

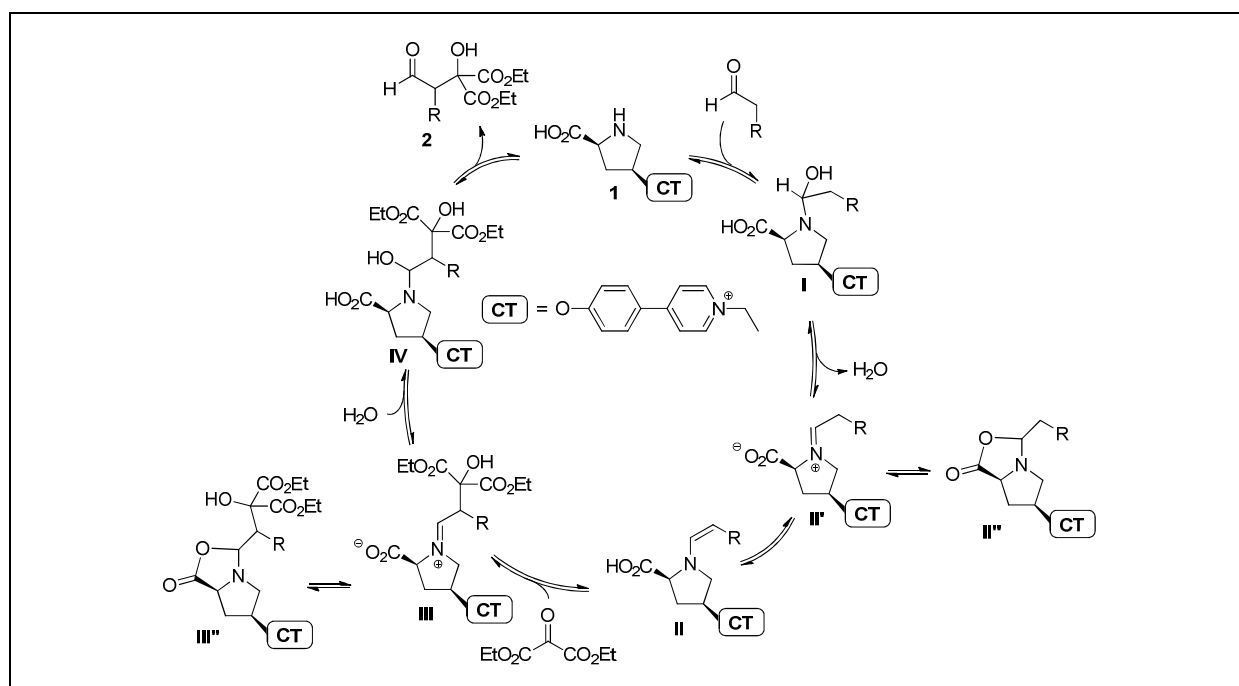
# ESI mass spectrometric mechanistic studies with a charge-tagged proline-based organocatalyst

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Proline-mediated enantioselective organocatalysis has become a major research topic in organic chemistry. The catalytic cycles typically are supposed to involve enamines or iminium ions as key intermediates. We have developed the synthesis of a charge-tagged L-proline-based organocatalyst **1** with the aim to elucidate mechanisms of organocatalyzed reactions by detecting reactive intermediates by ESI mass spectrometry.<sup>1</sup>

As an example, the markedly enhanced ESI response factor of catalyst **1** enabled us to detect two key intermediates as well as an off-cycle byproduct in the course of the asymmetric aldol reaction between aldehydes and diethyl ketomalonate. The species have been characterized by exact mass and CID MS/MS and their temporal evolution has been monitored.



1. Willms, J. A.; Beel, R.; Schmidt, M. L.; Mundt, C.; Engeser, M. *Beilstein J. Org. Chem.* **2014**, *10*, 2027-2037.