Supporting Information

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Catalytic Asymmetric Mannich-Type Reactions Activated by ZnF₂ Chiral Diamine in Aqueous Media

Tomoaki Hamada, Kei Manabe, and Shu Kobayashi*

Graduate School of Pharmaceutical Sciences
The University of Tokyo, The HFRE Division, ERATO
Japan Science and Technology Agency (JST)
Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
Fax: (+81) 3-5684-0634
E-mail: skobayas@mol.f.u-tokyo.ac.jp
For stereospecific, asymmetric Mannich-type reactions (Table 7)

While the \((E)\)-silyl enol ether derived from 3-pentanone (8E) gave the \textit{anti}-Mannich-type adduct (\textit{anti}-6d), the \textit{syn}-adduct (\textit{syn}-6d) was obtained from the \((Z)\)-silyl enol ether derived from 3-pentanone (8Z). We assumed an open transition state shown in Figure S-1. Due to steric and electronic repulsions between the CO$_2$Et and OSiMe$_3$ groups, the \(E\)- and \(Z\)-enolates gave \textit{anti-} and \textit{syn-}adducts, respectively.

![Figure S-1. Assumed Transition State Model (8E and 8Z)](image-url)

On the other hand, in the reactions with \((E)\)- and \((Z)\)-ketene silyl acetals derived from \textit{S-}tert-butyl thiopropionate (7E and 7Z), a different selectivity was observed. Namely, while the \(E\)-ketene silyl acetal (7E) gave the \textit{anti}-Mannich-type adduct (\textit{anti}-6c), the \textit{syn}-adduct (\textit{syn}-6c) was produced from the \((Z)\)-ketene silyl acetal (7Z). We also assumed an open transition state shown in Figure S-2. In this case, it was thought that the \textit{S’Bu} group was sterically larger than the OSiMe$_3$ group. Thus, we suppose that this interesting selectivity is due to the different steric influence of the Et and \textit{S’Bu} groups.
For transition state model

We assume the following transition state model based on the X-ray crystal structure shown in Figure 1 (Figure S-3). Zn(II) has a five-coordinated trigonal bipyramidal structure, in which one fluoride anion still remains on Zn(II). Due to basicity difference, it is assumed that an imino group and a carbonyl group of an amide in a hydrazone coordinate to Zn(II) via bidentate fashion. In the transition model, the $si$ face of the hydrazone is shielded by two aromatic rings, an enolate would attack the hydrazone from the $re$ face to afford the $R$ adduct selectively. Hydrogen bondings between the amine protons and the oxygen atoms of the $o$-MeO groups of 1c and 1i are suggested.
Figure S-3. Assumed Transition State Model