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Polymer-supported ytterbium perfluorooctanesulfonate [Yb(OPf)$_3$]: A recyclable catalyst for organic reactions

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ABSTRACT

Amberlyst A-21, a kind of well-known and cheap polymeric material, was treated with ytterbium perfluorooctanesulfonate [Yb(OPf)$_3$] giving a reagent with a ytterbium loading of 1.34 (wt%). The polymer-supported fluorous ytterbium catalyses the highly efficient nitration, esterification, Fridel-Crafts acylation, and aldol condensation. The catalyst can be recovered by simple filtration and used again without a significant loss of catalytic activity. The protocol avoids the use of fluorous solvents during the reaction or workup, which are expensive and can leach in small amounts.

1. Introduction

In the past decade transition metal-catalyzed reactions in a fluorous biphasic system (FBS) have become one of the most important methods for facile catalyst separation from the reaction mixture and recycling of the catalyst, since the technique of FBS was described by Horváth and Rábai [1]. In this catalytic system (Fig. 1), the metal catalyst coordinated by perfluoroalkylated ligands can dissolve into the fluorous phase containing the product after the reaction [2,3]. Furthermore, FBS has the advantage of possible use for water-sensitive reactions unlike aqueous biphase systems [3]. Various fluorous Lewis acids catalysts have exhibited their own advantages such as high activity and easy recycle in FBS [2]. Recently, novel Lewis acids of lanthanide tris(perfluorooctanesulfonyl)-methide {Ln[C(SO$_2$R$_{f8}$)$_3$]$_3$, R$_{f8}$ = (CF$_2$)$_7$CF$_3$, Ln(CPf$_3$)$_3$} [4,5], lanthanide bis(perfluorooctanesulfonyl)amide {Ln[N(SO$_2$R$_{f8}$)$_2$]$_3$, Ln(NPf$_2$)$_3$} [7] and lanthanide perfluorooctanesulfonate [Ln(O-SO$_2$R$_{f8}$)$_3$, Ln(OPf)$_3$] [6,7] have been of special interest in that they have characteristic features such as low hygroscopicity, ease of handling, robustness for the reuse and high solubility in fluorous solvent.

No catalyst recovery method is without potential drawbacks [8,9]. Accordingly, the fluorous solvent requirement in FBS has prompted various concerns involving cost, solvent leaching, and environmental persistence [10]. Small amounts of fluorous solvents are similarly found in the organic layers of fluorous/organic liquid/liquid biphase systems. This makes losses unavoidable upon phase separation. Therefore, the development of the strategy to eliminate the fluorous solvent requirement for fluorous Lewis catalyst is a topic of enormous importance.

From the environmental point of view several practical and economical aspects of organic reactions have to be developed for their industrialization. Therefore, the development of highly active and easily reusable immobilized catalysts is of great interest to chemists [11,12]. To date, numerous accomplishments on polymer-supported catalysts suggest that the polymer-supported catalytic system is a promising alternative [12]. Ideally, the catalytic synthesis is efficiently carried out, and the catalyst can be easily separated from the reaction mixture by simple filtration.

Based on the work of fluorous silica gel-supported fluorous palladium(0) for the Sonogashira coupling in Bannwarth group [13], Nishikido and co-workers reported the use of a fluorous silica gel-supported bis(perfluorooctanesulfonyl)amides Lewis acids, such as Sn(NPf$_2$)$_4$, Hf(NPf$_2$)$_4$, and Ln(NPf$_2$)$_3$, for various organic reactions. These reactions include Baeyer–Villiger oxidation [14], Diels–Alder reaction [14], and direct esterification [15]. At the same time, they reported aqueous reactions catalyzed by cyclodextrinepichlorohydrin copolymer-supported Ln(NPf$_2$)$_3$, due to the affinity of cyclodextrin for the perfluorobutyl groups [16]. Ln(CPf$_3$)$_3$ and Ln(NPf$_2$)$_3$ as solids catalyst without any support

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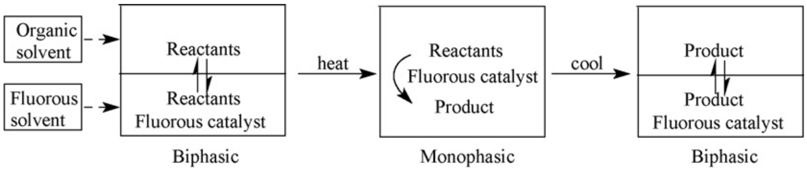


Fig. 1. Fluorous biphasic catalysis with fluorous solvent (the liquid/liquid FBS).

for Fridel-Crafts acylation were also described in Nishikido group [17].

