

On New N-Heterocyclic Carbene Derived Alkylidene Imidazolines

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Selected NMR Spectra

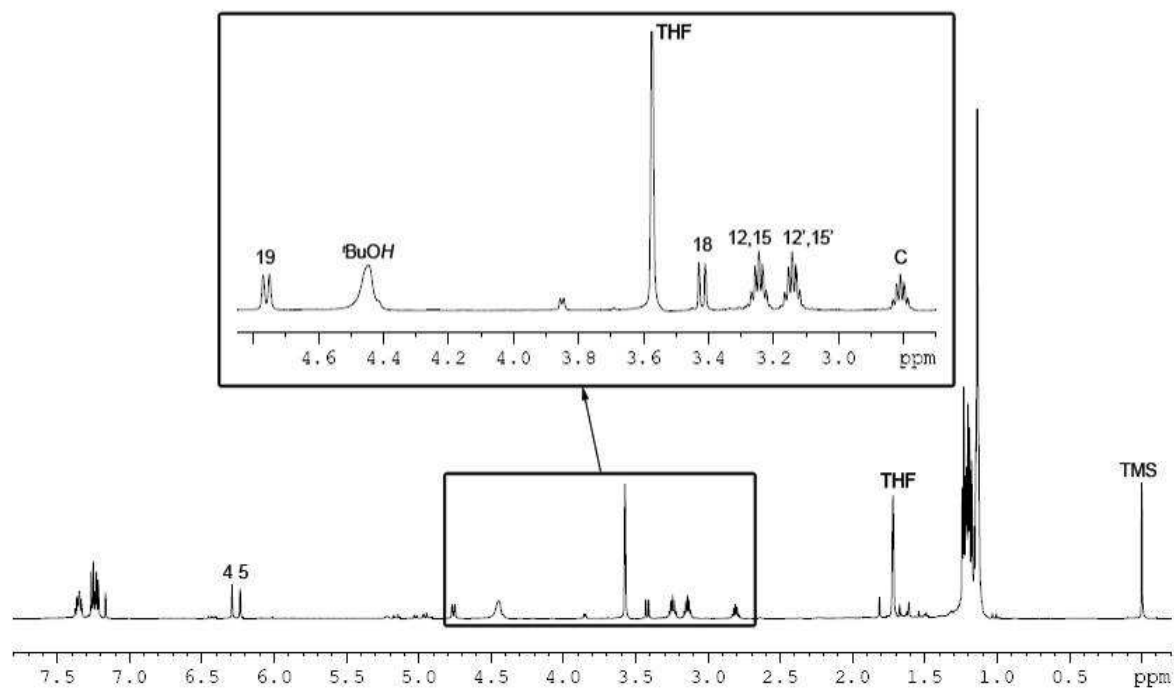


Figure S1: ¹H NMR of compound 5

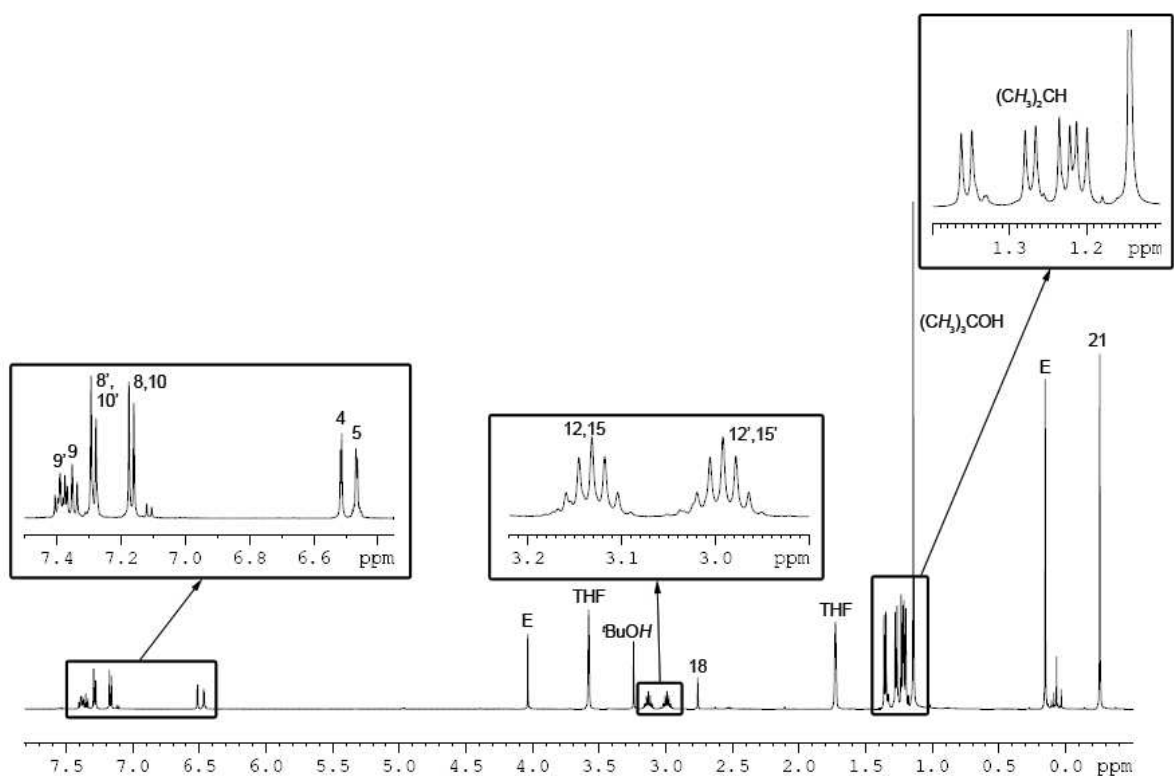


Figure S2: ¹H NMR of compound 6 (signals assigned with "E" belong to the electrophile, here: trimethylsilylpropargyl bromide)

