

Towards predictable application of *N*-heterocyclic carbenes in catalysis: Correlating structure, properties and catalytic efficacy

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Ideally, the most appropriate *N*-heterocyclic carbene catalyst for a given process could be designed based on the relationship between the catalyst's (physicochemical) properties and that required for the reaction in question. The laborious screening currently required demonstrates this is yet to be realised. This presentation will focus on the potential to correlate catalyst structure to nucleophilicity and catalyst efficacy. The use of the acidity of the corresponding azolium salts as an indirect measure (the Brønsted relationship,¹ Equation 1) for a suite of ca. 70 systems (Figure 1) will be discussed, particularly in terms of control of nucleophilicity through variation of structure.² Preliminary studies of the determination of relative nucleophilicities through competition experiments (Equation 2) we have developed³ and comparison to existing techniques will be highlighted.

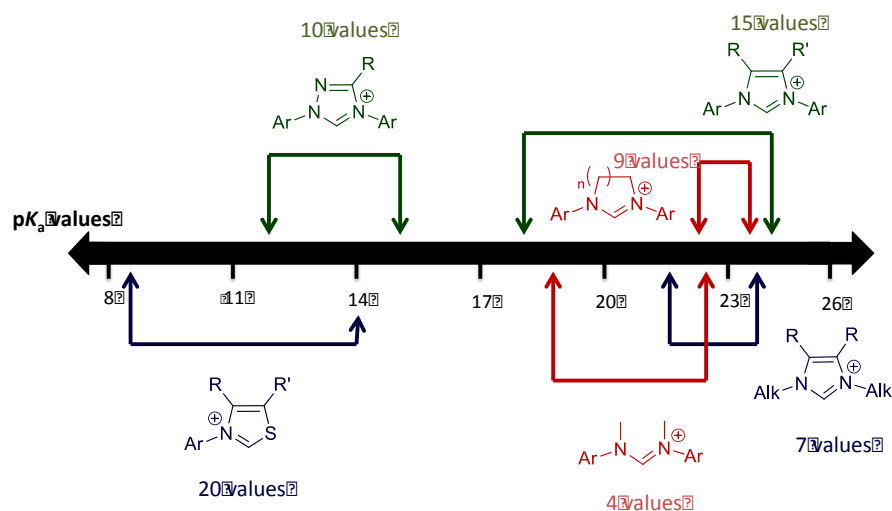


Figure 1. A pK_a scale, showing the range of acidities in DMSO covered by azolium (and related) salts.

$$\log(k) = \beta_{\text{Nuc}} pK_a + \log(C) \quad (1) \quad \frac{\ln\left(\frac{x_1}{x_{1,t=0}}\right)}{\ln\left(\frac{x_2}{x_{2,t=0}}\right)} = \frac{k_1}{k_2} = f(x) \Rightarrow N_1 = N_2 + \frac{\log(f(x))}{S_N} \quad (2)$$

1. *Modern Physical Organic Chemistry*, by E. V. Anslyn and D. A. Dougherty, University Science Books, 2006, Sausalito, CA, USA
2. Dunn, M. H., *Ph.D. Thesis*, University of New South Wales, 2015.
3. Yau, H. M.; Croft, A. K.; Harper, J. B. *Chem. Commun.* **2012**, *48*, 8937.