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# A novel ytterbium/perfluoroalkylated-pyridine catalyst for Baylis–Hillman reaction in a fluorous biphasic system

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**Abstract**

Ytterbium perfluorooctanesulfonate [$Yb(OPf)_3$] catalyses the highly efficient Baylis–Hillman reaction in the presence of a catalytic amount of a novel perfluoroalkylated-pyridine as a ligand in a fluorous biphasic system (FBS) composed of toluene and perfluorodecalin. The new process can be carried out successfully without the use of a stoichiometric amount of Lewis base. The fluorous phase containing the active catalytic species is easily separated and can be reused several times without significant loss of catalytic activity.


*Keywords:* Baylis–Hillman reaction; Ytterbium perfluorooctanesulfonate; Perfluorinated pyridine; Fluorous biphasic catalysis

## 1. Introduction

The Baylis–Hillman reaction and related processes have become increasingly important in synthetic organic chemistry because the resulting adducts have an array of multifunctional groups which can be subjected to numerous transformations [1]. This carbon–carbon bond formation was typically catalyzed by DABCO or tertiary phosphines. The major drawbacks of the Baylis–Hillman reaction are shown by its slow reaction rate and limited scope of substrates. To overcome its shortcomings, much effort has been made on using Lewis acids or adding additives to the reaction system to activate carbonyl electrophiles [2,3]. Among various Lewis acids, lanthanide triflates [$Ln(OSO_2CF_3)$, $Ln(OTf)_3$] have been successfully utilized to promote the Baylis–Hillman reaction in the presence of stoichiometric amount of Lewis base catalysts [3]. However, in those reported cases recycle of catalysts used has not heretofore been achieved.

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 [4] and Horváth and coworkers [5]. 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 recycling of the catalyst [5]. In this catalytic system, the metal catalyst coordinated by perfluoroalkylated ligands can dissolve into the fluorous phase containing the product after the reaction. Recently, novel Lewis acids of lanthanide tris(perfluorooctanesulfonyl)methide {$Ln[C(SO_2R_{f8})_3$, $R_{f8} = (CF_2)_7CF_3$], $Ln(CPf)_3$} [6], lanthanide bis(perfluorooctanesulfonyl)amide {$[LnN(SO_2R_{f8})_2]_3$, $[Ln(NPf_2)_3]$} [7] and lanthanide perfluorooctanesulfonate [$Ln(OSO_2R_{f8})_3$, $Ln(OPf)_3$] [8,9] 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.

During our studies to explore the utility of transition metal perflates-catalyzed reactions in fluorous solvents [9], we found that Baylis–Hillman reaction can proceed smoothly in the presence of ytterbium perfluorooctanesulfonate [$Yb(OPf)_3$, Scheme 1], and various perfluoroalkylated-pyridine ligands **1**–**3** (Scheme 2), in a FBS composed of toluene and perfluorodecalin. Concurrently, we also found that this new process can be carried out successfully with no need of a stoichiometric amount Lewis base and the robustness of the catalytic system for reuse can be obtained by simple phase-separation. Uemura and coworkers have previously reported the synthesis of ligands **1**–**3** and their application in the palladium-catalyzed oxidation reaction [10]. Gladysz and coworkers described the synthesis

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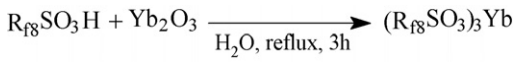
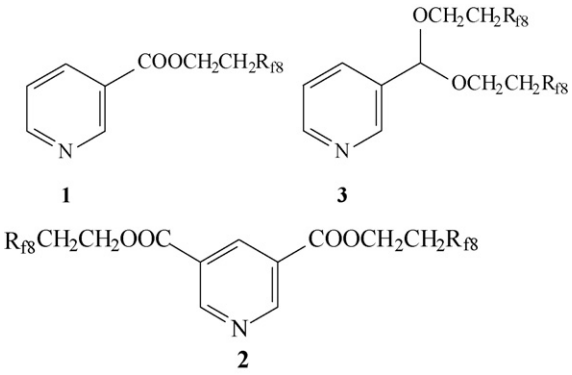



Scheme 1.




Scheme 2.

and physical properties of fluorous ligands containing simple hydrocarbon segments between the pyridine ring and perfluoroalkyl group, such as 2,6- and 3,5-$NC_5H_3(CH_2CH_2R_{f8})_2$ and 2,4,6-$NC_5H_2(CH_2CH_2R_{f8})_3$ [11].

