

Design of Novel Asymmetric Organocatalysts

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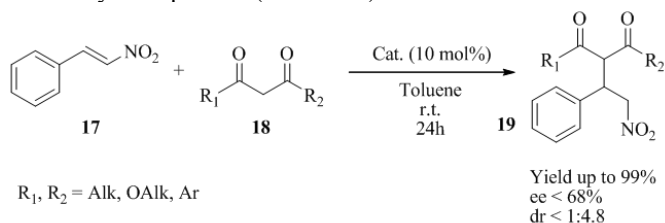
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In the past 10 years, chiral aminothioureas have gained increasing attention as excellent organocatalysts for asymmetric Michael reaction. However, a majority of these catalysts are based on chiral ethylene diamine scaffold, the most famous example being Takemoto's catalyst **1** [1]. In order to explore the potential of catalysts, based on propylene diamine motif, we report the synthesis and application of new aminothiourea derivatives.

A series of chiral 1,3-diamine containing thioureas **5-16** (Figure 1) has been synthesized to establish a relationship between the position of catalyst chiral centre and the level of enantiocontrol.

The synthesized aminothioureas **5-16** were tested in Michael reaction between nitrostyrene and various 1,3-dicarbonyl compounds (Scheme 1).



R₁, R₂ = Alk, OAlk, Ar

Scheme 1. Model reaction

The best results were obtained with catalysts **11** (94%, 68% ee), **12** (99%, 47% ee) and **15** (99% 60%) using ethyl benzoylacetate and benzoylacetone as 1,3-dicarbonyl donors. In general, yields and enantioselectivities are lower in many cases, compared to Takemoto's catalyst **1** and the previously reported catalysts **2-4** [1], [2]. However, our results provide a good insight into reaction TS and structure – reactivity relationships.

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- [2] Wang, W.H.; Abe, T.; Wang, X.B.; Kodama, K.; Hirose, T.; Zhang, G.Y. *Tetrahedron: Asymmetry* **2010**, *21*, 2925.

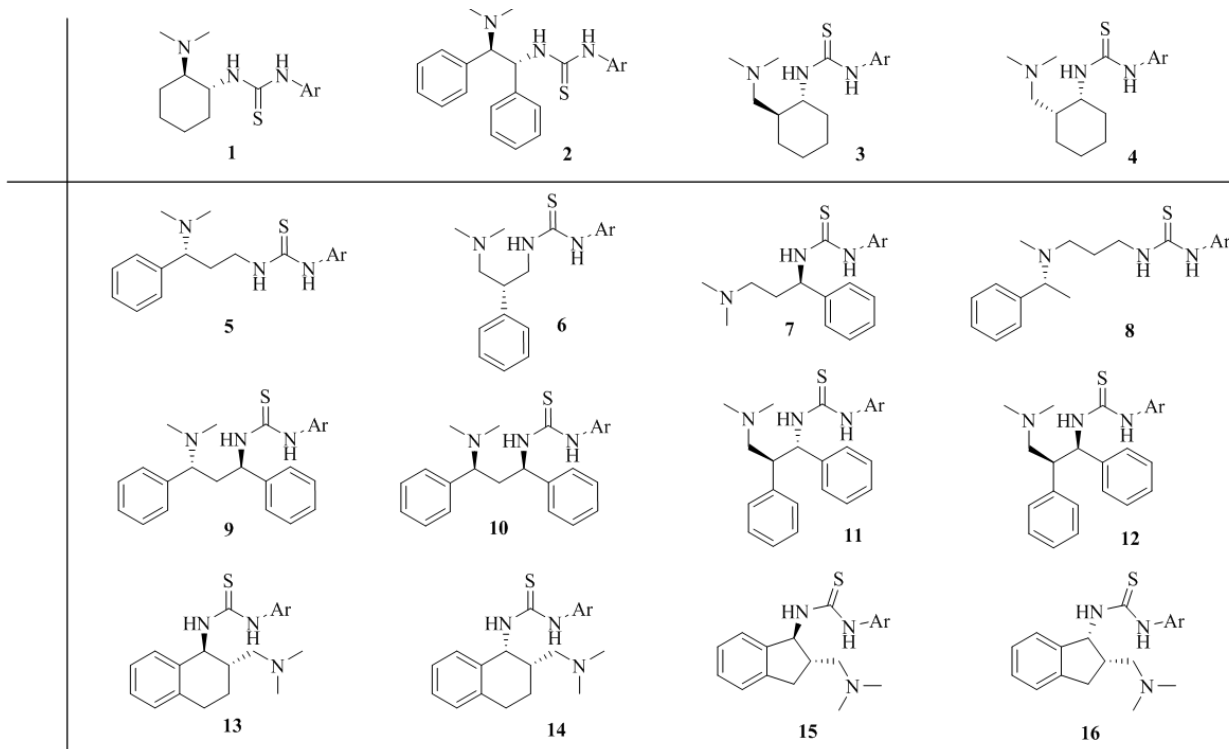


Figure 1. Known (1-4) and newly designed (5-16) organocatalysts