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ARTICLE

Establishing the Correlation between Catalytic Performance and N→Sb Donor-Acceptor Interaction: Systematic Assessment of Azastibocine Halide Derivatives as Water Tolerant Lewis Acids

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A series of organoantimony(III) halide complexes with tetrahydrodibenzo[*c,f*][*1,5*]azastibocine framework were synthesized and employed as water tolerant Lewis acid catalysts. The results of systematic structure-activity relationship study demonstrated that the strength of N→Sb donor-acceptor interaction could be synergistically modulated by tuning the property of the nitrogen substituents and halogen atoms adjacent to the central antimony atom, and consequently resulted in distinct catalytic performances towards organic reactions such as Mannich, cross-condensation, cyclization-aromatization and epoxides aminolysis reaction. The fluorinated organoantimony(III) derivatives were found to be more active than that of the chlorinated, brominated and iodinated analogues, owing to the use of Sb–F moiety as hydrogen bond acceptor. By comparison, the compound 6-cyclohexyl-12-fluoro-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*] azastibocine (**1d**) is found to exhibit the highest catalytic activity, together with facile reusability in scale enlarged synthesis.

Introduction

Given the growing concern on the economic and sustainability of chemical processes, continuous efforts have been devoted to the investigation of reaction systems for molecular transformations using naturally abundant main-group elements.[1] As a boundary element in group 15, antimony has drawn considerable attention since antimony-containing compounds are found in numerous synthetic, pharmaceutical and material molecules.[2] Over the past decades, inorganic antimony compounds e.g. $SbCl_3$, $SbBr_3$, and SbF_5, etc., have been investigated as catalysts in a diversity of organic reactions owing to their intrinsically high Lewis acidity.[3] Meanwhile, a number of antimony compounds with Sb–C covalent bond, the so-called organoantimony complexes, were synthesized and applied in organic synthesis.[4] In the pioneering works of Nomura and coworkers, antimony(V)-based organometallic complexes were used as effective catalysts for reactions such as chemical fixation of CO_2[5a–5c], polymerization[5d–5f], esterification[5g], and amidation[5i–5j]. However, the problem of instability of Sb–C bonds, sensitivity to air and/or moisture as well as the relatively low catalytic efficiency severely restricts the development of organoantimony catalysis.

The rich diversity of coordination chemistry provides an exciting prospect for the design of organoantimony compounds that are air-stable and water-tolerant.[6,7] Comprehensive studies have demonstrated that the incorporation of a bidentate or tridentate ligand to the antimony atom through the carbon atom of the aryl group as well as through the donor-acceptor interaction with coordinate bond from atoms such as B,[7a] N,[7b–7g] P,[7h–7j] O,[7k–7n] S[7o] or in some cases Ni,[7p] Pd,[7q] Pt,[7r] Au,[7s] Hg,[7t] would result in organoantimony complexes with high stability and unique reactivity. Furthermore, this strategy also provides a platform to execute previously unattainable reactions with more abundant and less expensive antimony-based catalysts[7i,7m,7n]. Most recently, Matile and coworkers have calculated binding energies of various highly fluorinated Lewis acids to chloridion, and found that antimony remained the most powerful donors for operational σ-hole interactions, which provided intriguing perspectives for future applications in catalysis.[8] Fascinated by these advances, we contemplate whether the intriguing correlation between donor-acceptor interaction and organoantimony catalysis could be explored for the purpose of developing effective antimony-based organometallic catalysts. Nonetheless, there is still lack of knowledge about the relationship between donor-acceptor interaction and catalytic performance of organoantimony complexes.

Our initial idea originated from a recent work on the utilization of azastibocine derivatives as potential antitumor agents against the human alveolar adenocarcinoma cell lines

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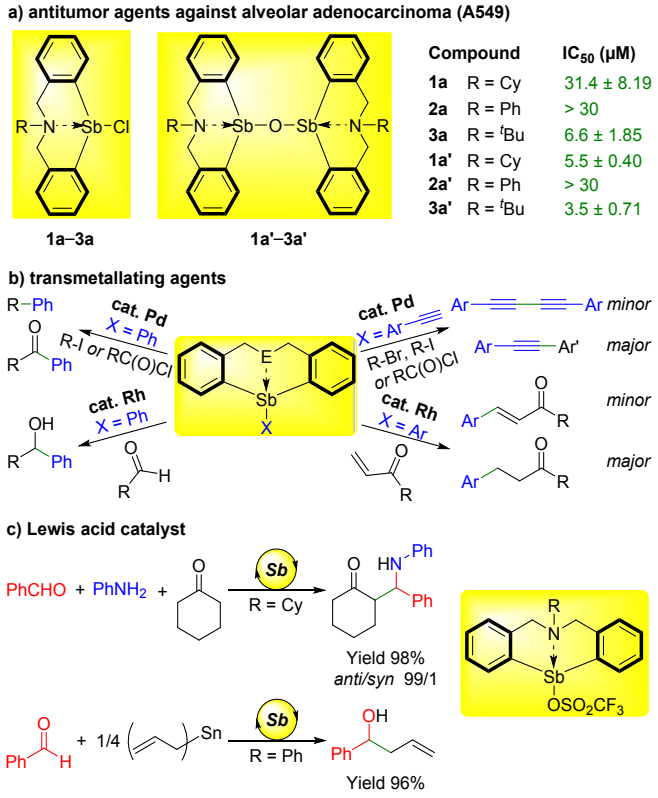


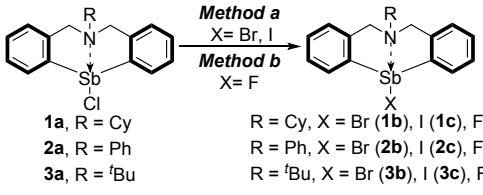
Fig.1 The importance of N→Sb inter-coordination in azastibocine derivatives.

(Fig. 1a). Preliminary data demonstrated that the anti-proliferative activity detected over these compounds could be attributed to the hypervalent coordination between the antimony and nitrogen atoms.[9] This observation is also supported by the functionalized azastibocine derivatives that were reported by Kurita and coworkers as transmetallating agents in the transition metal (Rh, Pd)-catalysed cross-coupling and addition reactions (Fig. 1b), wherein they found that the incorporation of the intramolecular N→Sb inter-coordination would remarkably enhance the reactivity of organoantimony compounds.[10] On the other hands, our group and Tan *et al.* have separately reported that organoantimony(III) triflates with azastibocine framework can efficiently catalyse the direct diastereoselective Mannich reaction[11] and allylation of aldehydes with tetraallyltin (Fig. 1c).[12] With this in mind, we went ahead to elucidate the correlation between N→Sb donor-acceptor interaction and catalytic activity of a series of halogenated azastibocine derivatives. To our delight, the nonlinear negative correlations between the lengths of N→Sb coordinate bond and the catalytic performances of organoantimony compounds were found. By comparison, we found that the complex 6-cyclohexyl-12-fluoro-5,6,7,12-tetrahydrodibenzo[*c,f*] [*1,5*]azastibocine (**1d**) exhibits the most potent catalytic efficiency towards organic reactions such as Mannich, cross-condensation, cyclization-aromatization and epoxides aminolysis reactions, and facile reusability in scale enlarged synthesis.