## 2. Results and discussion

We prepared $Yb(OPf)_3$ from ytterbium oxide ($Yb_2O_3$) by stirring it with heptadecafluorooctanesulfonic acid ($R_{f8}SO_3H$, PfOH) (Scheme 1), and perfluorinated pyridine **1–3** according to the method described by Uemura. $Yb(OPf)_3$ and **1–3** were soluble in perfluorodecalin ($C_{10}F_{18}$), perfluoromethylcyclohexane ($CF_3C_6F_{11}$) and $CF_3C_6H_5$. In perfluorodecalin, **3** was more soluble than other ligands. **1–3** also showed significant solubility in ether, THF, $CHCl_3$ and $CH_2Cl_2$. However, **1–3** always appeared to be less soluble in toluene, hexane and octane. $Yb(OPf)_3$ showed almost no solubility in traditional organic solvent such as methanol, $CH_3CN$, $CH_2Cl_2$ and toluene.

Quantitative data on fluorous phase affinities were sought. The perfluorodecalin/toluene partition coefficients were determined by GC or ICP according to the method previously reported [6,11]. These reflect *relative* as opposed to *absolute* solubilities and are summarized in Table 1. In pyridine ligand series, two $R_{f8}$ pony tails give high fluorous phase affinities (coefficients for **2** and **3** were 93.8:6.2 and 99.8:0.2, respectively), allowing essentially quantitative recovery. $Yb(OPf)_3$ retained in fluorous phase quantitatively, with the coefficients being >99.9:<0.1.

The Baylis–Hillman reaction of methyl acrylate with benzaldehyde in the presence of ytterbium complexes in a FBS composed of toluene and perfluorodecalin ($C_{10}F_{18}$) at 60 °C using **1–3** as ligands was firstly examined (Scheme 3 and Table 2). The results are summarized in Table 2. The reaction using $Yb(OPf)_3$ as catalyst alone failed to give the Baylis–Hillman product. Use of ligand **1** resulted in 64% yield of desired product, however, the recovered fluorous phases showed a lower catalytic activity, which could be ascribed to the loss of perfluorinated ligand in the toluene phase. Ligand **2** gave the poor result due to the weaker coordinative ability of ligand **2**, which has two electron-withdrawing substituents on an aromatic nuclei. Although the reaction became slower in the reaction of ligand **3**, in this process the toluene (upper) phase was colorless after the reaction, as opposed to the case of **1** and **2**, whose upper phase was yellowish, suggesting that $Yb(OPf)_3$ and ligand **3** could dissolve in the fluorous phase. Notably, the reaction using **3** as ligand gave 86% yield of Baylis–Hillman product in 6 h, longer reaction time did not significantly improve the result.

We then screened a range of lanthanide Lewis acids in the presence of ligand **3** (Table 2, entries 6–9). $Yb(OPf)_3$ and $Sc(OPf)_3$ provided the best result, and reaction with $Yb(OPf)_3$

Table 1
Partition coefficients (24 °C)

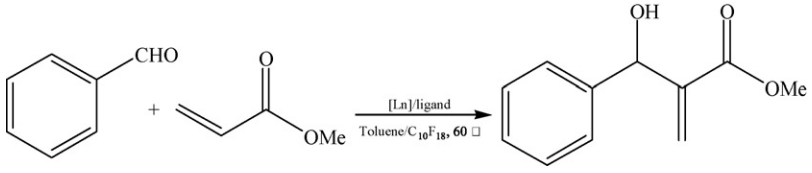
| Analyte | Perfluorodecalin/toluene |
|---|---|
| **1** | 88.7:11.3[a] |
| **2** | 93.8:6.2[a] |
| **3** | 99.8:0.2[a] |
| $Yb(OPf)_3$ | >99.9:<0.1[b] |

[a] Detected by GC.
[b] Detected by ICP.

Table 2
Data for the reactions in Scheme 3[a]

| Entry[b] | [Ln] | Ligand | Time (h) | Yield (%)[c] |
|---|---|---|---|---|
| 1 | $Yb(OPf)_3$ | – | 12 | – |
| 2 | $Yb(OPf)_3$ | **1** | 4 | 64 |
| 2a | $Yb(OPf)_3$ | **1** | 4 | 53 |
| 2b | $Yb(OPf)_3$ | **1** | 4 | 40 |
| 3 | $Yb(OPf)_3$ | **2** | 4 | 21 |
| 4 | $Yb(OPf)_3$ | **3** | 6 | 86 |
| 5 | $Yb(OPf)_3$ | **3** | 12 | 87 |
| 6 | $Sc(OPf)_3$ | **3** | 6 | 87 |
| 7 | $Eu(OPf)_3$ | **3** | 6 | 57 |
| 8 | $Sm(OPf)_3$ | **3** | 6 | 42 |
| 9 | $La(OPf)_3$ | **3** | 6 | 63 |