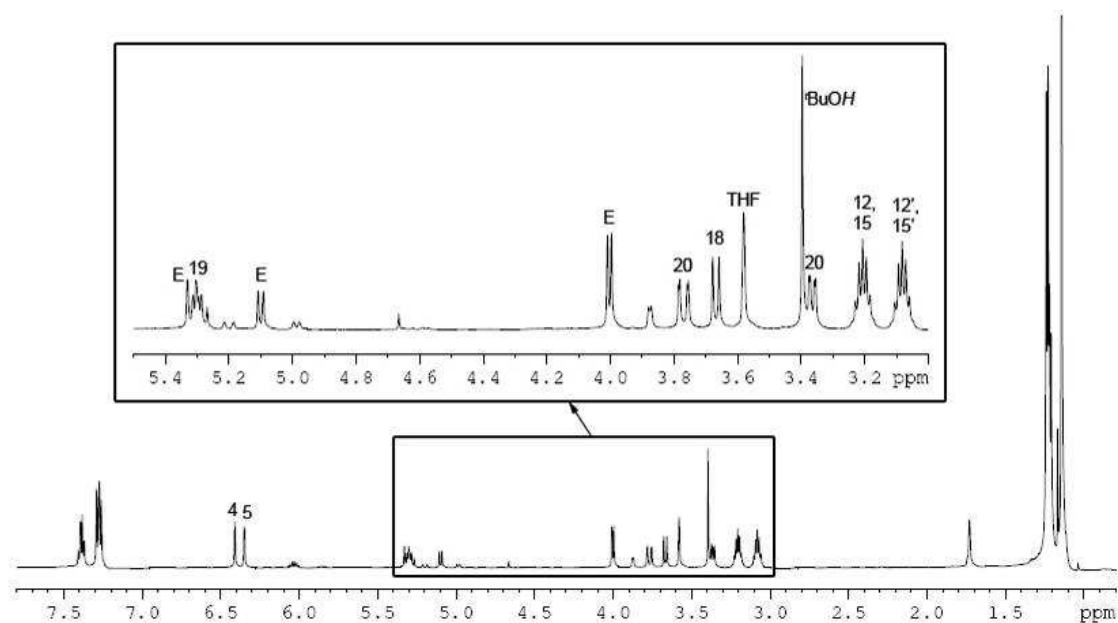


Figure S3: ¹H NMR of compound 8

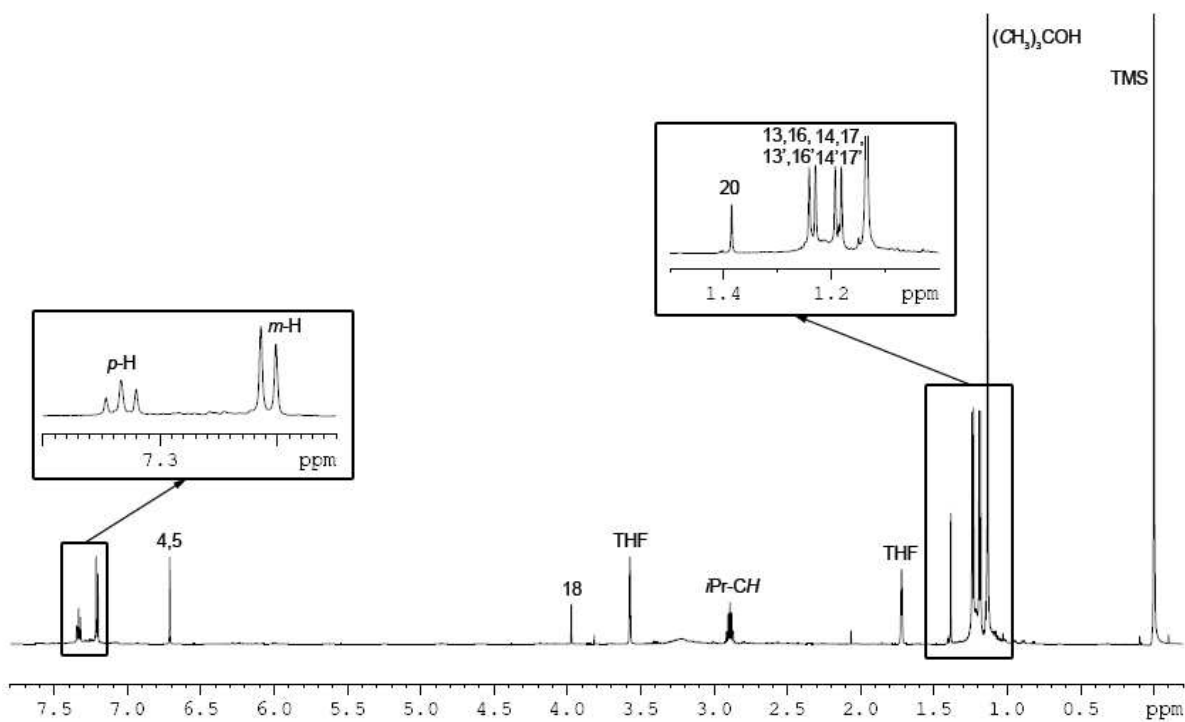


Figure S4: ¹H NMR of compound 9

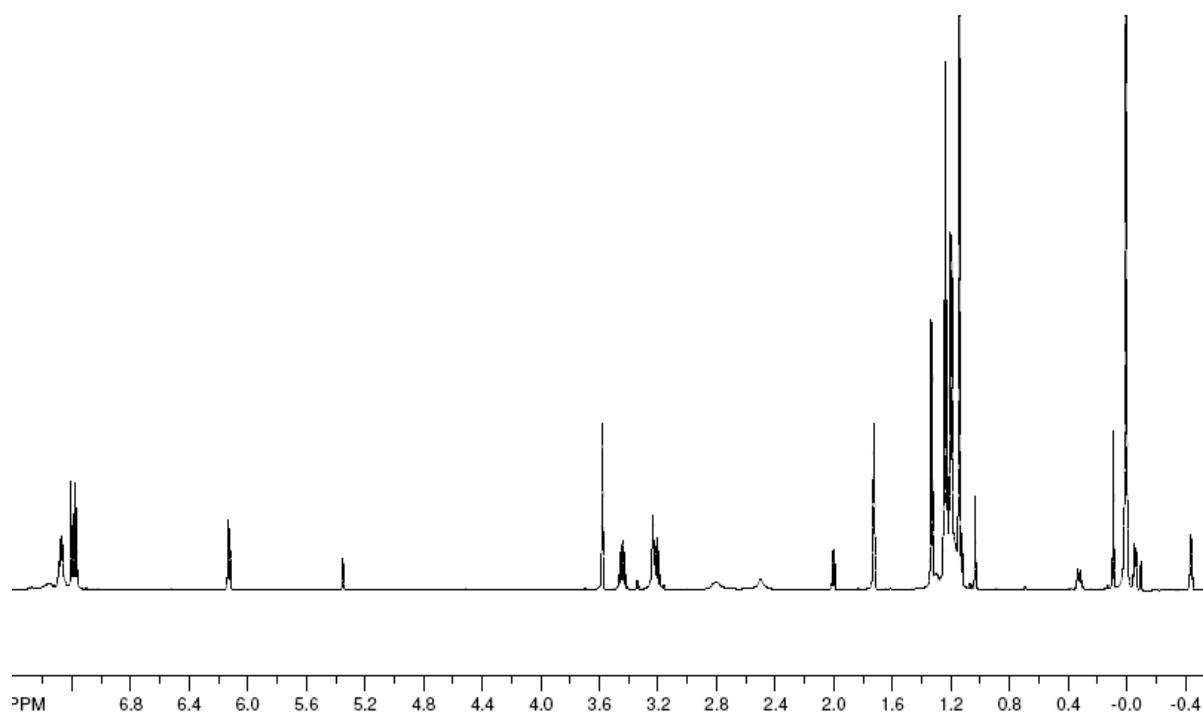


Figure S5: ^1H NMR of compound **10**

