, dimethylethylphenylammonium salts and some polyatomic anions such as $[\text{BF}_4]^-$, $[\text{PF}_6]^-$ etc. (Gabriel & Weiner, 1888) or halide ions such as Cl^- , Br^- etc. These ILs can be recycled and reused after an organic reaction is performed.

The very initial concept of IL was given by Gabriel and Weiner in 1888 with the synthesis of ethanolanmonium nitrate. (Gabriel & Weiner, 1888) Succeeding that, the synthesis of ethylammonium nitrate in 1914 by Paul Walden[5] marked the beginning of different approaches to design ILs. It was the first Room Temperature IL (RTIL) prepared by reacting HNO_3 and $\text{C}_2\text{H}_5\text{NH}_2$. As the IL designed by Walden was very unstable and explosive, later scientists discovered new methods to prepare stable, non-volatile, low-vapour pressure, non-toxic ILs. The 1st generation ILs were introduced in the year 1970 by Osteryoung *et al.* which were about AlCl_3 and the

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