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Air-stable Organoantimony (III) Perfluoroalkyl(aryl)sulfonate complexes as highly efficient, selective, and recyclable catalysts for C–C and C–N bond-forming reactions

Ningbo Li [a,b,c,*], Qi Fan [a], Li Xu [a], Rong Ma [a], Shitang Xu [d], Jie Qiao [b,c], Xinhua Xu [d,*], Rui Guo [a,c,*], Kemin Yun [e]

[a] Department of Biochemistry and Molecular Biology, School of Basic Medical Sciences, Shanxi Medical University, Taiyuan 030001, P. R. China
[b] Department of Chemistry, School of Basic Medical Sciences, Shanxi Medical University, Jinzhong 030619, P.R.China
[c] Key Laboratory of Cellular Physiology, Ministry of Education, Shanxi Medical University, Taiyuan 030001, China
[d] College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, P. R. China
[e] School of Forensic Medicine, Shanxi Medical University, Jinzhong 030619, P.R. China

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ABSTRACT

A series of air-stable organoantimony (III) perfluoroalkyl(aryl)sulfonate complexes with an azastibocine framework {*t*-BuN($CH_2C_6H_4$)$_2$SbOSO$_2$C$_4$F$_9$ (**2a**); [*t*-BuN($CH_2C_6H_4$)$_2$Sb(OH_2)]$^+$[OSO_2X]$^-$, [$X = C_6F_5$, (**2b**); C_8F_{17}, (**2c**)]} was synthesized and systematically characterized. These complexes exhibited good thermal stability and relatively strong Lewis acidity. Moreover, they showed high catalytic efficiency, selectivity and recyclability for Strecker reaction, Mannich-type reaction, cross-condensation of aldehydes with ketones, and amination of epoxides. Such complexes were applied to extend the synthesis of seven novel carbazole derivatives, which showed good inhibitory activity against CHT116 cells and HepG2 cells.

1. Introduction

Organoantimony complexes have attracted considerable attention in organic synthesis and as reagents in catalysis [1-6], pharmaceuticals [7-9], and materials science [10-13] because of their particular boundary (metal and non-metal, [Kr]4d^{10}5s^{2}5p^3) features [14], large reserves in nature [15], and relatively low cost antimony metal compared with transition metals (Pd, Pt, Ru, and Rh). Many groups have published their contributions in the synthesis and structure of organoantimony complexes [16,17] and their in vitro anti-tumor activity [18-22] and organic reactivity [23-27]. However, their application as a Lewis acid catalyst in organic synthesis has rarely been referred [28-32], which can be attributed to the weak acidity and activity given their stable and filled 4d- and 5s-obitals and half-filled 5p-obitals. Therefore, their Lewis acidity (empty 5p and/or 5 s orbitals) or basicity (fulfilled 5s-obitals) depends on the environment of the chelating or bonding ligand [33, 34]. For example, R_3Sb (Scheme 1a) has low catalytic efficiency, but it can be used as ligand to coordinate with a Pd catalyst, which is an additive, because of the lone pair of 5s^2 electrons [35]. After the 5s^2 electrons withdraw by the electron-deficient groups, the high Lewis acidity and electron-deficient complex of R_3SbX_2 is obtained [36-38] (Scheme 1b). For example, triphenylantimony (V) dichloride was first reported by Nomura et al. as a highly efficient catalyst in the chemical fixation of CO_2 to useful chemicals [39]. Our group disclosed two binuclear triphenylantimony (V) complexes, which showed high catalytic efficiency in C–C bond formation reaction [40]. In addition, a hypervalent organoantimony(III) complex, which was unknown until 2009, was used as a Lewis acid catalyst (Scheme 1c) [41]. In recent years, Yin and Tan reported several hypervalent organoantimony(III) complexes with an azastibocine framework, which could efficiently catalyze various organic reactions [42-45]. Meanwhile, the long pair of electrons in the nitrogen atom may not only coordinate with antimony to stabilize the complex but also serve as a basic site, thereby showing a bifunctional catalytic efficiency.

However, the R groups in the abovementioned complexes are rigid phenyl or cyclohexyl groups, and organoantimony complexes with a flexible group, such as tertiary butyl in the azastibocine framework, have been rarely reported as a Lewis catalyst. This finding may indicate that with the increase in the basicity of nitrogen (N) atom, the acidity of the antimony (Sb) center becomes weak. Therefore, perfectly balancing

* Corresponding authors.
E-mail addresses: ningboli@sxmu.edu.cn (N. Li), xhx1581@hnu.edu.cn (X. Xu), ruiguo@sxmu.edu.cn (R. Guo).

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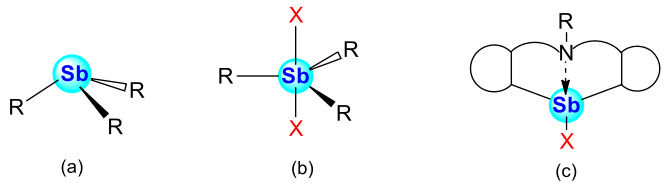


Scheme 1. Three types of organoantimony complexes.

the Lewis basicity of nitrogen atom and the Lewis acidity of central antimony atom remains a problem that needs to be solved.

This study adopted the azastibocine framework with tertiary butyl and modulated the electron-withdrawing nature of the perfluoroalkyl (aryl)sulfonate groups [46-51] connected to nitrogen and antimony atoms to modify the Sb→N coordination distance, increasing the Lewis acidity of antimony (Sb) center and maintaining the good performance of the nitrogen (N) atom as Lewis base. Consequently, we have successfully synthesized and characterized a series of air-stable and water-tolerant organoantimony (III) perfluoroalkyl(aryl)sulfonate complexes {*t*-Bu $N(CH_2C_6H_4)_2SbOSO_2C_4F_9$ (**2a**); [*t*-Bu $N(CH_2C_6H_4)_2Sb(OH_2)]^+[OSO_2X]^-$, [$X = C_6F_5$, (**2b**); C_8F_{17}, (**2c**)]}. Furthermore, we have systematically assessed their catalytic activities and selectivities using Lewis acid-catalyzed C–C and C–N bond-forming reactions, such as the Strecker reaction, Mannich-type reaction, cross-condensation of ketones and aldehydes, and amination of epoxides (Fig. 1).

2. Experimental section

All chemicals were purchased from Energy Chemical. Co., Ltd. and used as received unless otherwise indicated. Organoantimony chloride (**1**) was prepared as described previously [2]. The catalyst was prepared under the protection of nitrogen with fresh distilled solvent. The nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400 M Hz spectrometer (USA) in $CDCl_3$. Thermogravimetry-differential scanning calorimetry (TG-DSC) analysis was performed on an STA 449C instrument (NETZSCH, Shanghai, China). IR spectra were recorded on a Thermo Scientific Nicolet iS50 spectrophotometer (USA). Elemental analyses were performed using a PerkinElmer 2400 II instrument (USA). X-ray single crystal diffraction analysis was performed with a D8 Venture diffractometer (Bruker, Germany). Acidity was measured using the Hammett indicator method as described previously [47]. Two human cancer cell lines, namely, HCT 116 (colorectal carcinoma) and HepG2 (hepatoma) were kindly provided by Stem Cell Bank, Chinese Academy of Sciences (Shanghai, China).