UV/Vis Investigation

UV/Vis spectroscopy showed nearly the same absorption maxima (230-238 nm) for *p*-methylbenzyl bromide, carbene **2**, and imidazolium salt **3**. Enediamine **4** exhibited a strong red-shifted band at 350 nm.

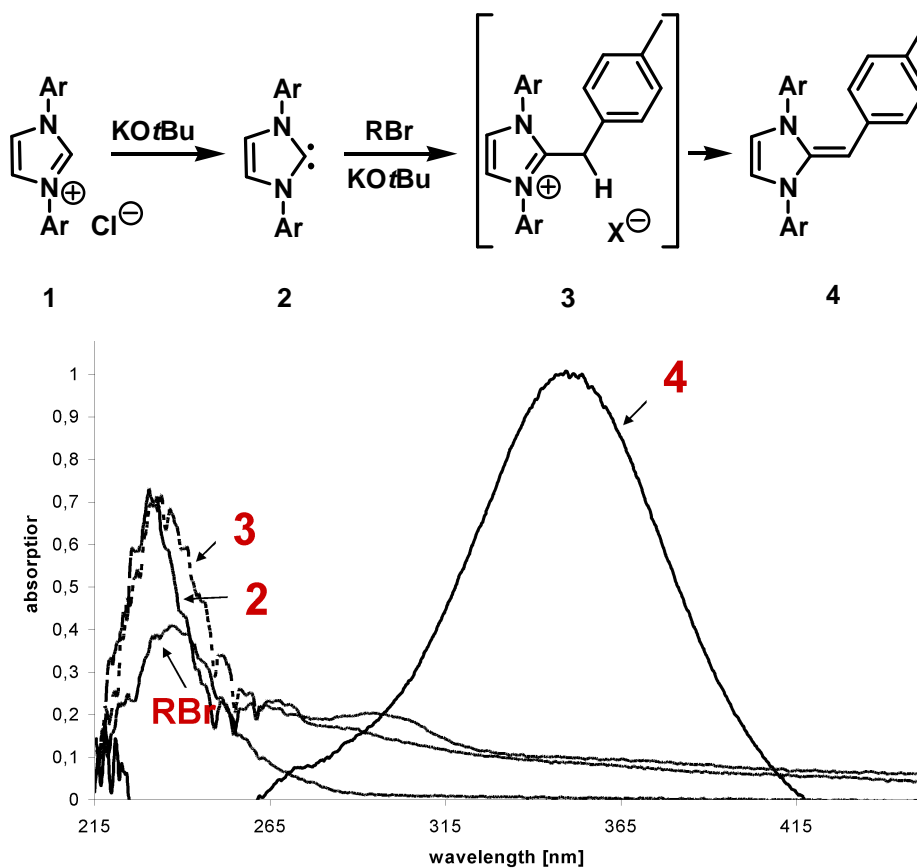


Figure S6: UV/Vis spectra of carbene **2**, imidazolium iodide **3**, enediamine **4** and *p*-methylbenzyl bromide (RBr). Ar = 2,6-diisopropylphenyl.

