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Synthesis and structure of an air-stable organoantimony complex and its use as a catalyst for direct diastereoselective Mannich reactions in water

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ABSTRACT

An air-stable organoantimony complex with a 5,6,7,12-tetrahydrodibenzo[c,f][1,5]azastibocine framework was synthesized, characterized, and found to exhibit high catalytic efficiency towards one-pot Mannich reaction with high diastereoselectivity in water. The catalyst can be recycled 10 times without showing any appreciable loss of efficiency. This catalytic system affords a simple and efficient approach for the synthesis of β-amino ketones.

1. Introduction

The Mannich reaction is a classical method for the preparation of β-amino carbonyl compounds as well as an important route for the formation of carbon–carbon bonds [1–4]. Nonetheless, the approach reported in the literature has shortcomings such as harsh conditions, long reaction time, and side reactions (such as aldol reaction) [1]. Hence the development of synthetic routes free of such drawbacks is highly desirable. Recent development of metal-free organocatalytic Mannich reaction has been reviewed by Ting and Schaus [2]. Impressive accomplishments have been made in diasteroselective synthesis over various Lewis acid catalysts [3]. Shibasaki and co-workers reported for the first time the direct Mannich-type reaction of unmodified ketones catalyzed by lanthanum complex [5]. Kobayashi et al. reported that $FeCl_2$ together with a (*R*)-3.3′-I_2BINOL complex is effective for the Mannich reaction of imines with silyl enolates [6]. Similar reactions were performed by using a novel chiral zirconium catalyst for the production of β-amino ester derivatives [7,8]. List and co-workers reported that the proline-catalyzed asymmetric Mannich reactions (with different ketones) displayed high enantioselectivity but accompanied by some aldol products [9,10]. Notz et al. and Ibrahem et al. disclosed that cyclic chiral amines can catalyze the direct Mannich reaction with good enantioselectivity under mild conditions [11,12]. Acidic ionic liquid as an effective organocatalyst for the one-pot Mannich reaction has also been developed [13]. Due to the use of organic solvents, the reactions have to be conducted at relatively low temperatures and under strictly anhydrous conditions. Recently, we reported a cationic organobismuth perchlorate complex ($[S(CH_2C_6H_4)_2Bi(OH_2)]^+[ClO_4]^-$) that is catalytically highly active, giving *anti*/*syn* molar ratio $\leqslant$ 95/5 in the direct diastereoselective Mannich reaction [14]. On the other hand, no diastereoselectivity was observed over covalent organobismuth(III) perfluorooctanesulfonate ($C_6H_{11}N(CH_2C_6H_4)_2$ $Bi(OSO_2C_8F_{17})$) although its catalytic efficiency towards the Mannich-type reactions was high [15].

Considering that antimony and bismuth are both group-15 elements, we turned our attention to the synthesis and application of new organoantimony compounds. Organoantimony compounds have been synthesized and used in organic reaction as well as in the fields of catalysis, biochemistry and medicine [16–26]. Most of the applications are focused on in vitro antitumour activity and organic reactivity [21–24]. Kakusawa et al. reported that hypervalent organoantimony compounds with a tetrahydrodibenzo[c,f][1,5]azastibocine framework are agents highly efficient for cross-coupling reactions [27]. Recently, organoantimony oxide was synthesized and found to be recoverable reagent efficient for CO_2 chemical fixation [28]. Ionic organoantimony

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complexes also have been developed [29–31]. However, the use of organoantimony compounds as catalysts in organic synthesis is rarely reported [25,26].

Generally, a stable metal–carbon bond is indispensable when organometallic compounds are used as catalysts. We have researched on organometallic compounds and found that the incorporation of perfluoroalkylsulfonate, perfluoroarylsulfonate or perchlorate groups into organometallic complexes can result in enhanced acidity critical for the improvement of catalytic activity [14,32–38]. In view of the stability of the tetrahydrodibenzo[c,f][1,5]azastibocine cyclic framework [27] and to study the potential applications of organoantimony compounds in catalysis, we adopted 5,6,7,12-tetrahydrodibenzo[c,f][1,5]azastibocine for the synthesis of organoantimony complex $[C_6H_{11}N(CH_2C_6H_4)_2SbOSO_2CF_3]$ **1**. We found that it could efficiently catalyze the direct diastereoselective Mannich reactions at room temperature in water.