In previous research on lanthanide perfluorooctanesulfonate catalyzed reactions, we found that the reported ytterbium perfluorooctanesulfonate [Yb(OPf)$_3$] is an efficient and relatively cheap catalyst for various organic reactions such as Fridel-Crafts alkylation [18] and acylation [19,20], esterification [21], nitration [22–24], and aldol condensation [25] in fluorous biphasic system. Taking concerns on fluorous solvents into consideration, we decided to concentrate on developing a supported-Yb(OPf)$_3$ catalytic system which is highly active and stable for organic reactions. Our goal was that it still be effective in the absence of fluorous solvent and can be recycled many times under aerobic conditions. In this paper, we develop a practical protocol for the esterification, nitration, Fridel-Crafts acylation, and aldol condensation under aerobic conditions with polymer supported Yb(OPf)$_3$ as a catalyst.

2. Experimental

2.1. General remarks

^{1}H NMR, and ^{19}F NMR spectra were characterized with a Bruker Advance RX300 spectrometer. GC analyse was performed on a Saturn 2000GC/MS instrument. IR spectra were recorded on a Bomen MB154S infrared analyzer. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. Inductively coupled plasma [ICP] spectra were measured on an Ultima2C apparatus. Amberlyst A-21 was commercially obtained from Weide Chemical Co. of Tianjin. Heptadecafluorooctanesulfonic acid ($R_{f8}SO_3H$, PfOS) and perfluorodecalin ($C_{10}F_{18}$, *cis* and *trans*-mixture) were commercially obtained from ARCOS Co. Amberlyst-21 (A-21) was dried at 80 °C in vacuum for 24 h before being used. Other commercially available reagents were used without further purification.

2.2. Preparation of Yb(OPf)$_3$

A mixture of a solution of PfOS (0.77 g, 1.5 mmol) in water (5 ml) and Yb_2O_3 (0.12 g, 0.25 mmol) powder was refluxed with stirring for 3 h. The resulting gelatin-like solid was collected, washed and dried at 150 °C in vacuum to give a white solid (0.82 g, 98%), which does not melt up to 500 °C, but shrinks around 380 °C and 450 °C. IR (KBr): 1237 (CF_3), 1152 (CF_2), 1081 (SO_2), 1059 (SO_2), 747 (S–O) and 652 (C–S) cm^{-1}. Anal. Calcd. for $C_{24}O_9F_{51}S_3Yb$: Yb, 10.36; C, 17.25. Found: Yb, 10.09; C, 17.13. ^{19}F NMR: δ -126.0, -121.2, -114.4, -81.1.

2.3. Preparation of A-21-Yb(OPf)$_3$

A mixture of Yb(OPf)$_3$ (0.6 g) and A-21 (4 g) in acetone (50 ml) was refluxed with stirring for 24 h. The mixture was allowed to stand at room temperature for *ca.* 2 h without stirring. Then the deposit was separated and washed with water (20 ml × 3) and toluene (20 ml × 2). The isolated solids were dried at 80 °C for 24 h in vacuum to give a gray solid (4.52 g). The solid contained 1.34% Yb by weight based on the ICP analysis.

