Tetrahedron 71 (2015) 4275–4281

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Strong Lewis acids of air-stable binuclear triphenylantimony(V) complexes and their catalytic application in C–C bond-forming reactions

Ningbo Li, Renhua Qiu *, Xiaohong Zhang, Yun Chen, Shuang-Feng Yin *, Xinhua Xu *

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

ARTICLE INFO

Article history:
Received 29 March 2015
Received in revised form 2 May 2015
Accepted 5 May 2015
Available online 9 May 2015

Keywords:
Organoantimony complexes
Pentafluorbezenesulfonate
Perfluorooctanesulfonate
C–C bond-forming

ABSTRACT

Two air-stable novel Lewis acids of triphenylantimony(V) pentafluorbezenesulfonates (**2**) and perfluorooctanesulfonates (**3**) were successfully synthesized and characterized. X-ray studies and thermogravimetric analysis found that these complexes showed high *anti*-hydrolyzability and thermal stability. The high catalytic activity and excellent recyclability of these complexes were achieved in the Michael addition reaction and the allylation reaction. On account of their stability, storability, as well as catalytic efficiency, these complexes should find a broad range of utility in organic synthesis.

1. Introduction

Organoantimony complexes have attracted much attention due to their structure and potential application in organic synthesis, pharmaceuticals and material science.[1] Recently, most of researchers mainly focused on the structural diversity of organoantimony(III) complexes since their stabilities.[2] For example, aryl ligands with the lone pair donor groups (sulfur, oxygen, or nitrogen), such as 2-$[Me_2NCH_2]C_6H_4$, 2,6-$(Me_2NCH_2)_2C_6H_3$, 2,6-$(ROCH_2)_2C_6H_3$ (R=Me, *t*-Bu) and $E(CH_2C_6H_4)_2$ (E=RN, O, S) help to stabilize organoantimony(III) halides, cations and compounds containing metal-metal bonds.[3] But these complexes' application as Lewis acid catalysts for organic synthesis was rarely reported since their low Lewis acidity.[4] By oxidizing the Sb(III) complexes to Sb(V) ones, e.g., Ph_3Sb is oxidized to Ph_3SbCl_2 (**1**), higher catalytic activity was successfully achieved.[5] Hence, design and synthesis of highly efficient organoantimony (V) complexes that free of hydrolysis and can be conveniently applied in various Lewis acid-catalyzed reactions are the key issues.

The synthesis of the organoantimony (V) complexes was chiefly concentrated in the tri- and tetraphenylantimony halides as starting material and further synthesis of their derivatives.[6] For instance, the μ-oxo-bridged binuclear triphenylantimony dihalide was easily synthesized from **1** in moisture solution, which possessing an appropriate stability,[7] but its low Lewis acidity limited its further application in catalysis. Recently, Otera et al.[8] and us[9] found the use of perfluoroalkyl(phenyl)sulfonate groups as effective counter anions could overcome the hydrolytic instability of the organometallic species and enhance the Lewis acidity.[10] This finding has led us to postulate that perfluoroalkyl(phenyl)sulfonate groups serve to overcome the hydrolytic instability of the organometallic species in a general sense. With this in mind, we herein successfully synthesized and characterized μ-oxo-bridged binuclear triphenylantimony(V) perfluorobezenesulfonates $[(Ph_3Sb)_2O](OSO_2C_6F_5)_2$ (**2**) and perfluorooctanesulfonates $[(Ph_3SbOH_2)_2O]^+[OSO_2C_8F_{17}]^-_2$ (**3**). Furthermore, their catalytic activities were assessed by using Lewis acid-catalyzed C–C bond-forming reactions such as the Michael addition reaction and the allylation reaction.

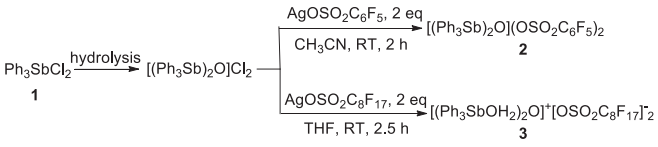
2. Results and discussion

Complexes **2** and **3** were synthesized by treatment of **1** with silver perfluorobezenesulfonate and perfluorooctanesulfonate (AgX, for **2**, X=$OSO_2C_6F_5$; for **3**, X=$OSO_2C_8F_{17}$) (2 equiv) in CH_3CN or THF solution, respectively (Scheme 1).

The crystal structures of **2** and **3** in the solid state were confirmed by X-ray analysis. An ORTEP representation of **2** and **3** and

* Corresponding authors. Fax: +86 731 88821546; e-mail addresses: renhuaqiu@hnu.edu.cn (R. Qiu), sf_yin@hnu.edu.cn (S.-F. Yin), xhx1581@hnu.edu.cn (X. Xu).

http://dx.doi.org/10.1016/j.tet.2015.05.013
0040-4020/



Scheme 1. Synthesis of complexes **2** and **3**.

selected bonds and angles were shown in Figs. 1 and 2. The crystal structure of the complex **2** shows it is covalent structure, which is similar with the complex $[(Ph_3Sb)_2O](OSO_2CF_3)_2$.[11] The unit cells of **2** contain four asymmetric molecules with a bent Sb1–O7–Sb2 bridge as a central. The atoms bound to the Sb1 and Sb2 atoms form distorted trigonal bipyramids with three C(phenyl) atoms in the equatorial plane and the bridging O7 and O1/O4 of the unidentate bonded sulfonate ligand in apical positions. The Sb1–O7 and Sb2–O7 bond distances of Sb1–O7–Sb2 bridge are 1.953(9), 2.028(18), respectively, while the Sb1–O1 and Sb2–O4 distances are 2.353(4), 2.233(3), respectively, which implies the Sb2–O4 and Sb1–O1 bonds connected with anions are more easily to dissociate when in catalytic solution than that of Sb1–O7 and Sb2–O7 bonds for substrate activating. The Sb1–O7–Sb2 angle of **2** is 135.8(16). The O1–Sb1–O7 and O4–Sb2–O7 angle of **2** are 175.9(2), 173.4(2) degree. The Sb–C(phenyl) distance varies from 2.042(11) to 2.095(4) Å.

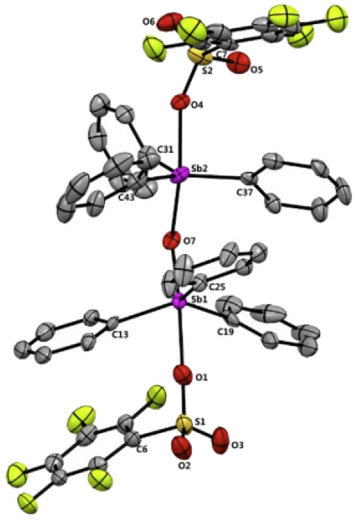


Fig. 1. The crystal structure of the complex **2** and selected bonds (A°) and angles (deg): The Sb1–O7 and Sb2–O7 distances are 1.953(9) and 2.028(18). The Sb1–O1 and Sb2–O4 distances are 2.353(4), 2.233(3). The Sb1–O7–Sb2 angle is 135.8(16) deg. The O1–Sb1–O7 and O4–Sb2–O7 angles are 175.9(2), 173.4(2) deg. The Sb1–C(phenyl) and Sb2–C(phenyl) distances are Sb1–C13, 2.081(17); Sb1–C19, 2.042(11); Sb1–C25, 2.109(6) and Sb2–C31, 2.095(4); Sb2–C37, 2.028(12), Sb2–C43, 2.085(8).

