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Short communication

$Yb[N(SO_2C_8F_{17})_2]_3$ -catalyzed allylation of 1,3-dicarbonyl compounds with allylic alcohols in a fluorous biphase system

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ABSTRACT

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1. Introduction

Allylation of 1,3-dicarbonyl compounds is an important type of carbon-carbon bond formation reaction in organic synthesis [1,2]. Many works have been devoted to this transformation in order to develop new methods consisting of inexpensive and readily available starting materials, atom-economy, mild reaction conditions, simple manipulation, and environmentally friendly catalysts [3–13]. A recent example is the establishment of new synthetic strategies that employ allylic alcohols as the allylating reagent in the presence of various transition-metal based reagents, such as palladium in the presence of a base or acid [3-5]; equimolar amounts of Cu(I) [6] and Co-salts [7,8]. Recently, Lewis acids such as BF₃·OEt₂ [9], InCl₃ [10], and FeCl₃ [11] or BrØnsted acids such as ptoluenesulfonic acid [12] and H-Montmorillonite [13] have also been reported to catalyze this reaction efficiently. However, most of these methods have problems including drastic reaction conditions, long reaction times and use of expensive, toxic and moisture sensitive reagents. Recently, Noji [14] and Huang [15] group reported that certain metal triflates can catalyze the allylation of 1.3-dicarbonyl compounds with allylic alcohols giving rise to the desired products in good to excellent yields. However, for the reuse of these catalysts, tedious work up procedures such as filtration, purification and drying should be required. Iodine (I_2) as a catalyst was also reported for the allylation of 1,3-dicarbonyl compounds by Rao's group [16]. However, the catalyst iodine cannot be recycled.

There has been rapidly increasing interest in the design and synthesis of compounds that exhibit high affinities for "fluorous" phases since the technique of "fluorous biphasic system" (FBS) was described by Horváth and Rabai [17-19]. The technique of FBS, as a phase-separation and catalyst immobilization technique, has become one of the most important methods for facile catalyst separation from the reaction mixture and recycle use of the catalyst [18,19]. In this catalytic system, the metallic catalyst coordinated by perfluoroalkylated ligands can dissolve into the fluorous phase after the reaction. Recently, novel Lewis acids of lanthanide tris(perfluorooctanesulfonyl)methide $\{Ln[C(SO_2R_{f8})]_3,$ $R_{f8} = (CF_2)_7 CF_3$, $Ln(CPf_3)_3$ [20,21], lanthanide bis(perfluorooctanesulfonyl)imide {Ln[N(SO₂R_{f8})₂]₃, Ln(NPf₂)₃} [22] and lanthanide perfluorooctanesulfonate [Ln(OSO₂R_{f8})₃, Ln(OPf)₃] [23–29] have been of special interest due to their characteristic features such as moisture insensitivity, ease of handling, robustness for the reuse and high solubility in fluorous solvent.

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Allylation of 1,3-dicarbonyl compounds with allylic alcohols was successfully accomplished using rare

earth metal (III) bis(perfluorooctanesulfonyl)imide $[RE(NPf_2)_3, RE = La \sim Lu]$ as catalysts in fluorous

solvents. Ytterbium bis(perfluorooctanesulfonyl)imide [Yb(NPf₂)₃] catalyzes the high efficient reaction

of allylation in fluorous solvents. By simple separation, fluorous phase containing only catalyst can be

During our studies to explore the utility of fluorinated Lewis acid catalysts in fluorous solvents [26–29], we found that the allylation of 1,3-dicarbonyl compounds with allylic alcohols can proceed smoothly in the presence of ytterbium bis(perfluorooctanesulfonyl)imide [Yb(NPf₂)₃] in a FBS system [Scheme 1]. Concurrently, we also found that the robustness of the catalytic system for reuse can be obtained by simple phase-separation.

2. Results and discussion

The reaction of allylic alcohol **1a** with 2,4-pentadione **2a** in perfluorodecalin ($C_{10}F_{18}$, *cis*- and *trans*-mixture) was selected as a model reaction for studying the effect of co-solvent and catalyst.

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Table 1 Allylation reaction in different co-solvents and the amount of catalyst loading^a.

