



Synthesis and structure of an air-stable hypervalent organobismuth (III) perfluorooctanesulfonate and its use as high-efficiency catalyst for Mannich-type reactions in water

Xiaowen Zhang^{a,b}, Shuangfeng Yin^{a,*}, Renhua Qiu^a, Jun Xia^a, Weili Dai^a, Zhenying Yu^a, Chak-Tong Au^{a,c,*}, Wai-Yeung Wong^{d,*}

^a College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, PR China

^b Key Laboratory of Pollution Control and Resource Use of Hunan Province, University of South China, Hengyang 421001, PR China

^c Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, PR China

^d Department of Chemistry and Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong, PR China

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ABSTRACT

An air-stable hypervalent organobismuth (III) perfluorooctanesulfonate was synthesized and characterized by spectroscopic and X-ray crystallographic techniques, and found to exhibit high catalytic efficiency towards one-pot Mannich-type reaction of ketones with aromatic aldehydes and aromatic amines in water. This catalyst also shows good recyclability and reusability. This catalytic system would provide a simple, efficient and 'green' avenue towards the synthesis of β -amino ketones.

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1. Introduction

Bismuth is low in toxicity and relatively cheap. Being environmentally friendly, bismuth compounds have been used in catalysis and organic synthesis. In the past two decades, bismuth(III) compounds (e.g., BiCl₃, BiBr₃, Bi(OTf)₃, Bi(NO₃)₃) have been studied as catalysts in a diversity of organic reactions, and review papers related to the catalysis of inorganic bismuth(III) compounds have been published [1–8]. However, up till now, there are only several reports on the use of organobismuth compounds as catalysts in organic synthesis, possibly due to the unstable nature of Bi–C bonds. With 'Green Chemistry' and 'Sustainable Development' in mind, we aim to synthesize stable organobismuth compounds and to investigate their potential uses. For example, organobismuth oxide, hydroxide and methoxide bearing a stable cyclic framework were synthesized and found to be good reagents and catalysts for CO₂ chemical fixation [9–11]. Very recently we reported that organobismuth complexes with equal or similar cyclic frameworks show *in vitro* antiproliferative activity [12]. Due to the stability of the cyclic frameworks, it is possible to conduct researches on the

synthesis of organobismuth derivatives and to exploit the compounds for catalytic applications. On the other hand, Qiu et al. postulated that the incorporation of long-chain perfluoroalkylsulfonate and perfluoroarylsulfonate groups into organometallic (e.g., Sn, Ti, Zr, Hf) complexes could result in enhanced acidity and stability of materials [13–16]. Hence, we envision that the incorporation of perfluorooctanesulfonate groups into organobismuth species can result in the generation of organobismuth compounds that are stable and have unique functionalities for catalytic reactions.

The Mannich reaction is one of the most useful reactions for the synthesis of nitrogen-containing compounds and is an effective method for the construction of C–C bonds [17–19]. The conventional catalysts for classical three-component Mannich reactions of aldehydes, ketones and amines are mineral and organic acids, and drawbacks such as long reaction time, harsh reaction condition, toxicity and difficulty in product separation are inevitable. It is hence desirable to develop synthetic routes that are free from such shortcomings.

It has been pointed out that organic synthesis using catalysts that are not based on transition metals is an important, interesting and challenging research topic in catalytic synthesis [3]. With the aim of developing new catalysts suitable for one-pot Mannich-type reaction and as an extension of our work on bismuth chemistry

* Corresponding authors. Tel./fax: +86 731 85118161.

E-mail addresses: sf_yin@hnu.cn (S. Yin), pctau@hkbu.edu.hk (C.-T. Au), rwyywong@hkbu.edu.hk (W.-Y. Wong).

[9–12,20], we synthesized an organobismuth (III) perfluorooctane-sulfonate ($C_6H_{11}N(CH_2C_6H_4)_2 Bi(OSO_2C_8F_{17})$) **1**. The compound is air-stable and shows high efficiency for the Mannich-type reaction under relatively mild conditions.

2. Results and discussion

2.1. Molecular structure

The quality of the crystals of compound **1** was verified by single-crystal X-ray diffraction. Listed in Table 1 are the crystal data, data collection and structure refinement details.

