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Ytterbium Triflate-Catalyzed Asymmetric Hetero Diels-Alder Cycloaddition of a 1-Thiabuta-1,3-diene with a Chiral *N*-Acryloyloxazolidinone Dienophile. Diastereoface Control by Solvents or Achiral Additives

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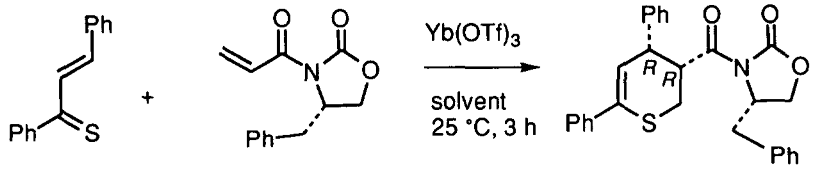
Abstract: Ytterbium triflate [Yb(OTf)$_3$]-catalyzed asymmetric hetero Diels-Alder cycloaddition reaction of 2,4-diphenyl-1-thiabuta-1,3-diene with (*S*)-*N*-acryloyl-4-benzyl-1,3-oxazolidin-2-one is described in which the sense of the π-facial selectivity can be controlled by solvents or additives employed without altering the auxiliary chirality for the asymmetric induction.

Recently, rare earth metal trifluoromethanesulfonates (triflates) have found their attractive use as Lewis acid catalysts in organic synthesis, particularly in carbon-carbon bond-forming reactions such as aldol, Michael, allylation, Friedel-Crafts acylation and Diels-Alder reactions, because of their unique properties, *viz*, high coordination numbers, exceedingly strong and hard Lewis acidity, large atomic radii, fast coordination-dissociation ability in equilibrium, and highly water-tolerant Lewis acidity.[1] These attractive unique properties of rare earth metal triflates prompted us to use them as Lewis acid promoters in asymmetric hetero Diels-Alder (AHDA) reaction of a 1-thiabuta-1,3-diene since thiabutadienes are generally unstable and particularly very sensitive to common Lewis acids and protic acids to readily decompose or deteriorate and since reported examples of Lewis acid-promoted AHDA reaction are very rare.[2] In this communication we wish to report that in the Yb(OTf)$_3$-catalyzed AHDA reaction of the thiabutadiene **1** with the dienophile **2**, the π-facial selectivity can readily and efficiently be controlled by the choice of achiral additives or solvents in combined use of the same chiral source for the asymmetric induction.



1 **2** **3** *endo* (3,4-cis)

When the reaction of thiabutadiene **1**[3] (1.2 equiv.) with the chiral dienophile **2** (1.0 equiv.) was performed without a Lewis acid at 25 °C for 3 h in CH_2Cl_2, the cycloadduct **3** was obtained in a 79:21 ratio of the *endo*:*exo* isomers (86 % yield) with (-) 67 % d.e. of the (3*S*,4*S*)-*endo* isomer[4] (Table 1). In contrast, the reaction in the presence of variable amounts of Yb(OTf)$_3$ resulted in a good to excellent diastereomeric excess of the π-facial selectivity (84 - >99 % d.e.) of the (3*R*,4*R*)-*endo* isomer in quantitative yields, though the *endo*:*exo* selectivity was low. Figure 1 shows variations of the *endo*:*exo* and π-facial selectivities as functions of Yb(OTf)$_3$ stoichiometry. Apparently, Yb(OTf)$_3$ accelerated the reaction and reversed completely the π-facial selectivity (*Cα-Re* → *Cα-Si*) from that in the thermal case by use of a small amount of the Lewis acid catalyst.

Table 1. Yb(OTf)$_3$-Catalyzed AHDA Reaction [a]

Run	Lewis acid mol %	Yield / %	Ratio [b] endo:exo	π-Facial (endo) d.e. / % [b]	Configuration[4]
1	none	86	79:21	-67	[3*S*,4*S*]
2	1	98	61:39	84	[3*R*,4*R*]
3	5	99	60:40	92	[3*R*,4*R*]
4	10	99	58:42	98	[3*R*,4*R*]
5	20	99	58:42	>99	[3*R*,4*R*]
6	50	99	53:47	>99	[3*R*,4*R*]
7	100	99	52:48	>99	[3*R*,4*R*]
8	200	99	52:48	>99	[3*R*,4*R*]

[a] Reactions were carried out at 25 °C for 3 h in CH$_2$Cl$_2$.