Entry	Catalyst loading (mol%)	Co-solvent	Time (h)	3aa yield (%) ^b
1	1	CH ₃ NO ₂	6	90
2	0.75	CH_3NO_2	6	80
3	0.5	CH_3NO_2	6	72
4	-	CH_3NO_2	12	-
5	1	MeCN	6	73
6	1	PhMe	6	35
7	1	1,4-Dioxane	6	70
8	1	THF	6	50

^a The reaction condition: Yb(NPf₂)₃ (0.31 g, 0.1 mmol), allylic alcohol **1a** (2.10 g, 10 mmol), 2,4-pentadione 2a (1.08 g, 12 mmol), co-solvent (2 mL) and perfluorodecalin (C10F18, cis- and trans-mixture, 2 mL), 80 °C.

^b Isolated yields.

Table 1 shows the influence of co-solvent and the amount of catalyst. We found that treating a solution of allylic alcohol 1a (1 equiv.) and 2,4-pentadione 2a (1.2 equiv.) in CH₃NO₂ with 1 mol% Yb(NPf₂)₃ as catalyst at 80 °C for 6 h gave the product **3aa** in 90% yield (Table 1, entry 1). Under the similar condition, lower product yields of 72-80% were obtained when decreasing the catalyst amount from 1 to 0.75, and 0.5 mol% (Table 1, entries 2 and 3), and no reaction was observed in the absence of $Yb(NPf_2)_3$ after 12 h (Table 1, entry 4). In contrast, the reactions operated in other co-solvent were less effective and lower product yields of 35-73% were obtained for reactions in MeCN, toluene, 1,4-dioxane or THF as the co-solvent (entries 5-8). Nitromethane proved to be the

Table 3

Table 2

Effect of the catalysts on the allylation reaction^a.

Entry	Catalyst	3aa yield (%) ^b
1	$Yb(NPf_2)_3$	90
2	$Ce(NPf_2)_3$	84
3	$Nd(NPf_2)_3$	81
4	Sm(NPf ₂) ₃	85
5	$Eu(NPf_2)_3$	69
6	$Tb(NPf_2)_3$	81
7	$Dy(NPf_2)_3$	76
8	$Er(NPf_2)_3$	76
9	$La(NPf_2)_3$	66
10	$Lu(NPf_2)_3$	66

^a The reaction condition: RE(NPf₂)₃ (0.31 g, 0.1 mmol), allylic alcohol **1a** (2.10 g, 10 mmol), 2,4-pentadione 2a (1.08 g, 12 mmol), CH₃NO₂ (2 mL) and perfluorodecalin (C_{10}F_{18}, cis- and trans-mixture, 2 mL), 80 $^\circ\text{C},$ 6 h.

^b Isolated yields.

most efficient and was selected as the co-solvent for the subsequent investigation.

Table 2 shows the catalytic activity of 10 different rare earth metal-imide complexes in perfluorodecalin. Yb(NPf₂)₃ was found to be the most efficient catalyst, which produced almost quantitative yield of the desired product in perfluorodecalin.

The use of the catalytic system $Yb(NPf_2)_3/C_{10}F_{18}$ was extended to explore the scope of the reaction to various allylic alcohols and 1,3dicarbonyl compounds. As shown in Table 3, 1,3-dicarbonyl compounds 2a and 2b were allylated by five different allylic alcohols to give the corresponding products in moderate to excellent



Table 3 (Continued)



^a The reaction condition: Yb(NPf₂)₃ (0.31 g, 0.1 mmol), allylic alcohol (10 mmol), 2,4-pentadione (12 mmol), CH₃NO₂ (2 mL) and perfluorodecalin (C₁₀F₁₈, *cis*- and *trans*mixture, 2 mL), 80 °C, 6 h. ^b Isolated yields base on the starting alcohol.

Table 4Recycling studies of catalyst.

	•	
Entry	Run	Yield (%) ^a
1 ^b	_	-
2	Run 1	90 ^c
3	Run 2	87
4	Run 3	88
5	Run 4	87

^a Isolated yields.

^b Blank experiment without using catalyst.