[a] The reaction condition: methyl acrylate, 0.02 mol; benzaldehyde, 0.01 mol; ligand, 0.5 mmol; [Ln], 0.05 mmol; fluorous solvent, 4 ml; toluene, 2 ml; 60 °C.
[b] Entries a and b correspond to the first and second recycling of the fluorous phase, respectively.
[c] Isolated yield based on benzaldehyde.




Scheme 3.

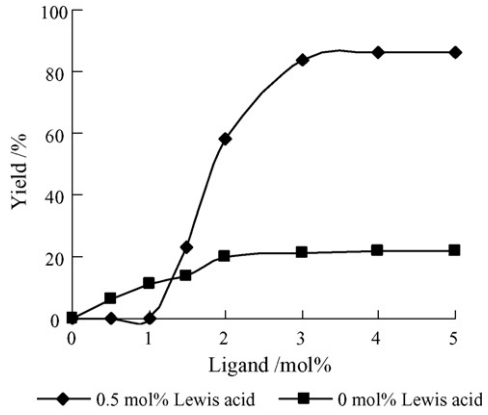



Fig. 1. Effect of amount of ligand **3** on reaction.

was studied in greater detail as it is more economical. Reactions were carried out with varied amounts of ligand **3** in the absence or presence (0.5 mol%) of $Yb(OPf)_3$. The results are depicted graphically in Fig. 1. For the case of no Lewis acid, the reaction only gave the product in nearly 20% yield with 2 mol% ligand **3**. Increase of ligand appeared not to work for the improvement of reaction. In the presence of Lewis acid, it was found that no reaction occurred until 1 mol% **3** had been added, possibly because all the perfluoroalkylated-pyridine ligand was associated with the Lewis acid to give a weaker and more labile complex [3]. This complex may still function as a Lewis acid as there should still be free sites on the metal to allow coordination of the aldehyde and therefore accelerate the reaction [3]. Concurrently, the perfluoroalkylated-pyridine ligand can perform its role as a nucleophilic catalyst at concentrations above 1 mol%. Notably, the system containing 0.5 mol% $Yb(OPf)_3$ and 3 mol% ligand **3** gave the Baylis–Hillman product in 86% yield. Further increases of amount of the ligand did not significantly improve the yield, which is consistent with the result of no Lewis acid.

The efforts were directed to the study of recycling of such catalytic system using the reaction with the ratio of ligand **3** to $Yb(OPf)_3$ being 6. After reaction, the separated fluorous phase could be reused for the next reaction without any specific treatment and the work-up procedure of recycling was accomplished by simple phase-separation. In order to analyze and quantify the 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 rate of Baylis–Hillman product at cycles 1, 3 and 5 within 6 h reaction time, which indicated that there was not only no loss of the catalyst but also no depression of catalytic activity during the recycling. Thus, it can be deduced that >99% of the catalyst [$Yb(OPf)_3$ and **3**] should still remain in the fluorous phase even after the fifth cycle. The problem on leaching in these catalyst recycling systems was studied. Based on $^{19}F$ NMR data, no loss of $Yb(OPf)_3$ to the organic phases can be detected. Only trace of ligand **3** (<0.1%) and perfluorodecalin was found by GC–MS in separated organic layer. In fact, we also investigated the exact amount of $Yb(OPf)_3$ and ligand **3** in the recovered fluorous phase by ICP and GC, finding that >99.9% of $Yb(OPf)_3$ and 99.8% of ligand

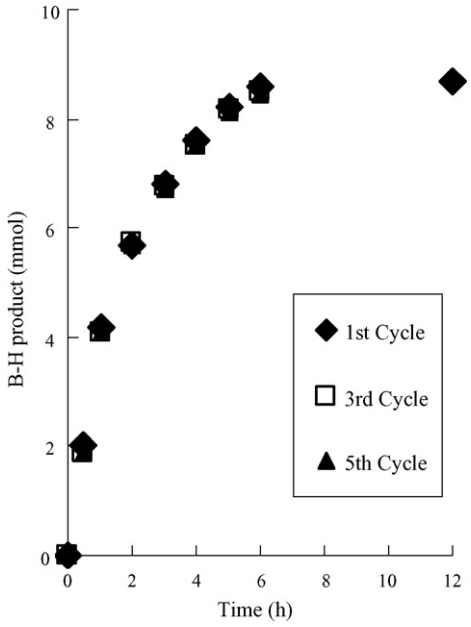
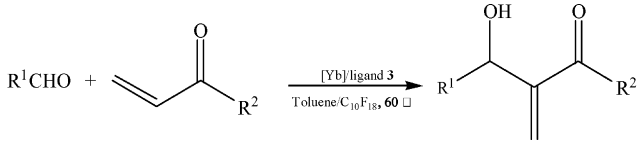