2.1. Preparation of organoantimony chloride *1*

A solution of *t*-$BuN(CH_2C_6H_4Br)_2$ (4.28 g, 10 mmol) in 100 mL of anhydrous Et_2O was added to *n*-BuLi (8.2 mL, 2.5 M) in hexane at −30 °C for 30 min. The temperature of the mixture was allowed to increase slowly to room temperature for 30 min. After $SbCl_3$ (2.33 g, 10.2 mmol) was added in 50 mL of anhydrous Et_2O solution to the mixture at −78 °C

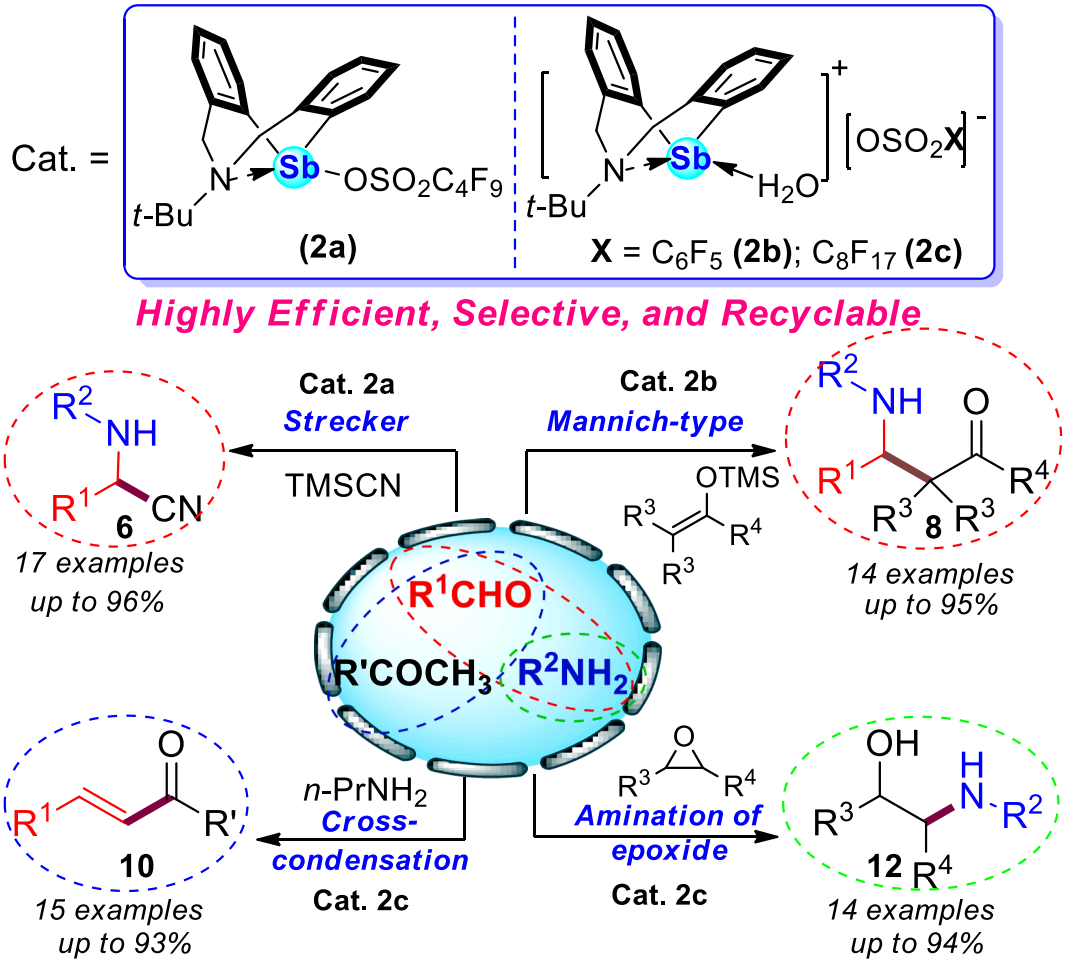


Fig. 1. Organoantimony complex-catalyzed C–C and C–N bond-forming reactions.

within 30 min, the as-obtained mixture was kept at −78 °C for 10 h. The reaction temperature was slowly increased to room temperature overnight. The resulting mixture was diluted with $CHCl_3$ (80 mL), washed with 1 M NH_4Cl in H_2O solution, and subjected to filtration. The organic layer was washed with deionized water (3 × 30 mL), dried with Na_2SO_4, and subjected to filtration and evaporation to obtain the crude product. After recrystallization in CH_2Cl_2/hexane solution, the colorless crystals of compound **1** were obtained (3.34 g, 82%). Mp:212–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.4 Hz, 2H), 7.20–7.10 (m, 6H), 4.46 (d, J = 15.6 Hz, 2H), 3.91 (d, J = 16.0 Hz, 2H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4, 145.1, 139.6, 139.5, 134.1, 133.1, 130.2, 65.8, 62.2, 31.5; Anal. Calc. for $C_{18}H_{21}ClNSb$: C, 52.91; H, 5.18; N, 3.43. Found: C, 52.88; H, 5.25; N, 3.40.

2.2. Preparation of complex *2a*

t-BuN$(CH_2C_6H_4)_2$SbCl (0.407 g, 1 mmol) was dissolved in THF(15 mL). A solution of $AgOSO_2C_4F_9$ (0.84 g, 2 mmol) in 10 mL of THF was added using a syringe under the protection of nitrogen, and the mixture was stirred for 2 h at room temperature in the absence of light. After filtering in air, the filtrate mixed with dry *n*-hexane (5 mL) was refrigerated for 24 h to obtain the colorless crystals (0.563 g, 84%). Mp: 185–187 °C, ^{1}H NMR (400 MHz, acetone-d_6): δ = 8.18 (d, J = 8.0 Hz, 2H), 7.76–7.63 (m, 6H), 5.00 (d, J = 16.0 Hz, 2H), 4.23 (d, J = 16.0 Hz, 2H), 1.32 (s, 9H); ^{19}F NMR (376 MHz, [d_6] acetone): δ: −81.73 to −81.80 (m, 3F; CF_3-), −114.85 (s, 2F; -CF_2-), −121.89 to −121.92 (m, 2F; -CF_2-), −126.54 to −126.63 (m, 2F; -CF_2-); IR(KBr): ν = 3474, 3056, 2978, 2926, 2855, 1465, 1385, 1350, 1307, 1220, 1141, 1047, 1004, 968, 905, 834, 755, 700, 653, 589 cm^{-1}; Anal. Calc'd for $C_{22}H_{21}F_9NO_3SSb$: C, 39.31; H, 3.15; N, 2.08; Found: C, 39.36; H, 3.20; N, 2.10.

2.3. Preparation of complex *2b*

t-BuN$(CH_2C_6H_4)_2$SbCl (0.407 g, 1 mmol) was dissolved in CH_3CN (15 mL). A solution of $AgOSO_2C_6F_5$ (0.71 g, 1.0 mmol) in 10 mL of CH_3CN was added under nitrogen atmosphere, and the mixture was stirred for 2 h at room temperature in the absence of light. After filtering in air, the filtrate was evaporated in a vacuum, and the resulting residue was diluted with THF (10 mL). Finally, the filtrate mixed with dry *n*-hexane (1 mL) was refrigerated for 24 h to obtain the colorless crystals (0.516 g, 81%). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by crystallization of **2b** from the THF/*n*-hexane solvent. Mp: 210–212 °C; ^{1}H NMR (400 MHz, acetone-d_6): δ = 8.01–7.98 (m, 2H), 7.38–7.32 (m, 6H), 4.84 (d, J = 15.6 Hz, 2H), 4.26 (d, J = 15.6 Hz, 2H), 3.08 (s, 2H), 1.48 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): −138.85 to −126.97 (m, 2F), −153.82 (s, 1F), −162.17 to −163.34 (m, 2F); IR (KBr): ν = 3259, 3043, 2989, 1645, 1517, 1491, 1411, 1309, 1265, 1221, 1105, 1046, 980, 907, 827, 754, 622, 520 cm^{-1}; Anal. Calc'd for $C_{24}H_{23}F_5NO_4SSb$: C, 45.16; H, 3.63; N, 2.19; Found: C, 45.22; H, 3.65; N, 2.25.

Crystal data for **2b**: $C_{24}H_{23}F_5NO_4SSb$; Mr = 638.24, Triclinic, space group *P-1*, a = 10.7995(5) Å, b = 10.9852 (5) Å, c = 10.39960 (4) Å; V = 1190.32(9) Å ^{3}; T = 293(2) K; Z = 2; Reflections collected/unique, 4186/3781, R_{int} = 0.0533, R_1 = 0.0311, wR_2 = 0.0506; GOF = 1.043; CCDC-1,565,687 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.

