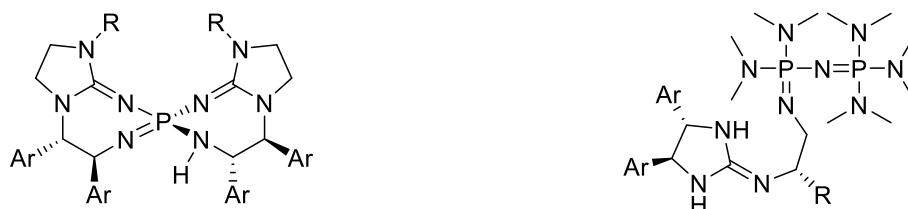


Enantioselective Catalysis by Chiral Higher Order Organosuperbase

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The development of new molecular catalysts is one of the keys for paving the way to novel transformations in organic synthesis. In the field of chiral Brønsted base catalysis, which is one of the most fundamental and environmentally benign methodologies for the direct synthesis of enantio-enriched compounds, a long-standing issue is the expansion of the scope of pronucleophiles that are applicable to the enantioselective reactions. Conventionally, chiral tertiary amines have been widely employed as chiral Brønsted base catalysts. Recently, chiral uncharged organobases with higher basicity than tertiary amines, such as chiral guanidines, P1-phosphazenes, and cyclopentenimines, have also emerged as efficient chiral Brønsted base catalysts. However, the insufficient basicity of these conventional chiral organobases limits the scope of pronucleophiles to highly acidic compounds, such as β -dicarbonyl compounds and nitroalkanes, which restricts the viable molecular transformations that are available under chiral Brønsted base catalysis. Therefore, the development of a new generation of chiral Brønsted base catalysts that can overcome the intrinsic limitations of pronucleophiles is highly desirable. In this context, our research program has been focusing on the development of much stronger chiral uncharged organobases, namely chiral higher order organosuperbase catalysts having a phosphazene core unit (Figure 1): 1) chiral bis(guanidino)iminophosphorane **1** possesses a C_2 symmetrical structure^[1-6] and 2) chiral cooperative binary base catalyst **2** consists of two different organobase functionalities,^[7] one of which functions as an organosuperbase and the other as the substrate recognition site. Our achievements for the enantioselective reactions of less acidic pronucleophiles have revealed the benefit of chiral Brønsted bases having high basicity in developing new catalytic enantioselective reactions and expanding the scope of pronucleophiles.



Chiral bis(guanidino)iminophosphorane catalyst (*M*)-**1**

Chiral cooperative binary base catalyst **2**

Figure 1. chiral higher order organosuperbase catalysts developed.

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