2.4. Typical procedure for the esterification with A-21-Yb(OPf)$_3$

Benzoic acid (1.23 g, 10 mmol) was added to a mixture of A-21-Yb(OPf)$_3$ (0.52 g, 0.4 mol% Yb) and toluene (10 ml) in a glass flask under vigorous stirring. After *ca.* 5 min, isopentanol (1.1 ml, 10 mmol) was introduced into the glass tube. After stirring at 100 °C for 6 h, the mixture was cooled and the catalyst was filtered. The filtrate was washed with 5% $NaHCO_3$ solution (10 ml), saturated NaCl solution (5 ml) and water (5 ml). The combined organic phases were dried over Na_2SO_4 and *p*-xylene (1.06 g, 10 mmol) was added as internal standard for GC analysis. After GC and GC/MS analyses, the solvents and volatiles were removed under vacuum, and then the residue was subjected to column chromatography on SiO_2 with hexane and ether (20:1, v/v) as eluent to give the esterification product (1.69 g, 88%).

2.5. Typical procedure for the esterification with Yb(OPf)$_3$ in FBS

Yb(OPf)$_3$ (0.067 g, 0.4 mol%) was added to a mixture of toluene (5 ml) and perfluorodecalin ($C_{10}F_{18}$, *cis* and *trans*-mixture, 5 ml) in a glass flask under vigorous stirring. After *ca.* 5 min, benzoic acid (1.23 g, 10 mmol) and isopentanol (1.1 ml, 10 mmol) were introduced into the glass tube. After stirring at 100 °C for 6 h, the mixture was cooled to room temperature. The fluorous layer on the bottom was separated for next esterification. The upper organic phase was washed with 5% $NaHCO_3$ solution (5 ml), saturated NaCl solution (5 ml) and water (5 ml). The combined organic phases were dried over Na_2SO_4 and *p*-xylene (1.06 g, 10 mmol) was added as internal standard for GC analysis. After GC and GC/MS analyses, the solvents and volatiles were removed under vacuum, and then the residue was subjected to column chromatography on SiO_2 with hexane and ether (20:1, v/v) as eluent to give the esterification product (1.82 g, 95%).

2.6. Typical procedure for the nitration with A-21-Yb(OPf)$_3$

65% HNO_3 (1.1 ml, 24 mmol) was slowly added to a mixture of A-21-Yb(OPf)$_3$ (3.1 g, 1 mol% Yb) and toluene (4.2 ml, 40 mmol) in a glass flask under vigorous stirring. After stirring at 60 °C for 1 h, the mixture was cooled and the catalyst was filtered. The filtrate was washed with 5% $NaHCO_3$ solution (5 ml) and water (5 ml). The combined organic phases were dried over $CaCl_2$ and evaporated under vacuum. Then, the residue was subjected to column chromatography on SiO_2 with EtOAC and petroleum ether (1:5, v/v) as eluent to give nitrotoluenes as yellowish liquid (3.09 g, 94%). The component of nitro isomers were measured by GC.

2.7. Typical procedure for the Fridel-Crafts acylation with A-21-Yb(OPf)$_3$

Acetic anhydride (1.1 ml, 12 mmol) was added to a mixture of A-21-Yb(OPf)$_3$ (1.55 g, 1 mol% Yb) and anisole (2.2 ml, 20 mmol) in chlorobenzene (6 ml) in a glass flask under vigorous stirring. After stirring at 80 °C for 1 h, the mixture was cooled and the catalyst was filtered. The filtrate was diluted with CH_2Cl_2 (10 ml), and washed with 5% $NaHCO_3$ solution (10 ml) and water (10 ml). The

Table 1
The esterifications of benzoic acid with isopentanol in two catalytic system[a]

Entry	Catalyst	Solvent	Yield (%)[b]				
			Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
1	$Yb(OPf)_3$	Toluene/perfluorodecalin	95	94	92	93	91
2	A-21-$Yb(OPf)_3$	Toluene	88	86	85	83	81

[a] The reaction condition: benzoic acid, 10 mmol; isopentanol, 10 mmol; [Yb], 0.4 mol%; toluene/perfluorodecalin, 5 ml/5 ml; toluene, 10 ml; 6 h, 100 °C.
[b] Isolated yields.

combined organic phases were dried over Na_2SO_4 and *p*-xylene (1.27 g, 12 mmol) was added as internal standard for GC or GC/MS analysis.

