

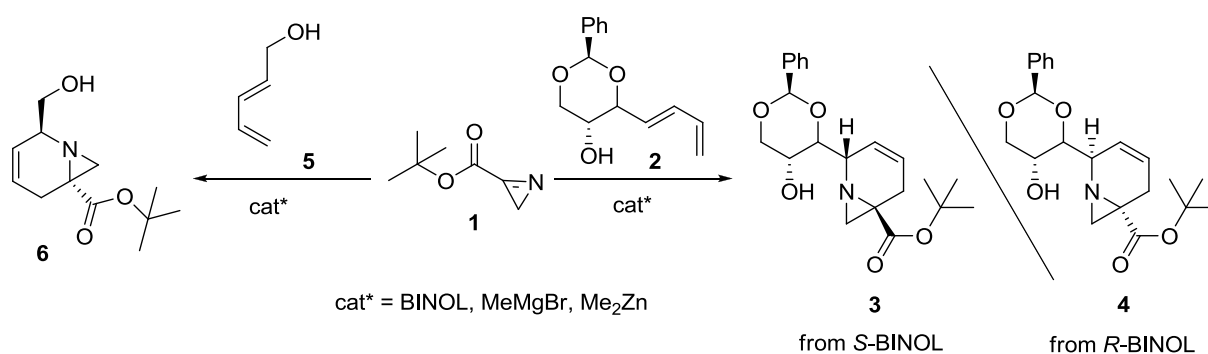
ASYMMETRIC DIELS-ALDER REACTION OF *tert*-BUTYL 2*H*-AZIRINE-3-CARBOXYLATE BY A SELF-ASSEMBLED COMPLEX OF BINOL, Mg AND Zn

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In the past the reaction of *tert*-butyl 2*H*-azirine-3-carboxylate (**1**) with 1,3-butadienes containing a glucosyl moiety as chiral auxiliary showed complete facial selectivity.^[1] However, the reaction of erythrose diene **2** with the same azirine **1** proceeds with low selectivity giving a 2.5:1 mixture of compounds **3** and **4**.

In an attempt to overcome this lack of selectivity the reaction components were tethered in a LACASA-Diels-Alder cycloaddition (LACASA-DA) using a bimetallic complex of Mg(II) and Zn(II) having R-/S-BINOL as chiral ligand. This method had been first developed by Inomata in reaction of dienol with nitroso dienophiles, in the presence of tartaric acid-zinc complex.^[2] Later Ward reported a highly enantioselective LACASA-DA reaction of diene **5** with methyl acrylate.^[3]



Bearing in mind the result obtained by Ward, we combined the same diene (**5**) with azirine **1**. The reaction proceeded at low temperature giving homochiral compound **6** in two diastereomeric forms depending on the stereochemistry of BINOL chiral inductor (R/S). Application of this methodology to reaction of chiral diene **2** with azirine **1** also gave complete facial control affording products **3** or **4** according to the BINOL chiral ligand. Non-optimized yields of products ranged from 30-50 %.

[1] Alves, M. J.; Gilchrist, T. L. *Tetrahedron Lett.*, **1998**, 39, 7579-7582.

[2] a) Ding, X.; Ukaji, Y.; Fujinami, S.; Inomata, K. *Chem. Lett.*, **2003**, 32, 582-583. b) Ukaji, Y.; Inomata, K. *Synlett*, **2003**, 1075-1087.

[3] a) Ward, D. E.; Souweha; M. S. *Org. Lett.*, **2005**, 3533-3536. b) Ward, D. E.; Mohammad; S. A. *Org. Lett.*, **2000**, 3937-3940.

Acknowledgements

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