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Supporting Information

Catalytic Asymmetric Mannich-Type Reactions Activated by ZnF_2 Chiral Diamine in Aqueous Media

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For stereospecific, asymmetric Mannich-type reactions (Table 7)

While the (*E*)-silyl enol ether derived from 3-pentanone (**8E**) gave the *anti*-Mannich-type adduct (***anti*-6d**), the *syn*-adduct (***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_2Et and $OSiMe_3$ groups, the *E*- and *Z*-enolates gave *anti*- and *syn*-adducts, respectively.

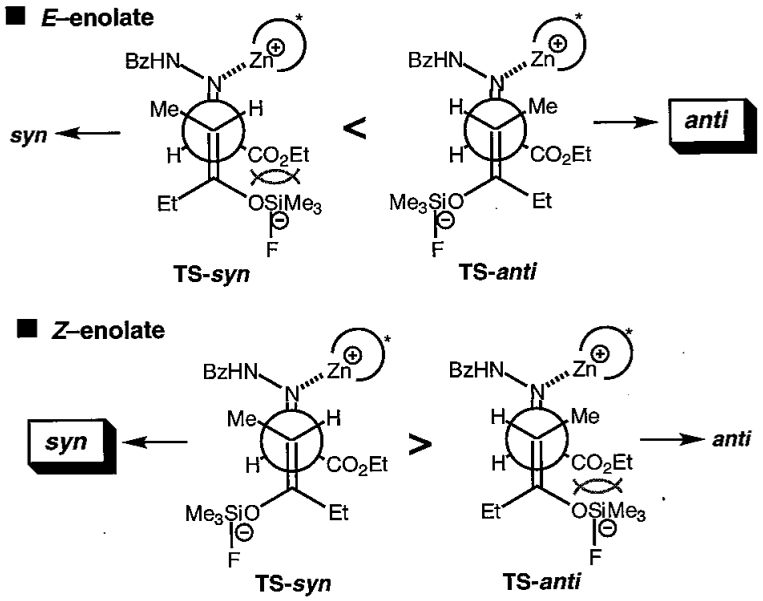

Figure S-1. Assumed Transition State Model (**8E** and **8Z**)

On the other hand, in the reactions with (*E*)- and (*Z*)-ketene silyl acetals derived from *S-tert*-butyl thiopropionate (**7E** and **7Z**), a different selectivity was observed. Namely, while the (*E*)-ketene silyl acetal (**7E**) gave the *anti*-Mannich-type adduct (***anti*-6c**), the *syn*-adduct (***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 S^{t}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 S^{t}Bu groups.

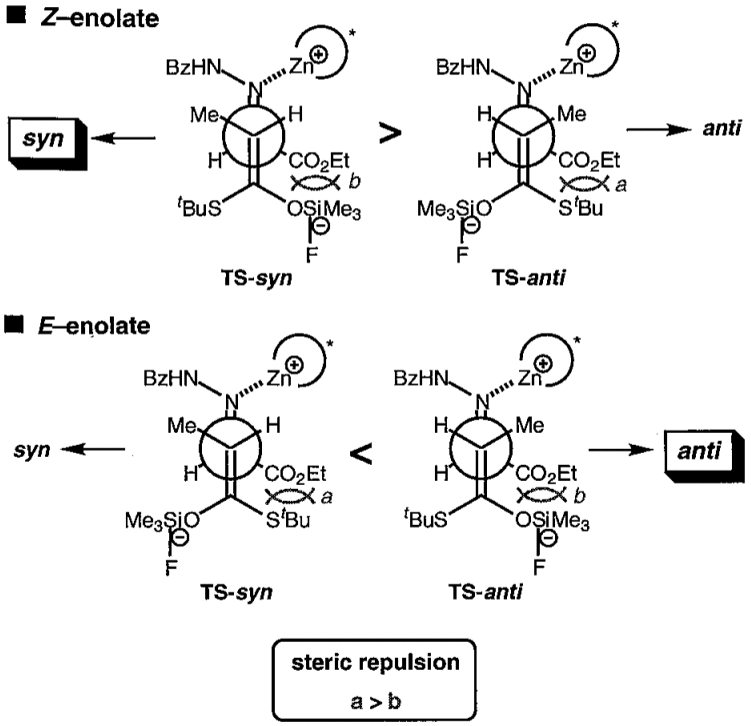

Figure S-2. Assumed Transition State Model (**7E** and **7Z**)

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.

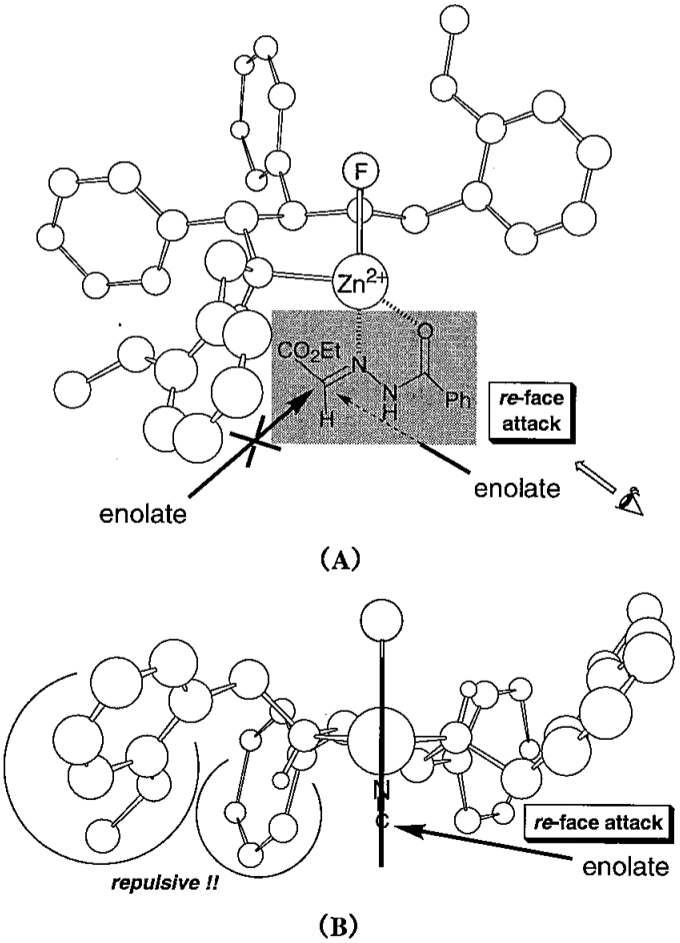

Figure S-3. Assumed Transition State Model