2.8. Typical procedure for aldol condensation with A-21-Yb(OPf)$_3$

Benzaldehyde (1.1 ml, 12 mmol) was added to a mixture of A-21-$Yb(OPf)_3$ (0.62 g, 0.4 mol% Yb) and acetophenone (2.4 ml, 20 mmol) in toluene (10 ml) in a glass flask under vigorous stirring. After refluxing for 1 h, the mixture was cooled and the catalyst was filtered. The filtrate was diluted with CH_2Cl_2 (10 ml), and washed with 5% $NaHCO_3$ solution (10 ml) and water (10 ml). The combined organic phases were dried over Na_2SO_4 and evaporated under vacuum. Then, the residue was recrystallized from ethanol to give chalcone product as a yellowish solid (2.09, 84%).

2.9. Typical procedure for catalyst recycling

After the reaction as described above, the mixture was allowed to stand for *ca.* 30 min without stirring at room temperature, and then filtered. The solids were washed with water (10 ml × 3) and toluene (10 ml × 3). The catalyst isolated was dried at 80 °C for 24 h in vacuum. The resulting catalyst was ready for further runs in the reaction.

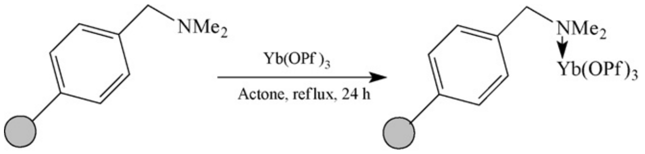
3. Results and discussion

3.1. Preparation of A-21-Yb(OPf)$_3$

We prepared $Yb(OPf)_3$ from ytterbium oxide (Yb_2O_3) by stirring it with heptadecafluorooctanesulfonic acid ($R_{f8}SO_3H$, PfOS) (Scheme 1) according to the previously reported method [18–23]. To select our catalytic system, we took into account that the ytterbium catalyst has to be fixed onto a polymer, possibly by chelation. Because recent developments on the polymeric material Amberlyst A-21 (A-21) provide a new possible candidate for a solid support for immobilization of catalysts [26], we selected to test the activity of $Yb(OPf)_3$ on A-21. This well-known polymer is a dimethylaminomethyl-grafted polystyrene and thus bears an amine group that can act as a chelatant [26]. The A-21-$Yb(OPf)_3$ can be conveniently prepared by stirring $Yb(OPf)_3$ and A-21 in acetone at elevated temperature (Scheme 2). After filtration and washing, the catalyst was dried and the content of ytterbium confirmed by weight and analysis.

$$R_{f8}SO_3H + Yb_2O_3 \xrightarrow[H_2O,\ \text{reflux, 3h}]{} (R_{f8}SO_3)_3Yb$$

Scheme 1. Preparation of Yb(OPf)$_3$.



Scheme 2. Preparation of A-21-Yb(OPf)$_3$.

The thermal studies (TGA) showed that A-21 resins were all stable up to 130 °C. Surprisingly the supported $Yb(OPf)_3$ catalyst was even more stable, with decomposition temperature being >140 °C. The $Yb(OPf)_3$ catalyst of this type are not only air and moisture stable, but also thermally robust.

3.2. Esterification

The esterification of benzoic acid with isopentanol was firstly investigated. The control experiment elucidated that only 5% of esterification product could be obtained in the absence of fluorous catalyst. Then, the esterification employing fluorous catalysis or polymer-supporting technology was examined with $Yb(OPf)_3$ catalyst. In stage of FBS, experiments were conducted in binary system perfluorodecalin/toluene (1:1, v/v). Reactions proceeded under one-phase conditions at 100 °C. After 6 h, esterification product was obtained in 96% isolated yield. As summarized in Table 1, good yields were maintained for three to five cycles. The stage was set for the experimental sequence in polymer-supported system. Benzoic acid, isopentanol, and A-21-$Yb(OPf)_3$ catalyst were combined in toluene at room temperature. The sample was next warmed to 100 °C. After stirring for 6 h, the reaction mixture was cooled. The catalyst precipitated as a white solid. The solid was separated, washed with toluene, dried at vacuum and then reused for the next reaction. Although a slight decease of the acidity of the Lewis acid $Yb(OPf)_3$ because of amino-group on the A-21 polymer was found, the reaction gave the esterification product in 88% yield and the supported fluorous catalyst can be reused several times without a significant loss of yield. To better gauge the extent of catalyst recovery, the reaction rates (=activity) at cycles 1, 3 and 5 were compared. The representative results are shown in Fig. 2. It was found that there was almost no difference for the formation