^c Experiment 1, reaction conditions as Table 2.

yields. The substituents on the allylic alcohols **1a**, **1b**, **1c** and **1d** had no obvious effect on the conversion (entries 1–4, 6–9). Allylic alcohol **1e** have the similar reaction activity with the other four allylic alcohols (entries 5, 10). In all cases, the double bonds on the allylic alcohols were not migrated (checked by ¹H NMR) and the reactions proceeded very cleanly (checked by TLC) and no side reaction products were observed.

To examine the reusability of the catalytic system, the catalyst recovered by simple phase-separation from the reaction mixture of allylation reaction was reused for the next experiment (up to four cycles) under the reaction condition described in Table 2. The results shown in Table 4 indicate that the catalyst can be reused without significant loss in activity. When the reaction was finished, and then the catalyst mixture was cooled to room temperature. The fluorous phase containing RE(NPf₂)₃ can be separated from the organic layer and returned to the bottom layer. Based on GC–MS and ¹⁹F NMR data, no distribution of Yb(NPf₂)₃ was found in organic layer and only trace amount of perfluorodecalin leached to organic phase was detected.

3. Conclusion

In conclusion, $RE(NPf_2)_3$ are demonstrated to be new and highly effective catalysts for the allylation of 1,3-dicarbonyl compounds with allylic alcohols in fluorous biphasic system (FBS). By simple separation of the fluorous phase containing only catalyst, the reaction can be repeated many times. Further study on the application of FBS to other reactions, which can be promoted by such Lewis acids, is under way in this laboratory.

4. Experimental

4.1. General

Chemicals used were obtained from commercial suppliers and used without further purifications. ¹H NMR and ¹⁹F NMR spectra were recorded with a Bruker Advance RX500 spectrometer. Mass spectra were recorded on a Saturn 2000GC/MS instrument. Inductively coupled plasma (ICP) spectra were measured on an Ultima2C apparatus. Elemental analyses were performed on a Yanagimoto MT3CHN recorder.

4.2. Typical procedure for preparation of RE(NPf)₃

RE(NPf₂)₃ was prepared according to the literatures [22]. A mixture of anhydrous methanol (10 mL), HN(SO₂C₈F₁₇)₂ (0.883 g, 0.9 mmol) and ytterbium (III) chloride (0.052 g, 0.3 mmol) was stirred continuously at 50 °C for 16 h. After being cooled to room temperature, the mixture was evaporated and dried at 80 °C/ 0.01 mmHg for 16 h to give white powders of ytterbium (III) bis(perfluorooctanesulfonyl)imide complex in 95% yield (0.843 g). ICP: Calcd. for C₄₈O₁₂N₃F₁₀₂S₆Yb: Yb, 5.56%. Found: Yb, 5.34%. Anal. Calcd. for Yb[N(SO₂C₈F₁₇)₂]₃: C, 18.52. Found: C, 18.44.

4.3. Typical procedure for allylation of 1,3-dicarbonyl compounds with allylic alcohols

A mixture of Yb(NPf₂)₃ (0.31 g, 0.1 mmol), allylic alcohol **1a** (2.10 g, 10 mmol), 2,4-pentadione **2a** (1.08 g, 12 mmol), CH₃NO₂ (2 mL) and perfluorodecalin (2 mL). The mixture was stirred at 80 °C for 6 h. Then, the fluorous layer on the bottom was separated for the next reaction. The organic solvent in the reaction mixture (organic phase) was removed under reduced pressure and the residue was purified by SiO₂ gel column chromatography using CH₂Cl₂:MeOH (99:1) as a eluent.

Compound **3aa** (Lit. [16]): 90% yield; ¹H NMR (500 MHz, CDCl₃) δ = 1.93 (s, 3H), 2.24 (s, 3H), 3.77–3.79 (d, *J* = 0.8 Hz, 1H), 4.25–4.27 (m, 1H), 6.02–6.08 (dd, *J* = 8.2, 15.7 Hz, 1H), 6.32 (d, *J* = 15.7 Hz, 1H), 6.77–7.20 (m, 10H); MS (EI) *m*/*z* 292 (M+).

