Nitrogen Functionalization with 2-Azido-1,3-dimethylimidazolinium Salts

2-Azido-1,3-dimethylimidazolinium salts 1 were found to be used for various nitrogen functionalization such as amination (N1 introduction), diazo-transfer reaction (N2 introduction), and azide-transfer reaction (N3 introduction).1–5 2-Azido-1,3-dimethylimidazolinium chloride (ADMC 1a) and its corresponding hexafluorophosphate (ADMP 1b) reacted with 1,3-dicarbonyl compounds under mild basic conditions to give 2-diazo-1,3-dicarbonyl compounds in high yields, which are easily isolated because the by-products are highly soluble in water. Naphthols also reacted with ADMC 1a to give corresponding diazonaphthoquinones (DNQ).

Furthermore, ADMP 1b shows efficient diazo-transfer ability to primary amines even without the aid of a metal salt such as Cu(II). Using this diazotization approach, various alkyl/aryl azides were obtained directly from corresponding primary amines. In addition, 2-azido-1,3-dimethylimidazolinium salts 1 were found to be employed as azide-transfer and amination reagents.

In the presentation, synthetic utility of DNQ will be also discussed.