[b] Determined by ^{1}H NMR spectroscopy and HPLC analysis.

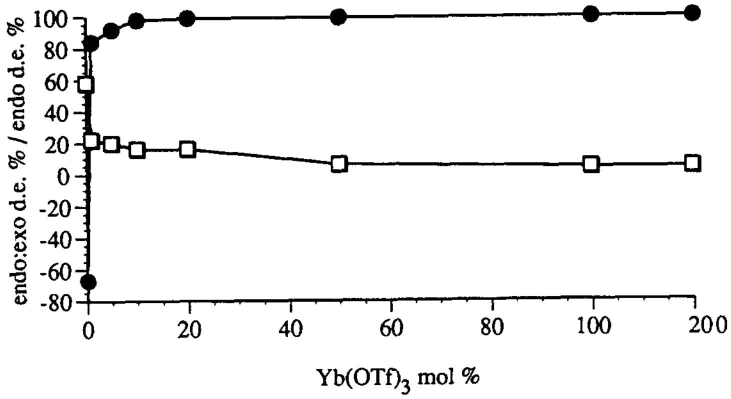


Fig. 1. Variation of diastereoselectivities in the Yb(OTf)$_3$-catalyzed AHDA reaction of **1** with **2**: *endo*:*exo* d.e.(□) as a function of Yb(OTf)$_3$ stoichiometry; *endo* d.e.(●) as a function of Yb(OTf)$_3$ stoichiometry.

We next examined effects of solvents on the diastereoselectivities under the influence of a Yb(OTf)$_3$ catalyst (Table 2). Noteworthy points are as follows: (1) *In either solvent employed, the reaction gave a good yield of the cycloadduct 3.* (2) *Even in the presence of the water in THF, the reaction worked well, no probable, but undesirable, hydrolysis or deterioration of the thioketone being observed.* (3) *In the two former solvents (Runs 1 and 2) the (3R, 4R)-isomer of the endo addition was formed exclusively (>99 % d.e.), whilst* *the three latter solvents (Runs 3-5) rendered the predominant formation of the (3S,4S)-isomer in -64, -64 and -66 % d.e., respectively.* These results suggest that polar solvents reverse the π-facial selectivity and have prompted us to gain more insight into the effects on the selectivity by employing DMSO (dimethyl sulfoxide) as an additive. The reactions were performed by varying the added amounts of DMSO (1 - 5 equiv. to Yb(OTf)$_3$) in CH_2Cl_2 in the presence of 100 mol % of the Lewis acid. The results are summarized in Table 3. By addition of ≥4 equiv. of DMSO, the sense of the π-facial selectivity is reversed.

Table 2. Solvent Effects on the D.e.s and *endo:exo* ratios [a]

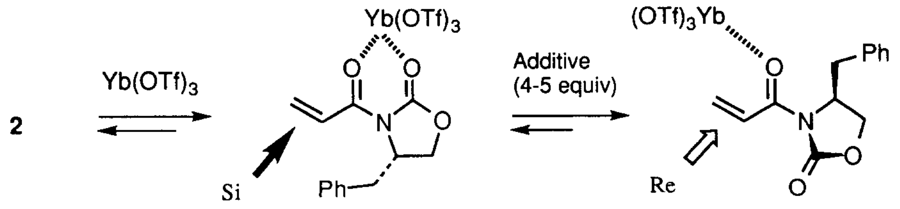
Run	Solvent	Yield / %	Ratio [b] endo:exo	π-Facial (endo) d.e./ % [b]	Configuration[4]
1	CH_2Cl_2	99	52:48	>99	[3*R*,4*R*]
2	THF	99	48:52	>99	[3*R*,4*R*]
3	THF-H_2O(9:1)	93	77:23	-64	[3*S*,4*S*]
4	DMSO	94	89:11	-64	[3*S*,4*S*]
5	DMF	94	87:13	-66	[3*S*,4*S*]

[a] Reactions were carried out using 100 mol % of Yb(OTf)$_3$ at 25 °C for 3 h.
THF: tetrahydrofuran; DMSO: dimethyl sulfoxide; DMF: dimethyl formamide.
[b] Determined by ^{1}H NMR spectroscopy and HPLC analysis.