2. Results and discussion

2.1. Crystal structure

The identity of the freshly recrystallized sample has been confirmed by ^{1}H NMR and elemental analysis. The molecular structure of compound **1** was determined by single-crystal X-ray diffraction. The crystal data and structure refinement details are listed in Table 1.

An ORTEP view of the structure of complex **1**, as well as selected bonds and angles are shown in Fig. 1. One can see that the central antimony-containing part of the complex exhibits a pseudo-trigonal bipyramidal structure. The N (1) and O (1) atoms are located at the apical positions while the C (1) and C (8) atoms exist at the equatorial positions. The Sb–C (8) and Sb–C (1) distance is 2.141 (6) Å and 2.145 (12) Å, respectively. The C(8)–Sb–C (1) angle is 98.6 (2)° while the N(1)–Sb–O (1) angle is 155.14 (16)° (rather than 180°). The Sb–N (1) distance (2.311 (4) Å) is shorter than the sum of the van der Waals radii of nitrogen and antimony atoms (3.74 Å) [27], indicating that coordination exists between the two.

Table 1
Crystal data, and structure refinement details for $C_6H_{11}N(CH_2C_6H_4)_2SbOSO_2CF_3$ **1**.[a]

Entry	$C_6H_{11}N(CH_2C_6H_4)_2SbOSO_2CF_3$ **1**
Formula	$C_{21}H_{23}F_3NO_3SSb$
Formula weight	548.21
Crystal system, space group	Monoclinic, *C*2/*c*
a (Å)	12.6394 (10)
b (Å)	14.8504 (11)
c (Å)	23.4741 (18)
β (°)	95.080 (2)
V (Å^3)	4388.8 (6)
Z, D_x, (Mg cm^{-3})	8, 1.659
μ (mm^{-1})	1.40 mm^{-1}
F(0 0 0)	2192
Crystal size (mm)	0.27 × 0.23 × 0.16
θ Range (°)	4.5–47.6
Limiting indices	$-9 \leqslant h \leqslant 16$, $-19 \leqslant k \leqslant 17$, $-26 \leqslant l \leqslant 30$
Reflections measured/unique (R_{int})	13 164/5009 (0.037)
Goodness-of-fit (GOF) on F^2	1.017
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0552$, $wR_2 = 0.1495$
R indices (all data)	$R_1 = 0.0765$, $wR_2 = 0.1614$
Largest diff. peak and hole (e Å^{-3})	2.085 and −1.138

[a] Temperature: 293(2) K; Wavelength: Mo/K*a*, 0.71073 Å; Refinement method: Full-matrix least-squares on F^2; $w = 1/[\sigma^2(F_o^2) + (0.090P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$; CCDC register number: CCDC 739931.

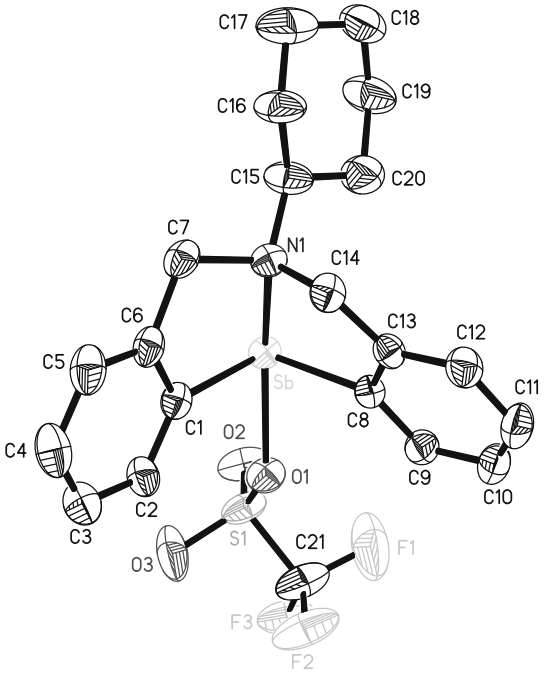


Fig. 1. An ORTEP view showing 50% probability ellipsoid of $[C_6H_{11}N(CH_2C_6H_4)_2SbOSO_2CF_3]$ **1**. Selected bond distance (Å) and angles (°): Sb–C(8), 2.141 (6); Sb–C(1), 2.145 (6); Sb–N(1), 2.311 (4); Sb–O(1), 2.373 (5); N(1)–C(14), 1.497 (7); N(1)–C(7), 1.506 (7); C(8)–Sb–C(1), 98.6 (2); C(8)–Sb–O(1), 84.99 (17); C(1)–Sb–O(1), 85.77 (18); C(8)–Sb–N(1), 79.23 (18); C(1)–Sb–N(1), 77.81 (19); C(14)–N(1)–C(7), 110.2 (5); N(1)–Sb–O(1), 155.14 (16).