An ORTEP representation of the structure of compound **1**, as well as selected bonds and angles are shown in Fig. 1. One can see that the central bismuth-containing part of the compound exhibits a pseudo-trigonal bipyramidal (TBP) structure, where both the C(1) and C(8) atoms exist in the equatorial position of the TBP structure along with a lone electron pair of bismuth, and the N(1) and O(1) atoms are at the apical positions; the N(1)–Bi–O(1) bond angle is $156.49(19)^\circ$. The Bi–C(1) and Bi–C(8) distance is 2.215(6) Å and 2.234(6) Å, respectively, while the C(1)–Bi–C(8) angle is $93.9(2)^\circ$. As previously reported, the Bi–N coordination distance in 5,6,7,12-tetrahydrodibenz[*c,f*][1,5]-azabismocines flexibly

changes in response to the electronic nature of bismuth [6,21–24]. The Bi–N(1) distance (2.397(5) Å) is shorter than that (2.631(4) Å) of precursor **2** [11]. As expected, the Bi–O(1) distance (2.497(5) Å) is longer than the covalent Bi–O bond (2.077 Å) and shorter than the Bi–O bond distance of $tBuN(CH_2C_6H_4)_2BiOH$ (2.691(4) Å) and $tBuN(CH_2C_6H_4)_2BiOCOME$ (2.730(4) Å) [10].

2.2. Physicochemical property

We found that the organobismuth perfluorooctanesulfonate **1** remained as dry crystals or a powder and suffered no color change in a test of one month in air. Therefore, it is air-stable. Its Lewis acidity is weak, showing strength of $4.8 < H_0 \leq 6.8$. The thermal stability of compound **1** was investigated by TG–DSC analysis under N_2 atmosphere (Fig. 2). Apparently there are two stages of weight loss. The plateau in the range of 29–246 °C suggests that **1** is thermally stable up to 246 °C. The weight loss in the 246–356 °C range should be due to the loss of $-OSO_2C_8F_{17}$ (weight loss 50.8%, theoretical loss 50.6%). The stage in the 356–631 °C range can be ascribed to the loss of organic ligand entities. The endothermic peak that appears at 187 °C reflects a step of fusion rather than desorption as there is no weight loss. The material is stable up to about 246 °C, and an exothermic peak appears at 246 °C followed by a significant decline in weight. It is suggested that the oxidation of $-OSO_2C_8F_{17}$ occurs at this stage. When the temperature is up to about 356 °C, another exothermic signal appears, plausibly due to

Table 1

Crystal data, data collection and structure refinement details for compound $C_6H_{11}N(C_6H_4)_2Bi(OSO_2C_8F_{17})$ **1**.

Entry	$C_6H_{11}N(C_6H_4)_2Bi(OSO_2C_8F_{17})$ (1)
Chemical formula, formula weight	$C_{28}H_{23}BiF_{17}NO_3S$, 985.51
Cryst. habit	Prismatic, colorless
Cryst. size (mm)	$0.39 \times 0.34 \times 0.17$
Cryst. syst, space group	Triclinic, $P\bar{1}$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.3897(12), 11.1263(13), 14.1172(16)
α , β , γ (°)	92.681(2), 100.123(2), 95.441(2)
<i>V</i> (Å ³), <i>Z</i> , <i>D_c</i> (g cm ⁻³)	1595.9(3), 2, 2.051
<i>F</i> (0 0 0)	948
<i>T</i> (°C), $2\theta_{max}$ (°)	20, 52.0
μ (Mo K α) (mm ⁻¹)	5.72
Number of reflections measured, number of unique reflections	8797, 6163
Number of observed reflections (<i>R_{int}</i>), <i>R</i> (<i>I</i> > 2 σ (<i>I</i>))	5226 (0.035), 0.042
<i>wR₂</i> (<i>F²</i> , all reflections)	0.094
Number of parameters	497
Goodness of fit (GOF) on <i>F²</i>	0.96

$$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2] \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