Results and discussion

In order to probe the effect of nitrogen substituents on the azastibocine derivatives, we began with the examination of the catalytic efficiency of our previously reported organoantimony chlorides **1a–3a** towards classical direct diastereoselective Mannich reactions of cyclohexanone with benzaldehyde and aniline in aqueous media at room temperature.[11] When the reaction proceeded under catalyst-free condition, only a trace amount of desired product **4a** was obtained, and there was no detection of diastereoselectivity (Table 1, entry 1). The use of organoantimony chlorides was crucial to improve both the yield and *anti*-selectivity of β-aminoketone (Table 1, entries 2–4). Among the three organoantimony chlorides, the catalytic performace of compound 12-chloro-6-cyclohexyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (**1a**) is superior to that of the phenyl (**2a**) and *tert*-butyl (**3a**) analogues. On the basis of crystallographic data of N→Sb coordinate bond lengths and experimental facts, we deduce that the increase of electron-donating ability of the nitrogen substituent would strengthen the coordination between nitrogen and antimony atoms as well as enhance the Lewis acidity, consequently resulting in the improvement of efficient for Mannich reaction. With such notation, it is reasonable to speculate that the nitrogen-containing ligand may serve as an auxiliary moiety to activate the Lewis acidity of organometal moiety, which is supported by the observation reported by Denmark and coworkers.[13] On the other hand, in the cases of phenyl (**2a**) and *tert*-butyl (**3a**) with opposite electronic effect, the lengths of N→Sb coordinate bonds are almost the same. The results might be attributed to the distortion of flexible tetrahydrodibenzo[*c,f*][*1,5*]azastibocine frameworks that are affected by both electronic and steric effect of the nitrogen substituents.[9]

Next, we systematically inspected the effect of the halogen atoms adjacent to the central antimony atom (Table 1). The organoantimony bromides (**1b–3b**), iodides (**1c–3c**) and fluorides (**1d–3d**) can be directly synthesized through halogen exchange by treating the precursor chlorides **1a–3a** with the corresponding inorganic salts, i.e. potassium bromide, potassium iodide or silver fluoride, in 1:10 or 1:1 molar ratio as specified in Scheme 1. These compounds readily recrystallized from the reaction mixtures as colourless crystals or white powders in moderate to excellent yields, and could be kept in open air or even in the presence of H_2O for a long-term period without showing any detectable change in ^1H NMR spectra,



Scheme 1 Preparation of organoantimony(III) compounds **1b**–**3d**. ***Method a***: KBr or KI (10 equiv.), H_2O/CH_2Cl_2, room temperature, 24 h; **1b**, 92%; **2b**, 87%; **3b**, 91%; **1c**, 86%; **2c**, 85%; **3c**, 81%. ***Method b***: AgF (1 equiv.), H_2O/CH_2Cl_2, room temperature, dark, 12 h; **1d**, 93%, **2d**, 95%, **3d**, 76%.

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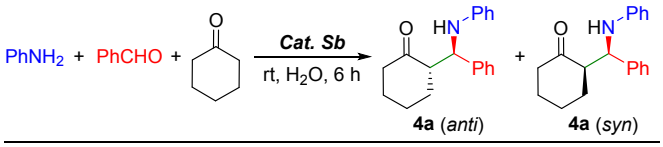
Table 1 Direct diastereoselective Mannich reaction catalysed by various halogenated azastibocine derivatives in aqueous media [a]



Entry	*Cat. Sb*	Length (Å)[b]	FIA (kJ/mol)[c]	*Anti/syn*[d]	Yield (%)[e]
1	none	–	–	51/49	trace[f]
2	**1a**	2.397(2)	254.3161300	93/7	54
3	**2a**	2.466(2)	182.0754975	83/17	39
4	**3a**	2.467(2)	175.0312810	82/18	37
5	**1b**	2.387(2)	260.0029630	95/5	64
6	**2b**	2.469(2)	159.6143450	80/20	34
7	**3b**	2.446(2)	233.2885005	88/12	47
8	**1c**	2.400(2)	245.6125975	90/10	51
9	**2c**	2.498(3)	133.8896960	75/25	30
10	**3c**	2.462(3)	193.3336415	85/15	40
11	**1d**	2.450(2)	209.7377655	98/2	98
12	**2d**	2.522(2)	128.8592380	90/10	82
13	**3d**	2.495(5)	143.7615760	96/4	86

[a] Reaction conditions: 5 mol% organoantimony catalyst, aniline (1 mmol), benzaldehyde (1 mmol) and cyclohexanone (3 mmol) in H_2O (2 mL) at room temperature for 6 h. [b] The length of N(1)→Sb(1) coordinate bond. [c] Fluoride ion affinity. [d] Determined by ^{1}H NMR analysis with crude reaction mixture. [e] Isolated yield of the major isomer after chromatography on silica gel. [f] Not isolated.

clearly indicating that the compounds are air-stable and water-tolerant. The structures of compounds **1b–3d** were unambiguously characterized by X-ray crystallography, all of which exhibit the *pseudo*-trigonal bipyramidal geometries with butterfly-shaped ligands. The nitrogen and halogen atoms are located at the apical positions, while the two adjacent carbon atoms are situated at the equatorial position along with a lone electron pair of antimony (see ESI†). The lengths of N→Sb coordinate bond in these compounds are within the range of 2.387(2)−2.522(2) Å, which are slightly longer than the sum of the covalent radii (2.11 Å)[14] but much shorter than the sum of the van der Waals radii (3.74 A)[15], indicating the existence of intramolecular coordination between the antimony and nitrogen atoms. Moreover, to measure the strength of Lewis acidity, the fluoride ion affinity (FIA) of these compounds were calculated at M06-2X/Def2TZVPP level by using COF_2 as a reference compound (eq.1). The resulting relative FIA values were converted to an absolute scale using the experimentally known value of 209 kJ/mol for the FIA of COF_2,[16] and the results demonstrated that the FIA, i.e. the strength of Lewis acidity, increased with the weakening of N→Sb interaction (Table 1).

$$CF_3O^- + Sb \longrightarrow COF_2 + SbF^- \qquad \text{(eq.1)}$$

The catalytic performances of these halogenated azastibocine derivatives were evaluated in a parallel manner under open-flask condition. In the cases of bromides and iodides, the yield and *anti*-selectivity of the desired product **4a** are favourable in the order of: **1b** > **1c** > **3b** > **3c** > **2b** > **2c**, which is in good agreement with the strength of N→Sb inter-coordination (Table 1, entries 5–10). To our delight, the incorporation of fluorine atom to the central antimony atom had a dramatic effect on the improvement of catalytic efficiency of the organoantimony(III) compounds, albeit the

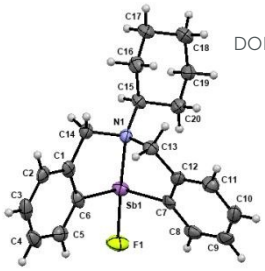
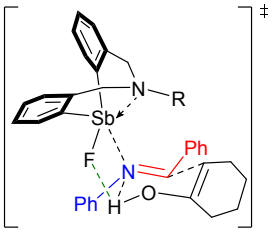


Fig.2 Crystal structure of 6-cyclohexyl-12-fluoro-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*] azastibocine **1d**.

