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Very Strong and Confined Acids Enable a General Approach to Asymmetric Lewis Acid Catalysis

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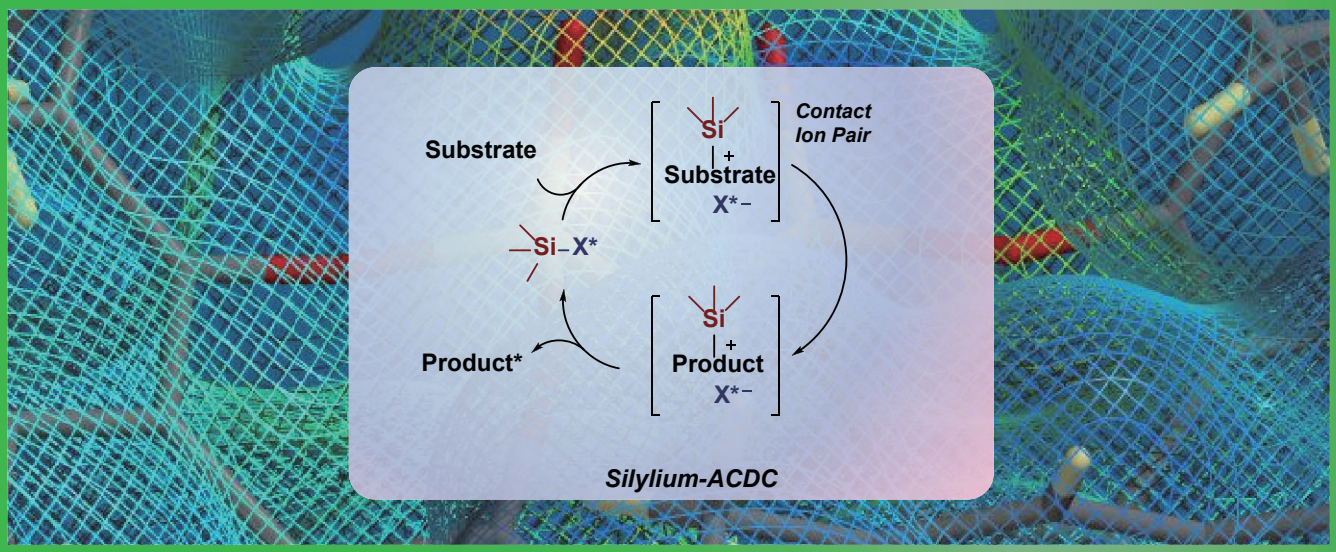
As a fundamental activation mode, Lewis acid catalysis enables key reactions in chemical synthesis, such as the Diels–Alder and Friedel–Crafts reactions, and various aldol, Mannich, and Michael reactions. Consequently, substantial efforts have been directed towards the development of enantiopure Lewis acids, which have enabled important asymmetric variations of such reactions. Despite the plethora of elegant catalysts and methodologies developed in this context, a key limitation of enantioselective Lewis acid catalysis is the frequent need for relatively high catalyst loadings, which result from issues such as insufficient Lewis acidity, product inhibition, hydrolytic instability, and background catalysis.

We have recently proposed a new design for asymmetric Lewis acid catalysis. We developed in situ silylated disulfonimide-based organocatalysts, which address some of the above problems in various highly enantioselective Mukaiyama-type reactions involving silicon-containing nucleophiles with unprecedentedly low catalyst loadings. As an example of asymmetric counteranion-directed catalysis (ACDC), these reactions proceed via silylation of an electrophile, generating a cationic reactive species that ion-pairs with an enantiopure counteranion and reacts with a silylated nucleophile. We became interested in expanding this “silylium-ACDC” concept to, in principle, all types of Lewis acid catalyzed reactions, including those that do not involve silylated reagents. In my presentation, I will discuss how the concept evolved from our studies on ACDC. I will furthermore describe its first realization with the development of extremely active organic Lewis acid catalysts that enable asymmetric versions of highly challenging Diels–Alder reactions. The confined acids that form the basis of our latest catalyst design not only enable the utilization of small and unbiased substrates but, because of their high acidity, also the activation of previously inaccessible substrates for organocatalysis.



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