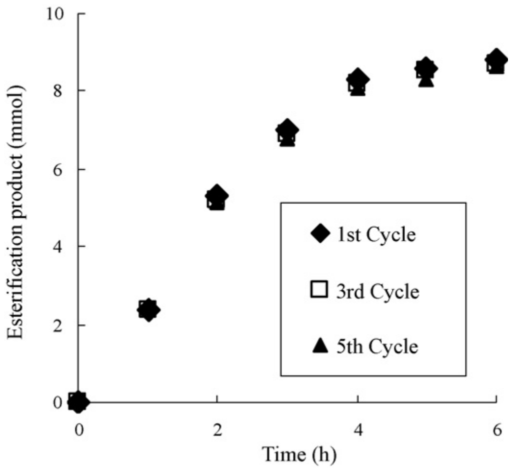
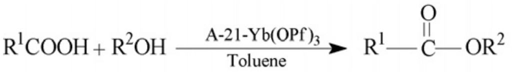


Fig. 2. The esterifications of benzoic acid with isopentanol at different cycles.

Table 2
The esterifications of various acids and alcohols with A-21-Yb(OPf)$_3$[a]



$$R^1COOH + R^2OH \xrightarrow[\text{Toluene}]{\text{A-21-Yb(OPf)}_3} R^1-\overset{O}{\overset{\|}{C}}-OR^2$$

Entry	R^1	R^2	Conditions	Yield (%)[b]
1	Ph	n-C_4H_9	70 °C, 6 h	95
2	Ph	$PhCH_2$	100 °C, 12 h	89
3	$Ph(CH_2)_2$	n-C_4H_9	70 °C, 5 h	94
4	CH_3CH_2	$CH(CH_3)_2$	50 °C, 8 h	86
5	CH_3	$Ph(CH_2)_2$	100 °C, 8 h	93

[a] The reaction condition: acid, 10 mmol; alcohol, 10 mmol; A-21-Yb(OPf)$_3$, 0.65 g (0.5 mol% of Yb); toluene, 10 ml.

[b] Isolated yields.

Table 4
Recycling of A-21-Yb(OPf)$_3$ catalyst in nitration of toluene

Cycle	Yb leaching (ppm)
1	2.5
2	4.8
3	7.4
4	10.3
5	14.5

rate of esterification product at cycles 1, 3, and 5 within 6 h reaction time, which indicate that there was not only no significant loss of the catalyst but also no depression of catalytic activity during the recycling. Thus, it can be deduced that >98% of the catalyst should still remain even after the fifth cycle.

From these observations it was revealed that using Yb(OPf)$_3$ as fluorous catalyst the technology of polymer supporting can be considered the most attractive alternative to existing FBS immobilizing protocol (Fig. 1). To examine the scope for this supported strategy in esterification, a variety of acids were carried out with different alcohols, and good to excellent results were obtained (Table 2). The efficacy of A-21-Yb(OPf)$_3$ was confirmed by the direct of esterification of benzoic acid/butanol, benzoic acid/benzyl alcohol, 3-phenylpropionic acid/butanol, propionic acid/isopropanol, acetic acid/2-phenylethyl alcohol.

3.3. Nitration

Nitration of aromatics using 65% nitric acid was then examined. In a typical experiment, the catalyst added to aromatic substrate, then the nitric acid (0.6 equiv.) was added. The reaction mixture was stirred at 80 °C. The course of the reaction was followed by GC. Thus, in the reaction of toluene in the presence of A-21-Yb(OPf)$_3$, the nitration product was obtained in 94% isolated yield after 1 h (Table 3, entry 1). Almost no by-products such as oxidative and polynitrated compounds were detected by GC. In the control experiment only 26% yield of nitrotoluenes were obtained (Table 3, entry 2).

