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Scandium Trifluoromethanesulfonate, a Novel Catalyst for the Addition of Allyltrimethylsilane to Aldehydes.

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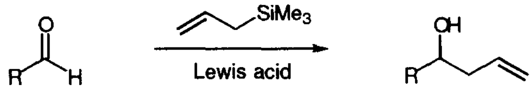
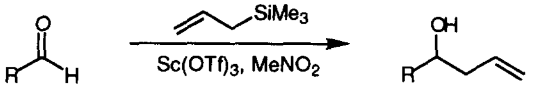
Abstract: *Scandium triflate (2-10 mol%) has been found to be a highly efficient catalyst for the addition of allyltrimethylsilane to both aromatic and aliphatic aldehydes.* Copyright © 1996 Elsevier Science Ltd

The addition of allylsilanes to aldehydes mediated by Lewis acids is an important synthetic transformation.[1] Generally, powerful Lewis acids (typically $TiCl_4$, $SnCl_4$, $BF_3.OEt_2$, $AlCl_3$) are needed to activate the aldehyde due to the inherent low nucleophilicity of allylsilanes. However, tight binding of the homoallylic alkoxide to the strong Lewis acids, together with poor efficiency of silicon transfer to oxygen results in poor turnover, thereby necessitating the use of stoichiometric (or greater) amounts of Lewis acid.[2] Alternative Lewis acids for the allylation process include active silyl reagents [Me_3SiOTf,[3a] Me_3SiI,[3b] $Me_3SiB(OTf)_4$ [3c,d]]. In such cases decomplexation of the homoallylic alkoxide from the metal ($SiMe_3$) is not required as the Lewis acid catalyst is regenerated from the allylsilane. With these Lewis acids it is possible to use sub-stoichiometric amounts, usually 20 mol% but in one case[3d] as little as 0.2 mol% [$Me_3SiB(OTf)_4$] was sufficient. However, these catalysts are somewhat sensitive and require careful handling, preparation and/or storage.



We have returned to the use of metal based Lewis acids, in particular the lanthanides, due to the success achieved by Kobayashi in the related (but much more reactive) Mukaiyama aldol reaction.[4] Indeed, such Lewis acids are effective catalysts in many fundamental reactions including Diels-Alder,[5a] Michael additions[5b] and Friedel-Crafts acylations.[5c] These Lewis acids are highly oxophilic and in general form strong but labile bonds with oxygen donor ligands. We have screened a number of metal salts [$Yb(OTf)_3$, $CeCl_3$, $Sc(OTf)_3$] in the reaction of allyltrimethylsilane with benzaldehyde and found that scandium triflate in nitromethane provided the greatest activation. Using as little as 2 mol% of $Sc(OTf)_3$, the reaction was complete within 14 hours.[6] A range of aldehydes were tested in this allylation process and the results are summarised in Table 1. We found that both unactivated and activated aromatic aldehydes worked well (entries 2, 3, 4 & 5). The most difficult allylation reactions are with aliphatic aldehydes due to their lower reactivity. We were pleased to find that allyltrimethylsilane (the least activated of all allylsilanes) coupled efficiently with aliphatic aldehydes (entries 6, 7, 8, & 9) although slightly higher catalyst loadings were required to achieve high yields.



entry	aldehyde	mol%. $Sc(OTf)_3$	time (hrs)	isolated yield(%)
1	benzaldehyde	0	48	0
2	benzaldehyde	2	14	79
3	2-naphthaldehyde	2	14	73
4	*p*-chlorobenzaldehyde	2	14	98
5	*p*-nitrobenzaldehyde	2	14	84
6	phenylacetaldehyde	10	14	53
7	valeraldehyde	10	18	56
8	cyclohexanecarboxaldehyde	10	18	62
9	pivalaldehyde	10	18	71

Table 1

In summary, we have found mild conditions for the reaction of allylsilanes with aldehydes which require very low catalyst loadings and provide the product in good to excellent yields after chromatographic purification. A real advantage of the procedure is the simplicity and robustness of the reaction: the catalyst is air stable, it is not necessary to carefully prepare or activate it and it is unnecessary to dry the solvent (both solvent and catalyst can be used as commercially supplied with no loss of yield). Asymmetric variants of this reaction are currently under investigation.

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6. Typical Experimental Procedure; Scandium triflate (0.02 mmol) was stirred in nitromethane (10 cm^3) at room temperature. To the mixture was added benzaldehyde (1 mmol) followed by allyltrimethylsilane (1.5 mmol). The mixture was stirred at room temperature until all of the aldehyde had been consumed (as monitored by tlc). The mixture was poured into brine (10 cm^3) and the products extracted into dichloromethane (3 x 10 cm^3). The mixture was dried (Na_2SO_4) and after removing the solvent under reduced pressure, the residue was treated with tetrabutylammonium fluoride (1.0 ml, 1.1M THF, 1.1 mmol). Evaporation of the solvent followed by flash chromatography [silica gel; 10% Et_2O/Petroleum (40-60)] gave the product as a colourless oil (79%).

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