2.4. Preparation of complex *2c*

t-BuN$(CH_2C_6H_4)_2$SbCl (0.407 g, 1 mmol) was dissolved in THF(15 mL). A solution of $AgOSO_2C_8F_{17}$ (1.21 g, 2 mmol) in 10 mL of THF was added using a syringe under the protection of nitrogen, the mixture was stirred for 2 h at room temperature in the absence of light. After filtering in air, the filtrate mixed with dry *n*-hexane (5 mL) was refrigerated for 24 h to obtain the colorless crystals (0.693 g, 78%). Mp: 189–191 °C; ^{1}H NMR (400 MHz, acetone-d_6): δ = 8.00 (s, 2H), 7.39–7.35 (m, 6H), 4.83 (d, J = 16.0 Hz, 2H), 4.27 (d, J = 16.0 Hz, 2H), 3.02 (s, 2H), 1.49 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): −81.62 to −81.68 (m, 3F; CF_3-), −115.22 to −115.33 (m, 2F; -CF_2-), −121.05 to −121.16 (m, 2F; -CF_2-), −122.10 to −122.20 (m, 4F; -CF_2-), −123.20 to −123.30 (m, 2F; -CF_2-), −126.69 to −126.76 (m, 2F; -CF_2-); IR(KBr): ν = 3328, 3198, 3076, 1650, 1483, 1444, 1411, 1365, 1252, 1137, 1059, 1024, 989, 939, 761, 739, 690, 626, 548 cm^{-1}; Anal. Calc'd for $C_{26}H_{23}F_{17}NO_4SSb$: C, 35.08; H, 2.60; N, 1.57; Found: C, 35.13; H, 2.64; N, 1.66.

2.5. Typical procedure for the Strecker reaction catalyzed by *2a*

Complex **2a** (0.05 mmol), aldehydes/ketones (1.0 mmol), anilines (1.0 mmol), and trimethylsilylcyanide (1.2 mmol) were mixed in a 25 mL round-bottom flask. Then, the mixture was stirred at room temperature under TLC analysis until the reaction was complete. The mixture was dissolved in Et_2O, and the catalyst was collected by filtration for the next cycle of reaction. After the filtrate solvent was evaporated, a pale yellow solid mixture was obtained. The crude products were purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1) to obtain the desired products **6**.

2.6. Typical procedure for the Mannich-Type reaction catalyzed by *2b*

Complex **2b** (0.05 mmol), aldehydes (1.0 mmol), anilines (1.0 mmol), and enol silyl ethers (1.2 mmol) were added to a 25 mL round-bottom flask. Then, the mixture was stirred at room temperature under TLC analysis until the reaction was complete. The mixture was dissolved in Et_2O, and the catalyst was collected by filtration for the next cycle of reaction. After the filtrate solvent was evaporated, a white solid mixture was obtained. The crude products were purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1) to obtain the desired products **8**.

2.7. Typical procedure for the cross-condensation reaction catalyzed by *2c*

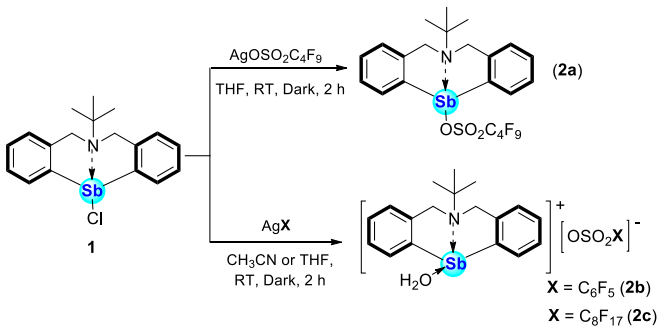
Complex **2c** (0.05 mmol), ArCHO (1.0 mmol), *n*-PrNH_2 (1.0 mmol), ketones (3.0 mmol), and H_2O (2.0 mL) were added to a 25 mL round-bottom flask. The mixture was stirred for 24 h and monitored by TLC analysis. After the reaction was completed, the solvent was removed under vacuum. Then, the residue was dissolved in Et_2O, and the catalyst was separated from the mixture by filtration for the next cycle of reaction. The filtrate was subjected to evaporation in vacuum. The crude products were purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8:1 to 4:1) to obtain the desired products **10**.

2.8. Typical procedure for epoxide ring-opening reaction with amines catalyzed by *2c*

Complex **2c** (0.05 mmol), epoxides (1.0 mmol), and amines (1.0 mmol) were added to a 25 mL round-bottom flask. Then, the mixture was stirred at room temperature for 2–6 h. After the reaction was completed (TLC analysis), the resulting mixture was subjected to evaporation, and the residue was dissolved in Et_2O. The catalyst was precipitated and separated by filtration for the next cycle of reaction. Then, the filtrate was evaporated under reduced pressure. The crude products were purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1) to obtain the desired products **12**.

2.9. Typical procedure for catalyst recovery and reuse (Strecker reaction as an example)

Complex **2a** (168 mg, 0.25 mmol), PhCHO (530 mg, 5 mmol), $PhNH_2$



Scheme 2. Synthesis of organoantimony complexes 2a–2c.

(530 mg, 5 mmol), and TMSCN (119 mg, 6 mmol) was mixed in a 50 mL round-bottom flask. The mixture was stirred at room temperature under TLC analysis until the reaction was complete (the intermediate *N*-benzylideneaniline was consumed completely). Then the mixture was diluted with Et_2O, and the catalyst was collected by filtration. The recovered catalyst was washed three times with Et_2O (10 mL × 3) for the next cycle of reaction. After the filtrate solvent was evaporated, a pale yellow solid mixture was obtained. The crude products were purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to obtain the desired products **6a**. Other reaction procedures for catalyst recovery are similar.

3. Results and discussion

3.1. Preparation, characterization, and physiochemical property of complexes 2a–2c

As shown in Scheme 2, organoantimony perfluoroalkyl(aryl)sulfonate complexes **2a**–**2c** were synthesized by treatment with organoantimony chloride (**1**) with $AgOSO_2X$ (X = C_4F_9, **2a**; C_6F_5, **2b**; C_8F_{17}, **2c**) in THF or CH_3CN for 2 h.

Complexes **2a**–**2c** remained stable as a white powder or colorless crystals in open air over 3 months and did not exhibit any detectable change upon ^{1}H NMR spectroscopic analysis (Fig. S1, ESI). The freshly prepared samples contained 0 or 1 water molecule for **2a, 2b**, and **2c**, as indicated by the results of ^{1}H NMR and elemental analysis. Therefore, complex **2a** may have a covalent structure, and complexes **2b** and **2c** are ionic complexes in solid state and are similar to the previously reported binuclear triphenylantimony complexes [40]. The scanning electron microscopy (SEM) image results of complexes **2a**–**2c** show a platelet-like crystal shape (Fig. S3, ESI). The crystal structure of complex **2b** was achieved by diffusion of hexane into a saturated solution of **2b** in THF. As shown in Fig. 2, complex **2b** is an ionic compound, and the cationic antimony-containing part shows a pseudo-trigonal bipyramidal structure with a butterfly-shaped ligand. This structure is where the nitrogen and oxygen atoms are located at the apical position, and the two adjacent carbon atoms exist in the equatorial positions along with a lone electron pair of Sb. The length of the N→Sb coordinate bond is 2.379(2) Å, which is between the length of the N-Sb covalent bonds (2.11 Å) [52] and the sum of the van der Waals radii (3.74 Å) [53], indicating that the intramolecular coordination between antimony and nitrogen atoms was weak. The anionic $C_6F_5SO_3^-$ion was packed around the antimony cation to improve water tolerance and enhance the Lewis acidity.

