Distinct Conformational Preferences of Prolinol and Prolinol Ether Enamines in Solution Revealed by NMR

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1 Experimental Details........................................................................................................S2

2 NMR Characterization of Enamines................................................................................S3

3 NMR Characterization of Organocatalysts....................................................................S5
1 Experimental Details

The enamines under investigation were created in situ by mixing freshly distilled aldehydes 1 or 2 (30 µmol) with a solution of 100 mol% of one the organocatalysts 3-9 in 0.6 mL of a deuterated solvent within a standard 5 mm NMR tube. The NMR tube was transferred to the spectrometer immediately after the preparation of the reaction mixture.

NMR measurements were performed at 300 K on a Bruker Avance DRX 600 (600.13 MHz) and on a Bruker Avance III 600 (600.25 MHz) spectrometer, the latter equipped with a TCI cryoprobe with z-gradient (53.5 G/cm). $^1$H-$^1$H-NOESY spectra were recorded using a mixing time of 700 ms. NMR data were processed and evaluated with Bruker’s TOPSPIN 2.1.

Spartan '06 (http://www.wavefun.com) was employed for the structure models displayed in Figure 4B. The structures were refined with the help of molecular mechanics conformer distribution calculations (MMFF force field).
2 NMR Characterization of Enamines

Scheme S1 Overview of the prolinol enamines, relevant $^1$H chemical shifts and coupling constants.
(Note: Chemical shifts of Hβ1, Hγ1 and Hδ1 are listed below those of Hβ2, Hγ2, Hδ2.)
Scheme S2 Overview of the prolinol ether enamines, relevant $^1$H chemical shifts and coupling constants.

(Note: Chemical shifts of H$\beta_1$, H$\gamma_1$ and H$\delta_1$ are listed below those of H$\beta_2$, H$\gamma_2$, H$\delta_2$.)

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Scheme S3 1H chemical shift assignment and relevant coupling constants of the prolinol organocatalysts.
(Note: Chemical shifts of Hβ1, Hγ1 and Hδ1 are listed below those of Hβ2, Hγ2, Hδ2.)
Scheme S4: $^1$H chemical shift assignment and relevant coupling constants of the prolinol ether organocatalysts.

(Note: Chemical shifts of $H\beta_1$, $H\gamma_1$ and $H\delta_1$ are listed below those of $H\beta_2$, $H\gamma_2$, $H\delta_2$.)

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