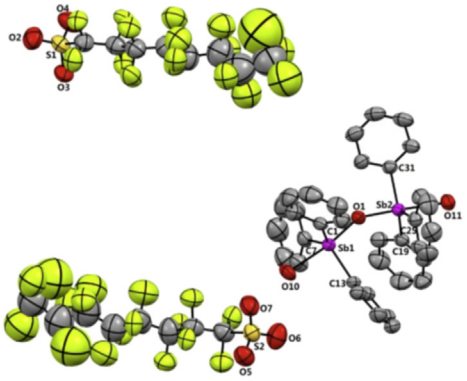


Fig. 2. The crystal structure of the complex **3** and selected bonds (A°) and angles (deg): The Sb1–O1 and Sb2–O1distances are 1.950(4) and 1.956(4). The Sb1–O1–Sb2 angle is 149.3(3) deg. The O1–Sb1–O10 and O1–Sb2–O11 angles are 171.62(19) and 177.15(19) deg. The Sb1–C(phenyl) and Sb2–C(phenyl) distances are Sb1–C1, 2.100(7); Sb1–C7, 2.093(8); Sb1–C13, 2.104(6) and Sb2–C19, 2.091(7); Sb2–C25, 2.105(7); Sb2–C31, 2.117(6). The Sb1–O10 and Sb2–O11 distances of Sb with water molecules are 2.402(5), 2.370(5).

The crystal structure of the complex **3** is depicted in Fig. 2. In contrast to covalent complex **2**, complex **3** is ionic complex in solid state. It shows that each pentavalent antimony center adopts a five-coordinate trigonal bipyramidal geometry surrounded by three equatorial phenyl C atoms, an axial O atom from coordinate water molecule and an axial bridging oxygen, with the bridging angle of 149.3(3)° for Sb1–O1–Sb2. The Sb–C(phenyl) distance varies from 2.091(7) to 2.117(6) Å, and the bridging Sb–O distances of 1.950(4) and 1.956(4) Å indicate that after the complex **3** dissociates as cationic ion, the distances of the two Sb–O bonds are almost same, which are consistent with reports for other trigonal bipyramidal μ-oxo bridged binuclear triphenylantimony complexes.[12]

Generally, water molecule is non-essential and even undesired since it may lead to decomposition of the catalyst. But its participation in the hydrogen bond significantly enhances the stability of the supermolecular structure of **3**. And the longer distances of 2.402(5) and 2.370(5) Å of terminal linkages between H_2O and Sb may benefit the common fluxional behavior of pentacoordinate molecular geometry, which provides easy access to an open coordination site for substrate attacking in catalysis.[13]

As shown in Fig. 3a, each diantimony moiety connects its neighbors through the O–H(water)···O(sulfonate) hydrogen bond(H···O=2.00, 1.98, 1.73 and 1.82 Å; O···O=2.742(9), 2.719(9), 2.683(8) Å, and 2.765(8) Å; O–H···O=132, 132, 172, and 166°) with the graph set $R_4^4(12)$, forming a one-dimensional infinite chain. By this way, the $C_8F_{17}SO_3^-$ anions are packed around the complex cation and produce hydrophobic domains. Furthermore, CH···π and π···π interactions (H···π=2.815 to 3.209 Å; C···π=3.59 to 3.85 Å; π···π=3.686 Å; C–H···π=128 to 153°) between phenyl groups connect chains into two-dimensional bilayer structure (Fig. 3b). Thus, the supermolecular nonbonded contacts and the characteristics of hydrophobicity and electron-withdrawing ability of perfluooctanesulfate counter anion can greatly enhance the stability and catalytic activity of the complex cation $[(Ph_3SbOH_2)_2O]^{2+}$.[5]

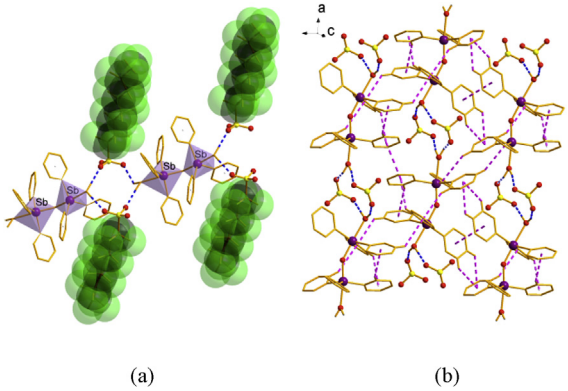


Fig. 3. (a) Perspective view of the coordination environment in complex **3**, and the one-dimensional infinite chain structure along the *c* axis linked by hydrogen bond between coordination water and sulfonate; (b) H atoms except for water molecules and the perfluorocarbon chain have been omitted for clarity. Nonbonded contacts of OH···O and CH···π as well as π···π interactions are indicated by dashed lines.

It is notable that the solid samples remain as dry crystals or powder after being kept in open air over three months, and exhibits no sign of skeleton change by ^{1}H NMR spectroscopy analysis (seeing SI). The thermal behaviors of **2** and **3** were investigated by

TG-DSC under N_2 atmosphere (Fig. S1). The thermal analysis curves showed that decomposition took places in three distinct stages. The first endothermic step below 100 °C can be assigned to the removal of two coordinate water molecules for complex **3**. Complexes **2** and **3** were stable up to about 300 °C. The weight loss of an exothermic nature at 350 °C is plausibly due to the oxidation of organic entities (Fig. 4).

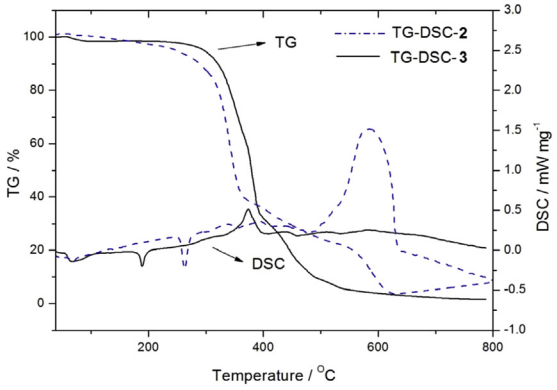


Fig. 4. TG-DSC curves of complexes **2** and **3**. Operation conditions: N_2, 5 °C/min heating rate.

Another notable feature is the unusual solubility of **2** and **3** in Acetone, THF, CH_3CN, EtOAc and MeOH (Table 1). One can see that **2** and **3** show higher solubility in common polar organic solvents. Another quite surprising behaviour is that these complexes is insoluble in CH_2Cl_2, because CH_2Cl_2 is usually the best solvent for similar binuclear triphenylantimony (V) bis(triflate) complexes.[11] Consistently, they are not soluble in much less polar toluene and nonpolar *n*-hexane. Furthermore, as it is apparently insoluble in water, these complexes are hydrophobic, which could be attributed to the fluoroalkyl(aryl) chain in the sulfonate ligand.