The efforts were directed to the study of recycling of such catalytic system using the nitration of toluene. After stirring at 80 °C for 1 h, the reaction mixture was filtered. The separated supported ytterbium catalyst could be reused for the next reaction after washing and drying. The nitration under the conditions mentioned above was run for five consecutive cycles respectively, furnishing the corresponding nitrotoluenes with 94%, 92%, 92%, 91%, 89% isolated yields (Table 3, entry 1). No noticeable loss of activity was observed as noted by yield. There were no significant differences between the IR spectra of the initial and recovered fluorous phase which may indicate that the supported fluorous ytterbium catalyst was recovered unaltered after the nitration process had taken place. As is shown in Table 4, ytterbium leaching from the catalyst is negligible with each cycle. The results demonstrate the A-21-Yb(OPf)$_3$ catalyst may have practical utility.

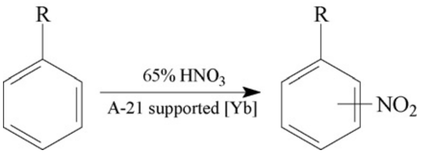
We then screened other ytterbium catalysts supported on Amberlyst A-21 for the nitration of toluene (Table 3, entries 3-4). It was found that supported Yb(OTf)$_3$ catalyst had similarly high activity for the reaction with a high conversion to the nitration product at 80 °C over 2 h. However, an obvious decrease in conversion was observed in the recycle of catalysts. In the case of YbCl$_3$, reaction only afforded the moderate conversion. The robustness of the A-21-Yb(OPf)$_3$ catalyst for recycling using may partly be attributed to the water-repellent nature of the perfluoroalkane chain "$(-CF_2-CF_2-)_n$" of Yb(OPf)$_3$ which refuses the approach of water molecules to the central metal cation, thus maintaining its high catalytic activity.

Next, we applied the supported catalytic system to other aromatic nitration (Table 3, entries 5–8). The results were summarized in Table 3. Accordingly, A-21-Yb(OPf)$_3$ is also applicable to the nitration of fluorobenzen, chlorobenzene, ethylbenzene, *p*-xylene.

3.4. Fridel-Crafts acylation

Fridel-Crafts acylation of anisole with acetic anhydride was carried out in this system to investigate the potential of supported ytterbium at low (1 mol%) catalytic loading (Table 5, entry 1). The

Table 3
Nitration of aromatics with supported ytterbium catalyst[a]

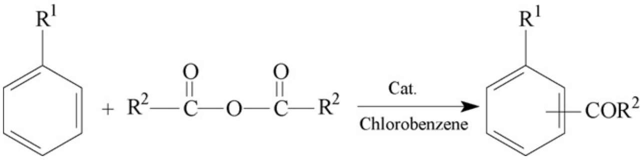


Entry	R	[Yb]	Time (h)	Yield (%)[b]	p:m:o
1	CH_3	Yb(OPf)$_3$	4	94, 92, 92, 91, 89	48:0:52
2	CH_3	–	4	26	39:1:60
3	CH_3	Yb(OTf)$_3$	6	86, 67, 40	42:0:58
4	CH_3	YbCl$_3$	8	58	40:1:59
5	F	Yb(OPf)$_3$	6	95	86:1:13
6	Cl	Yb(OPf)$_3$	10	96	71:0:29
7	CH_3CH_2	Yb(OPf)$_3$	5	94	68:2:30
8	*p*-Xylene	Yb(OPf)$_3$	2	98	–

[a] The reaction condition: aromatics, 40 mmol; 65% HNO$_3$, 24 mmol; A-21-Yb(OPf)$_3$, 1.55 g (1 mol% of Yb); 60 °C.

[b] Isolated yields based on HNO$_3$.