We evaluated the thermal stability of the complexes by TG-DTA analysis under N_2 atmosphere, and the result is shown in Fig. 3. Complexes **2a, 2b**, and **2c** are stable up to approximately 285 °C, 290 °C, and 340 °C, respectively, and the endothermic peak that appears at approximately 200 °C indicates that fusion occurred because no weight loss has been observed. Complex **2c** has better thermal stability than the other complexes, which may be due to the long-chain perfluorooctyl group. As shown in the TG-analysis results, complex **2a** did not contain coordinated water molecule, but complex **2b** or **2c** contained one water molecule, which was consistent with the results of ^{1}H NMR and

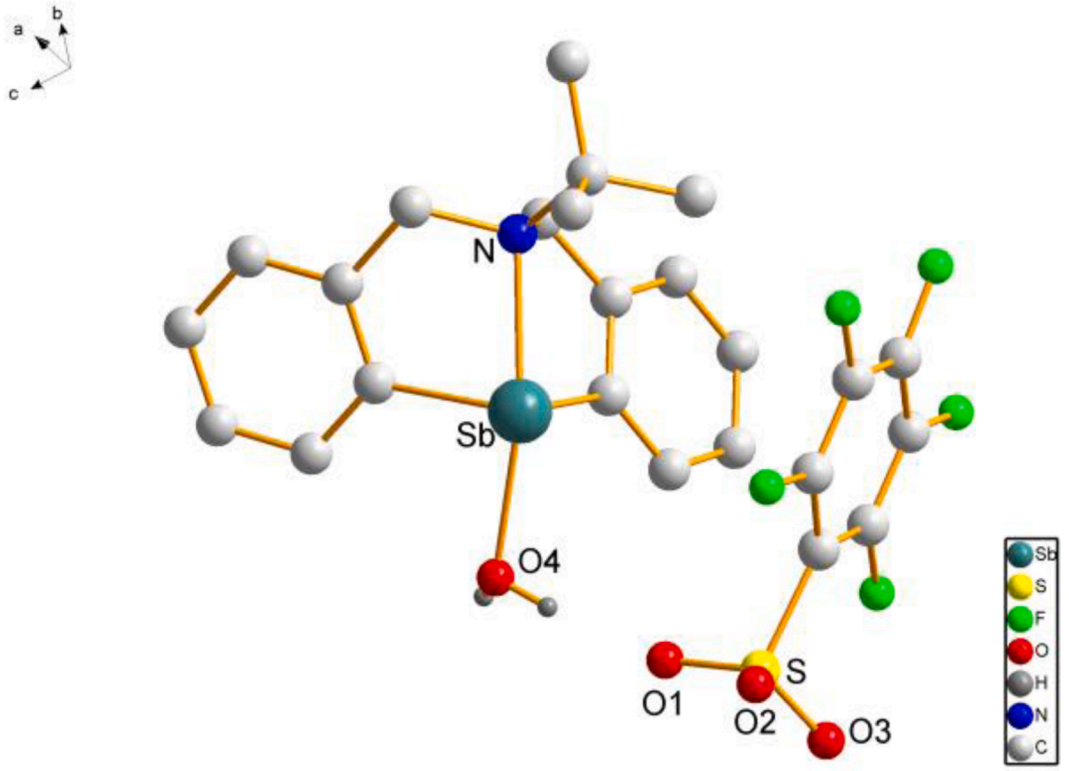


Fig. 2. ORTEP view of the crystal structure of 2b and selected bond lengths (Å) and angles (deg): Sb-C1, 2.147(3); Sb-C14, 2.26(3); Sb-N, 2.379(2); Sb-O4, 2.297(18); S-O2, 1.432(2); S-O1, 1.446(2); S-O3, 1.452(2); C14-Sb-C1 99.65(10); C14-Sb-O4 89.72(9); C1-Sb-O4 87.34(9); and O4-Sb-N1 158.09(7).

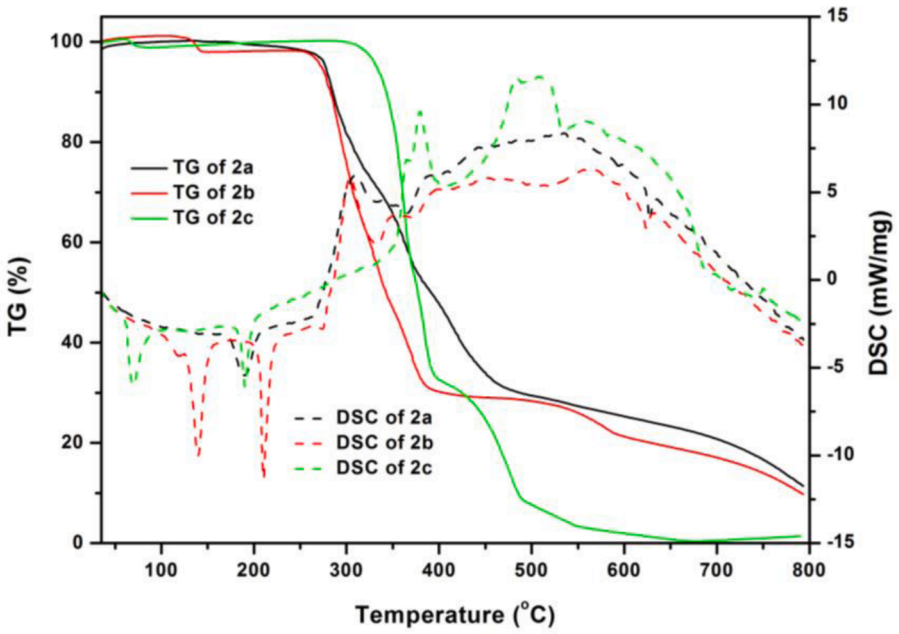
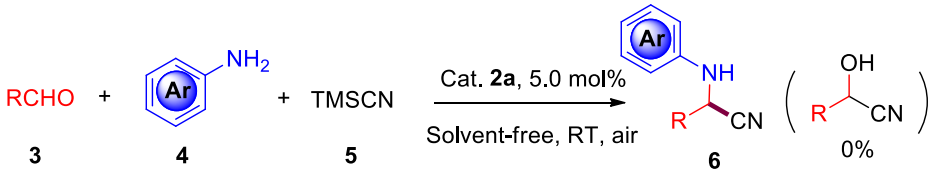
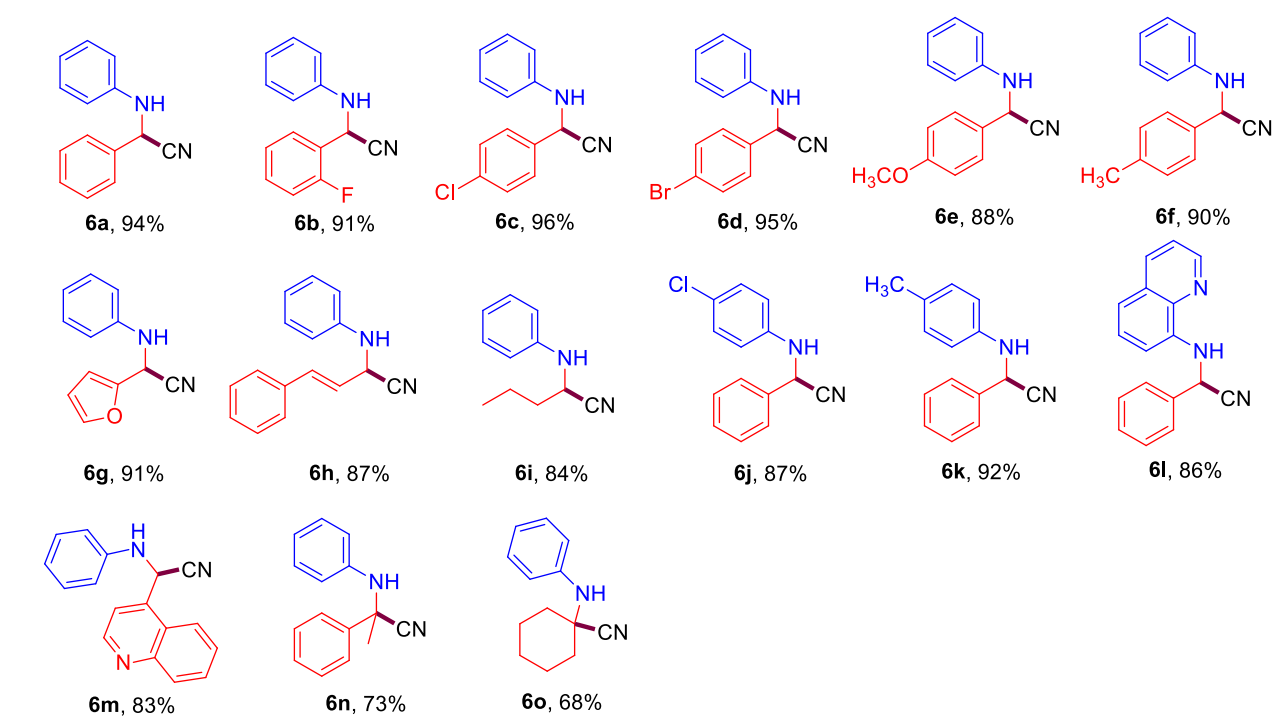


Fig. 3. TG-DTA curves of complexes 2a–2c.