Compound **3ba** (Lit. [16]): 88% yield; ¹H NMR (500 MHz, CDCl₃) $\delta = 1.91$ (s, 3H), 2.22 (s, 3H), 3.74–3.79 (m, 4H), 3.94 (s, 3H), 4.25–4.27 (m, 1H), 6.01–6.07 (dd, J = 8.2, 15.7 Hz, 1H), 6.30 (d, J = 15.7 Hz, 1H), 6.80–7.22 (m, 8H); MS (EI) m/z 320 (M+).

Compound **3ca** (Lit. [16]): 85% yield; ¹H NMR (500 MHz, CDCl₃) δ = 1.95 (s, 3H), 2.23 (s, 3H), 4.13–4.47 (m, 2H), 6.12 (dd, *J* = 8.2, 15.7 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 7.11–7.44 (m, 8H); MS (EI) *m*/*z* 361 (M+).

Compound **3da** (Lit. [15]): 92% yield; ¹H NMR (500 MHz, CDCl₃) δ = 1.92 (s, 3H), 2.23 (s, 3H), 3.77–3.79 (m, 7H), 4.25–4.27 (m, 1H), 6.02–6.08 (dd, *J* = 8.2, 15.7 Hz, 1H), 6.32 (d, *J* = 15.7 Hz, 1H), 6.80–7.22 (m, 8H); MS (EI) *m/z* 352 (M+).

Compound **3ea** (Lit. [16]): 90% yield; ¹H NMR 500 MHz, CDCl₃) δ = 1.20 (d, *J* = 8.7 Hz, 3H), 1.95 (s, 3H), 2.25 (s, 3H), 3.77–3.79 (d, *J* = 10.8 Hz, 1H), 4.25–4.27 (m, 1H), 6.02–6.08 (dd, *J* = 8.2, 15.7 Hz, 1H), 6.32 (d, *J* = 15.7 Hz, 1H), 6.80–6.89 (m, 5H); MS (EI) *m/z* 234 (M+).

Compound **3ab** (Lit. [12]): 88% yield; ¹H NMR 500 MHz, CDCl₃) $\delta = 1.03$ (t, *J* = 7.0 Hz, 3H), 1.95 (s, 3H), 3.87–3.96 (m, 3H), 4.18 (m, 1H), 6.04–6.09 (dd, *J* = 8.2, 15.7 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 1H), 6.77–7.20 (m, 10H); MS (EI) *m*/*z* 322 (M+).

Compound **3bb** (Lit. [16]): 85% yield; ¹H NMR 500 MHz, CDCl₃) $\delta = 1.05$ (t, *J* = 7.0 Hz, 3H), 1.98 (s, 3H), 3.74–3.78 (s, 6H), 3.87–3.96 (m, 3H), 4.18 (m, 1H), 6.02–6.08 (dd, *J* = 8.2, 15.7 Hz, 1H), 6.33 (d, *J* = 15.7 Hz, 1H), 6.82–7.24 (m, 8H); MS (EI) *m/z* 350 (M+).

Compound **3cb** (Lit. [16]): 82% yield; ¹H NMR 500 MHz, CDCl₃) $\delta = 1.05$ (t, *J* = 7.0 Hz, 3H), 1.95 (s, 3H), 3.87–3.96 (m, 3H), 4.18 (m, 1H), 6.04–6.09 (dd, *J* = 8.2, 15.7 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 1H), 6.77–7.20 (m, 8H); MS (EI) *m/z* 391 (M+).

Compound **3db** (Lit. [15]): 89% yield; ¹H NMR 500 MHz, CDCl₃) δ = 1.03 (t, *J* = 7.0 Hz, 3H), 1.95 (s, 3H), 3.77–3.79 (s, 6H), 3.89–3.99 (m, 3H), 4.18 (m, 1H), 6.04–6.09 (dd, *J* = 8.2, 15.7 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 1H), 6.77–7.20 (m, 8H); MS (EI) *m*/*z* 382 (M+).