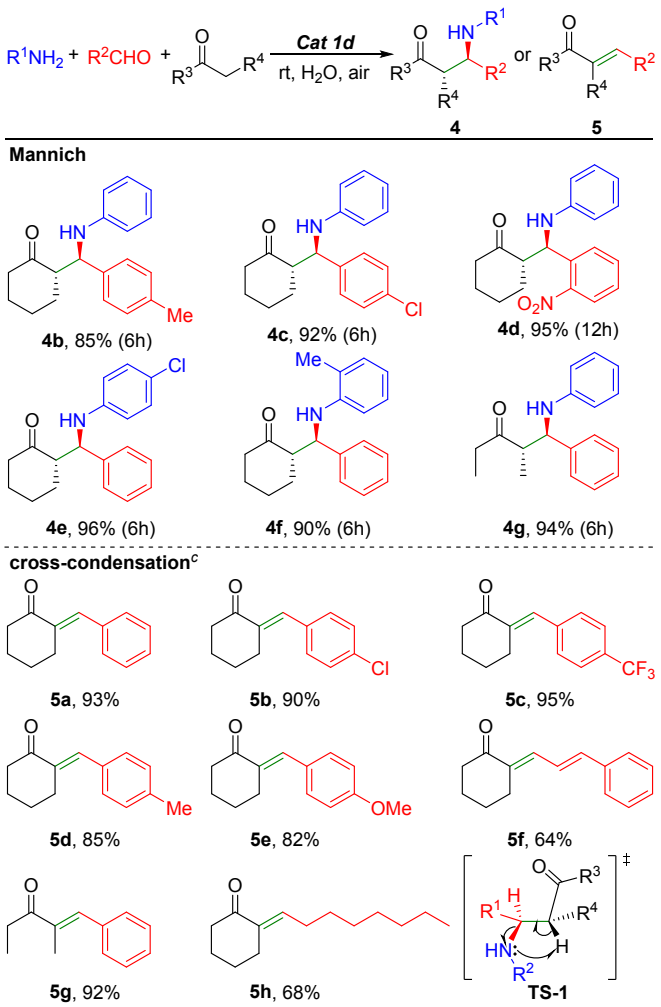
skeleton structures bearing remarkably long N→Sb bond of 2.450(2) Å for **1d**, 2.522(2) Å for **2d**, and 2.495(5) Å for **3d** (Table 1, entries 11–13). By comparison, we found that the compound 6-cyclohexyl-12-fluoro-5,6,7,12-tetrahydrodibenzo [*c,f*][*1,5*]azastibocine (**1d**) exhibits high diastereoselectivity and excellent yield towards the direct three-component Mannich reaction (*anti*:*syn* = 98/2, yield, 98%). It is worth noting that the FIA values, i.e. the Lewis acidity, of fluorides **1d–3d** are somewhat lower than those of compounds **1a**, **1b**, **1c**, and **3b**. Nevertheless, the catalytic performances of organoantimony fluorides is obviously more excellent, evidencing the importance of fluorine atom for enhancing catalytic activity. According to the crystal structures of fluorides **1d–3d** and the fact that organometallic fluoride is favourable for the formation of hydrogen bond[17], we postulate that the catalytic pathway undergoes a six-member cycle transition state comprised of the tetrahydrodibenzo[*c,f*][*1,5*]azastibocine framework and substrates, wherein the Sb–F moiety is employed as a hydrogen bond acceptor (Scheme 2).

Having extensively investigated the configuration of these organoantimony compounds and their catalytic performances towards Mannich reaction, we explored the generality and scope of this catalytic system over organoantimony fluoride **1d**. As shown in Table 2, aromatic aldehydes and amines with either an electron rich (e.g. methyl) or an electron deficient (e.g. chloro, nitro) group all are applicable for the current three-component reaction to produce the corresponding *anti*-selective β-aminoketones in good yields (85–96%). The aldehydes with electron-withdrawing groups (**4c** and **4d**) show relatively higher reactivity than that with an electron-donating group (**4b**). Despite larger in steric hindrance, 2-nitrobenzaldehyde proceeded smoothly to give *anti*-isomer **4d** in 95% yield, albeit a prolonged reaction time was required.



Scheme 2 Proposed transition state for direct diastereoselective Mannich reaction in the synthesis of *anti*-selective β-aminoketone **4a** catalysed by fluorinated azastibocine derivatives **1d–3d**.

Table 2 Direct Mannich and cross-condensation reactions of amines, aldehydes and ketones catalysed by compound **1d** [a,b]