Table 1
The solubility of complex **2** and **3** in Organic Solvents at 25 °C[a]

Solvent	Solubility (g/L) of **2**	Solubility (g/L) of **3**
Acetone	943	1071
CH_3CN	478	626
THF	432	641
EtOAc	398	537
MeOH	1025	1328
Et_2O	31	23
CH_2Cl_2	0	0
n-Hexane	0	0
Toluene	0	0

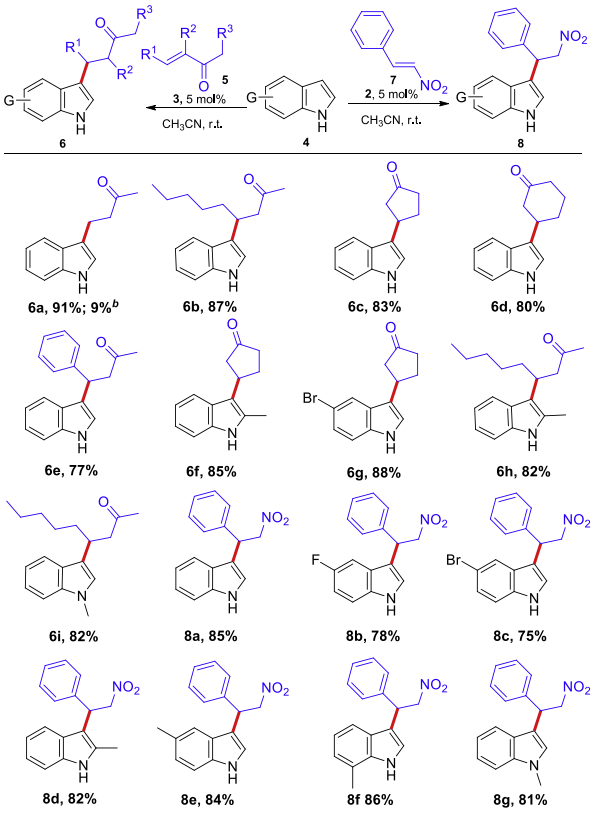
[a] All samples are fresh prepared and recrystallized in vacuum at room temperature in a period of 2 h.

In addition, we employed the Hammett indicator method to determine their acidities, and found that they show a relatively strong acidity with the acid strength of $3.3<H_0<4.8$ (H_0 being the Hammett acidity function).[14] These features facilitate their catalytic performance in C–C bond forming reactions.

The Michael addition reaction and the allylation reaction have been recently extensively used to assess the catalytic efficiency since these reactions required high Lewis acidity catalyst.[15] Hence, we evaluated the catalytic activities of complexes **2** and **3** in the Michael addition reaction of indoles to α, β-unsaturated carbonyl compounds or *trans*-β-nitrostyrene and the allylation reaction of aldehydes with tetraallyltin.

As shown in Table 2, the complex **3** showed high catalytic efficiency in Michael addition, good-to-excellent yields were obtained

Table 2
Product yields of the reactions of indole derivatives with enones/nitroalkenes catalyzed by **2** and **3**[a]



[a] **2** or **3**, 0.05 mmol; indoles **4**, 1.0 mmol; α, β-unsaturated carbonyl compounds **5** / nitroalkenes **7**, 1.0 mmol; CH_3CN, 1.0 mL; room temperature; 3-6 hours; isolated yields. [b] No catalyst, 12 h.

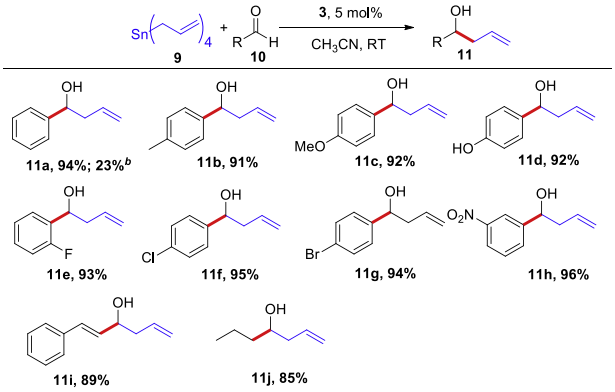
(**6a**–**i**, 77–91%). Gratifyingly, in the presence of 5.0 mol% of **2**, *trans*-β-nitro-styrene also showed good reactivity in good to excellent yields (**8a**–**g**, 75–86%). Controlled experiments were performed in the absence of **3**, the reaction basically did not take place; only 9% yield of the product (**6a**) was obtained.

Moreover, the complex **3** also showed high catalytic efficiency in the allylation reaction (Table 3, **11a**–**j**, 85–96%). The aromatic aldehydes with electron-withdrawing groups (e.g., Cl, Br, and NO_2) (**11d**–**h**, 92–96%) exhibited almost similar reactivity in the reaction as that with electron-donating groups in the *para*-position of the phenyl plane (e.g., methyl and methoxyl) (**11b**–**c**, 91–92%). The cinnamaldehyde with double bond was tolerated (**11i**, 89%). And the catalytic system can be easily extended to alkyl aldehyde (**11j**, 85%). Without the catalyst, only 23% yield of the desired product (**11a**) was obtained.

In addition, the activities of **1**, $(Ph_3SbCl)_2O$, **2**, and **3** together with $[(Ph_3SbOH_2)_2O](OSO_2CF_3)_2$ were estimated by the Michael addition reaction and allylation reaction (Table 4). High yields were attained over complexes **2** and **3**, while the other catalysts showed much lower yields, plausibly duo to their lower Lewis acidity or moisture-sensitive properties.

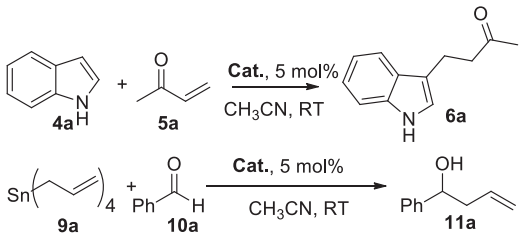
To test the reusability of the catalyst and reproducibility of catalytic performance, the complex **3** was subject to cycles of the Michael addition reaction (**4a**+**5a** → **6a**) and the allylation reaction (**9a**+**10a** → **11a**). The decline in product yield was minimal in a run of 5 cycles, indicating that the catalyst is stable and suitable for reuse (Table 5).

Table 3
Preparation of homoallyl alcohols catalyzed by **3**[a]



[a] **3**, 0.05 mmol; tetraallyltin **9**, 0.3 mmol; aldehydes **10**, 1.0 mmol; CH_3CN, 1.0 mL; room temperature; 1-3 hours; isolated yields. [b] No catalyst, 12 h.

Table 4
Catalyst comparison in the Michael addition reaction and allylation reaction of PhCHO with tetraallyltin[a]



Entry	Catalyst	**6a**[b]	**10a**[b]
1	Ph_3SbCl_2	12	58
2	$(Ph_3SbCl)_2O$	15	61
3	$[(Ph_3Sb)_2O]$ $(OSO_2C_6F_5)_2$	87	92
4	$[(Ph_3SbOH_2)_2O]^+$ $[OSO_2C_8F_{17}]^-{}_2$	91	94
5	$[(Ph_3SbOH_2)_2O](OSO_2CF_3)_2$	71	82

[a] **Cat.**, 0.05 mmol; tetraallyltin **9**, 0.3 mmol; benzaldehyde **10a**, 1.0 mmol; CH_3CN, 1.0 mL; room temperature; 1 h.
[b] Isolated yield.

Table 5
Yields of the Michael addition reaction (**4a**+**5a** → **6a**) and the allylation reaction (**9a**+**10a** → **11a**) catalyzed by recovered catalyst **3**[a]

Cycle	Yield (%)[b] **4a**+**5a** → **6a**	Cat (%)[c]	Yield (%)[b] **9a**+**10a** → **11a**	Cat (%)[c]
1	91	92	94	95
2	92	93	95	96
3	91	91	94	94
4	91	92	96	96
5	92	93	94	95

[a] **3**, 0.05 mmol; methyl vinyl ketone **4a**, 1.0 mmol; indole **5a**, 1 mmol; tetraallyltin **9**, 0.3 mmol; benzaldehyde **10a**, 1.0 mmol.
[b] Isolated yield of desired product.
[c] Isolated yield of recovered catalyst.

