# Chiral Brønsted Acid-Base Pyridinium Disulfonate Catalysts 

Organo- and Biocatalysis

## Key words

## disulfonic acids

Mannich-type

Tuning of acidity and bulkiness in situ:


1


1 (1 mol\%) $\xrightarrow[\substack{\mathrm{MgSO}_{4} \\ \mathrm{CH}_{2} \mathrm{Cl}_{2}, 0^{\circ} \mathrm{C}, 30 \mathrm{~min}}]{2,6-\mathrm{Ph}_{2} \mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}(2 \mathrm{~mol} \%)}$
$\mathrm{R}^{1}=\mathrm{Me}, \mathrm{Et}, \mathrm{Ph}$


10 examples
91 to $>99 \%$ yield
er = 92:8 to 99:1





## Selected examples:



99\% yield er $=92: 8$


99\% yield
er $=98: 2$


95\% yield
er $=97.5: 2.5$


99\% yield
$99 \%$
er $=92: 8$

Significance: By combining chiral disulfonic acid 1 and achiral 2,6-diphenylpyridine the authors obtain tailor-made Brønsted acid-base organocatalysts for a direct Mannich-type reaction. Excellent yields and enantioselectivities were achieved with this concept.

Comment: The authors use an original and elegant strategy for high enantioinduction in comparison to the generally applied strategy of substitution at the 3,3'-positions with bulky substituents in analogous binaphthyl phosphoric acid catalysts (e.g., see: Akiyama et al. Angew. Chem. Int. Ed. 2004, 43, 1566). By forming a salt of chiral disulfonic acid $\mathbf{1}$, which has been tested earlier as organocatalyst by List and co-workers (Chem. Asian J. 2008, 3, 430; Adv. Synth. Catal. 2008, 350, 962), and bulky pyridines, the authors circumvent the often tedious synthesis of the $3,3^{\prime}$-substituted derivatives. On the other hand, the acidity is reduced this way and therefore the substrate scope might be limited to easily activated compounds.