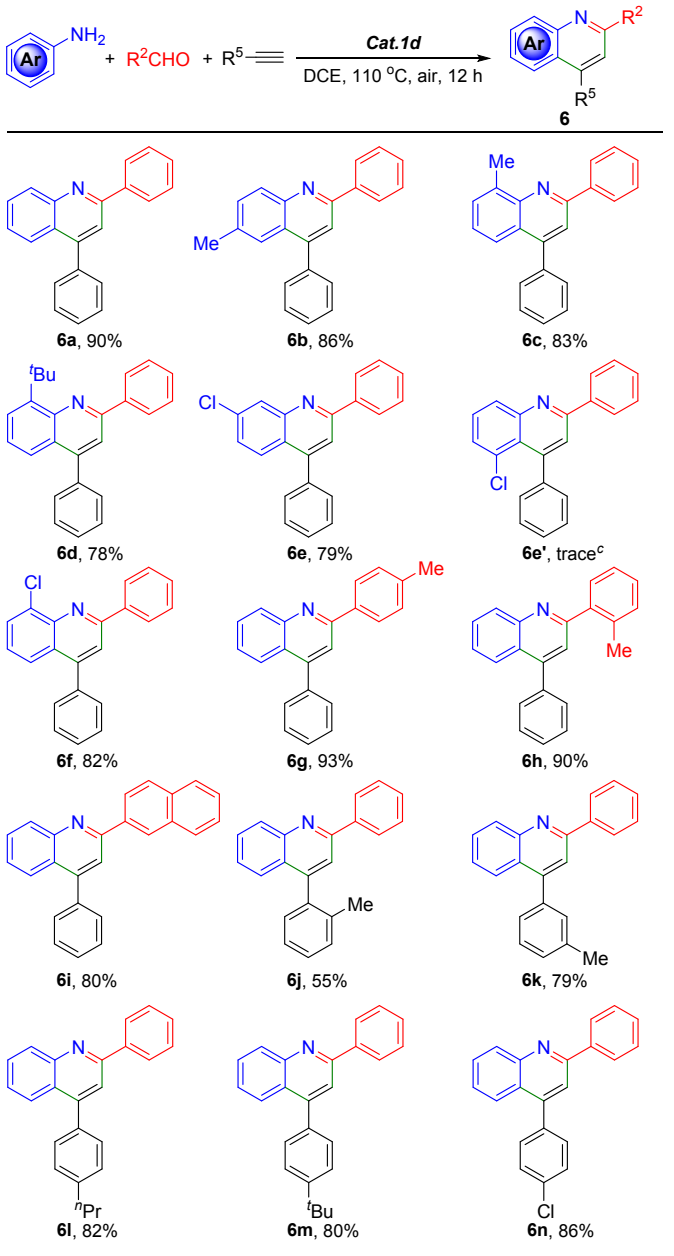


[a] Reaction conditions: organoantimony(III) fluoride **1d** (5 mol%), amine (1 mmol), aromatic aldehyde (1 mmol), ketone (3 mmol), H_2O (2 mL), air, room temperature. [b] Isolated yield of the major isomer after chromatography on silica gel. [c] Reaction conditions: organoantimony(III) fluoride **1d** (5 mol%), *n*-hexylamine (1 mmol), aldehyde (1 mmol), ketone (3 mmol), H_2O (2 mL), air, room temperature, 4 h.

The presence of substituent at the ortho position in aromatic amine had no obvious effect on the efficiency of the reaction, as in the case of **4f**. In addition, straight chain ketone such as pentan-3-one was also examined and good result was obtained (**4g**).

When an aliphatic amine was used instead, a cross-condensation reaction of benzaldehyde with cyclohexanone was found to take place (Table 2). By screening an array of amine sources and carefully tuning of solvents and catalyst **1d** loading during the cross-condensation procedure, we found that the reaction between benzaldehyde and cyclohexanone in the presence of *n*-hexylamine could afford the desired *(E)*-2-benzylidenecyclohexan-1-one (**5a**) in 93% isolated yield with **1d** (5 mol%) as the catalyst, and H_2O as the solvent (see ESI†). A variety of aromatic aldehydes could readily react with ketone substrates i.e. cyclohexanone and pentan-3-one, in aqueous media to afford the *E*-selective α,β-unsaturated ketones in moderate to good yields (**5b–5g**). Labile functional groups, such as chloro, methoxyl and trifluoromethyl, can be accommodated in this reaction. Moreover, the substrates are not limited to the mentioned aromatic aldehydes; *n*-octaldehyde which is relatively low in activity could be used as aldehyde source in this cross-condensation reaction to give respectable yield of **5i**. On the basis of the experimental results and previous reports,[18] we deduce that the *E*-selective products are formed through irreversible *syn*-elimination from the Mannich-type intermediates, as shown in **TS-1**, and the aliphatic amine was used as a co-catalyst in the cross-condensation reaction.

Table 3 Cyclization-aromatization reactions of amines, aldehydes and alkynes catalysed by compound **1d** [a,b]

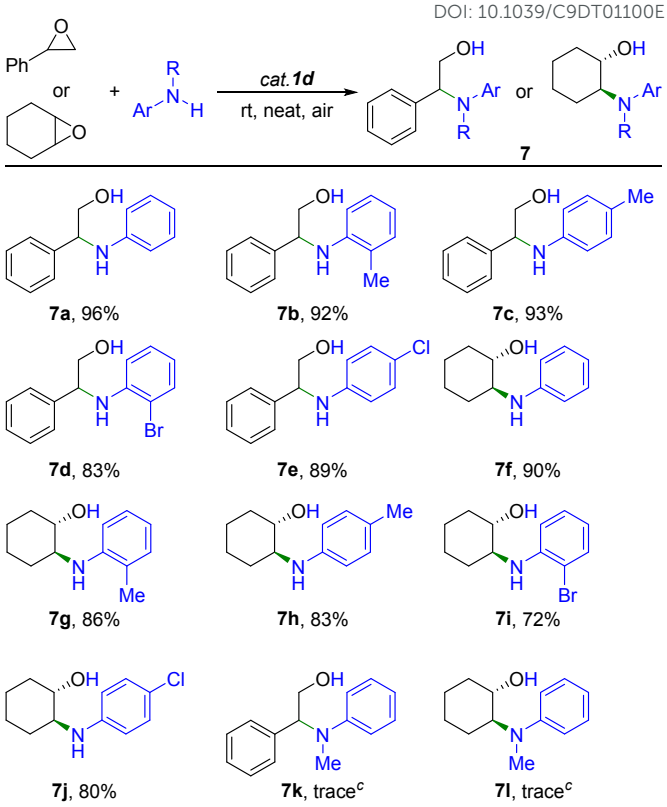


[a] Reaction conditions: organoantimony(III) fluoride **1d** (10 mol%), aromatic amine (1 mmol), aldehyde (1 mmol), alkyne (1 mmol), 1,2-DCE (2 mL), air, 110 °C, 12 h. [b] Isolated yield. [c] Not isolated.

Showing high compatibility of the organoantimony catalysis, the compound **1d** was adopted as a catalyst for the cyclization-aromatization reaction of aniline, benzaldehyde and phenylacetylene (Table 3). After judicious evaluation of reaction parameters, we identified that a protocol based on organoantimony fluoride **1d** (10 mol%) in 1,2-dichloroethane (1,2-DCE) at 110 °C in the presence of air delivered 2,4-diphenylquinoline (**6a**) in 90% isolated yield (see ESI†). The reactions were successful for a diversity of aromatic amines and aldehydes with either electron-rich (e.g. methyl, *tert*-butyl) or electron-poor (chloro) groups (**6b–6h**). It was observed that *meta*-substituted amine, such as 3-chloroaniline, showed high diastereoselectivity under the optimal conditions and produced almost exclusively **6e** in moderate yield (79%). Gratifyingly, 2-naphthaldehyde proceeded smoothly to give **6i** in 80% yield. The reaction also works well for an array of aromatic alkynes (**6j–6n**). The *ortho*-substituted substrate gave the product **6j** in only 55% yield. The somewhat lower yield of **6j** compared with the *meta*-substituted analogues **6k** is presumably due to steric hindrance by the *o*-Me group.