Table 1
Strecker reaction catalyzed by complex 2a[a].





[a]Catalyst **2a** (0.05 mmol); aldehydes/ketones (**3**; 1.0 mmol); 1.0 mmol; amines (**4**; 1.0 mmol); trimethylsilyl cyanide (**5**; 1.2 mmol); solvent-free; RT; **6a-6m**, 1 h; **6n** and **6o**, 6 h; isolated yield.

elemental analysis.

Next, we investigated the solubility and acidity of complexes **2a**–**2c**. These organoantimony complexes possess good solubility in common polar solvents, such as THF, acetone, acetonitrile, and MeOH, but are insoluble in CH_2Cl_2, Et_2O, *n*-hexane, and toluene (Table S1, ESI). The Lewis acidity of complexes **2a**–**2c** was estimated via the Hammett indicator method with strength of $3.3 < H_0 < 4.8$ (Fig. S2, ESI), indicating relatively strong acidity [54]. On the basis of the features of the abovementioned complexes, we assessed their catalytic activities and diastereoselectivities in four organic reactions: (i) the Strecker reaction, (ii) Mannich-type reaction, (iii) cross-condensation of aldehydes with ketones, and (iv) amination of epoxides.

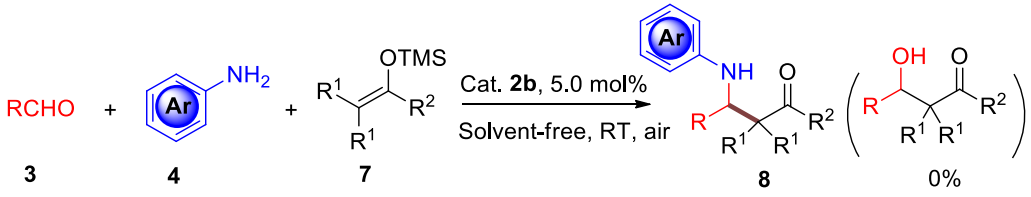
3.2. Strecker reaction catalyzed by complex *2a*

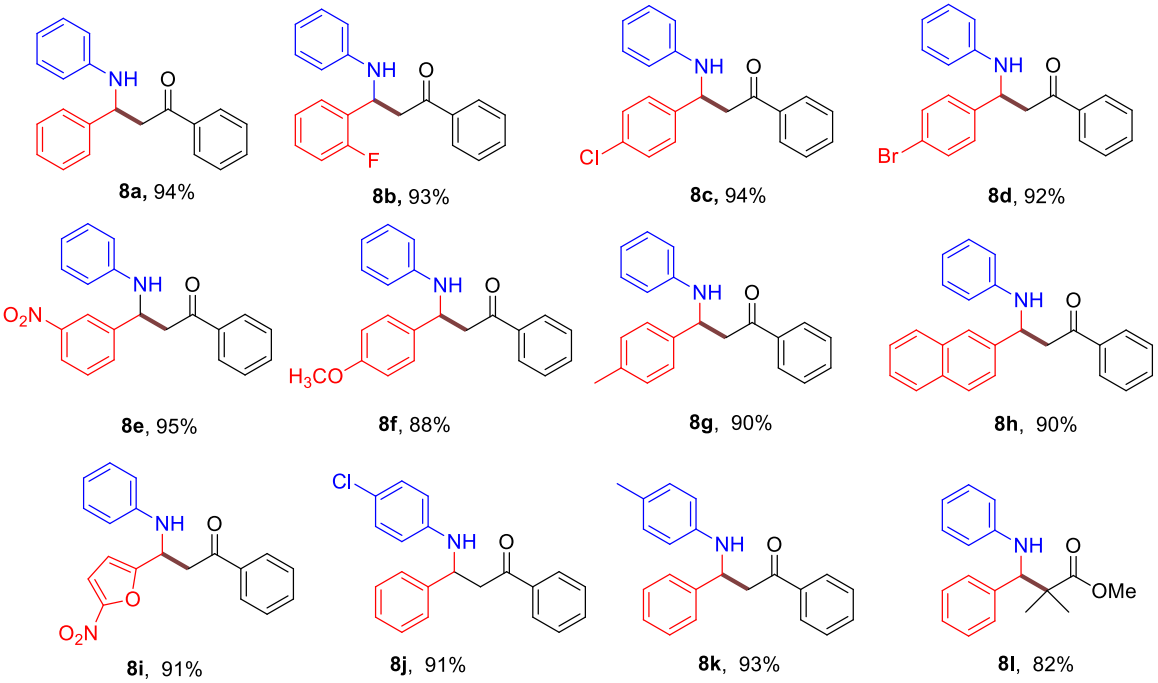
First, we assessed complex **2a** for the one-pot three-component Strecker reaction to demonstrate its catalytic efficiency (Table S2, optimal conditions in the ESI). As shown in Table 1, the Strecker reaction of aldehydes/ketones with anilines and trimethylsilyl cyanide proceeded well. The byproduct nitrile alcohol of the competitive reaction was not detected, indicating the good selectivity of **2a** for Strecker reaction. Aromatic aldehydes with electron-withdrawing (F, Cl, Br) and electron-donating (CH_3, OCH_3) groups can react smoothly with aniline and trimethylsilyl cyanide to obtain α-aminonitriles (**6a**–**6f**, 88%–96%), and aldehydes with electron-withdrawing groups showed higher reactivity. Furfural, cinnamaldehyde, and 4-quinolinecarboxaldehyde provide the corresponding products with respective 91%, 87%, and 83% isolated yield, thereby showing high compatibility for this reaction (**6 g, 6 h**, and **6 m** respectively). Meanwhile, *n*-butylaldehyde can react with aniline and trimethylsiloxynitrile, resulting in the 82% yield of **6i**. The presence of substituents in the phenylamine source and heterocyclic 8-aminoquinoline had a negligible effect on the reaction efficiency (**6j, 6k**, and **6l**). Acetophenone and cyclohexanone can also be transformed to the corresponding product with 73% and 68% yield (**6n** and **6o**).

3.3. Mannich-type reaction catalyzed by complex *2b*

The Mannich-type reaction is often used to prepare β-amino carbonyl compounds, which are important components of biologically active molecules [55-58]. However, solving the side reaction problem produced by aldehydes and enol silyl ethers remains a challenge [59]. Thus, the catalytic performance of complex **2b** was evaluated using the Mannich-type reaction of aldehydes with anilines and enol silyl ethers (Table S3, optimal conditions in the ESI). As shown in Table 2, a variety of β-amino carbonyl compounds can be conveniently and efficiently obtained via a complex **2b**-catalyzed Mannich-type reaction. In general, aromatic aldehydes with various functional groups (such as electron-rich and electron-deficient groups) at the para and meta positions, react smoothly to obtain the corresponding products with good-to-excellent yields (**8a**–**8 g**). Naphthaldehyde and 5-nitro-2-furaldehyde can be used in this reaction condition, providing compounds **8 h** and **8i** with 90% and 91% yields, respectively. Meanwhile, the reaction proceeds well with substituted anilines, providing the desired products with high yields (**8j** and **8k**). Notably,

Table 2
Mannich-type reaction by complex 2b [a].





[a]Catalyst **2b** (0.05 mmol); aldehydes (**3**; 1.0 mmol); amines (**4**; 1.0 mmol); enol silyl ethers (**7**; 1.2 mmol); solvent-free; RT; **8a-8k**, 0.5 h; **8l**, 3 h; isolated yield.

((1-Methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane is also suitable for the transformation, providing compound **8l** with 82% yield.

