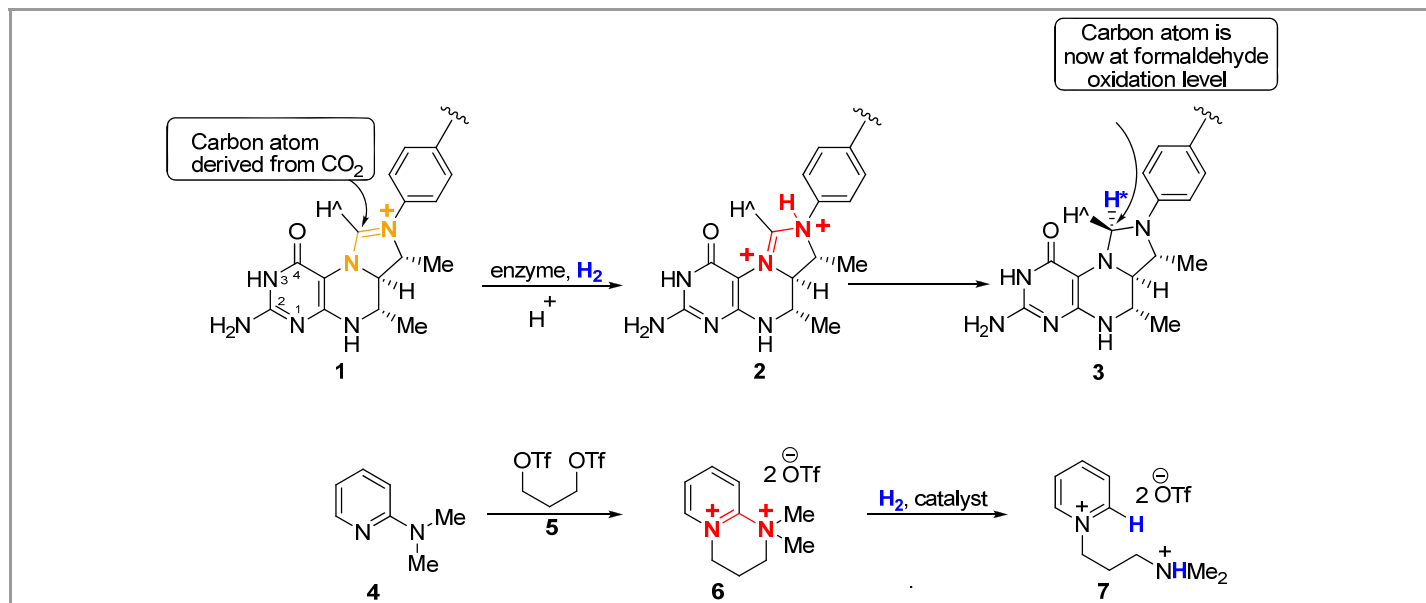


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Synthesis and Reactivity of Amidine Dications

One of the most mysterious processes seen in Nature is the conversion of carbon dioxide into methane. The transformation is important and topical: if we could harness such a process using economic catalysts, we could regenerate fuels from the world's growing levels of carbon dioxide.

This is a multi-step reaction sequence under the control of a group of bacterial enzymes. In the key reaction, the carbon dioxide-derived carbon, in substrate **1**, is at the formic acid oxidation level. This is reduced by the [Fe]-hydrogenase enzyme into the product **3**, where the carbon in question is at the formaldehyde oxidation level. The reaction involves abstraction of hydride from molecular hydrogen, H₂. A revolutionary proposal by Berkessel and Thauer in 1995, was that the substrate **1** underwent super-electrophilic activation in the enzyme active site, to form dication **2**; this compound would then be so electrophilic that it could accomplish the difficult reaction to **3**.



Scheme 1

Until now, nobody has been able to prepare amidine dications, of which **2** is an example. In 2009, we learned how to form alkylated amidine dications in high yield, forming disalt **6** and related compounds. Hydrogenation of **6** showed that it is indeed much more reactive than a normal pyridinium salt to hydrogen gas; thus **6** is converted into **7** cleanly and in high yield under very mild conditions. Under these conditions, no further reaction of normal pyridinium mono-salt **7** is seen. Our work has thus involved unusual and highly reactive dications (and, more recently, trications). Analysis of these compounds has not been easy, but mass spectrometry has been central to their identification, allowing unambiguous determinations of the multiple charges on the polycations. The excellent work of the Mass Spectrometry Service Centre in Swansea has been critical to our success.

References.

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2. Corr, M.; Gibson, K.; Kennedy, A. R.; Murphy, J. A. *J. Am. Chem. Soc.*, **2009**, *131*, 9174.