The versatility of the organoantimony(III) catalyst **1d** was not limited to the reactions that proceed through imine intermediates, as can be seen in the catalysis of ring-opening reaction of epoxides with amines (Table 4). In the presence of 5 mol% of **1d**, 2-phenyloxirane could efficiently react with various primary aromatic amines that are structurally and electronically different in diastereoselective ring opening at benzylic carbon atom and furnished the corresponding β-amino-alcohols in good yields (**7a–7e**). In the cases of *o*-toluidine and 2-bromoaniline that are sterically more hindered, satisfactory yields can still be achieved (**7b** and **7d**). Moreover, such an observation is also supported by the reactions using 7-oxabicyclo[4.1.0]heptane as epoxide source (**7f–7j**). In all cases, only the major *trans*-isomers can be isolated, again illustrating the high diastereoselectivity of organoantimony(III) fluoride **1d**. The secondary aromatic amine, for example, *N*-methylaniline was also tested but the yields of corresponding products are low to negligible (**7k–7l**).

Table 4 Aminolysis reactions of epoxides with amines catalysed by compound **1d** [a,b]



[a] Reaction conditions: organoantimony(III) fluoride **1d** (5 mol%), epoxides (1 mmol) and amine (1 mmol), air, room temperature for 6 h. [b] Isolated yield of the major isomer after chromatography on silica gel. [c] Not isolated.

Finally, to further demonstrate the correlation between intramolecular N→Sb donor-acceptor interaction and catalytic performance, we compared the efficiency of other synthesized halogenated azastibocine derivatives towards the above cross-condensation (**I**: reaction substrates are *n*-hexylamine benzaldehyde and cyclohexanone, and the product is (*E*)-2-benzylidenecyclohexan-1-one), cyclization-aromatization (**II**: reaction substrates are aniline, benzaldehyde and

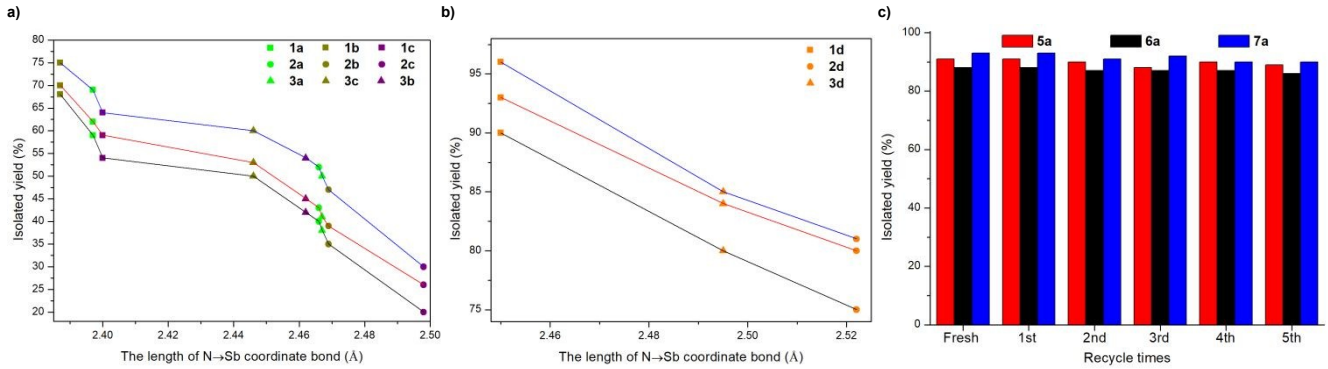


Fig. 3 a) Correlation between N→Sb coordinate bond length in organoantimony(III) chlorides (**1a**, ■; **2a**, ●; **3a** ▲), bromides (**1b**, ■; **2b**, ●; **3b** ▲) and iodides (**1c**, ■; **2c**, ●; **3c** ▲) and corresponding catalytic performances towards cross-condensation (**I**, red line), cyclization-aromatization (**II**, black line) and aminolysis reactions of epoxides (**III**, blue line) reactions. b) Correlation between N→Sb coordinate bond length in organoantimony(III) chlorides (**1d**, ■; **2d**, ●; **3d** ▲) and corresponding catalytic performances towards selected organic reactions (**I**, **II**, and **III**). c) Recyclability of compound **1d** for the scale enlarged synthesis (5 times) of (*E*)-2-benzylidenecyclohexan-1-one (**5a**), 2,4-diphenylquinoline (**6a**), and 2-phenyl-2-(phenylamino)ethan-1-ol (**7a**).

phenylacetylene, and the product is 2,4-diphenylquinoline) and aminolysis reactions of epoxides (**III**: reaction substrates are 2-phenyloxirane and aniline, and the product is 2-phenyl-2-(phenylamino)ethan-1-ol). By comparison, the alternative organoantimony(III) halides exhibited somewhat lower catalytic activity for the selected reactions than that of fluoride **1d**. More to the point, the nonlinear negative correlations between the N→Sb coordinate bond lengths and the catalytic performances of organoantimony(III) chlorides, bromides and iodides (Fig. 3a) as well as in the special cases of the three fluorides (Fig. 3b) were repeatedly found. In addition, the reusability of compound **1d** in scale enlarged synthesis (5 times) were also evaluated (Fig. 3c). The efficiency of the small-scale reaction was retained, delivering the corresponding products in 91% (**5a**), 88% (**6a**) and 93% (**7a**) yields, respectively. Furthermore, the catalyst can be easily recycled five times without showing significant decline of catalytic efficiency as well as maintaining the freshly prepared skeleton structure, which points to a potential industrialization window for the antimony-based catalytic systems.

Conclusions

In conclusion, by adopting the 5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine framework and through modulating synergistically the property of nitrogen substituent and halogen atom adjacent to the central antimony(III) atom, we successfully adjusted the strength of N→Sb donor-acceptor interaction on a series of azastibocine derivatives and employed them as water tolerant Lewis acid catalysts towards Mannich, cross-condensation, cyclization-aromatization and aminolysis reactions of epoxides. The compound 6-cyclohexyl-12-fluoro-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (**1d**) is found to exhibit the highest catalytic efficiency, together with facile reusability in scale enlarged synthesis, owing to the use of Sb–F moiety as hydrogen bond acceptor. More to the point, the nonlinear negative correlations between the N→Sb coordinate bond lengths and catalytic performances of the corresponding organoantimony(III) compounds were found, which provide theoretical and experimental basis for in-depth study on the mechanism of organoantimony catalysis and for further design of antimony-based organometallic complexes as water tolerant Lewis acids. More detailed investigations on the reaction mechanism and correlation between the strength of N→Sb intramolecular interaction and the biological activity of these organoantimony(III) compounds are currently underway in our laboratory.

Experimental

General information

The commercially available chemicals were purchased from Adamas-beta, and were used as received unless indicated otherwise. The *N*-containing precursors and organoantimony chlorides were prepared according to previous literature[10f]. Melting points were determined over a XT-4 micro melting point apparatus (Beijing Tech Instrument Co., Ltd.). Proton, carbon and fluorine nuclear magnetic resonance spectra were recorded on a Bruker-400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR spectroscopy) spectrometer with solvent resonance as the internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). Chemicals shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS). Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q= quartet, m = multiplet), Coupling constants (*J*) are reported in hertz. Elemental analysis was performed using VARIO EL III. X-ray single crystal diffraction analysis was performed with SMART-APEX and RASA-7A by Shanghai Institute Organic Chemistry, China Academy of Science. The fluoride ion affinity was performed with Tianhe-2 in the national super computer centre, in Guangzhou, China.