Crystal Structures

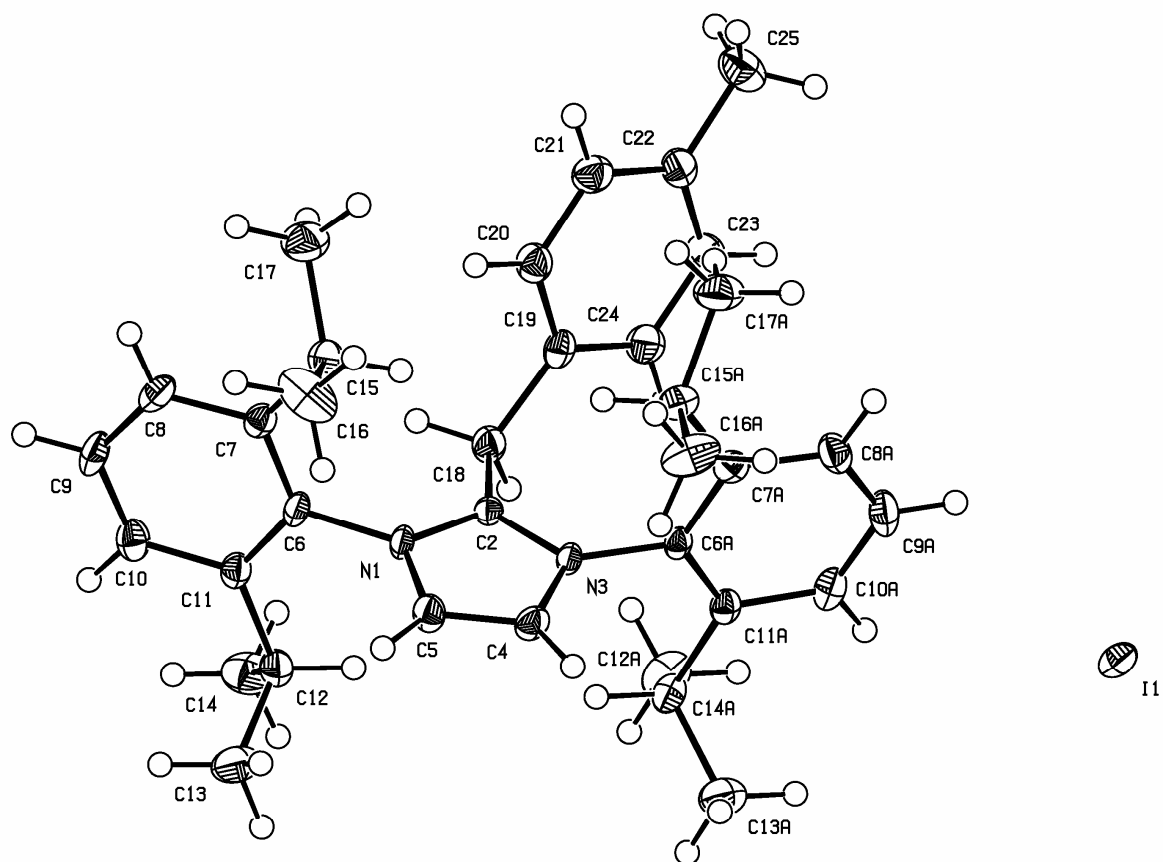


Figure S7: Crystal structure of imidazolium iodide **3** (ellipsoids at 50% probability).