Fig. 2. The reaction of methyl acrylate with benzaldehyde at different cycles.




Scheme 4.

**3** retained in perfluorodecalin. This result suggests the robustness of the catalytic system for recycled use.

The Baylis–Hillman reaction catalyzed by $Yb(OPf)_3$ and ligand **3** were extended to various aldehydes and Michael acceptors (Scheme 4, Table 3). The results collected in Table 3 indicated that both aliphatic and aromatic aldehydes can be employed as electrophilic acceptors among which aromatic aldehydes gave better yields. For aromatic aldehydes, attachment

Table 3
Data for the reactions in Scheme 4

| Entry | $R^1$ | $R^2$ | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | 4-$NO_2$Ph | OMe | 2 | 92 |
| 2 | 4-ClPh | OMe | 3 | 87 |
| 3 | 4-MePh | OMe | 8 | 79 |
| 4 | 4-MeOPh | OMe | 24 | 46 |
| 5 | 2-Naphthyl | OMe | 8 | 85 |
| 6 | 2-Furyl | OMe | 8 | 78 |
| 7 | $C_2H_5$ | OMe | 12 | 51 |
| 8 | *i*-$C_3H_7$ | OMe | 12 | 54 |
| 9 | *n*-$C_5H_{11}$ | OMe | 12 | 48 |
| 10 | Ph | $OC(Me)_3$ | 6 | 86 |
| 11 | 4-$NO_2$Ph | $OC(Me)_3$ | 2 | 93 |
| 12 | Ph | Me | 6 | 81 |
| 13 | 4-$NO_2$Ph | Me | 3 | 90 |

The reaction condition: methyl acrylate, *tert*-butyl acrylate, methyl vinyl ketone, 0.02 mol; aldehyde, 0.01 mol; ligand, 0.3 mmol; [Yb], 0.05 mmol; fluorous solvent, 4 ml; toluene, 2 ml; 60 °C.

[a] Isolated yield based on aldehyde.

of electron withdrawing group is favorable to the reaction. Hetereocyclic aldehyde such as 2-furylaldehyde showed high reactivity, although there was difficulty in identifying the major side-products (>6%) for this case. About 4% of diene side-products were found in aliphatic cases of entries 7–9, which were generated from the dehydration of Baylis–Hillman adducts. *tert*-Butyl acrylate and methyl vinyl ketone afforded reasonable yield of Baylis–Hillman product.

## 3. Experimental

### 3.1. General

MPs were obtained with a Shimadzu DSC-50 thermal analyzer. IR spectra were recorded on a Bomem MB154S infrared analyzer. $^1$H NMR and $^{19}$F NMR spectra were recorded with Bruker Advance RX300. Mass spectra were recorded on Saturn 2000GC/MS or Agilent 1100 LC/MS instrument. Inductively coupled plasma (ICP) spectra were measured on an Ultima2C apparatus. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. The perfluorodecalin and rare earth (III) salts were purchased from Aldrich Co. Heptadecafluorooctanesulfonic acid was commercially obtained from ARCOS Co. Commercially available reagents were used without further purification.

### 3.2. Preparation of $Yb(OPf)_3$

A mixture of a solution of PfOH (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 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: $\delta$ −126.0, −121.2, −114.4, −81.1.

### 3.3. Typical procedure for Baylis–Hillman reaction in a FBS

To a mixture of $Yb(OPf)_3$ (83 mg, 0.05 mmol) and toluene (2 ml) in a glass tube was added ligand **3** (306 mg, 0.3 mmol) under vigorous stirring. After a few minutes, perfluorodecalin (4 ml), methyl acrylate (1.9 ml, 20 mmol) and benzaldehyde (1 ml, 10 mmol) were introduced into the glass tube. After stirring at 60 °C for the appropriate time, the mixture was cooled with in an ice bath. Then, the fluorous layer on the bottom was separated for the next reaction. The reaction mixture (organic phase) was dried over anhydrous sodium sulfate, filtered, and then concentrated in vacuo. The resulting crude oil was further purified by flash column chromatography on silica gel, using the mixed solvent of ethyl acetate and hexane (1:3 or 1:4, v/v), to give the desired product. All desired products were known products and fully characterized by IR, $^1$H NMR and MS.

