



## Short communication

Y(OTf)<sub>3</sub>-catalyzed addition reaction of alcohol to  $\beta$ -nitrostyrene

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## ABSTRACT

A concise and efficient addition reaction of alcohol to  $\beta$ -nitrostyrene promoted by Y(OTf)<sub>3</sub> has been established for the synthesis of  $\beta$ -nitroether derivatives. The present approach shows attractive properties, such as the high efficiency of catalyst, operational simplicity, and the tolerance of a wide range of functional groups. This strategy not only provides a variety of  $\beta$ -nitroethers but also expands the scope of application of early transition metals.

## 1. Introduction

Lewis acid-catalyzed organic synthesis reactions are of great interest because of their unique reactivities and selectivities and mild reaction conditions used [1–4]. Recently, many reactions catalyzed by Lewis acids have been reported, and they have been applied to the synthesis of a variety of organic compounds [5–10]. However, conventional Lewis acids such as AlCl<sub>3</sub>, TiCl<sub>4</sub>, etc. have one or more disadvantages, such as moisture sensitivity, easily decomposed or deactivated even in small amount of water, unrecoverable, and stoichiometric amounts catalyst being necessary in many cases, which strictly limited the scope of application. Since the first report of water-compatible lanthanide triflates [Ln(OTf)<sub>3</sub>] in 1991, lanthanide triflates have become literature-known compounds, which have been regarded as new types of Lewis acids [11]. Many useful organic synthesis reactions (including asymmetric synthesis) were catalyzed by rare-earth metal triflates successfully [12–20]. In many cases, rare-earth metal triflates can be recovered easily after reactions and reused without loss of activity. Rare-earth metal triflates are available in various solvents and are still active in the coexistence of many Lewis bases containing nitrogen, phosphorus, and sulfur atoms [21–22]. Moreover, rare-earth metal triflates are easily prepared by mixing the corresponding metal oxide chlorides in an aqueous trifluoromethanesulfonic acid solution under selective temperature [23–24].

Addition reaction of alcohol to  $\beta$ -nitrostyrene has emerged as a powerful method for the construction of C–O bonds with control of the contiguous C–O stereocentres products. This reaction generates  $\beta$ -nitroethers with higher levels of functionality, which may be further produce a range of useful intermediates. As addition product of alcohol to  $\beta$ -nitrostyrene, the most characteristic feature of  $\beta$ -nitroether derivatives is that they are unstable, thus, only a few reports on the

synthesis of them. Moreover, most of these syntheses were achieved via addition reaction in the presence of active metal or special catalysts, such as sodium alkoxide [25], sodium and corresponding alcohol [26], and others [27–30]. Herein, the catalysts usually suffer from more or less problems, such as moisture sensitive and easily decomposed or deactivated, large amount of catalyst loading, complicated preparation procedures, and so on, which greatly restrict the following application of such compounds. For example, NiFe<sub>2</sub>O<sub>4</sub> NPs [30], which is suitable to many Michael additions with broad substrate scope is an efficient, green and reusable catalyst. However, the complicated preparation procedure of the catalyst, which may be lead into uncertainty of structure or activity limits the application of it. Therefore, the development of effective synthetic methods, producing diversity of  $\beta$ -nitroether derivatives, continues to be considerable interest and important. To the best of our knowledge, the synthesis  $\beta$ -nitroether derivatives using acid as catalyst has not been reported yet. In the past several years, we have been engaging in the development of heterocyclic compounds that can provide easy access to new core structures of biological and pharmaceutical interest [31]. As the unexpected result, herein we report a new method for the synthesis of  $\beta$ -nitroether derivatives using catalytic amount of yttrium triflate as catalyst. Yttrium triflate, which is stable and can work as Lewis acids in water and many organic solvents is readily prepared by heating the yttrium chloride in an aqueous trifluoromethanesulfonic acid solution.