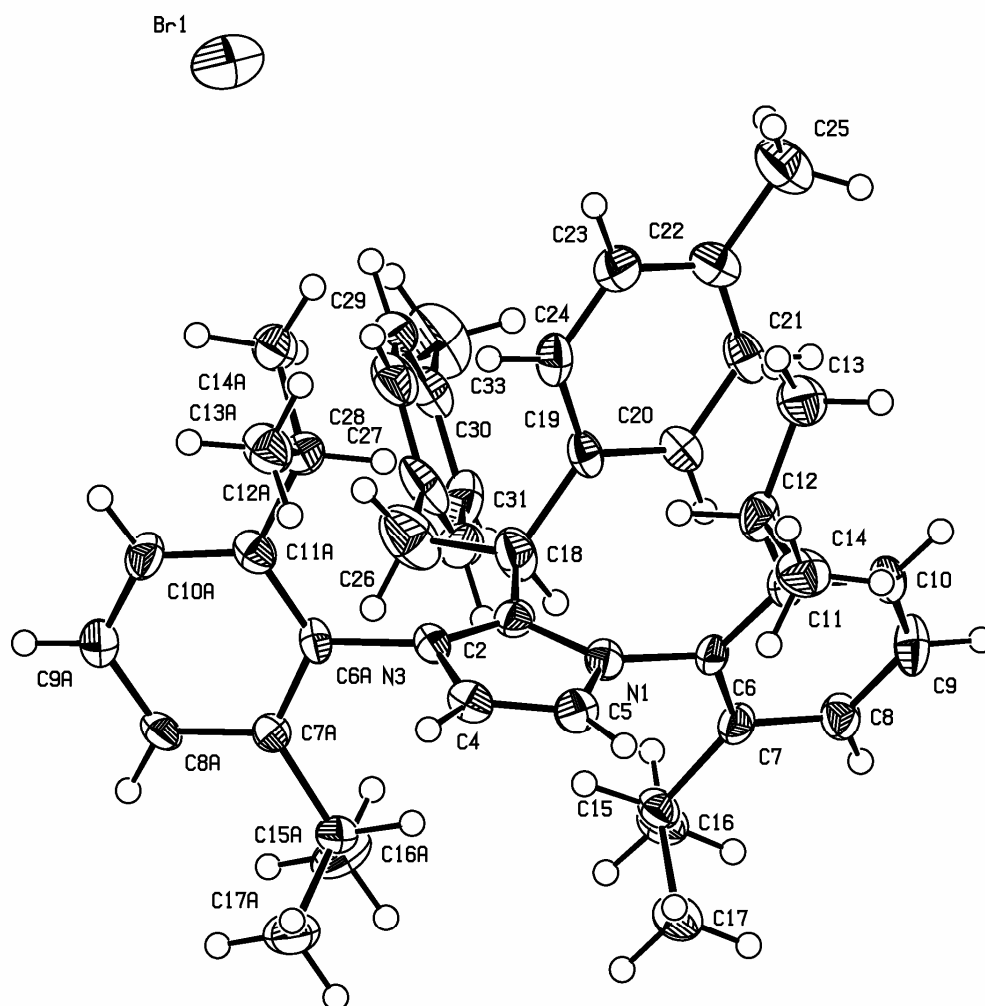


Figure S8: Crystal structure of imidazolium bromide **16** (ellipsoids at 50% probability).