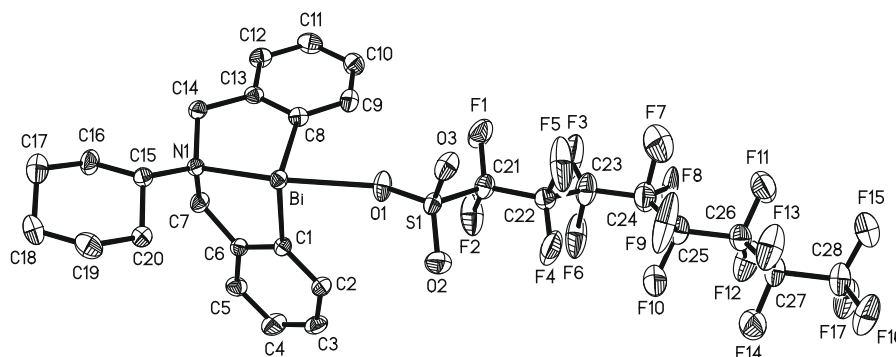


Fig. 1. Thermal ellipsoid plot of $C_6H_{11}N(C_6H_4)_2Bi(OSO_2C_8F_{17})$ (50% probability level). Hydrogen atoms on the carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Bi–C(1) 2.215(6); Bi–C(8) 2.234(6); Bi–N(1) 2.397(5); Bi–O(1) 2.497(5); N(1)–C(14) 1.487(7); N(1)–C(7) 1.491(8); N(1)–C(15) 1.521(8); S(1)–O(1) 1.455(5); C(1)–Bi–C(8) 93.9(2); C(1)–Bi–N(1) 77.97(19); C(8)–Bi–N(1) 75.3(2); C(1)–Bi–O(1) 90.1(2); C(8)–Bi–O(1) 85.5(2); N(1)–Bi–O(1) 156.49(19); S(1)–O(1)–Bi 150.2(4); O(1)–S(1)–C(21) 99.4(3).

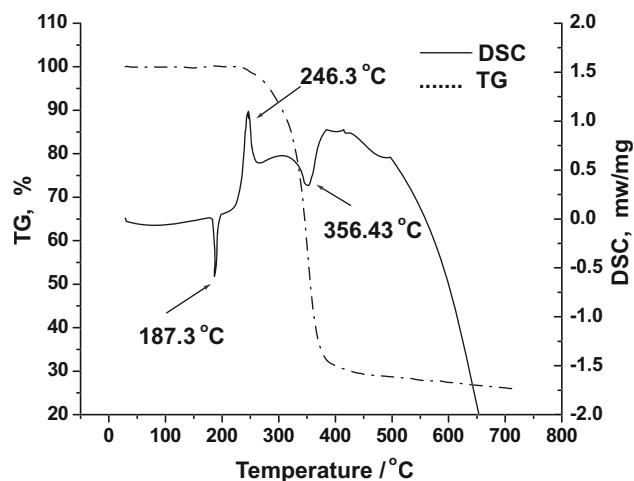
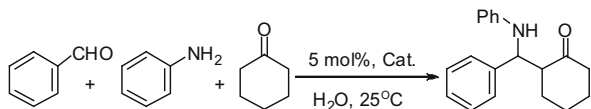


Fig. 2. TG–DSC curves of compound **1**.

Table 2

$C_6H_{11}N(CH_2C_6H_4)_2Bi(OSO_2CF_3)_3$ -catalyzed three-component Mannich-type reactions of benzaldehyde, aniline and cyclohexanone in different solvents.^a



Entry	Solvent	Time (h)	Yield (%) ^b
1	H ₂ O	2	96
2	CH ₃ OH	2	99
3	C ₂ H ₅ OH	2	98
4	THF	2	90
5	Toluene	2	95
6	CH ₃ CN	6	87
7	CH ₂ Cl ₂	3	85

^a Reaction conditions: benzaldehyde (1.0 mmol), aniline (1.0 mmol), cyclohexanone (1.0 mmol), cat. (0.05 mmol), H₂O (2.0 ml), 25 °C.

^b Isolated yield.

the oxidation of the organic entities. The final substance that left behind after heating to 700 °C as identified by XRD analysis is BiF₃ [25] (overall weight loss 73.0%, theoretical loss 73.0%).