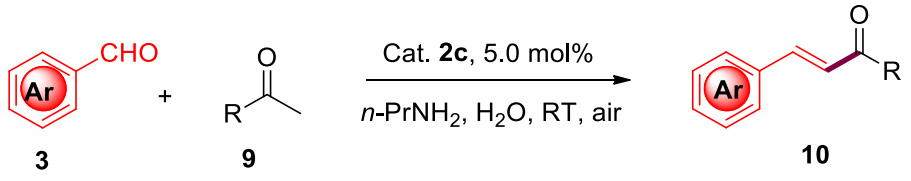
3.4. Cross-condensation reaction catalyzed by complex *2c*

We adopted complex **2c** as a catalyst for the cross-condensation reaction of aromatic aldehydes and ketones to explore its stereoselectivity (Table S4, optimal conditions in the ESI). As shown in Table 3, using organoantimony complex **2c** as a catalyst, we obtained moderate-to-good yields of (*E*)-*α, β*-unsaturated ketones (70%–90%) with trace of *Z*-isomer (not isolable). Previous reports indicated that syn-elimination of the Mannich intermediates is the primary cause of *E*-selective product formation [60]. Therefore, a particular butterfly-shaped structure and anion with large electron-withdrawing ability can significantly improve the stereoselectivity and catalytic efficiency for cross-condensation reaction. Aromatic aldehydes and ketones with electron-withdrawing groups (F, Cl and Br) showed better stereoselectivity than those with electron-donating groups (CH_3 and *t*-Bu) (**10b**–**10j**). The reaction was compatible with the CN group in terms of achieving high yields of the desired *E* configuration products (**10k** and **10l**). Next, other ketones, such as 2-acetonaphthone and acetone are suitable substrates for this transformation and can generate the corresponding products (**10 m** and **10n**). Thus, the high stereoselectivity can be attributed to the bifunctional Lewis acidic/basic feature of complex **2c** in synthesizing *E*-selective *α, β*-unsaturated ketones.

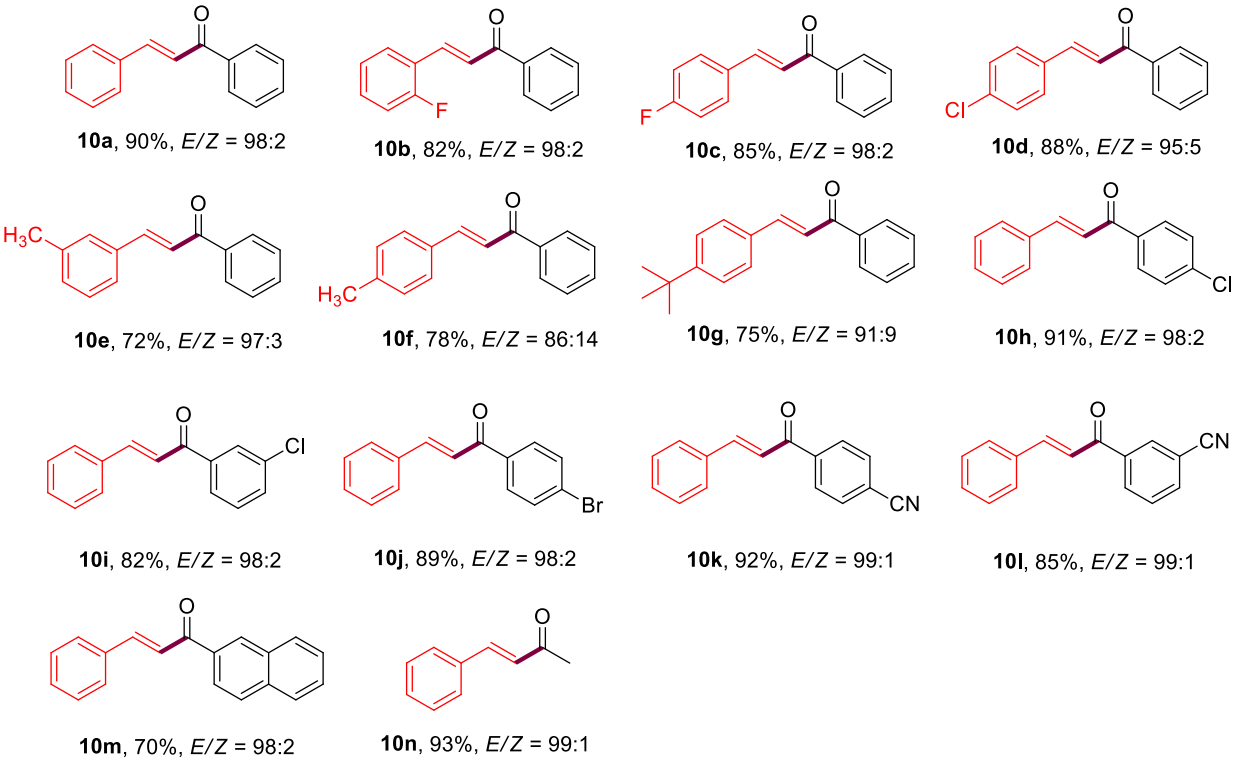
3.5. The epoxide ring-opening reaction catalyzed by complex *2c*

Finally, we applied complex **2c** as a catalyst for epoxide ring-opening reaction with aromatic amines to explore the stereoselectivity of cis and trans isomers (Table S5, optimal conditions in the ESI). As shown in Table 4, non-activated aromatic amines with either an electron-deficient (F, Cl) or an electron-rich (CH_3, OCH_3) group show good reactivity with cyclohexene oxide in obtaining the only trans-β-aminoalcohol products (**12a**–**12 g**), indicating the high stereoselectivity of catalyst **2c**. In the cases of *o*-toluidine and 2, 5-dimethoxyaniline with a large steric effect (**12e** and **12 g**), satisfactory yields (84% and 90%) can be achieved. When 2-phenyloxirane, which can react with different aromatic amines, was adopted as the epoxide, the *α*-amino product with high regioselectivity was obtained (α/β>97/3, **12h**–**12j**, 90%–94% yield). Moreover, epoxypropane with low activity can be used as an epoxy source to provide the only β-aminoalcohol product with 80% yield. Remarkably, enantiomerically pure chiral (*R*)−2-phenyloxirane was converted into their corresponding ring-opening products without racemization (**12h′**), indicating that catalyst **2c** had no effect on the chiral center of the product (chromatograms in the ESI).

Table 3
Cross-condensation reaction catalyzed by **2c**[a].

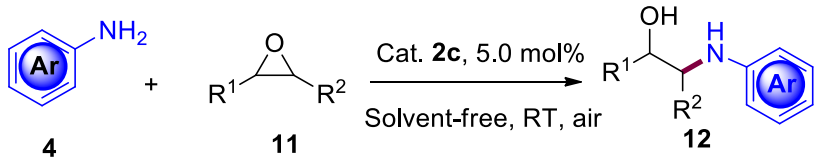


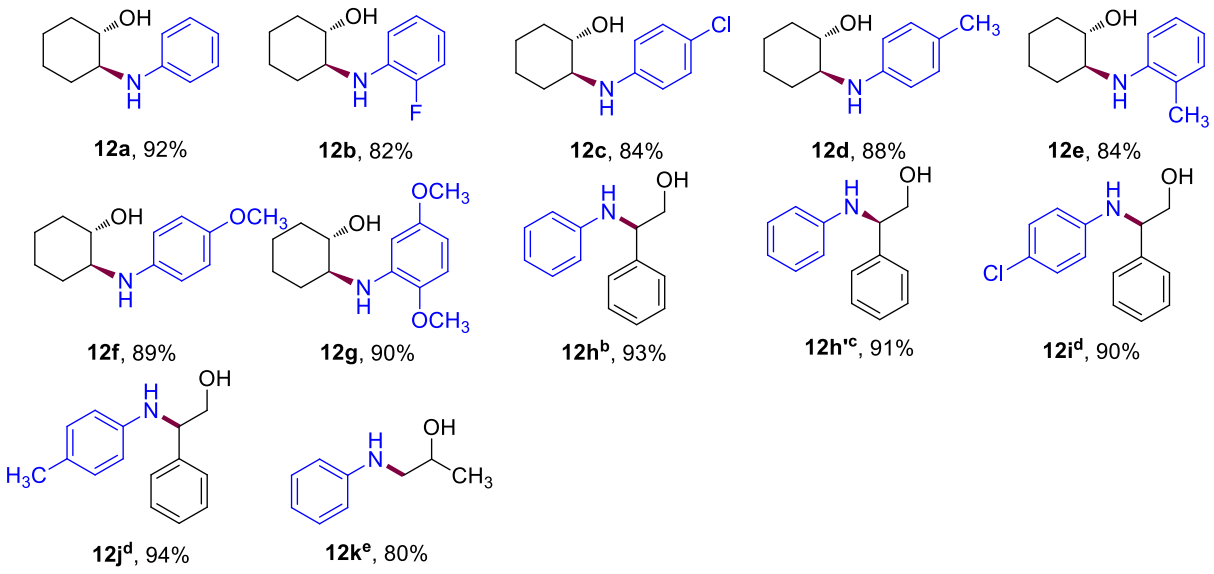
3 9 10



[a]Catalyst **2c** (0.05 mmol); aldehydes (**3**; 1.0 mmol); *n*-$PrNH_2$ (1.0 mmol); ketones (**9**; 1.2 mmol); solvent: H_2O (2 mL); RT; 24 h; isolated yield; determined by ^1H NMR for *E/Z ratio*.