Table 5
Fridel-Crafts acylation[a]

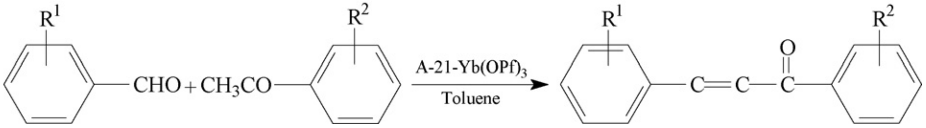


Entry	R^1	R^2	Cat.	Time (h)	Yield (%)[b]	p:m:o
1	OCH_3	CH_3	A-21-Yb(OPf)$_3$	2	86, 83, 81	98:0:2
2	OCH_3	CH_3	–	2	<1	95:0:5
3	OCH_3	CH_3	AlCl$_3$	2	3	94:0:6
4	OCH_3	CH_3	Yb(OPf)$_3$	2	42	96:0:4
5	OCH_3	Ph	A-21-Yb(OPf)$_3$	3	92	99:0:1
6	CH_3	CH_3	A-21-Yb(OPf)$_3$	12	10	96:0:4
7	CH_3	Ph	A-21-Yb(OPf)$_3$	12	9	99:0:1
8	*p*-xylene	CH_3	A-21-Yb(OPf)$_3$	12	16	–

[a] The reaction condition: aromatics, 20 mmol; acid anhydride, 12 mmol; Cat., 1 mol%; 100 °C.

[b] GC yields based on acid anhydrides.

Table 6
Aldol condensation with A-21-Yb(OPf)$_3$[a]



Entry	R^1	R^2	Time (h)	Yield (%)[b]
1	H	H	12	84, 84, 82
2	4-CH_3O	H	16	68
3	4-NO_2	H	8	94, 93
4	H	4-Cl	12	87
5	H	4-CH_3	16	75
6	H	4-CH_3O	24	62
7	H	4-NO_2	6	95

[a] The reaction condition: benzaldehydes, 12 mmol; acetophenones, 20 mmol; toluene, 10 ml; A-21-Yb(OPf)$_3$, 0.62 g (0.4 mol% of Yb); reflux.

[b] Isolated yields based on benzaldehyde.

control experiment elucidated that <1% product of acylation was obtained in the absence of catalyst (Table 5, entry 2). In addition, the activity of $AlCl_3$, a traditional industrially catalyst for Fridel-Crafts acylation, was significantly low under the present mild reaction conditions (Table 5, entry 3).

Inspired by the work on the Ln(NPf$_2$)$_3$ catalysts without supports [17], we tried the Yb(OPf)$_3$ Lewis acid as solids catalyst for the acylation directly (Table 5, entry 4). However, the reaction gave a low yield of the aromatic ketones because of low solubility of the solid catalyst in the reaction mixture. In addition, it was difficult to collect or recover Yb(OPf)$_3$ by filtration, which led to unavoidable and significant loss of Yb(OPf)$_3$. From these observations it can be concluded that the presence of A-21 as support is essential to obtain good yields of acylation and robustness of the catalytic system for recycling using without fluorous solvents. Thus, the acylation was extended to other anhydride such as benzoic anhydride under the above reaction conditions. Although the reaction became slower, benzoic anhydride gave 92% of the corresponding aromatic ketones after 3 h (Table 5, entry 5). However, the less electron rich toluene (Table 5, entries 6-7) and *p*-xylene (Table 5, entry 8) underwent acylation much less smoothly than anisole, and produced ketones in poor yields.

3.5. Aldol condensation

The aldol condensation of various aldehydes and aromatic ketones was examined to evaluate this supporting system. Not surprisingly, the high catalytic activity and high efficiency of recycle of A-21-Yb(OPf)$_3$ were further clearly proven by the aldol condensation (Table 6). All the reaction products were isolated and identified as α,β-unsaturated ketones, and no side reactions were observed. Based on ^1H NMR and GC–MS data, the reaction was found to give *E*-stereoisomer as sole product. The purity of the products thus obtained was consistently high, probably because the perflates-catalyzed reactions took place under neutral conditions. In general, reactions between aromatic aldehydes and ketones gave good results. The condensations of *p*-substituted benzaldehyde with *p*-substituted acetophenones yielded the corresponding chalcones and the product yields were remarkably affected by the substituent groups of either aldehydes or ketones: reactants having electron-withdrawing substituents gave high yields and those having electron-donating ones gave low yields.