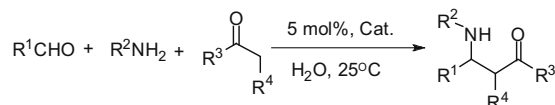
2.3. $C_6H_{11}N(CH_2C_6H_4)_2Bi(OSO_2C_8F_{17})_3$ -catalyzed Mannich reaction

We adopted the one-pot three-component Mannich reaction for the study of catalytic activity of compound **1** (Tables 2–4). One can see that the reaction that involves benzaldehyde, aniline and cyclohexanone occurs smoothly in MeOH, EtOH, THF, H₂O, and CH₃C₆H₅ (Table 2, entries 1–5), but slowly in CH₃CN and CH₂Cl₂ (Table 2, entries 6–7). The yield of the target product (i.e., β -amino ketone) is above 96% in 2 h when water, methanol or ethanol was used as the solvent. It is apparent that a polar solvent benefits this reaction. Since the use of water as a medium for organic synthesis is known to be environmentally friendly [26], we selected water as the solvent for further investigations.

In order to show the generality and scope of the new protocol, we selected aldehydes, aromatic amines and ketones of various

Table 3

The one-pot three-component Mannich-type reaction in water.^a



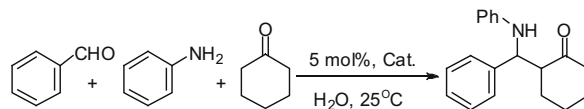
Entry	Aldehyde	Amine	Ketone	Time (h)	Yield (%) ^b
1	PhCHO	PhNH ₂	Cyclohexanone	15	99
2	<i>p</i> -ClC ₆ H ₄ CHO	PhNH ₂	Cyclohexanone	16	98
3	<i>p</i> -CF ₃ C ₆ H ₄ CHO	PhNH ₂	Cyclohexanone	12	95
4	<i>p</i> -O ₂ NC ₆ H ₄ CHO	PhNH ₂	Cyclohexanone	16	99
5	<i>p</i> -CH ₃ OC ₆ H ₄ CHO	PhNH ₂	Cyclohexanone	17	99
6	<i>p</i> -CH ₃ C ₆ H ₄ CHO	PhNH ₂	Cyclohexanone	18	99
7	C ₇ H ₁₅ CHO	PhNH ₂	Cyclohexanone	14	95
8	PhCHO	<i>o</i> -CH ₃ C ₆ H ₄ NH ₂	Cyclohexanone	16	30
9	PhCHO	<i>p</i> -NO ₂ C ₆ H ₄ NH ₂	Cyclohexanone	17	50
10	PhCHO	PhNH ₂	Acetone	19	60
11	PhCHO	PhNH ₂	Acetophenone	36	30
12	PhCHO	PhNH ₂	1-(3-nitrophenyl)ethanone	15	88

^a Reaction conditions: aldehyde (1.0 mmol), amine (1.0 mmol), ketone (1.0 mmol), cat. (0.05 mmol), H₂O (2.0 ml), 25 °C.

^b Isolated yield.

Table 4

Catalytic activity of different bismuth compounds in Mannich reaction of benzaldehyde, aniline and cyclohexanone.^a



Entry	Catalyst (5 mol%)	Solvent	Time (h)	Yield (%) ^b
1	no catalyst added	H ₂ O	5	8
2	$C_6H_{11}N(CH_2C_6H_4)_2BiCl$	H ₂ O	3	50
3	$C_6H_{11}N(CH_2C_6H_4)_2Bi(OSO_2C_8F_{17})_3$ (1)	H ₂ O	2	95
4	$^tBuN(CH_2C_6H_4)_2Bi^+[B(C_6F_5)_4]^-$	H ₂ O	2	92
5	$Bi(OSO_2CF_3)_3$	H ₂ O	2	84 ^c
6	$Bi(O_2CCF_3)_3$	H ₂ O	5	77 ^c
7	$S(CH_2C_6H_4)_2BiCl$	H ₂ O	2	20
8	$C_6H_{11}N(CH_2C_6H_4)_2Bi[OCO_2(CH_2)_2GePh_3]$	H ₂ O	3	80
9	$C_6H_5N(CH_2C_6H_4)_2Bi[OCO_2(CH_2)_2GePh_3]$	H ₂ O	3	75
10	$^tBuN(CH_2C_6H_4)_2Bi[OCO_2(CH_2)_2GePh_3]$	H ₂ O	3	55

^a Reaction conditions: benzaldehyde (1.0 mmol), aniline (1.0 mmol), cyclohexanone (1.0 mmol), cat. (0.05 mol), H₂O (2.0 ml), 25 °C.