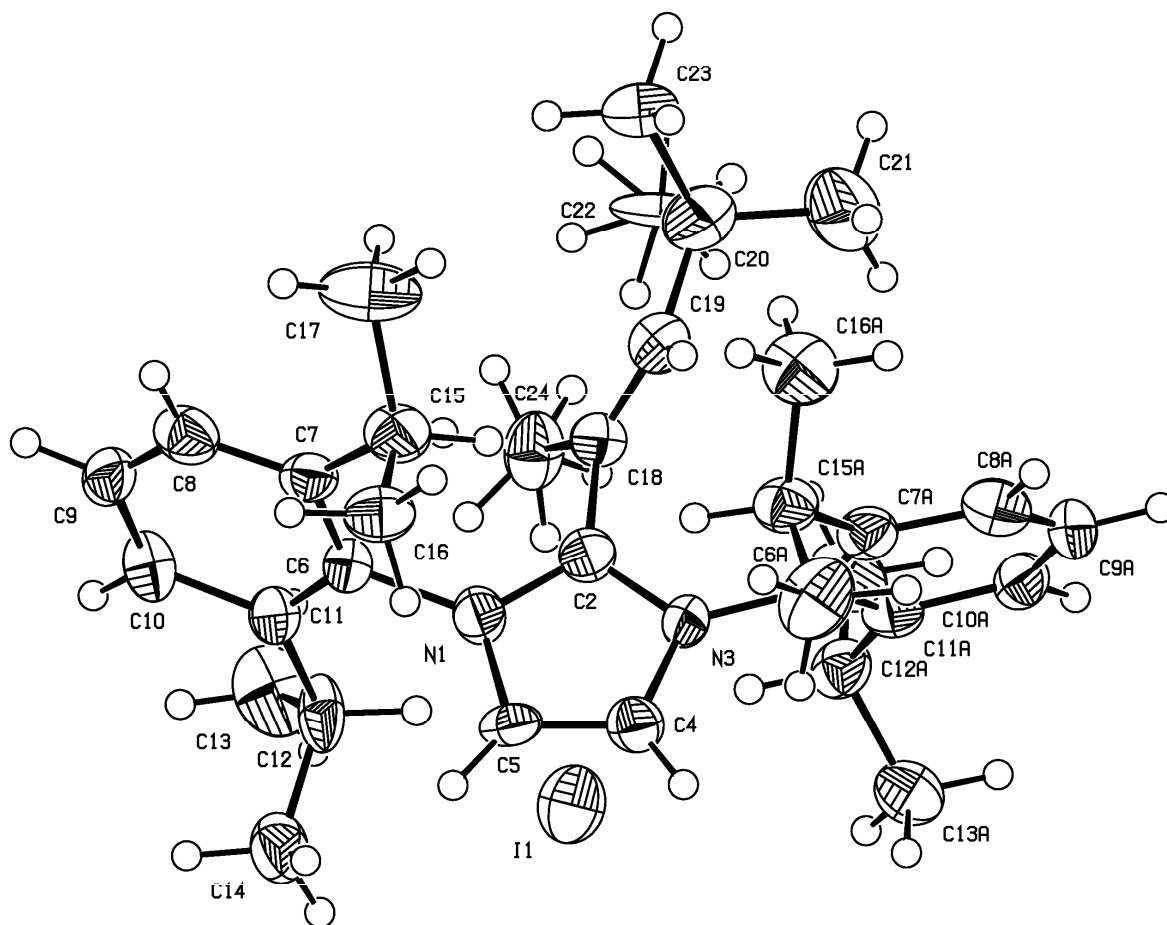


Figure S9: Crystal structure of imidazolium iodide **19** (ellipsoids at 50% probability).

Proposed mechanism for the reaction of carbene 2 with epibromohydrin

In the reaction of epibromohydrin with **1** in the presence of 2 equivalents KO^tBu surprisingly 2-propanonylidene **9** was formed. This compound contains a methyl vinyl ketone moiety¹ and was presumably formed via *t*-butoxide-mediated ring-opening of the intermediate imidazolylidene-methyl oxirane (Fig. S11). The mechanism is supported by the following observations: a) simple epoxides (methyl oxirane, styrene oxide, *t*-butoxymethyl oxirane) were unreactive toward **2** under identical conditions; b) epichlorohydrin also afforded **9** albeit at slower rate; c) epibromohydrin was not prone to isomerization to bromoacetone under basic (KO^tBu) conditions; d) with non-nucleophilic NaH as base **9** was not formed. As a by product methylene adduct **28** was observed.²

Alternatively a mechanism, that involves intramolecular epoxide opening via formation of a cyclopropanolate can be discussed.