2.2. Physicochemical properties

The compound is air-stable and remains as dry colorless crystals or white powder in a test period of one year in air. The acidity of complex **1** measured by the Hammett indicator method is $3.3 < H_0 \leqslant 4.8$. Influenced by the $-OSO_2CF_3$ group that is strongly electron-withdrawing, the exposed antimony can function as a Lewis acid site. It is envisaged that complex **1** can work as a Lewis acid catalyst. The thermal behavior of complex **1** was investigated by TG-DSC under N_2 atmosphere (Fig. 2). Apparently, there are two stages of weight loss. The weight loss (4 wt%) within temperature of 60–100 °C is from the absorbing water molecule on the complex **1**. The plateau in the range of 100–290 °C suggests that **1** is thermally stable up to 290 °C. The weight loss (67 wt%) in the range of 290–500 °C is ascribed to the loss of counter anion OSO_2CF_3 and the organic framework $[C_6H_{11}N(CH_2C_6H_4)_2]$.

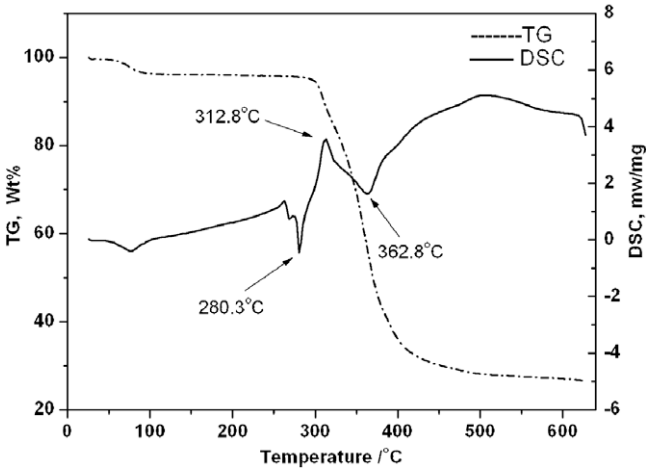
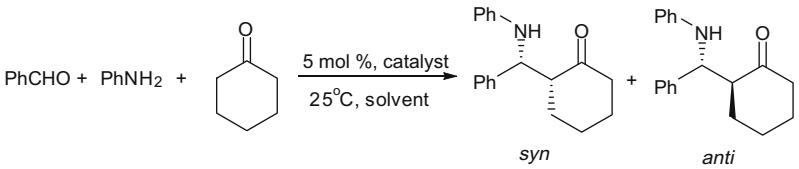


Fig. 2. TG-DSC curves of complex **1**.

2.3. Organoantimony complex **1**-catalyzed direct Mannich reaction

In the present study, the organoantimony complex **1** is adopted as a catalyst for the Mannich reaction of benzaldehyde, aniline, and cyclohexanone in water as well as in various solvents (Table 2). One can see that the reaction occurs quickly and efficiently, and higher yields are obtained when the reactions are conducted in polar solvents. Particularly, high catalytic efficiency and stereoselec-

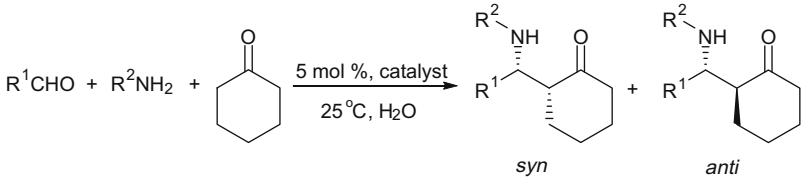
Table 2
Direct Mannich reaction of benzaldehyde, aniline and cyclohexanone in various solvents.[a]



Entry	Solvent	Time (h)	*anti*/*syn*[b]	Yield (%)[c]
1	MeOH	4	98/2	98
2	EtOH	4	98/2	97
3	CH_3CN	4	97/3	91
4	THF	4	98/2	93
5	CH_2Cl_2	4	97/3	90
6	Et_2O	4	98/2	90
7	H_2O	4	99/1	98
8	Hexane	5	98/2	89

[a] PhCHO, 1.0 mmol; $PhNH_2$, 1.0 mmol; cyclohexanone, 1.0 mmol; Cat., 0.05 mmol; solvent, 2.0 mL, 25 °C.
[b] Determined by ^1H NMR.
[c] Isolated yield.