^b Isolated yield.

^c See Ref. [40].

kinds. Table 3 demonstrates that excellent yields of β -amino ketones are obtained across the selected aldehydes including those that bear an electron-withdrawing group (Table 3, entries 2–4). The use of electron-rich aromatic aldehydes also leads to good yields of products (Table 3, entries 5–6). However, a change of substituted groups in phenyl plane of aromatic amines results in a poor reaction rate (Table 3, entries 8–9). Three other ketones are also examined (Table 2, entries 10–12). As expected, *m*-NO₂PhCOCH₃ exhibits higher activity than PhCOCH₃ due to the electron-withdrawing ability of –NO₂.

In Table 4, the catalytic performance of compound **1** is compared with that of other bismuth compounds. One can see that in a blank run the isolated yield of β -amino carbonyl compound is only 8%. Over C₆H₁₁N(CH₂C₆H₄)₂BiCl, ^tBuN(CH₂C₆H₄)₂Bi⁺[B(C₆F₅)₄][–], Bi(OSO₂CF₃)₃, Bi(O₂CCF₃)₃, C₆H₁₁N(CH₂C₆H₄)₂Bi[OCO₂(CH₂)₂GePh₃], and C₆H₅N(CH₂C₆H₄)₂Bi[OCO₂(CH₂)₂GePh₃], the

yields are above 70%. The catalytic activity can be ranked in the order of C₆H₁₁N(CH₂C₆H₄)₂Bi(OSO₂C₈F₁₇) > ^tBuN(CH₂C₆H₄)₂Bi⁺[B(C₆F₅)₄][–] > Bi(OSO₂CF₃)₃ > C₆H₁₁N(CH₂C₆H₄)₂Bi[OCO₂(CH₂)₂GePh₃] > Bi(O₂CCF₃)₃ > C₆H₅N(CH₂C₆H₄)₂Bi[OCO₂(CH₂)₂GePh₃] > ^tBuN(CH₂C₆H₄)₂Bi[OCO₂(CH₂)₂GePh₃]. As reported in the literature, HCl [27], HBF₄ [28], InCl₃ [29], Y(OTf)₃ [30], Yb(OPf)₃ (Ytterbium perfluorooctanoate) [31], Zn(BF₄)₂ [32], ZrOCl₂·8H₂O [33], SiO₂–OAlCl₂ [34], PS–SO₃H (polystyrene-supported sulfonic acid) [35], heteropoly acid (H₃PW₁₂O₄₀) [36], NbCl₅ [37], HClO₄–SiO₂ [38] and Bi(OTf)₃ [39] were used as catalysts in the Mannich-type reactions. Despite individual feature(s) and/or merit(s) of the catalysts, drawbacks such as difficulty of product separation, impossible recycling and reuse of catalyst caused much concerns. Despite the low solubility of aldehydes, ketones, and amines in water, Mannich reactions proceed efficiently at ambient temperature in the presence of compound **1**. The catalyst remains in solid