3. Conclusions

In summary, we have synthesized and characterized two binuclear triphenylantimony (V) complexes. These complexes are strongly acidic and air-stable, and show highly catalytic efficiency in the Michael addition reaction and the allylation reaction. Moreover, these complexes possess good reusability. On account of their stability, storability, as well as catalytic efficiency, these complexes should find a broad range of utility in organic synthesis.

4. Experimental section

4.1. General

All chemicals were purchased from Aldrich. Co. Ltd and used as received unless otherwise indicated. The NMR spectra were recorded at 25 °C on INOVA-400M (USA) calibrated with tetramethylsilane (TMS) as an internal reference. Elemental analyses were performed by VARIO EL III. TG-DSC analysis was performed on an HCT-1 (HENVEN, Beijing, China) instrument. IR spectra were recorded on NICOLET 6700 FTR spectrophotometer (Thermo Electron Corporation). X-ray single crystal diffraction analysis was performed with SMART-APEX and RASA-7A by Shanghai Institute Organic Chemistry, China Academy of Science. Catalyst acidity was measured by Hammett indicator method.

*4.1.1. Preparation of $[(Ph_3Sb)_2O](OSO_2C_5F_6)_2$ (**2**).* To a solution of Ph_3SbCl_2 (0.419 g, 0.99 mmol) in 10 mL CH_3CN, a solution of $AgOSO_2C_6F_5$ (0.724 g, 2 mmol) in 5 mL CH_3CN was added. After the mixture was stirred in the absence of light at room temperature for 2 h, it was filtrated and evaporated in the vacuum and the resulted residue was diluted with 10 mL THF and followed by five drops of dry hexane and then was maintained in the refrigerator for 24 h, and the colorless crystals were obtained (0.94 g, 78%). Mp: 262–263 °C, ^{1}H NMR (400 MHz, [d_6] acetone) δ: 7.46–7.50 (m, 2H, Ph), 7.62–7.69 (m, 9H, Ph), 8.14–8.17 (m, 4H, Ph). ^{19}F NMR (376M, [d_6] acetone): δ: −138.82 to −138.90 (m, 2F; ArF), 155.04 (s, 1F; ArF),−163.83 to −163.94 (m, 2F; ArF). IR(KBr): ν=3085, 3020, 1652, 1488, 1257, 1139, 1074, 987, 936, 783, 685, 650, 547 cm^{-1}. Anal. Calcd for $C_{48}H_{30}F_{10}Sb_2O_7S_2$: C, 47.40; H, 2.49; found: C 47.38; H, 2.47.

Crystal data for **2**: $C_{96}H_{62}F_{20}Sb_4O_{15}S_4$; *Mr*=2450.70, Monoclinic, space group *P 21/c*, *a*=9.5078(10) Å, *b*=31.297 (3) Å, *c*=15.9879 (14) Å; *V*=4488.4(7) Å^3; *T*=296(2) K; *Z*=2; Reflections collected/unique, 34601/8334, R_{int}=0.0225, Final *R* indices [$I>2\sigma(I)$] R_1=0.0325, wR_2=0.0895; *R* indices (all data), R_1=0.0380, wR_2=0.0938. *GOF*=1.073; CCDC No. 949212.

*4.1.2. Preparation of $[(Ph_3SbOH_2)_2O](OSO_2C_8F_{17})_2$ (**3**).* To a solution of Ph_3SbCl_2 (0.419 g, 0.99 mmol) in 20 mL THF, a solution of $AgOSO_2C_8F_{17}$ (1.212 g, 2 mmol) in 10 mL THF was added. After the mixture was stirred in dark at room temperature for 2.5 h, it was filtered in air. The filtrate mixed with 40 mL hexane was refrigerated for 24 h, and the colorless crystals were obtained (1.27 g, 73%). Mp: 188–189 °C, ^{1}H NMR (400 MHz, [d_6] acetone) δ: 4.64 (s, 2H, H_2O), 7.58–7.60 (m, 3H, Ph), 7.70–7.75 (m, 9H, Ph), 8.14–8.16 (m, 3H, Ph). ^{19}F NMR (376M, [d_6] acetone): d=−76.05 to −76.10 (m, 3F; $-CF_3$), −109.52 to −109.60 (m, 2F; $-CF_2-$), −115.59 (s, 2F; $-CF_2-$), −116.63 to −116.92 (d, 6F; $-(CF_2)_3-$), −117.82 (s, 2F; $-CF_2-$), −121.20 to −121.24 ppm (m, 2F; $-CF_2-$); IR(KBr): ν=3421, 2923, 2854, 1649, 1482, 1442, 1247, 1148, 1066, 1031, 996, 940, 778, 735, 687, 650, 620, 557, 517, 450 cm^{-1}. Elemental analysis calculate (%) for $C_{52}H_{34}F_{34}Sb_2O_9S_2$: C, 35.56; H, 1.95; found: C 35.58; H, 1.94.

Crystal data for **3**: $C_{52}H_{34}F_{34}Sb_2O_9S_2$; *Mr*=1756.41, Triclinic, space group *P-1*, *a*=13.0383(12) Å, *b*=15.0200(12) Å, *c*=17.9200(16) Å; *V*=3288.7(5) Å^3; *T*=153(2) K; *Z*=2; Reflections collected/unique, 19878/12870, R_{int}=0.0305, Final *R* indices [$I>2\sigma(I)$] R_1=0.0635, wR_2=0.1735; *R* indices (all data), R_1=0.0941, wR_2=0.2022. *GOF*=1.082; CCDC No. 895178.

*4.1.3. Typical procedure for solubility of complexes **2** and **3**.*[10] Acetone (0.5 mL) was placed in a test tube; the complex of $[(Ph_3Sb)_2O](OSO_2C_5F_6)_2$ (**2**) was added gradually at room temperature. When the amount of added **2** exceeds 471.5 mg, insoluble **2** appeared. Based on this data, solubility of **2** was determined to be

471.5 g L^{-1}. According to the same procedure, the solubility of complex **3** was determined.

4.1.4. General procedure for the Michael addition reaction of indoles to α, β-unsaturated carbonyl compounds and trans-β-Nitrostyrene. A mixture of α, β-unsaturated carbonyl compound/*trans*-β-Nitrostyrene (1.0 mmol), indoles (1 mmol) and **2** or **3** (0.05 mmol) in acetonitrile (1 mL) was stirred at room temperature for the appropriate reaction time and monitored by TLC. Then the solvents of the resulted mixture were removed by evaporation in vacuum, CH_2Cl_2 (10 mL×3) was added to the reaction mixture and the catalyst was filtered for the next cycle of reaction. To the filtrate, after evaporation of the solvent a Pinkish solid mixture was obtained. The residue was performed by a short column chromatography eluted with ethyl acetate/petroleum ether (80/20).