Table 3. Effects of Added Amounts of DMSO on the D.e.s and *endo:exo* ratios [a]

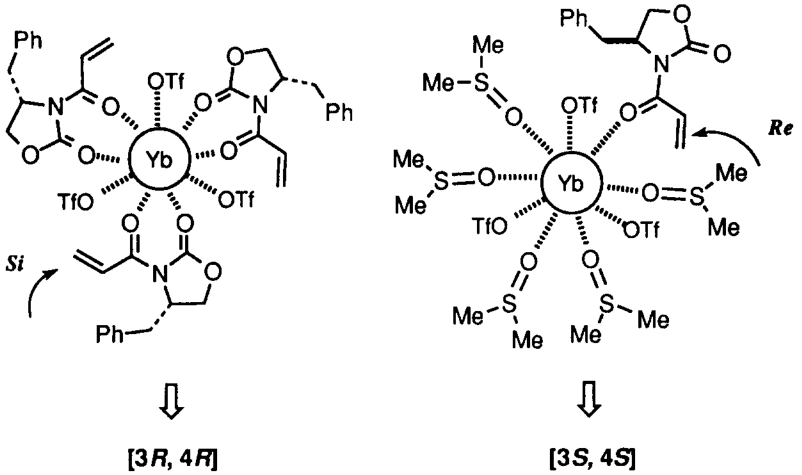
Run	DMSO equiv.	Yield / %	Ratio [b] endo:exo	π-Facial (endo) d.e. / % [b]	Configuration[4]
1	0	99	52:48	>99	[3*R*,4*R*]
2	1	99	58:42	>99	[3*R*,4*R*]
3	2	99	61:39	60	[3*R*,4*R*]
4	3	99	68:32	20	[3*R*,4*R*]
5	4	97	70:30	-30	[3*S*,4*S*]
6	5	99	78:22	-60	[3*S*,4*S*]
7	in DMSO	97	89:11	-64	[3*S*,4*S*]

[a] Reactions were carried out using 100 mol % of Yb(OTf)$_3$ in CH_2Cl_2 at 25 °C for 3 h.
[b] Determined by ^{1}H NMR spectroscopy and HPLC analysis.



The following explanation of these phenomena can be considered: In the absence of a coordinative additive (or a solvent) such as DMSO, the two-points binding dienophile **2** is able to chelate with the ytterbium cation, whilst in the presence of the additive (DMSO) at least four or five molecules of DMSO can coordinate the ytterbium cation competitively with the dienophile to form the chelation, resulting in the monodentate coordination in equilibrium. The diene attacks the dienophile from the less hindered *Si*-face of the chelation complex and from the *Re*-face of the monocoordination form.

Further studies to develop new AHDA reactions along this line are now in progress.



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References and Notes

1. Kobayashi, S. *Synlett*, **1994**, 689.

(a) Kobayashi et al. and Takaki et al. recently reported the lanthanide triflate-catalyzed hetero Diels-Alder reaction of imines with carbodienes or alkenes to give cycloadducts such as pyridine and/or quinoline derivatives. Kobayashi, S.; Ishitani, H.; Nagayama, S. *Synthesis*, **1995**, 1195. Ishitani, H.; Kobayashi, S. *Tetrahedron Lett.*, **1996**, *37*, 7357. Makioka, Y.; Shindo, T.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *Synthesis*, **1995**, 801.

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3. A 1,2-dithiin-type dimer was used as the precursor of **1**. See literature in reference 2.
4. The absolute configuration was determined by comparisons of HPLC and ^{1}H NMR spectral data with the authentic data reported in the literature.[2]

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