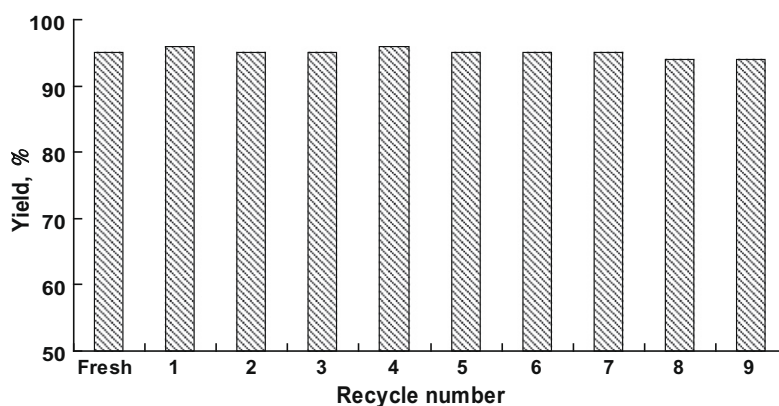
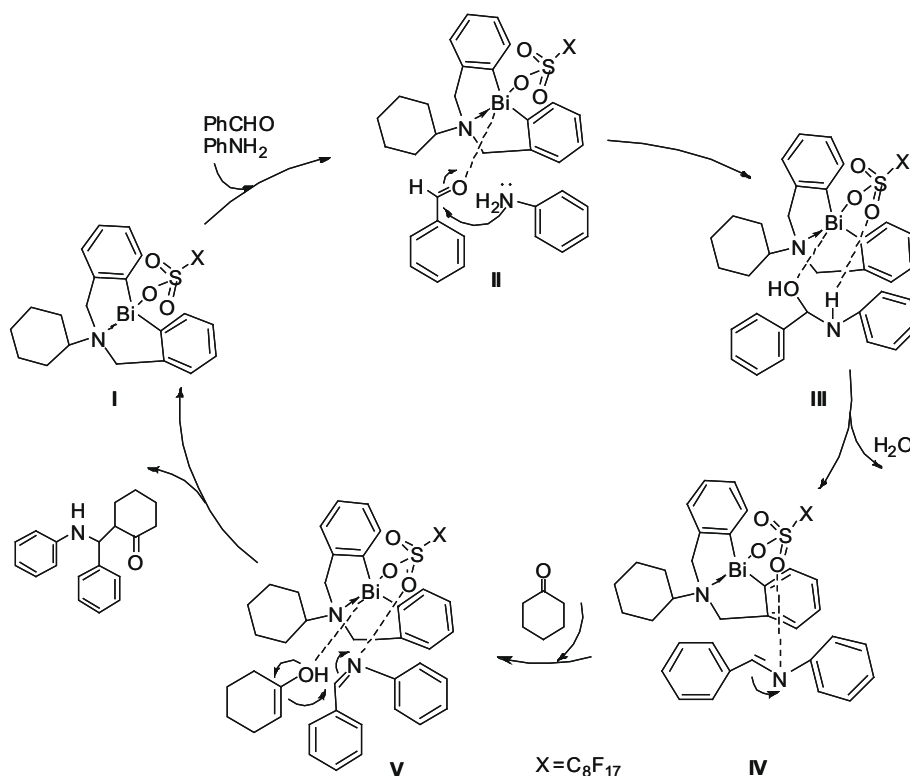


Fig. 3. Catalyst recycling. (For each cycle: PhCHO 1.06 g, 10.0 mmol, PhNH₂ 0.93 g, 10.0 mmol, cyclohexanone 0.98 g, 10.0 mmol, and H₂O 20.0 ml.)



Scheme 1. Proposed mechanism on the direct Mannich reaction catalyzed by organobismuth perfluorooctanesulfonate **1**.

form throughout the reaction, suggesting the catalysis is heterogeneous. Compared the results in Table 2, when some organic solvents (e.g., THF) was used as the solvent, the catalytic process was homogeneous, while the isolated yield of Mannich product was lower in THF than that in water. We deduced that the difference in yield could be explained by dynamical equilibrium. As is well known that the Mannich product is insoluble in water but has good solubility in THF. Thus the use of water as solvent is beneficial for the formation of the desired product.

To examine the reusability and applicability of the catalyst, compound **1** was subject to cycles of the Mannich reaction. When (*E*)-*N*-benzylideneaniline was consumed completely, the mixture was subject to methylene chloride extraction and the residue after vacuum evaporation was analyzed by column chromatograph (petroleum ether/ethyl acetate = 5/1). The recovered catalyst was reused directly. In a test of 10 cycles, the change of product yield is minimal (isolated yield only slightly declined from 95% to 94%), indicating that the catalyst is stable and reusable (Fig. 3).