*4.1.5. General procedure for allylation of benzaldehyde with tetrallyltin catalyzed by complex **3**.* Complex **3** (0.05 mmol) was added to a solution of benzaldehyde (1.0 mmol) in CH_3CN (1 mL). Tetrallyltin (0.3 mmol) was then added to the mixture at room temperature. After the mixture was stirred at room temperature for three hours and monitored by TLC, it was evaporated in vacuum at room temperature. *n*-Hexane (10 mL×3) was added to the residue; the catalyst precipitated and was recovered by filtration for the next reaction cycle. The combined *n*-hexane solution was concentrated, and then MeOH and HCl (aq) was added and stirred for 15 min $NaHCO_3$ (aq) was added for neutralization. After the mixture was subject to evaporation, the as-obtained solids were dissolved in AcOEt and water. After extraction with AcOEt (three times), the organic layer was washed with NaCl (aq) and dried over $MgSO_4$. After evaporation, GLC yield was measured. Alternatively, the residue was subject to silica gel column chromatography (petroleum ether/ethyl acetate=8:1) and 6a was obtained as a colorless oil (139 mg, isolated yield 94%).

4.2. Characterization data

*4.2.1. **6a**–**6i**, **8a**–**8g** are known compounds, and ^1H NMR, ^{13}C NMR spectral data are summarized as follows*

*4.2.1.1. 4-(1H-3-Indolyl)-2-butanone (**6a**).*[16a] Red solid, mp: 70–71 °C; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 2.15 (s, 3H, CH_3), 2.84–2.87 (m, 2H, CH_2), 3.04–3.07 (m, 2H, CH_3), 6.99 (d, *J*=2.4 Hz, 1H, ArH), 7.11 (t, *J*=8.0 Hz, 1H, ArH), 7.20 (t, *J*=7.6 Hz, 1H, ArH), 7.36 (d, *J*=8.0 Hz, 1H, ArH), 7.59 (d, *J*=7.6 Hz, 1H, ArH), 7.96 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 19.31, 29.86, 44.06, 111.11, 115.20, 118.64, 119.28, 121.41, 122.04, 127.14, 136.27, 208.75.

*4.2.1.2. 4-(1H-3-Indolyl)-2-nonanone (**6b**).*[16b] Yellow oil, ^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.82 (t, *J*=6.6 Hz, 3H, CH_3), 1.16–1.27 (m, 6H, CH_2), 1.70–1.79 (m, 2H, CH_2), 2.02 (s, 3H, CH_3), 2.81 (dd, *J*=16.0 Hz, 6.8 Hz, 1H, CH_2), 2.88 (dd, *J*=16.0 Hz, 7.6 Hz, 1H, CH_2), 3.44–3.48 (m, 1H, CH), 6.97 (d, *J*=2.4 Hz, 1H, ArH), 7.10 (t, *J*=7.4 Hz, 1H, ArH), 7.18 (d, *J*=7.8 Hz, 1H, ArH), 7.35 (d, *J*=7.8 Hz, 1H, ArH), 7.65 (d, *J*=8.0 Hz, 1H, ArH), 7.99 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.20, 22.71, 27.42, 29.85, 30.59, 32.03, 35.90, 50.36, 109.76, 111.22, 119.14, 119.29, 121.18, 121.87, 126.51, 136.50, 209.08.

*4.2.1.3. 3-(3-Indolyl)-cyclopentan-1-one (**6c**).*[16b] Yellow oil, ^1H NMR (400 MHz, $CDCl_3$): δ ppm 2.10–2.19 (m, 1H, CH_2), 2.29–2.46 (m, 3H, CH_2),;2.51–2.55 (m, 1H, CH_2), 2.75 (dd, *J*=18.4 Hz, 7.6 Hz, 1H, CH_2), 3.69–3.77 (m, 1H, CH), 6.98 (d, *J*=1.6 Hz, 1H, ArH), 7.15 (t, *J*=7.8 Hz, 1H, ArH), 7.23 (t, *J*=8.0 Hz, 1H, ArH), 7.38 (d, *J*=8.4 Hz, 1H, ArH), 7.64 (d, *J*=8.0 Hz, 1H, ArH), 8.10 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 29.90, 33.53, 38.16, 45.20, 112.71, 112.90, 118.24, 121.27, 121.69, 125.18, 128.41, 135.32, 219.34.

*4.2.1.4. 3-(3-Indolyl)-cyclohexan-1-one (**6d**).*[16c] Red solid, mp: 103–104 °C; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 1.81–1.89 (m, 1H, CH_2), 1.91–2.07 (m, 2H, CH_2),;2.25–2.29 (m, 1H, CH_2), 2.36–2.46 (m, 2H, CH_2), 2.60–2.67 (m, 1H, CH_2), 2.79–2.83 (m, 1H), 3.42–3.49 (m, 1H, CH), 6.98 (d, *J*=2.4 Hz, 1H, ArH), 7.12 (t, *J*=7.8 Hz, 1H, ArH), 7.19 (t, *J*=8.0 Hz, 1H, ArH),7.37 (d, *J*=8.0 Hz, 1H, ArH), 7.62 (d, *J*=8.0 Hz, 1H, ArH), 8.02 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 29.34, 31.90, 35.91, 41.56, 48.04, 111.27, 118.37, 119.00, 119.37, 119.72, 120.28, 126.12, 136.41, 211.79.

*4.2.1.5. 4-(1H-Indol-3-yl)-4-phenyl-2-butanone (**6e**).*[16d] Red solid, mp: 97–99 °C; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 2.07 (s, 3H, CH_3), 3.15 (dd, *J*=16.0 Hz, 8.0 Hz, 1H, CH_2), 3.24 (dd, *J*=16.0 Hz, 7.2 Hz, 1H, CH_2), 4.83 (t, *J*=7.6 Hz, 1H, CH), 6.96 (d, *J*=2.4 Hz, 1H, ArH), 7.03 (t, *J*=7.6 Hz, 1H, ArH), 7.14 (t, *J*=8.0 Hz, 2H, ArH), 7.24 (t, *J*=7.6 Hz, 2H, ArH), 7.28 (d, *J*=8.8 Hz, 3H, ArH), 7.42 (d, *J*=8.0 Hz, 1H, ArH), 8.03 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 29.83, 30.46, 30.51, 38.49, 38.58, 50.48, 111.28, 118.95, 119.55, 121.46, 121.51, 122.31, 126.50, 126.65, 127.82, 128.61, 136.71,144.07, 207.83.

*4.2.1.6. 3-(2-Methyl-3-indolyl)-cyclopentan-1-one (**6f**).*[17a] Red solid, mp: 140–142 °C; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 2.28–2.36 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.45–2.51 (m, 1H, CH_2),;2.53–2.60 (m, 2H, CH_2), 2.75–2.82 (m, 1H, CH_2), 3.58–3.65 (m, 1H, CH), 7.06 (t, *J*=7.4 Hz, 1H, ArH), 7.13 (t, *J*=7.4 Hz, 1H, ArH), 7.29 (t, *J*=7.6 Hz, 1H, ArH), 7.54 (d, *J*=7.6 Hz, 1H, ArH), 7.88 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 12.28, 29.89, 34.66, 39.63, 44.45, 110.83, 111.98, 118.80, 119.32, 121.15, 126.87, 131.00, 135.64, 219.95.

*4.2.1.7. 3-(5-Bromo-methyl-3-indolyl)-cyclopentan-1-one (**6g**).*[16b] Red oil, ^1H NMR (400 MHz, $CDCl_3$): δ ppm 2.04–2.11 (m, 1H, CH_2), 2.27–2.44 (m, 3H, CH_2),;2.48–2.53 (m, 1H, CH_2), 2.74 (dd, *J*=18.0 Hz, 7.6 Hz, 1H, CH_2), 3.61–3.71 (m, 1H, CH), 6.98 (d, *J*=2.4 Hz, 1H, ArH), 7.24–7.31 (m, 2H, ArH), 7.74 (s, 1H, ArH), 8.21 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 29.85, 33.49, 38.04, 45.11, 112.68, 112.77, 118.26, 121.12, 121.17, 121.60, 121.65, 125.14, 128.36, 135.26, 218.99.