## 2. Results and discussion

## 2.1. Optimization of the reaction conditions

To begin this study, we chose (*E*)-(2-nitrovinyl)benzene (1a), and methanol (2a) as the standard substrates to search for suitable

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**Table 1**  
Optimization of the catalysts.<sup>a</sup>

Entry	Catalyst (mol%)	Time (h)	Yield (%) <sup>b</sup>
1	–	24	0
2	HOAc (10)	24	0
3	TsOH (10)	24	0
4	TfOH (10)	24	0
5	TFA (10)	24	0
6	H <sub>2</sub> SO <sub>4</sub> (10)	24	0
7	C-SO <sub>3</sub> H (10) <sup>c</sup>	24	0
8	Sc(OTf) <sub>3</sub> (10)	6	86
9	Y(OTf) <sub>3</sub> (10)	6	85
10	Yb(OTf) <sub>3</sub> (10)	6	80
11	Y(OTf) <sub>3</sub> (20)	6	86
12	Y(OTf) <sub>3</sub> (5)	6	84
13	Y(OTf) <sub>3</sub> (3)	6	72

<sup>a</sup> Reaction conditions: 1a (1.0 mmol), 2a (1.5 mL), and catalyst at reflux temperature.

<sup>b</sup> Isolated yields.

<sup>c</sup> C-SO<sub>3</sub>H (10 mg) was prepared using furaldehyde and hydroxyethylsulfonic acid.

conditions. It is worth noting that in the absence of catalyst, no goal product was obtained even after 24 h at reflux. Then, the model reaction was performed in MeOH at reflux using various Brønsted acids, such as HOAc, TsOH, TfOH, TFA, and H<sub>2</sub>SO<sub>4</sub> as catalyst. Unfortunately, none of the goal product was found (Table 1, entries 2–6). Then, the carbonaceous material (C-SO<sub>3</sub>H) [31] was used to catalyze the model reaction under same conditions, but none of the goal product was obtained (Table 1, entry 7). Next, different Lewis acids such as Sc(OTf)<sub>3</sub>, Y(OTf)<sub>3</sub>, and Yb(OTf)<sub>3</sub> were used to promote the model reaction. To our delight, the Lewis acids catalysts exhibited remarkably high activity for the formation of (1-methoxy-2-nitroethyl)benzene (3a). Taking into account the cost, the reaction was performed catalyzed by Y(OTf)<sub>3</sub> in all the subsequent reactions. The screening of results catalyst loading revealed that Y(OTf)<sub>3</sub> (5 mol%) was enough to put the reaction forward. Therefore, Y(OTf)<sub>3</sub> (5 mol%) was chosen for all further reactions.

To further optimize reaction conditions, the above reactions were

performed at 65 °C catalyzed by Y(OTf)<sub>3</sub> in various solvents including CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>CN, THF, Toluene, and MeOH (Table 2, entries 2–6). It was observed that MeOH was proven to be the best solvent (Table 2, entry 7). Subsequently, the reaction was performed in MeOH in different temperatures. The results indicated that the 65 °C was proper reaction temperature for all further reactions.

## 2.2. Reaction scope of substrates

To examine the efficiency of this reaction, a series of  $\beta$ -nitrostyrene (1) and alcohol (2) were submitted to the optimized reaction conditions (Table 3). Firstly, we explored the nitrostyrene substrate scope, using MeOH (1a) as model substrate (Table 3). To our delight, the nitrostyrenes bearing either electron withdrawing functional groups, such as fluoro, chloro, bromo, nitro, or trifluoromethyl or electron donating functional groups, such as methyl, or methoxyl, all gave goal products

**Table 2**  
Screening of solvent and temperature for model reaction.<sup>a</sup>

Entry	Solvent	T (°C)	Yield (%) <sup>b</sup>
1	–	65	56
2	CH <sub>2</sub> Cl <sub>2</sub>	Reflux	38
3	CHCl <sub>3</sub>	65	56
4	CH <sub>3</sub> CN	65	57
5	THF	65	51
6	Toluene	65	53
7	MeOH	65	84
8	MeOH	60	81
9	MeOH	20	11
10	MeOH	40	32
11	MeOH	80 <sup>c</sup>	86
12	MeOH	100 <sup>c</sup>	87

<sup>a</sup> Reaction conditions: 1a (1.0 mmol), 2a (10.0 mmol), Y(OTf)<sub>3</sub> (5 mol%), and solvent (1.5 mL), in 6 h.

<sup>b</sup> Isolated yields.

<sup>c</sup> The reaction was carried out at sealed tube.

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