2.4. Proposed mechanism

A possible mechanism of the Mannich-type reaction that involves the use of compound **1** as catalyst in water is proposed (Scheme 1). When compound **1** (**I**) is added to the reaction solution, the carbonyl oxygen atom of benzaldehyde coordinates with the bismuth atom and is activated; and this results in the formation of an intermediate **II**. Then aniline (a nucleophile) attacks the activated carbonyl group of benzaldehyde and forms a hydrogen-bond (between H and O) with $\text{OSO}_2\text{C}_8\text{F}_{17}$, producing the intermediate imine **IV**. With the release of a water molecule, there is an intramolecular rearrangement. Meanwhile, the carbonyl oxygen atom of cyclohexanone coordinates with the bismuth atom and is activated, forming a 1-cyclohexen-1-ol intermediate **V**. Then the π -electrons of the activated (or unstabilized) imine delocalize towards the activated 1-cyclohexen-1-ol, forming a new carbon-carbon bond through the *re*-face of the double bond plane. Then the π -electrons of the activated 1-cyclohex-1-enol redistribute to form cyclohexanone (accompanied by the transfer of hydrogen atom to nitrogen atom). It is worth pointing out that all of the electron-transfer processes occur simultaneously and it is impossible for the substrates to adjust into positions that would cause side reactions (such as aldol addition and condensation). Finally, the Mannich adduct is formed and catalyst **1** renewed.

3. Conclusion

In summary, we synthesized and characterized for the first time a stable hypervalent organobismuth (III) perfluorooctanesulfonate of Lewis acidity. The compound shows good catalytic efficiency in three-component Mannich reactions of aldehydes, amines, and ketones in water under mild reaction conditions. Moreover, the catalyst can be easily recycled and reused. The adoption of this catalytic system would afford a simple, efficient and 'green' approach for the synthesis of β -amino ketones.

4. Experimental

4.1. General

All manipulations of air-sensitive materials were conducted in a glovebox filled with argon or under the protection of N_2 atmosphere according to the standard Schlenk tube techniques. The commercially available chemicals were purchased from Aldrich or Sinopharm Chemical Reagent Co. Ltd., and were used as received without further purification. NMR spectra were recorded at

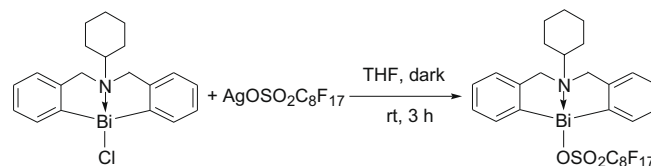
400 MHz for proton and at 100 MHz for carbon nuclei (in CDCl_3) using a INOVA-400 M (Varian) spectrometer. The chemical shifts of ^1H (δ ppm) were examined using tetramethylsilane as the internal standard (δ 0.0) while those of ^{13}C NMR were recorded using CDCl_3 as the internal standard (δ 77.0). Melting points of compounds were determined over a XT-4 micro apparatus (Beijing Tech Instrument Co. Ltd.). Elemental analysis was conducted over a VARIO EL III (Elementar) instrument. Single-crystal X-ray diffraction analysis was performed in Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences using a SMART-APEX instrument. TG-DSC analysis was performed on a NETZSCH-STA-449C equipment (operation condition: N_2 , 5 °C/min heating rate). The acidity was measured by the Hammett indicator method [41,42]. The employed indicators were crystal violet ($\text{p}K_a = 0.8$), dimethyl yellow ($\text{p}K_a = 3.3$), methyl red ($\text{p}K_a = 4.8$), and neutral red ($\text{p}K_a = 6.8$). Acid strength was expressed by the Hammett acidity function (H_0) as scaled by $\text{p}K_a$ value of the indicators.