*4.2.1.8. 4-(2-Methyl-1H-3-indolyl)-2-nonanone (**6h**).*[16c] Yellow oil, ^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.80 (t, *J*=6.4 Hz, 3H, CH_3), 1.13–1.22 (m, 6H, CH_2), 1.65–1.76 (m, 2H, CH_2), 1.83–1.90 (m, 1H, CH_2), 1.93 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.79 (dd, *J*=16.0 Hz, 6.0 Hz, 1H, CH_2), 3.04 (dd, *J*=15.6 Hz, 8.4 Hz, 1H, CH), 3.33–3.38 (m, 1H, CH_2), 7.02–7.10 (m, 2H, ArH), 7.23 (d, *J*=7.6 Hz, 1H, ArH), 7.58 (d, *J*=8.0 Hz, 1H, ArH), 7.77 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 12.03, 14.01, 25.55, 27.60, 30.74, 31.72, 32.67, 35.08, 49.28, 111.40, 113.29, 118.77, 118.93, 120.53, 127.06, 131.40, 135.56, 209.04.

*4.2.1.9. 4-(1-Methyl-1H-3-indolyl)-2-nonanone (**6i**).*[17b] Yellow oil, ^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.82 (t, *J*=6.4 Hz, 3H, CH_3), 1.22–1.26 (m, 6H, CH_2), 1.65–1.78 (m, 2H, CH_2), 2.01 (s, 3H, CH_3), 2.76 (dd, *J*=16.0 Hz, 7.2 Hz, 1H, CH_2), 2.83 (dd, *J*=16.4 Hz, 7.6 Hz, 1H, CH), 3.42–3.49 (m, 1H, CH_2), 3.71 (s, 3H, CH_3), 6.81 (s, 1H, ArH), 7.07 (t, *J*=8.0 Hz, 1H, ArH), 7.22 (t, *J*=8.0 Hz, 1H, ArH), 7.26 (t, *J*=8.4 Hz, 1H, ArH), 7.63 (t, *J*=8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.02, 25.51, 27.26, 30.36, 31.79, 32.52, 32.72, 35.91, 50.33, 109.21, 117.43, 118.49, 119.29, 121.33, 125.91, 126.89, 137.10, 208.79.

*4.2.1.10. 3-(2-Nitro-1-phenylethyl)-1H-indole (**8a**).*[17c] Yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 4.94 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.07 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.20 (t, *J*=8 Hz, 1H, CH), 7.03 (d, *J*=2.8 Hz, 1H, ArH), 7.07 (t, *J*=7.6 Hz, 1H, ArH), 7.18–7.38 (m, 7H, ArH), 7.44 (d, *J*=7.6 Hz, 1H, ArH),8.11 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 41.50, 79.48, 111.33, 118.89, 119.92, 121.55, 122.67, 127.53, 127.72, 128.88, 136.43, 139.11.

*4.2.1.11. 5-Fluoro-3-(2-nitro-1-phenylethyl)-1H-indole (**8b**)*[S12]. Red oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 4.92 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.04 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.15 (t, *J*=7.6 Hz, 1H, CH), 6.82 (t, *J*=9.0 Hz, 1H, ArH), 7.30 (d, *J*=9.2 Hz, 2H, ArH), 7.25–7.35 (m, 6H, ArH), 8.12 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 41.54, 79.60, 97.63, 97.87, 108.78, 109.02, 114.66, 119.79, 121.77, 122.77, 127.77, 129.05, 136.47, 136.60, 159.09, 161.47.

*4.2.1.12. 5-Bromo-3-(2-nitro-1-phenylethyl)-1H-indole (**8c**)*.[17d] Red solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 4.91 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.02 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.12 (t, *J*=8.2 Hz, 1H, CH), 7.06 (d, *J*=2.4 Hz, 1H, ArH), 7.20–7.35 (m, 7H, ArH), 7.54 (s, 1H), 8.17 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 41.27, 79.36, 112.81, 113.22, 114.02, 121.45, 122.69, 125.64, 127.63, 127.75, 127.83, 129.02, 135.05, 138.65.

*4.2.1.13. 2-Methyl-3-(2-nitro-1-phenylethyl)-1H-indole (**8d**)*:.[17c] Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.29 (s, 3H, CH_3), 5.04 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.10 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.16 (t, *J*=8.0 Hz, 1H, CH), 6.95 (t, *J*=7.4 Hz, 1H, ArH), 7.03 (t, *J*=7.6 Hz, 1H, ArH), 7.22–7.26 (m, 6H, ArH), 7.29 (d, *J*=8.0 Hz, 1H, ArH), 7.79 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 11.91, 40.37, 78.55, 108.72, 110.64, 118.51, 119.66, 121.25, 126.75, 127.00, 127.23, 128.70, 132.80, 135.32, 139.42.

*4.2.1.14. 5-Methyl-3-(2-nitro-1-phenylethyl)-1H-indole (**8e**)*:.[17d] White solid, mp: 127–128 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.40 (s, 3H, CH_3), 4.91 (dd, *J*=12.8 Hz, 8.4 Hz, 1H, CH_2), 5.02 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.15 (t, *J*=8.0 Hz, 1H, CH), 6.92 (d, *J*=2.4 Hz, 1H, ArH), 7.01 (t, *J*=8.0 Hz, 1H, ArH), 7.21–7.33 (m, 7H, ArH), 7.95 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 21.59, 41.58, 79.58, 111.13, 113.91, 118.48, 121.85, 124.40, 126.38, 127.58, 127.81, 128.96, 129.34, 134.85, 139.29.

*4.2.1.15. 7-Methyl-3-(2-nitro-1-phenylethyl)-1H-indole (**8f**)*:.[17d] Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.46 (s, 3H, CH_3), 4.93 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.06 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.18 (t, *J*=8.0 Hz, 1H, CH), 7.00 (d, *J*=5.2 Hz, 2H, ArH), 7.01 (d, *J*=2.0 Hz, 1H, ArH), 7.24–7.32 (m, 5H, ArH), 8.02 (br s, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 16.50, 41.61, 79.48, 114.85, 116.60, 120.15, 120.57, 121.26, 123.17, 125.59, 127.49, 127.71, 128.86, 136.04, 139.17.

*4.2.1.16. 1-Methyl-3-(2-nitro-1-phenylethyl)-1H-indole (**8g**)*.[17d] Red oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 3.69 (s, 3H, CH_3), 4.90 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.02 (dd, *J*=12.4 Hz, 8.4 Hz, 1H, CH_2), 5.12 (t, *J*=8.0 Hz, 1H, CH), 7.00–7.28 (m, 9H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 32.94, 41.61, 79.64, 109.60, 112.88, 119.06, 119.54, 122.31, 126.46, 127.60, 127.82, 129.00, 137.37, 139.44.

*4.2.2. **11a–11j** are known compounds, and the ^{1}H NMR, ^{13}C NMR spectral data are summarized as follows*

*4.2.2.1. 1-Phenyl-3-buten-1-ol(**11a**)*.[18a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.11 (br, 1H, OH), 2.48–2.54 (m, 2H, CH_2), 4.74 (t, *J*=6.4 Hz, 1H, CH), 5.13–5.16 (m, 2H, two vinyls), 5.77–5.83 (m, 1H, vinyl), 7.28–7.37 (m, 5H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 43.87, 73.31, 118.50, 125.84, 127.60, 128.45, 134.51, 143.88.