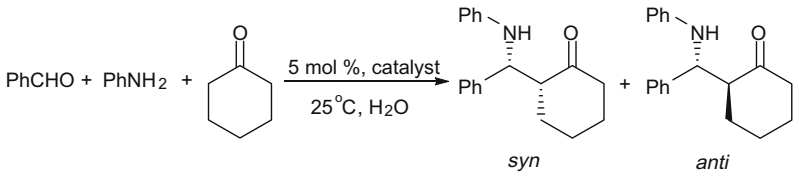
Table 3
Direct Mannich reaction of various aldehydes, amines, and cyclohexanone catalyzed by organoantimony complex **1** in water.[a]



Entry	R^1	R^2	Time (h)	*anti*/*syn*[b]	Yield (%)[c]
1	Ph	Ph	4	99/1	98
2	*p*-$CH_3C_6H_4$	Ph	5	96/4	90
3	*p*-$CH_3OC_6H_4$	Ph	4	97/3	92
4	*p*-$CF_3C_6H_4$	Ph	3	97/3	95
5	*p*-ClC_6H_4	Ph	4	96/4	97
6	Ph	*o*-$CH_3C_6H_4$	10	95/5	90

[a] R^1CHO, 1.0 mmol; R^2NH_2, 1.0 mmol; cyclohexanone, 1.0 mmol; Cat., 0.05 mmol; H_2O, 2.0 mL, 25 °C.
[b] Determined by ^1H NMR.
[c] Isolated yield.

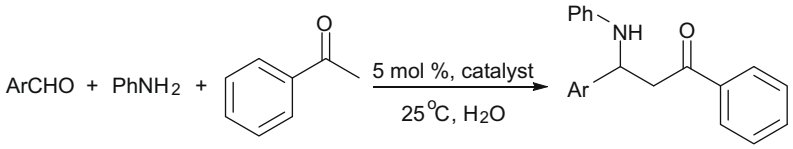
Table 4
Direct Mannich reaction of benzaldehyde, aniline and cyclohexanone over various catalysts.[a]



Entry	Catalyst	Time (h)	*anti*/*syn*[c]	Yield (%)[d]
1	$C_6H_{11}N(C_6H_4CH_2)_2SbOSO_2CF_3$ **1**	4	99/1	98
2	$C_6H_{11}N(C_6H_4CH_2)_2SbCl$ **2**	5	96/4	45
3	$[S(CH_2C_6H_4)_2Bi(OH_2)]^+[ClO_4]^-$ **3**	2	95/5	98
4	$SbCl_3$[b] **4**	8	68/32	78

[a] PhCHO, 1.0 mmol; $PhNH_2$, 1.0 mmol; cyclohexanone, 1.0 mmol; Cat., 0.05 mmol; H_2O, 2.0 mL, 25 °C.
[b] PhCHO, 2.0 mmol; $PhNH_2$, 2.0 mmol; cyclohexanone, 3.0 mmol; Cat., 0.2 mmol; CH_3CN, 10.0 mL, 25 °C.
[c] Determined by ^1H NMR.
[d] Isolated yield.

Table 5
Direct Mannich reaction of aromatic aldehydes, aniline, and acetophenone catalyzed by organoantimony complex **1** in water.[a]



Entry	Ar	Time (h)	Yield (%)[b]
1	Ph	24	65
2	*p*-ClC_6H_4	24	72
3	*p*-$CF_3C_6H_4$	24	70
4	*p*-$CH_3C_6H_4$	24	81
5	*p*-$CH_3OC_6H_4$	24	78

[a] ArCHO, 1.0 mmol; $PhNH_2$, 1.0 mmol; acetophenone, 1.1 mmol; Cat., 0.05 mmol; H_2O, 2.0 mL, 25 °C.
[b] Isolated yield.

tivity are observed when water is used as solvent (Table 2, entry 7, *anti*/*syn* = 99/1, yield, 98%). Compared to the reports on direct three-component Mannich reactions conducted in media of organic solvents, the reports on those conducted in water are relatively few [39–42]. We found that *anti*-selectivity is almost independent of the adopted solvents. Since the use of water as reaction medium for organic synthesis is environmentally benign [43], we chose water as solvent for further investigations.

