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Ytterbium Trifluoromethanesulfonate [Yb(OTf)3] as a Novel Catalyst for the Allylation of Aldehydes

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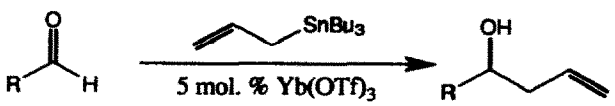
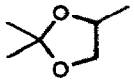
Abstract: *Ytterbium triflate has been found to be an excellent Lewis acid catalyst for the reaction of aldehydes with allyltributylstannane.*

The Lewis acid promoted allylation of aldehydes using allylstannanes or silanes is a versatile synthetic tool. Whilst numerous Lewis acids will *promote* the reaction, there is little precedent for Lewis acid *catalysis*. Recently however, Keck[1] and Tagliavini[2] have shown that chiral titanium complexes are capable of catalysing the reaction of aldehydes with allyltributylstannane with excellent enantioselectivity, although reaction times are very long (up to 70 hours). Kobayashi has also reported the $Sc(OTf)_3$ catalysed reaction of aldehydes with the more reactive tetraallyltin.[3]

Lanthanide triflates have been reported to catalyse a range of Lewis acid promoted reactions, including the Aldol reaction,[4] Diels Alder reaction,[5] and Michael addition.[6] The catalysts are readily prepared from the corresponding lanthanide oxide and triflic acid.[7] As part of a study directed towards the development of asymmetric Lewis acid catalysts, we have found that ytterbium triflate, $Yb(OTf)_3$, will catalyse the reaction of a range of aldehydes with allyltributylstannane under very mild conditions. Using as little as 5 mol. % of the catalyst, the reactions were all found to be complete after 24 hours at room temperature, using dichloromethane as solvent. We found it essential to dry the catalyst prior to use; inefficient drying of the complex led to very low yields of the products, even with extended reaction periods. An aqueous work-up, followed by column chromatography led to isolation of the desired alcohols in excellent yields.[8]



Entry	R	Isolated yield (%)[a]	Remarks
1	Ph	85	
2	4-NO_2Ph	93	
3	C_6H_{11}	94	
4	1-naphthyl	88	
5	PhCH(Me)	87	*ca.* 2:1 mixture of diastereoisomers.
6	2-furyl	85	
7		66	*ca.* 2:1 mixture of diastereoisomers.
8	C_5H_{11}	93	
9	$CH_3CH(Me)$	86	Product isolated as the OBz ester.

[a] After chromatography. All reactions were complete (as observed by GC) after 24 hours.

In conclusion, ytterbium triflate has been found to be an excellent Lewis acid catalyst for the allylation of aldehydes under very mild conditions. The yields for the process are very high, even with catalyst concentrations as low as 5 mol. %.

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8. Typical experimental procedure: Ytterbium triflate (100 mg) was dried under vacuum (0.1 mmHg, 140 °C) for 16 hours. On cooling, the flask was filled with argon and the complex was dissolved in dichloromethane (5 ml). Benzaldehyde (330 µl, *ca.* 3.25 mmol) was added, followed by allyltributylstannane (1.1 ml, 3.55 mmol) and the mixture was allowed to stir at room temperature for 24 hours. The reaction was quenched by addition of saturated $NaHCO_3$ solution (5 ml), and the products extracted into dichloromethane (3 x 20 ml). After drying ($MgSO_4$) the solvent was removed under reduced pressure, and the resulting oil was purified by flash chromatography (eluent petroleum ether (b.p. 40-60 °C) / diethyl ether 10:1) to give the product as a clear oil.

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