*4.2.2.2. 1-(p-Methylphenyl)-3-buten-1-ol (**11b**)*.[18a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.98 (d, *J*=3.2 Hz, 1H, OH), 2.35 (s, 3H, CH_3), 2.48–2.52 (m, 2H, CH_2), 4.71 (t, *J*=6.4 Hz, 1H, CH), 5.12–5.15 (m, 2H, 2 vinyls), 5.76–5.85 (m, 1H, vinyl), 7.15 (d, *J*=8.0 Hz, 2H, Ar), 7.24 (d, *J*=7.8 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 21.15, 43.81, 73.18, 118.36, 125.78, 129.13, 134.61, 137.26, 140.86.

*4.2.2.3. 1-(p-Hydroxyphenyl)-3-buten-1-ol (**11c**)*.[18b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.11 (d, *J*=4.0 Hz, 1H, OH), 2.25–2.42 (m, 2H, CH_2), 4.67 (t, *J*=6.6 Hz, 1H, CH), 4.90–4.98 (m, 2H, 2 vinyls), 5.59–5.68 (m, 1H, vinyl), 6.75–7.23 (m, 4H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 44.74, 73.10, 115.11, 115.33, 116.03, 127.36, 128.77, 136.94.

*4.2.2.4. 1-(p-Methoxyphenyl)-3-buten-1-ol (**11d**)*.[18a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.12 (d, *J*=4.0 Hz, 1H, OH), 2.48 (t, *J*=7.4 Hz, CH_2, 2H), 3.79 (s, 3H, CH_3), 4.67 (t, *J*=6.6 Hz, 1H, CH), 5.10–5.16 (m, 2H, 2 vinyls), 5.75–5.82 (m, 1H, vinyl), 6.87 (d, *J*=8.8 Hz, 2H, ArH), 7.26 (d, *J*=8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 43.77, 55.29, 72.99, 113.78, 118.25, 127.11, 134.66, 136.08, 159.01.

*4.2.2.5. 1-(o-Fluorophenyl)-3-buten-1-ol (**11e**)*.[18c] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.11 (d, *J*=3.6 Hz, 1H, OH), 2.45–2.63 (m, 2H, CH_2), 4.22 (t, *J*=6.0 Hz, 1H, CH), 5.14–5.18 (m, 2H, 2 vinyls), 5.73–5.81 (m, 1H, vinyl), 7.03 (t, *J*=9.4 Hz, 1H, ArH), 7.16 (t, *J*=7.0 Hz, 1H, ArH); 7.22–7.28 (m, 1H, ArH), 7.48 (t, *J*=7.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 42.61, 67.22, 115.15, 115.20, 118.81, 124.24, 127.22, 128.82, 128.90, 132.42, 134.07.

*4.2.2.6. 1-(p-Chlorophenyl)-3-buten-1-ol (**11f**)*.[18a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.13 (d, *J*=3.2 Hz, 1H, OH), 2.41–2.50 (m, 2H, CH_2), 4.71 (t, *J*=6.4 Hz, 1H, CH), 5.14–5.20 (m, 2H, 2 vinyls), 5.72–5.81 (m, 1H, vinyl), 7.26–7.33 (m, 4H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 43.90, 72.55, 118.94, 127.22, 128.55, 133.16, 133.99, 142.20.

*4.2.2.7. 1-(p-Bromophenyl)-3-buten-1-ol (**11g**)*.[18b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.16 (d, *J*=3.2 Hz, 1H, OH), 2.40–2.48 (m, 2H, CH_2), 4.70 (t, *J*=6.4 Hz, 1H, CH), 5.14–5.17 (m, 2H, 2 vinyls), 5.72–5.78 (m, 1H, vinyl), 7.22 (d, *J*=8.8 Hz, 2H, ArH), 7.46 (d, *J*=8.4 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 43.85, 72.58, 118.96, 121.28, 127.58, 131.50, 133.96, 142.81.

*4.2.2.8. 1-(m-Nitrophenyl)-3-buten-1-ol (**11h**)*.[18d] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.33 (d, *J*=3.6 Hz, 1H, OH), 2.44–2.57 (m, 2H, CH_2), 4.86 (t, *J*=6.0 Hz, 1H, CH), 5.17–5.22 (m, 2H, 2 vinyls), 5.75–5.84 (m, 1H, vinyl), 7.53 (t, *J*=8.0 Hz, 1H, ArH), 7.70 (d, *J*=7.6 Hz, 1H, ArH); 8.14 (d, *J*=7.4 Hz, 1H, ArH); 8.24 (t, *J*=3.6 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 43.57, 72.06, 119.74, 120.88, 122.49, 129.37, 131.99, 133.28, 145.93, 148.32.

*4.2.2.9. 1-Phenyl-1,5-hexadien-3-ol (**11i**)*.[18a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.88 (d, *J*=4.0 Hz, 1H, OH), 2.35–2.44 (m, 2H, CH_2), 4.36 (t, *J*=6.0 Hz, 1H, CH), 5.15–5.18 (m, 2H, 2 vinyls), 5.80–5.89 (m, 1H, vinyl), 6.24 (dd, *J*=16.0 Hz, 6.4 Hz, 1H, vinyl), 6.59 (d, *J*=16.0 Hz, 1H, ArH), 7.24 (t, *J*=7.2 Hz, 1H, ArH); 7.31 (t, *J*=7.6 Hz, 2H, ArH); 8.24 (d, *J*=7.2 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 42.03, 71.73, 118.59, 126.51, 127.70, 128.61, 130.38, 131.55, 134.06, 136.65.

*4.2.2.10. Heptyl-1-en-4-ol (**11j**)*.[18e] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.97 (t, *J*=7.4 Hz, 1H, CH_3), 1.30–1.38 (m, 2H, CH_2), 1.45–1.54 (m, 2H, CH_2), 1.96 (s, 1H, OH), 2.18–2.36 (m, 2H, CH_2), 3.80–3.88 (m, 1H, CH), 5.11–5.19 (m, 2H, vinyl), 5.76–5.85 (m,

1H, vinyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.16, 19.06, 38.77, 47.05, 72.70, 117.81, 135.28.

Acknowledgements

The authors thank the NSFC (Nos. 21273068, 21373003, J1210040), the NSF of Hunan Province (2014JJ7027), and the Fundamental Research Funds for the Central Universities, Hunan University, for financial support. The authors thank the Prof. A. Orita (Okayama University of Science), Prof. N. Kambe (Osaka University) and Profs. C.T. Au and W.-Y. Wong (HKBU) for helpful discussion.

Supplementary data

Supplementary data (The crystal data of complex **2** and **3**, copies of the ^1H NMR and ^{13}C NMR of all the products; additional information as needed can be seen in the Supplementary data.).

CCDC 949212 and 895178 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/ata_request/cif.) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.05.013.