#### 3.3.1. Methyl 2-[1-hydroxy-1-(phenyl)methyl]acrylate (product for Table 2)

A colorless oil (Literature [2b]); IR ($CHCl_3$) 3480, 1720 cm$^{-1}$. $^1$H NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.38 (s, 3H), 3.23 (brs, 1H), 5.65 (s, 1H), 6.02 (s, 1H), 6.23 (s, 1H), 6.92 (m, 1H), 7.05–7.16 (m, 4H). MS (EI) *m/z* 192 ($M^+$).

#### 3.3.2. Methyl 2-[1-hydroxy-1-(4-nitrophenyl)methyl]acrylate (Table 3, entry 1)

A yellowish oil (Literature [2c]); IR ($CHCl_3$) 3490, 1715 cm$^{-1}$. $^1$H NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.36 (s, 3H), 3.28 (brs, 1H), 5.70 (s, 1H), 6.08 (s, 1H), 6.29 (s, 1H), 7.56 (d, $J$ = 8.6 Hz, 2H), 8.19 (d, $J$ = 8.6 Hz, 2H). MS (EI) *m/z* 237 ($M^+$).

#### 3.3.3. Methyl 2-[1-hydroxy-1-(4-chlorophenyl)methyl]acrylate (Table 3, entry 2)

A yellowish oil (Literature [2b]); IR ($CHCl_3$) 3480, 1720 cm$^{-1}$. $^1$H NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.30 (s, 3H), 3.26 (brs, 1H), 5.70 (s, 1H), 6.11 (s, 1H), 6.29 (s, 1H), 7.18 (d, $J$ = 8.6 Hz, 2H), 7.30 (d, $J$ = 8.6 Hz, 2H). MS (EI) *m/z* 226 228 ($M^+$).

#### 3.3.4. Methyl 2-[1-hydroxy-1-(4-methylphenyl)methyl]acrylate (Table 3, entry 3)

A colorless oil (Literature [2b]); IR ($CHCl_3$) 3480, 1710 cm$^{-1}$. $^1$H NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.18 (s, 3H), 2.32 (s, 3H), 3.21 (brs, 1H), 5.68 (s, 1H), 6.09 (s, 1H), 6.30 (s, 1H), 6.88 (d, $J$ = 7.8 Hz, 2H), 7.09 (d, $J$ = 7.8 Hz, 2H). MS (EI) *m/z* 206 ($M^+$).

#### 3.3.5. Methyl 2-[1-hydroxy-1-(4-methoxyphenyl)methyl]acrylate (Table 3, entry 4)

A colorless oil (Literature [2b]); IR ($CHCl_3$) 3480, 1725 cm$^{-1}$. $^1$H NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.32 (s, 3H), 2.42 (s, 3H), 3.30 (brs, 1H), 5.49 (s, 1H), 6.02 (s, 1H), 6.28 (s, 1H), 6.80 (d, $J$ = 7.8 Hz, 2H), 7.01 (d, $J$ = 7.8 Hz, 2H). MS (EI) *m/z* 222 ($M^+$).

#### 3.3.6. Methyl 2-[1-hydroxy-1-(2′-naphthyl)methyl]acrylate (Table 3, entry 5)

A colorless oil (Literature [2b]); IR ($CHCl_3$) 3480, 1720 cm$^{-1}$. $^1$H NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.35 (s, 3H), 3.28 (brs, 1H), 5.68 (s, 1H), 5.97 (s, 1H), 6.25 (s, 1H), 6.92 (m, 1H), 7.06–7.16 (m, 4H). 7.20–7.28 (m, 3H). MS (EI) *m/z* 242 ($M^+$).

#### 3.3.7. Methyl 2-[1-hydroxy-1-(2′-furyl)methyl]acrylate (Table 3, entry 6)

A colorless oil (Literature [2b]); IR ($CHCl_3$) 3485, 1720 cm$^{-1}$. $^1$H NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.34 (s, 3H), 2.89 (m, 3H), 3.20 (brs, 1H), 5.68 (s, 1H), 5.99 (s, 1H), 6.10 (s, 1H). MS (EI) *m/z* 182 ($M^+$).

