

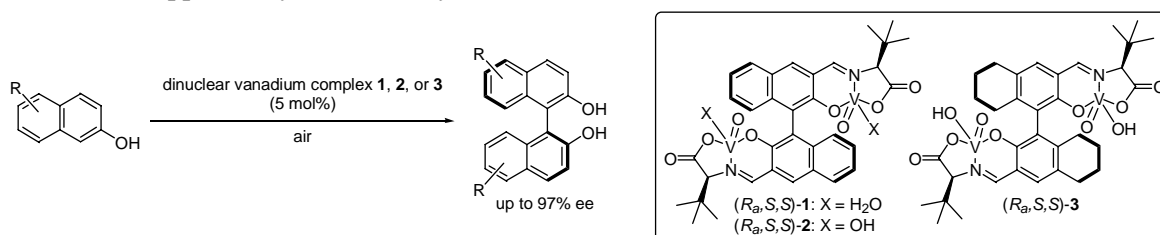
DEVELOPMENT OF DINUCLEAR VANADIUM CATALYSTS AND ACID-BASE ORGANOCATALYSTS FOR ENANTIOSELECTIVE REACTIONS VIA DUAL ACTIVATION MECHANISM

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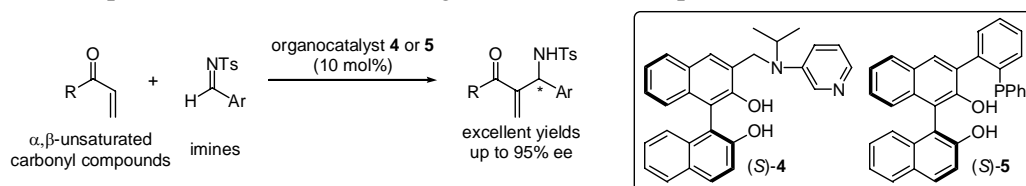
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Dual activation by reaction promoting functionalities in asymmetric catalysis leads to high reaction rate and orientational control for substrates resulting in excellent asymmetric induction. To achieve the dual activation concept in radical coupling reaction and organocatalytic reaction, we have developed dinuclear vanadium catalysts (R_a,S,S)-**1**, **2**, **3** and acid-base organocatalysts (S)-**4** and **5**.

Chiral dinuclear vanadium complexes (R_a,S,S)-**1**, **2** and **3** have been found to promote the oxidative coupling of 2-naphthols to afford (S)-BINOLs with up to 97% ee. The two vanadium metals in the chiral complex activate two molecules of 2-naphthols simultaneously in an intramolecular manner coupling reaction, achieving a high reaction rate with high enantiocontrol. This dual activation mechanism is supported by kinetic analysis.



Brønsted acid - Lewis base organocatalysts (S)-**4** and **5** have been established as efficient asymmetric bifunctional organocatalysts for the aza-Morita-Baylis-Hillman reaction of α,β -unsaturated carbonyl compounds with imines. The acid-base functionalities cooperatively activate the substrate to promote the reaction with high enantiocontrol (up to 95% ee).



References: *Tetrahedron Lett.*, **45**, 1841 (2004); *Tetrahedron Lett.*, **46**, 1943 (2005); *J. Am. Chem. Soc.*, **127**, 3680 (2005); *Tetrahedron: Asymmetry*, **17**, 578 (2006); *Synlett*, **2006**, 761; *J. Synth. Org. Chem. Jpn.*, **65** 1089 (2007); *Chem. Commun.*, **2008**, 1810; *Tetrahedron*, **64**, 3361 (2008); *Chem. Commun.*, **2008**, 4113.