References and notes

1. (a) Fujiwara, Y.; Mitani, M.; Yasuike, S.; Kurita, J.; Kaji, T. *J. Health Sci.* **2005**, *51*, 333; (b) Rat, C. I.; Silvestru, C.; Breunig, H. J. *Coord. Chem. Rev.* **2013**, *257*, 818 references cited therein; (c) Yang, H. F.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2014**, *136*, 10866.
2. (a) May, B. M.; Coles, M. P. *Organometallics* **2013**, *32*, 4270; (b) Ke, I. S.; Gabbaï, F. P. *Inorg. Chem.* **2013**, *52*, 7145; (c) Ke, I. S.; Myahkostupov, M.; Castellano, F. N.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2014**, *134*, 15309; (d) Jiang, J.; Yin, H. D.; Wang, F. L.; Han, Z.; Wang, F.; Cheng, S.; Hong, M. *Dalton Trans.* **2013**, *42*, 8563; (e) Chitnis, S. S.; Burford, N.; McDonald, R.; Ferguson, M. J. *Inorg. Chem.* **2014**, *53*, 5359.
3. (a) Preda, A. M.; Rat, C. I.; Silvestru, C.; Breunig, H. J.; Lang, H.; Rüffer, T.; Mehring, M. *Dalton Trans.* **2013**, *42*, 1144; (b) Dostál, L.; Jambor, R.; Růžička, A.; Jiřasko, R.; Holèček, J.; De Proft, F. *Dalton Trans.* **2011**, *40*, 8922; (c) Conrad, E.; Burford, N.; McDonald, R.; Ferguson, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 5066; (d) Tan, N. Y.; Chen, Y.; Yin, S. F.; Qiu, R. H.; Zhou, Y. B.; Au, C. T. *Dalton Trans.* **2013**, *42*, 9476.
4. (a) Tan, N. Y.; Chen, Y.; Yin, S. F.; Qiu, R. H.; Zhou, Y. B.; Au, C. T. *Curr. Org. Chem.* **2012**, *16*, 2462; (b) Xia, J.; Qiu, R. H.; Yin, S. F.; Zhang, X. W.; Luo, S. L.; Au, C.-T.; Wong, W. Y. *J. Organomet. Chem.* **2010**, *17*, 1497.
5. Pan, B. F.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2014**, *136*, 9564.
6. (a) Šimon, P.; de Proft, F.; Jambor, R.; Růžička, A.; Dostál, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 5468; (b) Yin, H. D.; Wu, Q. K.; Hong, M.; Li, W. K. *Z. Anorg. Allg. Chem.* **2012**, *638*, 725; (c) Quan, L.; Yin, H. D.; Cui, J. C.; Hong, M.; Wang, D. Q. *J. Organomet. Chem.* **2009**, *694*, 3708; (d) Yin, H. D.; Wen, L. Y.; Cui, J. C.; Li, W. K. *Polyhedron* **2009**, *28*, 2919.
7. Meinema, H. A.; Rivarola, M. E.; Noltes, J. G. *J. Organomet. Chem.* **1969**, *17*, 71.
8. (a) Chen, J.; Otera, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 91; (b) Li, X.; Kurita, A.; Man-e, S.; Orita, A.; Otera, J. *Organometallics* **2005**, *24*, 2567.
9. (a) Qiu, R. H.; Yin, S. F.; Zhang, X. W.; Xia, J.; Xu, X. H.; Luo, S. L. *Chem. Commun.* **2009**, 1679; (b) Qiu, R. H.; Xu, X. H.; Peng, L. F.; Zhao, Y. L.; Li, N. B.; Yin, S. F. *Chem.—Eur. J.* **2012**, *18*, 6172; (c) Li, N. B.; Zhang, X. H.; Xu, X. H.; Chen, Y.; Qiu, R. H.; Chen, J. Y.; Wang, X.; Yin, S. F. *Adv. Synth. Catal.* **2013**, *355*, 2430; (d) Li, N. B.; Wang, J. Y.; Zhang, X. H.; Qiu, R. H.; Wang, X.; Chen, J. Y.; Yin, S. F.; Xu, X. H. *Dalton Trans.* **2014**, *43*, 11696; (e) Zhang, X. H.; Qiu, R. H.; Zhou, C. C.; Yu, J. X.; Li, N. B.; Yin, S. F.; Xu, X. H. *Tetrahedron* **2015**, *71*, 1011.
10. An, D. L.; Peng, Z. H.; Orita, A.; Kurita, A.; Man-e, S.; Ohkubo, K.; Li, X.; Fukuzumi, S.; Otera, J. *Chem.—Eur. J.* **2006**, *12*, 1642.
11. Perut, H.; Rüther, R.; Huber, F. *Acta Crystallogr.* **1986**, *42*, 1154.
12. (a) Goel, R. G.; Prasad, H. S. *Inorg. Chem.* **1972**, *11*, 2141; (b) Long, G. G.; Doak, G. O.; Freedman, L. D. *J. Am. Chem. Soc.* **1964**, *86*, 209; (c) Rüther, R.; Huber, F.; Preut, H. *Angew. Chem.* **1987**, *99*, 948; (d) Taylor, M. J.; Baker, L. J.; Rickard, C. E. F.; Surman, P. W. J. *J. Organomet. Chem.* **1995**, *498*, 14.
13. (a) Matsukawa, S.; Yamamichi, H.; Yamamoto, Y.; Ando, K. *J. Am. Chem. Soc.* **2009**, *131*, 3418; (b) Robertson, A. P. M.; Burford, N.; Mcdonald, R.; Ferguson, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 3480.
14. (a) Benesi, H. A. *J. Am. Chem. Soc.* **1956**, *78*, 5490; (b) Benesi, H. A. *J. Phys. Chem.* **1957**, *61*, 970.
15. (a) Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; John Wiley & Sons: New York, NY, 1997; (b) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207; (c) Cai, Q.; Liu, C.; Liang, X. W.; You, S. L. *Org. Lett.* **2012**, *14*, 4588; (d) Gu, Y. L.; Ogawa, C.; Kobayashi, J.; Mori, Y.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 7217.
16. (a) Singh, D. U.; Singh, P. R.; Samant, S. D. *Synth. Commun.* **2006**, *36*, 1265; (b) Zhou, B. H.; Yang, J.; Li, M. H.; Gu, Y. L. *Green Chem.* **2011**, *13*, 2204; (c) Bartoli, G.; Bartolacci, M.; Bosco, M.; Foglia, G.; Giuliani, A.; Marcantoni, E.; Sambri, L.; Torregiani, E. *J. Org. Chem.* **2003**, *68*, 4594; (d) Yadav, J. S.; Reddy, B. V. S.; Baishya, G.; Reddy, K. V.; Narsaiah, A. V. *Tetrahedron* **2005**, *61*, 9541.
17. (a) Alam, M. M.; Varala, R.; Adapa, S. R. *Tetrahedron Lett.* **2003**, *44*, 5115; (b) Schwalm, C. S.; Ceschi, M. A.; Russowsky, D. *J. Braz. Chem. Soc.* **2011**, *22*, 623; (c) Jia, Y. X.; Zhu, S. F.; Yang, Y.; Zhou, Q. L. *J. Org. Chem.* **2006**, *71*, 75; (d) Peng, J. H.; Du, D. M. *Eur. J. Org. Chem.* **2012**, 4042.
18. (a) Qiu, R. H.; Zhang, G. P.; Zhu, Y. Y.; Xu, X. H.; Shao, L. L.; Li, Y. H.; An, D. L.; Yin, S. F. *Chem.—Eur. J.* **2009**, *15*, 6488; (b) Yao, Q. W.; Sheets, M. *J. Org. Chem.* **2006**, *71*, 5384; (c) Huang, J. W.; Ren, H. R. *Chem. Commun.* **2010**, 2286; (d) Gnanamani, E.; Someshwar, N.; Ramanathan, C. R. *Adv. Synth. Catal.* **2012**, *354*, 2101; (e) Zhang, X. W.; Qiu, R. H.; Tan, N. Y.; Yin, S. F.; Xia, J.; Luo, S. L.; Au, C.-T. *Tetrahedron Lett.* **2010**, *51*, 153.