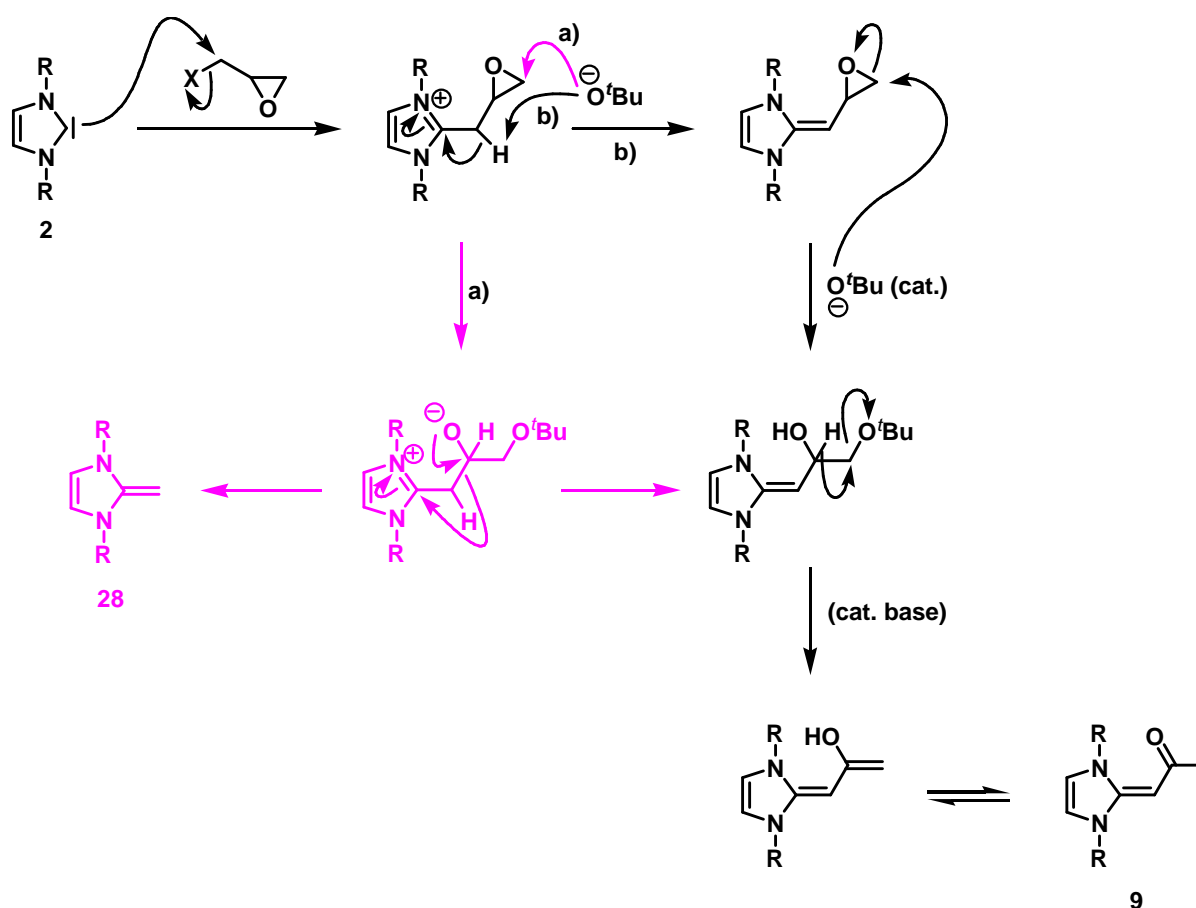
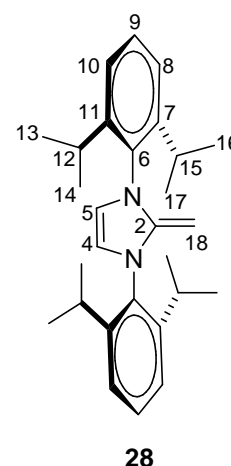


Figure S10: Proposed mechanism for the reaction of carbene **2** with epibromohydrin.

¹ For structurally related compounds, see also: (a) A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angew. Chem.* **2008**, *120*, 3254-3258; *Angew. Chem. Int. Ed.* **2008**, *47*, 3210-3214; (b) J. Bourson, *Bull. Soc. Chim. Fr.* **1971**, 152-159.

² ¹H-NMR (600 MHz, THF-*d*₈): δ = 7.33 (m; 2H, H-9), 7.23 (m; 4H, H-8, H-10), 6.24 (s; 2H, H-4, H-5), 3.20 (sep; 4H, ³J_{HH} = 6.9 Hz, H-12, H-15), 1.91 (s; 2H, H-18), 1.27-1.10 (m; 24H, H-13, H-14, H-16, H-17); ¹³C-NMR (151 MHz, THF-*d*₈): δ = 153.1 (d; 1C, C2), 149.5 (d; 4C, C7, C11), 135.51 (d; 2C, C6), 129.6 (u; 2C, C9), 124.9 (u; 4C, C8, C10), 115.4 (u; 2C, C4, C5), 43.6 (d; 1C, C18), 29.2 (u; 4C, C12, C15), 24.4 (u; 4C, C13, C16), 24.0 (u; 4C, C14, C17); ESI-MS: m/z: 403.00 [M+H]⁺.