In order to show the generality and scope of the new protocol, various aromatic aldehydes with electron-withdrawing and electron-donating groups were tested (Table 3). It is clear that the aldehydes react readily to generate the products in very good yields and diastereoselectivity. In the present investigation, the aldehydes with electron-withdrawing groups (Table 3, entries 4 and 5) show slightly higher reaction activity than the aldehydes with electron-donating groups (Table 3, entries 2 and 3). The reaction of octanal, aniline, and cyclohexanone produces the corresponding β-amino ketone in 50% yield even in prolonged reaction time (8 h), similar to that reported by Eftekhari-Sis et al. [44]. Other aromatic amines such as *o*-toluidine was also tested (Table 3, entry 6), and good result was obtained. The lower activity of the substrate with a methyl group in the *ortho*-position may be due to steric effect of CH_3.

To demonstrate the superiority of complex **1**, its catalytic performance is compared with that of precursor $C_6H_{11}N(C_6H_4\ CH_2)_2SbCl$ **2**, cationic organobismuth $[S(CH_2C_6H_4)_2Bi(OH_2)]^+[ClO_4]^-$ **3** [15], and antimony trichloride **4** [45]. As shown in Table 4, catalyst **1** is superior to the others in efficiency as well as in diastereoselectivity. In contrast to the case of complex **3**, product of single configuration with nearly 100% *anti*-selectivity is obtained in the case of complex **1**. Interestingly, we found that high diastereoselectivity is also obtained using precursor $C_6H_{11}N(C_6H_4CH_2)_2$ SbCl **2** as catalyst. It implies that there is a correlation between the framework of the catalyst and the diastereoselectivity of Mannich products.

Encouraged by the good results, we investigated acetophenone (Table 5), and the corresponding β-amino ketone was obtained in good yields. Acetophenone was less reactive than cyclohexanone, and longer reaction time was needed to afford the desired products. It was found that the electronic effect of substitutes has some influence on the yields. Aromatic aldehyde with an electron-withdrawing group (Table 5, entries 2 and 3) gives lower yield than that with an electron-donating group (Table 5, entries 4 and 5).

To examine the reusability and reproducibility of the catalyst, complex **1** was subjected to cycles of the Mannich reaction of benzaldehyde, aniline and cyclohexanone. Within a test of 10 cycles, the change of product yield is minimal, indicating that the catalyst is stable and reusable (Fig. 3).

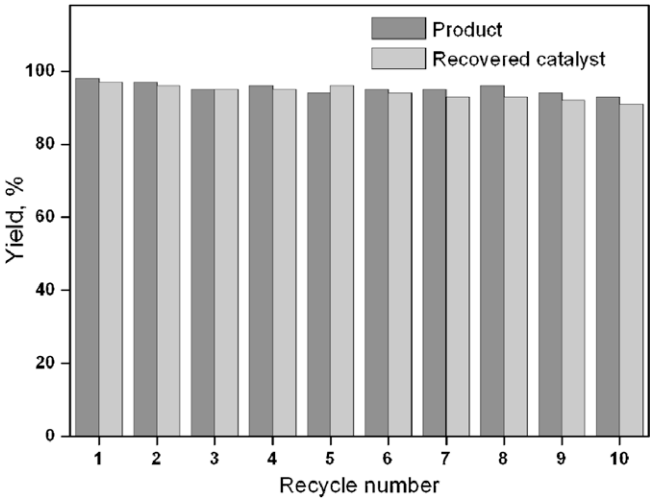


Fig. 3. Direct Mannich reaction of benzaldehyde, aniline and cyclohexanone over recovered catalyst **1**.

3. Conclusion

In summary, an air-stable organoantimony complex **1** has been synthesized and characterized. The compound exhibits good catalytic efficiency and high diastereoselectivity for the direct Mannich reaction in water under mild conditions. Moreover, the catalyst shows good stability and reusability. It can be expected that the complex will find broad applications in organic synthesis.