General procedure for the synthesis of organoantimony(III) bromides and iodides

To a solution of organoantimony chloride (5 mmol) in CH_2Cl_2 (30 mL), a solution of KBr or KI (50 mmol) in deionized water was added under open-flask conditions. After stirred at room temperature for 24 h, the solution was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and subject to filtration. After filtrate concentration in vacuo, the solution was mixed with *n*-hexane and kept at room temperature to afford the corresponding products by recrystallization.

$Cy(CH_2C_6H_4)_2SbBr$ (1b): Colourless crystal (2.2 g, 92% yield); mp 245–247 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.34 (2H, d, *J* = 7.0 Hz, C5 & C11–H), 7.27 (4H, dt, *J* = 23.4, 7.2 Hz, C3, C4, C12 & C13–H), 7.07 (2H, d, *J* = 7.3 Hz, C2 & C14–H), 4.09 (4H, dd, *J* = 58.1, 15.2 Hz, C7 & C8–H), 3.05 (1H, t, *J* = 10.8 Hz, C15–H), 1.99 (2H, d, *J* = 11.4 Hz, C16 & C20–H), 1.79 (2H, d, *J* = 12.5 Hz, C16' & C20'–H), 1.63 (1H, d, *J* = 12.8 Hz, C18–H), 1.40–1.21 (4H, m, C19 & C17–H), 1.12–1.08 (1H, m, C18'–H); ^{13}C NMR (100 MHz,$CDCl_3$, TMS): δ 144.0 (C6 & C10), 138.0 (C5 & C11), 136.2 (C1 & C9), 128.9 (C2 & C14), 128.6 (C3 & C13), 124.7 (C4 & C12), 65.5 (C15), 57.8 (C7 & C8), 29.6 (C16 & C20), 25.6 (C18), 25.3 (C17 & C19); Anal. Calc. for $C_{20}H_{23}BrNSb$: C, 50.14; H, 4.84; N, 2.92. Found: C, 50.29; H, 4.95; N, 2.99; Selected bond distances (Å) and angles (°): Sb(1)–C(6) 2.143(2), Sb(1)–C(10) 2.157(2), Sb(1)–N(1) 2.387(2), Sb(1)–Br(1), 2.7142(5), C(6)–Sb(1)–C(10) 99.23(8), Br(1)–Sb(1)–N(1) 163.53(4).

$Ph(CH_2C_6H_4)_2SbBr$ (2b): Colourless crystal (2.0 g, 87% yield); mp 233–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.35 (2H, d, *J* = 7.4 Hz, C3 & C20–H), 7.40 (2H, t, *J* = 7.3 Hz, C5 & C18–H), 7.33 (4H, dd, *J* = 13.5, 7.2 Hz, C4, C6, C17 & C19–H), 7.26–7.24 (3H, m, C11 & C13–H), 7.19 (3H, d, *J* = 7.6Hz, C10, C12 & C14–H), 4.62 (4H, dd, *J* = 66.4 ,14.9 Hz, C8 & C15–H); ^{13}C NMR (100 MHz,$CDCl_3$, TMS) δ 147.8 (C9), 143.0 (C1 & C2), 138.2 (C7 & C16), 136.8 (C3 & C20), 129.6 (C11 & C13), 129.4 (C5 & C18), 129.3 (C6 & C17), 125.5 (C4 & C19), 125.3 (C12), 119.8 (C10 & C14), 61.2 (C8 & C15); Anal. Calc. for $C_{20}H_{17}BrNSb$: C, 50.78; H,

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3.62; N, 2.96. Found: C, 50.89; H, 3.69; N, 3.07; Selected bond distances (Å) and angles (°): Sb(1)–C(1) 2.158(3), Sb(1)–C(8) 2.156(3), Sb(1)–N(1) 2.469(2), Sb(1)–Br(1), 2.6620(4), C(1)–Sb(1)–C(8) 100.4(1), Br(1)–Sb(1)–N(1) 163.22(6).

^{t}Bu($CH_2C_6H_4$)$_2$SbBr (3b): Colourless crystal (2.0 g, 91% yield); mp 244–246 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 8.42 (2H, d, *J*= 7.4 Hz, C5 & C8–H), 7.38–7.28 (4H, m, C3, C4, C9 & C10–H), 7.14 (2H, d, *J* = 7.4 Hz, C2 & C11–H), 4.23 (4H, dd, *J* = 156.2, 15.4 Hz, C13 & C14–H), 1.39 (9H, s, C16, C17 & C18–H); ^{13}C NMR (100 MHz,$CDCl_3$, TMS): δ 144.9 (C6 & C7), 139.6 (C5 & C8), 134.3 (C1 & C12), 129.2 (C2 & C11), 128.7 (C3 & C10), 124.5 (C4 & C9), 60.8 (C15), 57.1 (C13 & C14), 27.2 (C16, C17 & C18). Anal. Calc. for $C_{18}H_{21}$BrNSb: C, 47.72; H, 4.67; N, 3.09. Found: C, 47.82; H, 4.75; N, 3.16; Selected bond distances (Å) and angles (°): Sb(1)–C(6) 2.153(2), Sb(1)–C(7) 2.151(2), Sb(1)–N(1) 2.446(2), Sb(1)–Br(1) 2.7631(5), C(6)–Sb(1)–C(7) 96.18(8), Br(1)–Sb(1)–N(1) 162.99(4).

Cy($CH_2C_6H_4$)$_2$SbI (1c): Colourless crystal (2.3 g, 86% yield); mp 253–255 °C; 1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.52 (2H, d, *J* = 6.9 Hz, C5 & C8–H), 7.74–7.31 (4H, m, C3, C4, C9 & C10–H), 7.11 (2H, d, *J* = 7.0 Hz, C2 & C11–H), 4.13 (4H, dd, *J* = 53.0, 15.1 Hz, C13 & C14–H), 3.12 (1H, t, *J* = 11.3 Hz, C15–H), 2.05 (2H, d, *J* = 11.8 Hz, C16 & C20–H), 1.87 (2H, d, *J* = 12.9 Hz, C16' & C20'–H), 1.70 (1H, d, *J* = 13.0 Hz, C18–H), 1.47–1.28 (4H, m, C19 & C17–H), 1.19–1.10 (1H, m, C18–H); ^{13}C NMR (100 MHz,$CDCl_3$, TMS): *δ* 143.8 (C6 & C7), 139.4 (C5 & C8), 134.5 (C1 & C12), 129.2 (C2 & C11), 129.0 (C3 & C10), 124.7 (C4 & C9), 65.6 (C15), 57.6 (C13 & C14), 29.7 (C16 & C20), 25.7 (C18), 25.4 (C17 & C19); Anal. Calc. for $C_{20}H_{23}$INSb: C, 45.66; H, 4.41; N, 2.66. Found: C, 45.74; H, 4.54; N, 2.79; Selected bond distances (Å) and angles (°): Sb(1)–C(6) 2.154(3), Sb(1)–C(7) 2.166(3), Sb(1)–N(1) 2.400(2), Sb(1)–I(1) 2.9650(4), C(6)–Sb(1)–C(7) 98.8(1), I(1)–Sb(1)–N(1) 163.34(6).