Table 4
Amination reaction of epoxides catalyzed by **2c** [a].





[a]Catalyst **2c** (0.05 mmol); epoxides (**11**; 1.0 mmol); aromatic amines (**4**; 1.0 mmol); solvent-free; RT; **12a-12g**, 4 h; **12h-12j** 2 h; **12k**, 6 h; isolated yield; [b]α/β = 97/3, determined by GC-MS and 1H NMR analysis of the product; [c]stereoisomer was determined by chiral HPLC (AD-H column); [d]100% α-amino pruduct; [e]100% β-amino product.

3.6. Comparison of the catalyst with other catalytic systems

We compared the catalytic activities and stereoselectivities of organoantimony perfluoroalkyl(aryl)sulfonate complexes with other antimony compounds, such as $SbCl_3$, Ph_3SbCl_2, *t*-BuN$(CH_2C_6H_4)_2SbCl$, and *t*-BuN$(CH_2C_6H_4)_2SbOTf$, to demonstrate their advantage. Table 5 shows that catalysts, such as antimony trichloride, triphenylantimony dichloride, and organoantimony chloride with an azastibocine framework had low yields (entries 1–3), probably because of their sensitivity to moisture or their weak Lewis acidity. Although catalysts such as *t*-BuN$(CH_2C_6H_4)_2SbOTf$ exhibited good catalytic efficiency, their diastereoselectivity was poor (entry 4). By contrast, complexes **2a**–**2c** showed high yields and stereoselectivities (entries 5–7), particularly, complex **2c**, which was sui` for catalyzing the cross-condensation reaction, thereby indicating its potential industrial application for organoantimony bifunctional catalytic systems. For comparison, previous reports on other homogeneous and heterogeneous catalysts are summarized in Table 5 (entries 8–18) [56,61-70]. The results showed suggest the advantages of complexes 2a–2c as follows i) mild conditions ii) solvent-free or H_2O as a solvent condition, iii) a wide substrate scope, iv) high efficiency, and v) good reusability.

3.7. Reusability of complexes *2a–2c*

We evaluated the reusability of these catalysts, which were subjected to the following reactions (Eq 1: **3a** + **4a** + **5** →**6a**; Eq 2: **3a** + **4a** + **7a** → **8a**; Eq 3: **3a** + **9a** → **10a**; Eq 4: **4a** + **11a** → **12a**). Catalysts **2a**–**2c** had good recycling ability at least five times without a significant decrease in catalytic efficiency (Fig. 4). The ^1H NMR and SEM results indicated that the skeleton structures of recycled sample and the freshly prepared catalyst were the same, and their morphological structures were similar after the recycling run (Fig. S3–S6, ESI), indicating that the catalyst is suitable for reuse.

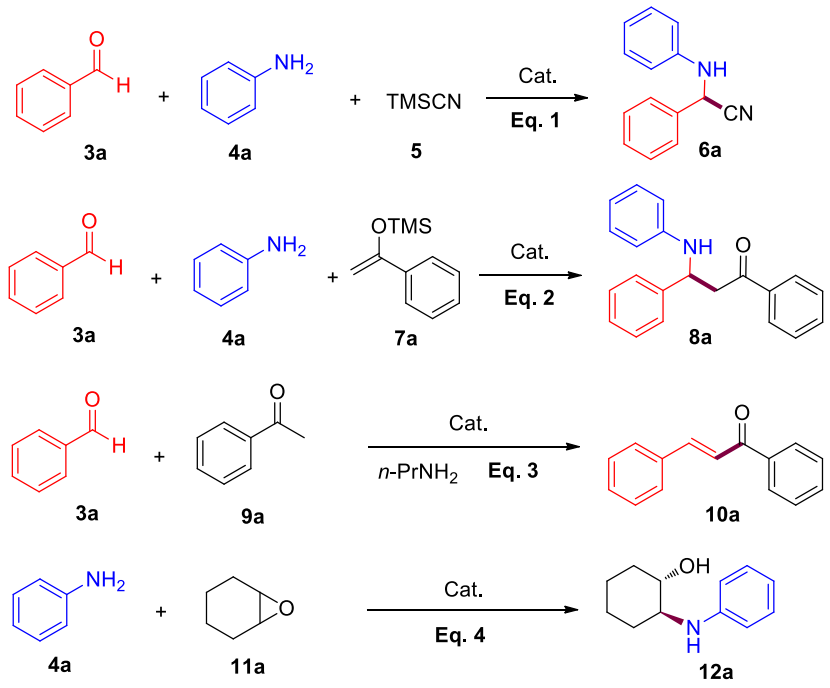
3.8. Synthesis of carbazole derivatives and antitumor activity study

Carbazole derivatives are a class of important heterocyclic compounds possessing high biological activity, such as anticancer, anti-inflammatory, and anti-HIV effects [71]. Given their good catalytic performance, we synthesized a series of novel carbazole derivatives (**6p, 6q, 8 m, 8n, 10o, 12l**, and **12 m**) using the abovementioned reactions catalyzed by complexes **2a**–**2c** (Fig. 5a). Furthermore, we screened the antiproliferative activities of such compounds in two human cancer cell lines (colorectal carcinoma HCT116 cells and hepatoma HepG2 cells) using the CCK-8 assay (Fig. 5b). The compounds showed good inhibitory activity for the two human cancer cell lines at the low μM level, with IC_{50} values of approximately 30 μM. Notably, compound 6p, with IC_{50} of 21.25 μM in HCT116, had a better inhibitory activity than the other compounds. However, the presence of a $C=C$ double bond in compound **10o** resulted in a remarkable decrease in activity in the two cell lines. Therefore, these carbazole derivatives showed slightly enhanced activity against CHT116 cells compared with that against HepG2 cells. Further bioactivity investigation is still underway in our laboratory.

4. Conclusions

In conclusion, we adopted an azastibocine framework with tertiary butyl and synergistically modulated the properties of tert-butyl nitrogen and the electron-withdrawing nature of the perfluoroalkyl(aryl)sulfonate groups adjacent to the antimony atom to synthesize and

Table 5
Catalyst comparison of antimony compounds and other catalytic systems.