4. Experimental

4.1. General

The commercially available chemicals were purchased from Aldrich. Co. Ltd. as well as from other chemical providers and used as received without further purification unless otherwise specified. All manipulations of air-sensitive materials were conducted in a glove box filled with argon or under the protection of N_2 atmosphere according to the standard Schlenk tube techniques. The NMR spectra were recorded on a INOVA-400M (Varian) instrument (^1H NMR, 400 MHz; ^{13}C NMR 100 MHz); chemical shifts of ^1H (δ ppm) were calibrated using tetramethylsilane (TMS) as internal standard (δ 0.0), while those of ^{13}C NMR were calibrated using $CDCl_3$ as internal standard (δ 77.0). Elemental analysis was conducted using a VARIO EL III (Germany) 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-409-PC/PG equipment (Operation condition: in N_2, 10 °C/min heating rate). Melting points of compounds were determined over a XT-4 micro apparatus (Beijing Tech Instrument Co. Ltd.). The acidity was measured by Hammett indicator method. Acid strength was expressed by Hammett acidity function (H_0) as scaled by pK_a value of indicators.

4.2. General procedure for synthesizing of complex *1*

The precursor $C_6H_{11}N(CH_2C_6H_4)_2SbCl$ **2** of complex **1** was prepared according to the procedure described elsewhere [46]. The synthetic process of catalyst **1** was conducted in air using THF as solvent as shown in Scheme 1 of the article. To a solution of $C_6H_{11}N(C_6H_4CH_2)_2SbCl$ (0.435 g, 1.0 mmol) in 15 mL THF, a solution of $AgOSO_2CF_3$ (0.257 g, 1.0 mmol) in 10 mL THF was added. After stirred in the dark at room temperature for 3 h, the mixture was subject to filtration. The filtrate was mixed with 1.0 mL hexane and kept at room temperature for 24 h for the generation of colorless crystals of complex **1** (537 mg, 98%). Good crystals qualified for single-crystal X-ray diffraction analysis were obtained by crystallizing **1** in a THF/*n*-hexane solvent. *Compound* ***1***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.12 (1H, td, J = 3.2 Hz), 1.25–1.46 (4H, m), 1.67 (1H, d, J = 13.2 Hz,), 1.85 (2H, d, J = 13.6 Hz), 2.03 (2H, d, J = 12 Hz), 3.11 (1H, td, J = 2.8 Hz), 4.18 (2H, d, J = 14.8 Hz), 4.35 (2H, d, J = 15.6 Hz), 7.18 (2H, d, J = 7.2 Hz, Ph), 7.29 (2H, t, J = 7.2 Hz, Ph), 7.37 (2H, t, J = 7.2 Hz, Ph), 7.96 (2H, d, J = 7.2 Hz, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 25.11, 25.54, 30.21, 60.28, 67.53, 124.66,129.64, 129.74, 134.75, 140.99. 143.98. ^{19}F NMR($CDCl_3$): −77.04 (3F, s). Mp: 282–284 °C. Anal. Calc. for $C_{21}H_{23}F_3NO_3SSb$: C, 46.01; H, 4.23; N, 2.55. Found: C, 45.96; H, 4.25; N, 2.58%.

4.3. Typical procedure for acidity measurement of complex *1*

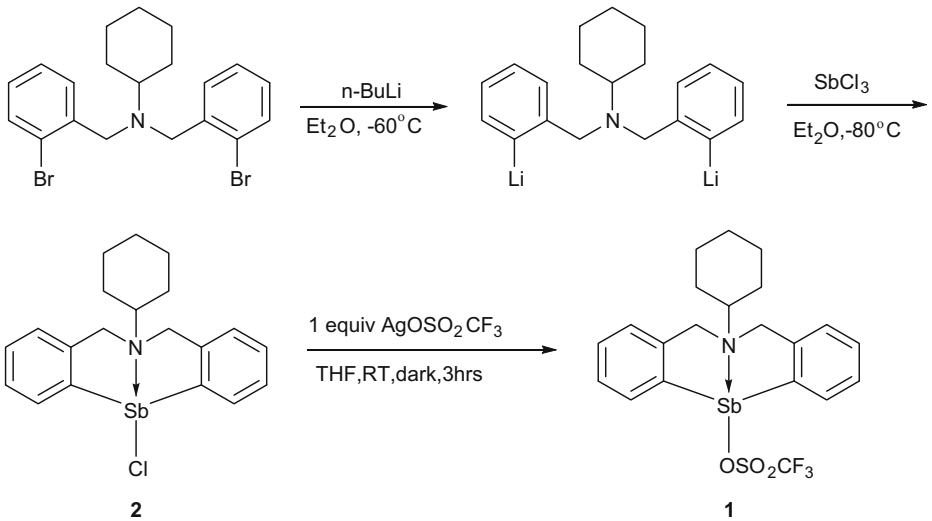
The acidity was measured by Hammett indicator method as previously described [47–49]. Benzene was chosen as solvent and dehydrated over 3 Å zeolite prior to use. The employed indicators included crystal violet (pK_a = 0.8), dimethyl yellow (pK_a = 3.3), methyl red (pK_a = 4.8), and neutral red (pK_a = 6.8). Each indicator was dissolved in benzene to generate a 0.1 wt% solution. Acid strength was expressed by the Hammett acidity function (H_0), which was scaled by pK_a value of the indicators. The procedure for determining the acidity of complex **1** is as follows: 5.0 mg complex **1** was mixed with 0.5 mL benzene in a test tube (10 mL), followed by sonication until complete dissolution. Then one drop of indicator was added to the solution (by the use of a 1.0 mL plastic syringe), and acidity strength was estimated in terms of color change.