#### 3.3.8. Methyl 2-[1-hydroxy-1-(ethyl)methyl]acrylate (Table 3, entry 7)

A colorless oil (Literature [2m]); IR ($CHCl_3$) 3490, 1710 cm$^{-1}$. $^1$H NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 1.89 (m,

3H), 2.10 (m, 2H), 2.37 (s, 3H), 3.19 (brs, 1H), 5.62 (s, 1H), 6.00 (s, 1H), 6.24 (s, 1H). MS (EI) *m/z* 144 ($M^+$).

*3.3.9. Methyl 2-[1-hydroxy-1-(propyl)methyl]acrylate (Table 3, entry 8)*

A colorless oil (Literature [2m]); IR ($CHCl_3$) 3470, 1730 $cm^{-1}$. $^1H$ NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 1.60 (t, 3H), 2.04 (m, 4H), 2.40 (s, 3H), 3.26 (brs, 1H), 5.68 (s, 1H), 6.10 (s, 1H), 6.20 (s, 1H). MS (EI) *m/z* 158 ($M^+$).

*3.3.10. Methyl 2-[1-hydroxy-1-(pentyl)methyl]acrylate (Table 3, entry 9)*

A colorless oil (Literature [2m]); IR ($CHCl_3$) 3480, 1720 $cm^{-1}$. $^1H$ NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 1.56 (t, 3H), 1.96–2.19 (m, 8H), 2.38 (s, 3H), 3.23 (brs, 1H), 5.65 (s, 1H), 6.02 (s, 1H), 6.23 (s, 1H). MS (EI) *m/z* 186 ($M^+$).

*3.3.11. tert-Butyl 2-[1-hydroxy-1-(phenyl)methyl]acrylate (Table 3, entry 10)*

A colorless oil (Literature [2g]); IR ($CHCl_3$) 3465, 1730 $cm^{-1}$. $^1H$ NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.08 (m, 9H), 3.32 (brs, 1H), 5.75 (s, 1H), 6.09 (s, 1H), 6.24 (s, 1H), 6.90 (m, 1H), 7.04–7.16 (m, 4H). MS (EI) *m/z* 234 ($M^+$).

*3.3.12. tert-Butyl 2-[1-hydroxy-1-(4-nitrophenyl)methyl]acrylate (Table 3, entry 11)*

A yellowish oil (Literature [2g]); IR ($CHCl_3$) 3465, 1720 $cm^{-1}$. $^1H$ NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.06 (m, 9H), 3.36 (brs, 1H), 5.76 (s, 1H), 6.12 (s, 1H), 6.26 (s, 1H), 7.59 (d, $J$ = 8.6 Hz, 2H), 8.17 (d, $J$ = 8.6 Hz, 2H). MS (EI) *m/z* 279 ($M^+$).

*3.3.13. 3-[(Phenyl)hydroxymethyl]-3-buten-2-one (Table 3, entry 12)*

A colorless oil (Literature [2e]); IR ($CHCl_3$) 3485, 1715 $cm^{-1}$. $^1H$ NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.36 (s, 3H), 3.28 (brs, 1H), 5.68 (s, 1H), 6.07 (s, 1H), 6.34 (s, 1H), 6.95 (m, 1H), 7.02–7.18 (m, 4H). MS (EI) *m/z* 176 ($M^+$).

*3.3.14. 3-[(4-Nitrophenyl)hydroxymethyl]-3-buten-2-one (Table 3, entry 12)*

A yellowish solid (Literature [2c]); mp 66–68 °C. IR ($CHCl_3$) 3475, 1720 $cm^{-1}$. $^1H$ NMR (500 MHz, TMS, $CDCl_3$) $\delta$ 2.07 (m, 9H), 3.42 (brs, 1H), 5.80 (s, 1H), 6.09 (s, 1H), 6.35 (s, 1H), 7.61 (d, $J$ = 8.5 Hz, 2H), 8.19 (d, $J$ = 8.5 Hz, 2H). MS (EI) *m/z* 221 ($M^+$).

## 4. Conclusions

In conclusion, the novel fluorous biphasic system of a combination of $Yb(OPf)_3$ and perfluoroalkylated-pyridine **3** showed a high catalytic activity for Baylis–Hillman reaction. The reaction can be carried out successfully without the use of a stoichiometric amount Lewis base and robustness of the catalytic system for reuse can be obtained by simple phase-separation. These new procedures could provide novel strategies in order to achieve their asymmetric versions in the future.

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