4. Conclusion

In conclusion, A-21-Yb(OPf)$_3$ was found to be an interesting and highly efficient catalyst for esterification, nitration, Fridel-Crafts acylation, and aldol condensation. The catalyst performed is easily separated and can be reused several times without a noticeable change in activity under fluorous solvent free conditions. Further investigations of more favourable strategy and conditions for recycle of Yb(OPf)$_3$, as well as synthetic applications, are currently in progress and will be reported in due course.

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References

[1] I.T. Horváth, J. Rábai, Science 266 (1994) 72–73.
[2] J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley-VCH, Weinheim, 2004.
[3] K. Mikami (Ed.), Green Reaction Media in Organic Synthesis, Blackwell, Oxford, 2005.
[4] K. Mikami, Y. Mikami, Y. Matsumoto, J. Nishikido, F. Yamamoto, H. Nakajima, Tetrahedron Lett. 42 (2001) 289–292.
[5] J. Nishikido, M. Kamishima, H. Matsuzawa, K. Mikami, Tetrahedron 58 (2002) 8345–8349.
[6] X.-H. Hao, A. Yoshida, J. Nishikido, J. Fluorine Chem. 127 (2006) 193–199.
[7] X.-H. Hao, A. Yoshida, J. Nishikido, Green Chem. (2004) 566–569.
[8] J.A. Gladysz, Pure Appl. Chem. 73 (2001) 1319–1324.
[9] J.A. Gladysz, Chem. Rev. 102 (2002) 3215–3216.
[10] M. Wende, J.A. Gladysz, J. Am. Chem. Soc. 125 (2003) 5861–5872.
[11] B.M.L. Dioos, I.F.J. Vankelecom, P.A. Jacobs, Adv. Synth. Catal. 348 (2006) 1413–1446.
[12] P.-W. Zheng, W.-Q. Zhang, J. Catal. 250 (2007) 324–330, and references therein.
[13] C.H. Tzschucke, C. Markert, H. Glatz, W. Bannwarth, Angew. Chem. Int. Ed. 41 (2002) 4500–4503.
[14] O. Yamazaki, X.-H. Hao, A. Yoshida, J. Nishikido, Tetrahedron Lett. 44 (2003) 8791–8795.
[15] A. Yoshida, X.-H. Hao, O. Yamazaki, J. Nishikido, Molecules 11 (2006) 627–640.
[16] J. Nishikido, M. Nanbo, A. Yoshida, H. Nakajima, Y. Matsumoto, K. Mikami, Synlett (2002) 1613–1616.
[17] K. Mikami, Y. Mikami, H. Matsuzawa, Y. Matsumoto, J. Nishikido, F. Yamamoto, H. Nakajima, Tetrahedron 58 (2002) 4015–4021.
[18] W.-B. Yi, C. Cai, J. Fluorine Chem. 126 (2005) 831–833.
[19] W.-B. Yi, C. Cai, J. Fluorine Chem. 126 (2005) 1191–1195.
[20] M. Shi, S.-C. Cui, J. Fluorine Chem. 116 (2002) 143–147.
[21] W.-B. Yi, C. Cai, Chin. J. Org. Chem. 25 (2005) 1434–1436.
[22] M. Shi, S.-C. Cui, Chem. Commun. (2002) 994–995.
[23] W.-B. Yi, C. Cai, J. Energy Mater. 25 (2007) 129–139.
[24] W.-B. Yi, C. Cai, Synth. Commun. 36 (2006) 2957–2961.
[25] W.-B. Yi, C. Cai, J. Fluorine Chem. 126 (2005) 1553–1558.
[26] C. Girard, M. Aufort, Org. Lett. 8 (2006) 1689–1692.