Ph($CH_2C_6H_4$)$_2$SbI (2c): Colourless crystal (2.2 g, 85% yield); mp 249–251 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 8.47–8.45 (2H, m, C3 & C20–H), 7.39–7.30 (6H, m, C4, C5, C6, C17, C18 & C19–H), 7.26–7.23 (2H, m, C11 & C13–H), 7.19–7.16 (3H, m, C10, C12 & C14–H), 4.60 (4H, dd, *J* = 66.6, 14.9 Hz, C8 & C15–H); ^{13}C NMR (100 MHz,$CDCl_3$, TMS): *δ* 147.6 (C9), 142.9 (C1 & C2), 140.0 (C7 & C16), 134.0 (C3 & C20), 129.6 (C11 & C13), 129.5 (C5 & C18), 129.4 (C6 & C17), 125.5 (C4 & C19), 125.3 (C12), 119.8 (C10 & C14), 60.9 (C8 & C15); Anal. Calc. for $C_{20}H_{17}$INSb: C, 46.19; H, 3.30; N, 2.69. Found: C, 46.27; H, 3.33; N, 2.76; Selected bond distances (Å) and angles (°): Sb(1)–C(1) 2.166(3), Sb(1)–C(8) 2.175(3), Sb(1)–N(1) 2.498(3), Sb(1)–I(1) 2.8995(3), C(1)–Sb(1)–C(8) 96.3(1), I(1)–Sb(1)–N(1) 163.92(6).

^{t}Bu($CH_2C_6H_4$)$_2$SbI (3c): Colourless crystal (2.0 g, 81%); mp 228–230 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 8.48 (2H, t *J* = 3.8 Hz, C5 & C8–H), 7.30–7.26 (4H, m, C3, C4, C9 & C10–H), 7.06 (2H, d, *J* = 4.7 Hz, C3 & C11–H), 4.15 (4H, dd, *J* = 151.6, 12.9 Hz, C13 & C14–H), 1.34 (9H, s, C16, C17 & C18–H); ^{13}C NMR (100 MHz,$CDCl_3$, TMS): *δ* 144.9 (C6 & C7), 139.6 (C5 & C8), 134.3 (C1 & C12), 129.2 (C2 & C11), 128.8 (C3 & C10), 124.5 (C4 & C9), 60.8 (C15), 57.1 (C13 & C14), 27.2 (C16, C17 & C18); Anal. Calc. for $C_{18}H_{21}$INSb: C, 43.24; H, 4.23; N, 2.80. Found: C, 43.33; H, 4.35; N, 2.96; Selected bond distances (Å) and angles (°): Sb(1)–C(6) 2.166(3), Sb(1)–C(7) 2.157(3), Sb(1)–N(1) 2.462(3), Sb(1)–I(1) 2.9463(3), C(6)–Sb(1)–C(7) 97.6(1), I(1)–Sb(1)–N(1) 163.59(6).

General procedure for the synthesis of organoantimony(III) fluorides

To a solution of organoantimony chloride (5 mmol) in CH_2Cl_2 (30 mL), a solution of AgF (5 mmol) in deionized water (25 mL) was added under open-flask condition. After stirred in the dark at room temperature for 12 h, the mixture was subject to filtration. The filtrate was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic layer was dried over anhydrous Na_2SO_4. After filtrate concentration in vacuo, the solution was mixed with *n*-hexane and kept at room temperature to afford the corresponding products by recrystallization.

Cy($CH_2C_6H_4$)$_2$SbF (1d): Colourless crystal (1.9 g, 93% yield); mp 237–239 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.91 (2H, d, *J* = 7.2 Hz, C5 & C8–H), 7.32 (2H, t, *J* = 7.2 Hz, C3 & C10–H), 7.21 (2H, t, *J* = 7.2 Hz, C3' & C10'–H), 7.09 (2H, t, *J* = 7.3 Hz, C2 & C11–H), 4.04 (4H, dd, *J* = 71.6, 15.1 Hz, C13 & C14–H), 2.97 (1H, d, *J* = 10.5 Hz, C15), 2.00 (2H, d, *J* = 11.2 Hz, C16 & C20–H), 1.80 (2H, d, *J* = 12.0 Hz, C16' & C20'–H), 1.63 (1H, d, *J* = 12.4 Hz, C18–H), 1.39–1.21 (4H, m, C17 & C19–H), 1.12–1.03 (1H, m, C18'–H); ^{13}C NMR (100 MHz,$CDCl_3$, TMS): *δ* 144.1 (C6 & C7), 143.9 (d, *J* = 6.3 Hz, C5 & C8), 133.4 (d, *J* = 5.9 Hz, C1 & C12), 128.5 (C2 & C11), 128.3 (C3 & C10), 124.7 (C4 & C9), 65.2 (C15), 57.7 (C13 & C14), 29.4 (C16 & C20), 25.6 (C18), 25.5 (C17 & C19); ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -185.15 (s, F1); Anal. Calc. for $C_{20}H_{23}$FNSb: C, 57.45; H, 5.54; N, 3.35. Found: C, 57.53; H, 5.59; N, 3.44; Selected bond distances (Å) and angles (°): Sb(1)–C(6) 2.140(3), Sb(1)–C(7) 2.145(3), Sb(1)–N(1) 2.450(2), Sb(1)–F(1) 2.015(2), C(6)–Sb(1)–C(7) 98.5(1), F(1)–Sb(1)–N(1) 156.42(7).

Ph($CH_2C_6H_4$)$_2$SbF (2d): Colourless crystal (2.0 g, 95% yield); mp 216–218 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.92 (2H, d, *J* = 7.3 Hz, C2 & C9–H), 7.38 (2H, t, *J* = 7.2 Hz, C4 & C11–H), 7.27–7.26 (4H, m, C3, C5, C10 & C12–H), 7.20 (4H, t, *J* = 7.2 Hz, C16, C17, C19 & C20–H), 7.12 (1H, t, *J* = 7.1 Hz, C18–H), 4.55 (4H, dd, *J* = 85.2, 15.0 Hz, C7 & C14–H); ^{13}C NMR (100 MHz,$CDCl_3$, TMS): *δ* 148.5 (C15), 144.6 (d, *J* = 6.6 Hz, C1 & C8), 143.1 (C6 & C13), 133.4 (d, *J* = 6.2 Hz, C2 & C9), 129.4 (C17 & C19), 128.9 (C4 & C11), 128.8 (C5 & C12), 125.2 (C3 & C10), 125.0 (C18), 119.4 (C16 & C20), 61.1 (C7 & C14); ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -198.48 (s, F1); Anal. Calc. for $C_{20}H_{17}$FNSb: C, 58.29; H, 4.16; N, 3.40. Found: C, 58.39; H, 4.24; N, 3.58; Selected bond distances (Å) and angles (°): Sb(1)–C(1) 2.131(3), Sb(1)–C(8) 2.153(3), Sb(1)–N(1) 2.522(2), Sb(1)–F(1) 1.998(2), C(1)–Sb(1)–C(8) 91.80(9), F(1)–Sb(1)–N(1) 162.92(7).