Entry	Catalyst	Yield (%) [e]				
		Eq.1[a]	Eq.2[b]	Eq. 3 (*E*/*Z*) [c]	Eq.4 [d]	Ref
1	$SbCl_3$	38	45	0	46	-
2	Ph_3SbCl_2	51	60	40(64/36)	62	-
3	*t*-BuN$(CH_2C_6H_4)_2$SbCl	48	55	36(71/19)	58	-
4	*t*-BuN$(CH_2C_6H_4)_2$SbOTf	87	91	88 (82/18)	87	-
5	Complex **2a**	94	94	90 (90/10)	91	-
6	Complex **2b**	93	94	89 (95/5)	90	-
7	Complex **2c**	94	93	90 (98/2)	92	-
8	TMSOTf (5 mol%)-Eq.1	Conditions: CH_2Cl_2; RT.; 3 h; Yield: 87%; non-recyclable				[61]
9	Silica sulfuric acid (25 mol%)-Eq.1	Conditions: CH_2Cl_2; RT.; 6 h; Yield: 88%; non-recyclable				[62]
10	NHC-Amidate Palladium (II) Complex (3 mol%)-Eq.1	Conditions: CH_2Cl_2; RT.; 24 h; Yield: 79%; non-recyclable				[63]
11	$Bi(OTf)_3{\cdot}4H_2O$ (2 mol%)- Eq.2	Conditions: dry CH_3CN, RT.; 0.1 h; Yield: 89%; recyclable				[56]
12	PS–SO_3H (1 mol%)- Eq.2	Conditions: H_2O; 30 °C; 2 h; Yield: 91%; non-recyclable				[64]
13	P/S-Yb$(OTf)_3$ (5 mol%)- Eq.2	Conditions: CH_3CN/ CH_2Cl_2, RT.; 2 h; Yield: 92%; recyclable				[65]
14	$RuCl_3$ (3 mol%)-Eq.3	Conditions: solvent-free; 120 °C; 6 h; Yield: 95%; non-recyclable				[66]
15	GO-MnO_2 (8 wt%)-Eq.3	Conditions: solvent-free; 110 °C; 1 h; Yield: 98%; recyclable				[67]
16	Fe_3O_4@MOF (3 mol%)-Eq.3	Conditions: solvent-free; 110 °C; 24 h; Yield: 96%; recyclable				[68]
17	$Cu(OTf)_2$ (5 mol%)-Eq.4	Conditions: CH_3CN; RT.; 30 h; Yield: 95%; non-recyclable				[69]
18	$InBr_3$ (5 mol%)−Eq.4	Conditions: CH_3CN; RT.; 12 h; Yield: 84%; non-recyclable				[70]

[a]Cat. (0.05 mmol); PhCHO (1.0 mmol); $PhNH_2$ (1.0 mmol); TMSCN (1.2 mmol); solvent-free; RT.; 1 h; [b]Cat. (0.05 mmol); PhCHO (1.0 mmol); $PhNH_2$ (1.0 mmol); trimethyl((1-phenylvinyl)oxy)silane (1.2 mmol); solvent-free; RT.; 0.5 h; [c]Cat. (0.05 mmol); PhCHO (1.0 mmol); n-$PrNH_2$ (1.0 mmol); $PhCOCH_3$ (1.2 mmol); solvent: H_2O (2 mL); RT.; 24 h; [d]Cat. (0.05 mmol); cyclohexene oxide (1.0 mmol); $PhNH_2$ (1.0 mmol); solvent-free; RT.; 4 h; [e]isolated yield.

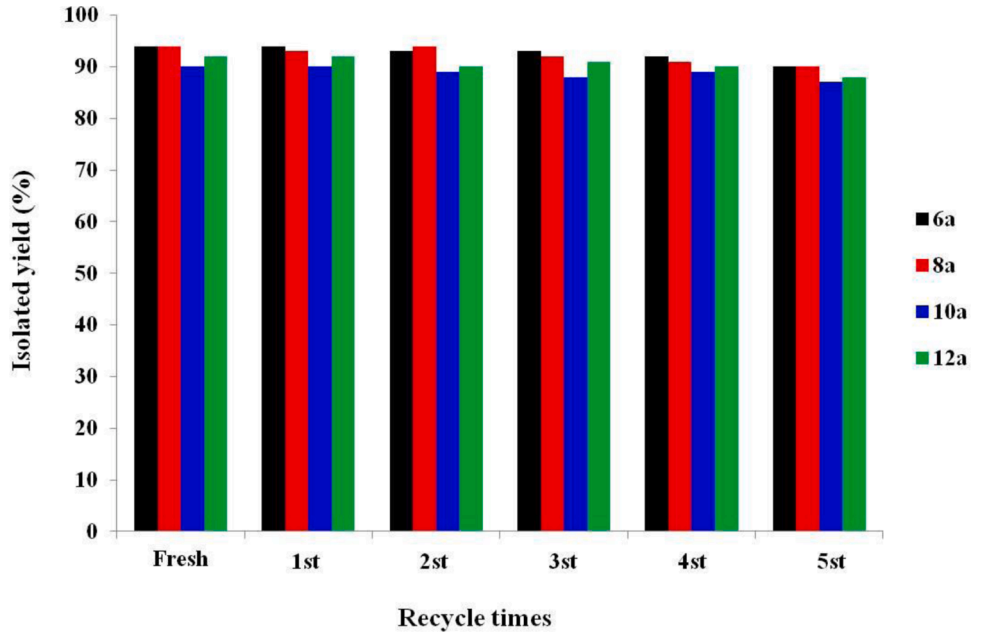
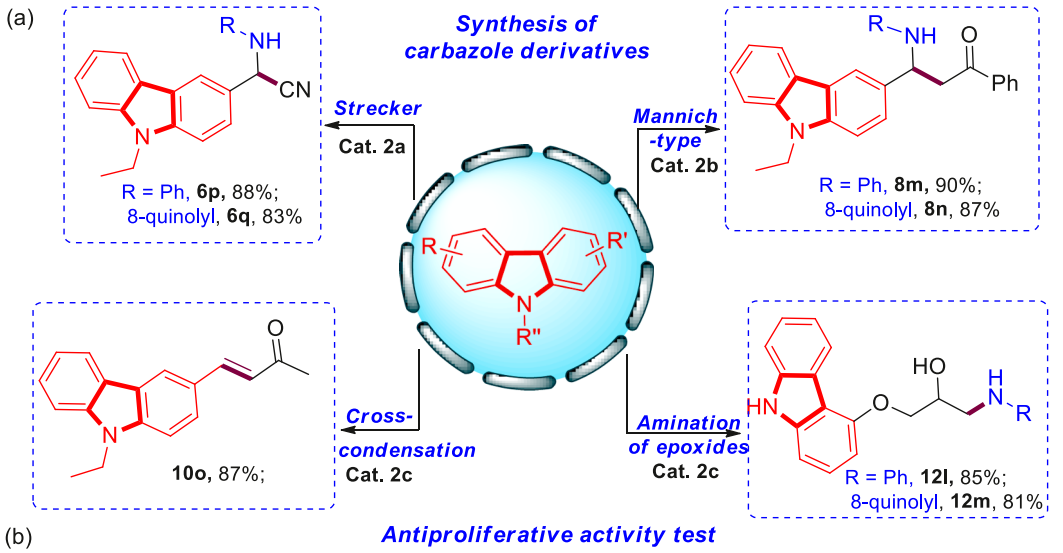


Fig. 4. Recycling tests for complexes 2a–2c.



(b) **Antiproliferative activity test**

IC_{50} Values (μmol/L)	6p	6q	8m	8n	10o	12l	12m
HCT116	21.25 ± 0.91	30.77 ± 0.99	29.46 ± 0.39	30.61 ± 1.21	35.51 ± 0.83	29.93 ± 0.34	29.71 ± 0.41
HepG2	32.45 ± 0.38	46.54 ± 0.73	32.24 ± 0.42	39.43 ± 0.57	43.14 ± 0.45	34.41 ± 1.72	35.65 ± 1.96

Fig. 5. (a) Synthesis of carbazole derivatives and (b) antiproliferative activity test against CHT116 cells and HepG2 cells.

characterize a series of air-stable and water-tolerant organoantimony (III) perfluoroalkyl(aryl)sulfonate complexes. They exhibited good thermal stability and relatively strong Lewis acidity. The complexes, as bifunctional Lewis acidic/basic catalysts, showed high catalytic efficiency, selectivity, and recyclability in the Strecker reaction, Mannich-type reaction, cross-condensation of aldehydes with ketones, and amination of epoxides. The butterfly-shaped structure and anion with large electron-withdrawing ability can significantly improve the stereoselectivity and catalytic efficiency for cross-condensation reaction. Compared with other catalytic systems, complexes exhibited an efficient, mild, highly selective and recyclable protocol for the synthesis of α-aminonitriles, β-amino carbonyl compounds, chalcones and β-amino-alcohol. Moreover, we applied such complexes to extend the synthesis of seven novel carbazole derivatives, which showed good inhibitory activity against CHT116 and HepG2 cells. Based on such excellent performance, these complexes had high application potential in organic synthesis and fine chemicals.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2021.111727.

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