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## New Strategies for Acid-Acid-Catalyzed Reactions with Auto-Tandem Catalysis

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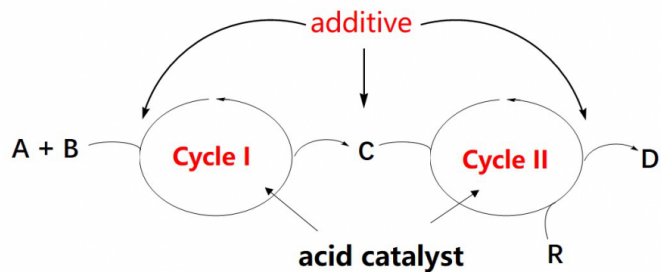
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**PURPOSE OF THE ABSTRACT**

Acid-acid-catalyzed tandem reactions in a one-pot system have been frequently used in organic synthesis. Basically, this chemistry can be considered as an acid-driven subdivision of auto-tandem catalysis. To establish the reaction sequence, a substrate-design strategy was often adopted, in which complex molecules have to be designed and used as substrates. However, the practical usefulness of the methodologies was weakened to some extent because preparation of the starting materials lengthened the synthesis procedure and marginalized the potential advantages. To solve this problem and strengthen the usefulness, we have developed in the past five years the following strategies on the basis of our previous substrate-design-based studies:

1. Additive-induced auto-tandem catalysis with an acid catalyst.[2] By means of adding some inexpensive chemicals, such as trialkyl orthoformates, light alcohols or NBS into the reaction system, tandem catalysis can be established that can drive assembly of simple molecules to form complex products (Figure 1).
2. Co-product acts as an acid catalyst for relay catalysis.[3] HBr released in Friedel-Crafts reaction can play a role of an acid, which cooperates with the F-C reaction catalyst to establish a relay catalysis process for the synthesis of complex molecules (Figure 2).
3. Polar aprotic salt-driven acid-catalyzed two-step reactions in homogeneous-to-heterogeneous systems. A sulfone-containing zwitterion salt that is insoluble in organic solvent was added into the reaction system at the end of the first reaction step. A unique polar and aprotic phase can be established by the salt, which created a polar microenvironment to guide progress of the second step of the reaction (Figure 3).

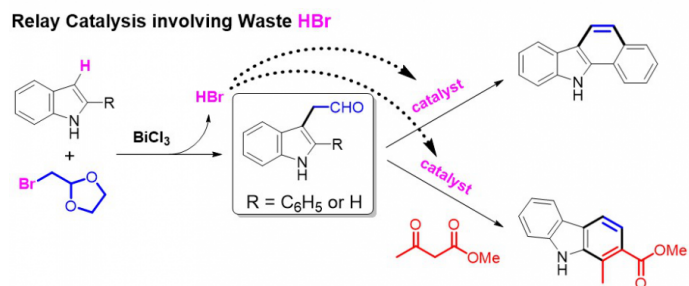
## FIGURES



**FIGURE 1**

Figure 1

Additive-induced auto-tandem catalysis with acid catalyst.



**FIGURE 2**

Figure 2

Relay catalysis established by BiCl<sub>3</sub> and a co-product HBr.

## KEYWORDS

auto-tandem catalysis | acid catalysis | tandem reaction | organic synthesis

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