4.4. Typical procedure for the synthesis of β-amino carbonyl compounds catalyzed by recovered catalyst *1*

To a 100 mL round bottomed glass flask was added catalyst **1** (0.28 g, 0.5 mmol), PhCHO (1.06 g, 10.0 mmol), $PhNH_2$ (0.93 g, 10.0 mmol), cyclohexanone (0.98 g, 10.0 mmol) and H_2O (20.0 mL). Then the mixture was stirred for 4 h under TLC (Thin Layer Chromatography) analysis until the PhCHO and $PhNH_2$ as well as the (*E*)-N-benzylideneaniline (generated from PhCHO and $PhNH_2$) intermediate was completely consumed. With the removal of water, the mixture was extracted with Et_2O and subject to filtration. The filtrate was dried over anhydrous $MgSO_4$ and subject to evaporation in vacuum to give a solid substance. The recovered catalyst was washed several times with Et_2O before reuse.

4.5. General procedure for the synthesis of β-amino carbonyl compounds

To a 25 mL round bottomed glass flask with a magnetic stirrer was added catalyst **1** (28 mg, 0.05 mmol), aldehydes (1.0 mmol), amines (1.0 mmol), cyclohexanone (1.0 mmol) or acetophenone (1.1 mmol) and H_2O (2.0 mL). The mixture was stirred for 4–24 h under TLC analysis until complete consumption of aldehydes and amines as well as the intermediate imines. After completion of the reaction, water was removed. Then the residue was dissolved in Et_2O and the catalyst was separated from the mixture by filtration. The filtrate was dried over anhydrous $MgSO_4$ and subject to evaporation in vacuum. The crude products obtained were purified by column chromatograph on a silica gel (petroleum ether/ethyl acetate = 5/1, v/v). Products of Mannich reaction were confirmed according to their spectroscopic data (NMR) by means of comparison with those reported in the literature [50–52]. One of NMR data of the products is listed here: 2-(phenyl(phenylamino)methyl)cyclohexanone (Table



Scheme 1. Synthesis of organoantimony complex **1**.

2, entry 1): ^{1}H NMR(400 MHz, $CDCl_3$, TMS): δ 1.64–1.75 (2H, m, CH_2 of Cy), 1.81–1.96 (4H, m, $(CH_2)_2$ of Cy), 2.29–2.36 (1H, m, one proton of CH_2 in Cy), 2.40–2.46 (1H, m, one proton of CH_2 in Cy), 2.72–2.78 (1H, m, one proton of Cy), 4.61 (0.99 H, d, J = 7.2 Hz, CH, *anti*-isomer), 6.52 (2H, d, J = 7.6 Hz, Ph), 6.60 (1H, t, J = 7.6 Hz, Ph), 7.04 (2H, t, J = 8.0 Hz, Ph), 7.19 (1H, t, J = 7.6 Hz, Ph), 7.28 (2H, t, J = 7.2 Hz, Ph), 7.36 (2H, d, J = 7.2 Hz, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 23.68, 27.88, 31.30, 41.79, 57.44, 58.16, 113.76, 117.68, 127.20, 127.30, 128.49, 129.07, 141.62, 147.10, 212.85.

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Appendix A. Supplementary material

CCDC 739931 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.2010.03.003.

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