Compound **3eb** (Lit. [15]): 87% yield; ¹H NMR 500 MHz, CDCl₃) $\delta = 1.03$ (t, J = 7.0 Hz, 3H), 1.20 (d, J = 8.7 Hz, 3H), 1.95 (s, 3H), 3.77– 3.99 (m, 3H), 4.25–4.27 (m, 1H), 6.02–6.08 (dd, J = 8.2, 15.7 Hz, 1H), 6.32 (d, J = 15.7 Hz, 1H), 6.80–6.89 (m, 5H); MS (EI) m/z 264 (M+).

References

- [1] J. Tsuji, I. Minami, Acc. Chem. Res. 20 (1987) 140-145.
- [2] B.M. Trost, Acc. Chem. Res. 13 (1980) 385–393.
- [3] H. Kioshita, H. Shinokubo, K. Oshima, Org. Lett. 6 (2004) 4085-4088.
- [4] Y. Kayaki, T. Koda, T. Ikariya, J. Org. Chem. 69 (2004) 2595–2597.
- [5] M. Kimura, R. Mukai, N. Tanigawa, S. Tanaka, Y. Tamaru, Tetrahedron 59 (2003) 7767–7777.
- [6] J.B. Baruah, A.G. Samuelson, J. Organomet. Chem. 361 (1989) C57-C60.
- [7] M. Mukhopadhyay, J. Iqbal, Tetrahedron Lett. 36 (1995) 6761-6764.
- [8] J. Marqet, M. Moreno-Manas, Chem. Lett. (1981) 173-176.
- [9] F. Bisaro, G. Pretat, M. Vitale, G. Poli, Synlett (2002) 1823–1826.
- [10] M. Yasuda, T. Somyo, A. Baba, Angew. Chem., Int. Ed. 45 (2006) 793–796.
 [11] U. Jana, S. Biswas, S. Maiti, Tetrahedron Lett. 48 (2007) 4065–4069.
- [12] R. Sanz, A. Martinez, D. Miguel, J.M. Alvarez-Gutierrez, F. Rodriguez, Adv. Synth. Catal. 348 (2006) 1841–1845.

- [13] K. Motokura, N. Fujita, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, Angew. Chem., Int. Ed. 45 (2006) 2605-2609.
- [14] M. Noji, Y. Konno, K. Ishii, J. Org. Chem. 72 (2007) 5161-5167.
- [15] W. Huang, J.-L. Wang, Q.-S. Shen, X.-G. Zhou, Tetrahedron Lett. 48 (2007) 3969-3973.
- [16] W. Rao, A.H.L. Tay, P.J. Goh, J.M.L. Choy, J.K. Ke, P.W.H. Chan, Tetrahedron Lett. 49 (2008) 122–126.
- [17] I.T. Horváth, J. Rabai, Science 266 (1994) 72-74.
- [18] J.A. Gladysz, D.P. Curran, I.T. Horváth, Handbook of Fluorous Chemistry, Wiley-VCH, Weinheim, 2004.
- [19] K. Mikami (Ed.), Green Reaction Media in Organic Synthesis, Blackwell, Oxford, 2005, p. 7.
- [20] K. Mikami, Y. Mikami, Y. Matsumoto, J. Nishikido, F. Yamamoto, H. Nakajima, Tetrahedron Lett. 42 (2001) 289-292.
- [21] J. Nishikido, M. Kamishima, H. Matsuzawa, K. Mikami, Tetrahedron 58 (2002) 8345-8349.
- [22] X.-H. Hao, A. Yoshida, J. Nishikido, J. Fluorine chem.. 127 (2006) 193-199.
- [23] M. Shi, S.-C. Cui, Y.-H. Liu, Tetrahedron 61 (2005) 4965-4970.
- [24] M. Shi, S.-C. Cui, Chem. Commun. (2002) 994–995.
- [25] M. Shi, S.-C. Cui, J. Fluorine Chem. 116 (2002) 143-147.
- [26] M.-G. Shen, C. Cai, J. Fluorine Chem. 128 (2007) 232-235.
- [27] M.-G. Shen, C. Cai, Catal. Commun. 8 (2007) 871-875.
- [28] M.-G. Shen, C. Cai, W.-B. Yi, J. Fluorine Chem. 128 (2007) 1421–1424.
 [29] W.-B. Yi, C. Cai, X. Wang, J. Fluorine Chem. 128 (2007) 919–924.