^{t}Bu($CH_2C_6H_4$)$_2$SbF (3d): Colourless crystal (1.5 g, 76% yield), mp 206–208 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.80 (2H, d, *J* = 7.3 Hz, C5 & C11–H), 7.16 (2H, t, *J* = 7.3 Hz, C3 & C13–H), 7.07 (2H, t, *J* = 7.3 Hz, C4 & C12–H), 6.96 (2H, d, *J* = 7.7 Hz, C2 & C14–H), 3.95 (4H, dd, *J* = 171.1, 15.4 Hz, C7 & C8–H), 1.13 (9H, s, C16, C17 & C18–H); ^{13}C NMR (100 MHz,$CDCl_3$, TMS): *δ* 145.1 (C6 & C10), 143.8 (d, *J* = 5.8 Hz, C5 & C11), 133.2 (d, *J* = 6.5 Hz, C1 & C9), 128.5 (C2 & C14), 128.0 (C3 & C13), 124.5 (C4 & C12), 59.7 (C15), 57.1 (C7 & C8), 26.9 (C16, C17 & C18); ^{19}F NMR (376 MHz, $CDCl_3$): δ -185.16 (s, F1); Anal. Calc. for

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$C_{18}H_{21}FNSb$: C, 55.13; H, 5.40; N, 3.57. Found: C, 52.25; H, 5.46; N, 3.62; Selected bond distances (Å) and angles (°): Sb(1)–C(6) 2.127(7), Sb(1)–C(10) 2.135(7), Sb(1)–N(1) 2.495(5), Sb(1)–F(1) 2.026(6), C(6)–Sb(1)–C(10) 98.2(3), F(1)–Sb(1)–N(1) 155.9(2).

General procedure for the direct diastereoselective Mannich reactions

To a 25 mL Schlenk tube was charged with organoantimony complex (0.05 mmol), aromatic amine (1 mmol), aldehyde (1 mmol), cyclohexanone (1 mmol) and H_2O (2 mL). Then the mixture was stirred at room temperature under TLC analysis until the amine and aldehyde as well as the imine intermediate was completely consumed. With the removal of water, the mixture was extracted with Et_2O (3×5 mL) and subject to filtration. The filtrate was then dried over anhydrous Na_2SO_4 and concentrated in vacuo. The diastereoselectivity of product was determined by ^1H NMR spectra of the filtrate and the residue was purified by silica gel flash chromatography column to give the corresponding *anti*-selective product.

General procedure for the cross-condensation reactions

To a 25 mL Schlenk tube was charged with organoantimony complex (0.05 mmol), *n*-hexylamine (1 mmol), aldehyde (1 mmol), cyclohexanone (1 mmol) and H_2O (2 mL). Then the mixture was stirred at room temperature under open-flask condition for 4 h. With the removal of water, the mixture was extracted with Et_2O (3×5 mL), subject to filtration and dried over anhydrous Na_2SO_4. After concentration of the filtrate in vacuo, the residue was purified by silica gel flash chromatography column to give the corresponding *E*-selective product.

General procedure for the cyclization-aromatization reactions

To a 25 mL Schlenk tube was charged with organoantimony complex (0.1 mmol), aromatic amine (1 mmol), aldehyde (1 mmol), alkyne (1 mmol) and 1,2-dichloroethane (2 mL). Then the mixture was stirred at 110 °C under air atmosphere for 12 h. The mixture was cooled to room temperature, diluted with dichloromethane (5 mL), and concentrated in vacuo. The residue was dissolved in Et_2O (10 mL) and the catalyst was separated from the mixture by filtration. After the concentration of the filtrate in vacuo, the residue was purified by silica gel flash chromatography column to give the corresponding product.

General procedure for the aminolysis reactions of epoxides

To a 25 mL Schlenk tube was charged with organoantimony complex (0.05 mmol), aromatic amine (1 mmol), and epoxide (1 mmol). Then the mixture was stirred at room temperature under open-flask condition for 6 h. The mixture was dissolved in Et_2O (10 mL) and the catalyst was separated from the mixture by filtration. After the concentration of the filtrate in vacuo, the residue was purified by silica gel flash chromatography column to give the corresponding product.

General procedure for the scale enlarged synthesis of α,β-unsaturated ketone 5a catalysed by recovered complex 1d

To a 50 mL Schlenk tube was charged with organoantimony complex **1d** (0.25 mmol), *n*-hexylamine (5 mmol), aldehyde (5 mmol), cyclohexanone (5 mmol) and H_2O (10 mL). Then the mixture was stirred at room temperature under open-flask condition for 4 h. With the removal of water, the mixture was extracted with Et_2O (3×20 mL), and the complex **1d** was precipitated and separated by filtration. After concentration of the filtrate in vacuo, the residue was purified by silica gel flash chromatography column to give the corresponding *E*-selective product **5a**. The recovered complex was washed with ethyl ether for five times before being used for the next reaction cycle.

General procedure for the scale enlarged synthesis of 2,4-diphenylquinoline 6a catalysed by recovered complex 1d

To a 50 mL Schlenk tube was charged with organoantimony complex **1d** (0.5 mmol), aromatic amine (5 mmol), aldehyde (5 mmol), alkyne (5 mmol) and 1,2-dichloroethane (10 mL). Then the mixture was stirred at 110 °C under air atmosphere for 12 h. The mixture was cooled to room temperature, diluted with dichloromethane (20 mL), and concentrated in vacuo. The residue was dissolved in Et_2O (30 mL) and the complex **1d** was separated from the mixture by filtration. After the concentration of the filtrate in vacuo, the residue was purified by silica gel flash chromatography column to give the corresponding product **6a**. The recovered complex was washed with ethyl ether for five times before being used for the next reaction cycle.

General procedure for the scale enlarged synthesis of β-amino-alcohol 7a catalysed by recovered complex 1d

To a 50 mL Schlenk tube was charged with organoantimony complex **1d** (0.25 mmol), aromatic amine (5 mmol), and epoxide (5 mmol). Then the mixture was stirred at room temperature under open-flask condition for 6 h. The mixture was dissolved in Et_2O (40 mL) and the complex **1d** was separated from the mixture by filtration. After the concentration of the filtrate in vacuo, the residue was purified by silica gel flash chromatography column to give the corresponding product **7a**. The recovered complex was washed with ethyl ether for five times before being used for the next reaction cycle.

Conflicts of interest

There are no conflicts to declare.

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