4.2. Synthesis of compound **1**

The precursor $\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiCl}$ **2** of **1** was prepared according to the procedure described elsewhere [11]. The synthetic process of compound **1** is shown in Scheme 2. $\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiCl}$ **2** (2.61 g, 5.0 mmol) was dissolved in 90.0 ml THF, then a solution of $\text{Ag}(\text{OSO}_2\text{C}_8\text{F}_{17})$ (3.04 g, 5.0 mmol) in 60.0 ml THF was added. After the mixture was stirred in the dark at room temperature for 3 h, it was filtered. The filtrate mixed with 10.0 ml hexane was refrigerated for 24 h, giving colorless crystals (4.93 g, 98.0%). Good crystals qualified for single-crystal X-ray diffraction analysis were obtained by the recrystallization of compound **1** in a mixed solvent of THF/hexane (volume ratio: 10/1). Compound **1**: ^1H NMR (D_6 acetone, 400 MHz, TMS): δ 1.14 (1H, td, $J = 7.0$), 1.24–1.33 (4H, m), 1.63 (1H, d, $J = 14.0$), 1.84 (2H, d, $J = 13.0$), 1.98 (2H, d, $J = 11.5$), 2.94 (1H, td, $J = 11.5$), 4.33 (2H, d, $J = 15.5$), 4.53 (2H, d, $J = 15.0$), 7.31 (2H, td, $J = 8.0$, ArH), 7.49 (2H, d, $J = 7.5$, ArH), 7.55 (2H, t, $J = 7.5$, ArH), and 8.29 (2H, d, $J = 7.5$, ArH). ^{13}C NMR (D_6 acetone, 100 MHz): δ 25.88, 26.318, 31.99, 64.95, 67.71, 129.24, 129.43, 131.59, 137.98, 154.32 and 206.21. ^{19}F NMR (D_6 acetone, 376 MHz): δ -121.16 (2F, m), -117.70 (2F, s), -116.88 (4F, b), -116.54 (2F, s), -115.31 (2F, s), -109.01 (2F, t), -76.05 (3F, t). Melting point: 184–185 °C. Anal. Calc. for $\text{C}_{28}\text{H}_{23}\text{BiF}_{17}\text{NO}_3\text{S}$ (985.09): C, 34.12; H, 2.35; Bi, 21.21; F, 32.77; N, 1.42; O, 4.87; S, 3.25. Found: C, 34.07; H, 2.39; Bi, 21.24; F, 32.71; N, 1.46; O, 4.90; S, 3.21%.

4.3. X-ray crystallography

Crystals suitable for X-ray diffraction study were grown by slow evaporation of the solution (compound dissolved in THF/hexane) at room temperature. Geometric and intensity data were collected at 293 K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker AXS SMART 1000 CCD diffractometer. The crystallinity, orientation matrix, and accurate unit-cell parameters were determined according to standard procedures. The collected frames were processed with the software SAINT [43], and absorption correction (SADABS) [44] was applied to the acquired



Scheme 2. Synthesis of organobismuth perfluorooctanesulfonate **1**.

reflection peaks. The structure was solved by the Direct or Patterson method (SHELXS97, Sheldrick, 1990) [45] in conjunction with standard difference Fourier techniques, and subsequently refined by full-matrix least-squares analyses on F^2 . Hydrogen atoms were generated in their idealized positions and all non-hydrogen atoms were assigned with anisotropic displacement parameters.

4.4. Mannich reaction

All the Mannich reactions were performed in a 25 ml round bottom glass flask equipped with a magnetic stirrer. Typically, a mixture of compound **1** (0.05 mmol), PhCHO (106 mg, 1.0 mmol), PhNH₂ (93 mg, 1.0 mmol), cyclohexanone (98 mg, 1.0 mmol) and H₂O (2.0 ml) was charged into the flask. Then the mixture was stirred under TLC (Thin Layer Chromatography) analysis until complete consumption of PhCHO and PhNH₂ as well as no indication of the presence of intermediate (*E*)-*N*-benzylideneaniline (generated from PhCHO and PhNH₂); the process usually took around 2 h. The resulting solid substance was filtered out and Et₂O was added for the dissolution of the target product. After filtration, the filtrate was subject to vaporization at room temperature for the generation of product in the form of colorless crystals.

4.5. Typical procedure for catalyst recovery and reuse

To a 100 ml round bottomed flask was added compound **1** (0.46 g, 0.5 mmol), PhCHO (1.06 g, 10.0 mmol), PhNH₂ (0.93 g, 10.0 mmol), cyclohexanone (0.98 g, 10.0 mmol) and H₂O (20.0 ml). Then the mixture was stirred for 2 h under the TLC analysis until the PhCHO and PhNH₂ as well as the intermediate (*E*)-*N*-benzylideneaniline obtained from PhCHO and PhNH₂ was consumed completely. Water was removed from the mixture to leave residue. Then the residue was suspended by 30.0 ml diethyl ether, followed by filtration. After the filter cake of the catalyst was washed three times with diethyl ether (10.0 × 3 ml), it was used for catalyzing the next reaction cycle. The combined filtrate was evaporated in vacuum, and the product was purified by column chromatograph on silica gel (200–300 mesh) (petroleum ether/ethyl acetate = 5/1).

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Appendix A. Supplementary material

CCDC 733861 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.07.018](https://doi.org/10.1016/j.jorganchem.2009.07.018).

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