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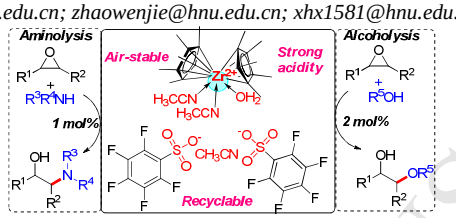

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ABSTRACT

An air-stable mononuclear complex of bis(pentamethylcyclopentadienyl) zirconium pentafluorbezenesulfonate was successfully synthesized by treating $C_6F_5SO_3Ag$ with $[(CH_3)_5Cp]_2ZrCl_2$, which showed the cationic uninuclear structure of $[\{(CH_3)_5Cp\}_2Zr(CH_3CN)_2(H_2O)][OSO_2C_6F_5]_2\cdot CH_3CN$ (**1**) confirmed by the X-ray analysis. Complex **1** was also characterized by other techniques and found to have the good nature of air-stability, water tolerance, thermally-stability and strong Lewis-acidity. Moreover, the complex showed high catalytic activity and recyclability in catalytic epoxide ring-opening reactions by amines or alcohols. This catalytic system affords a simple and efficient approach for synthesis of *β*-amino alcohols or *β*-alkoxy alcohols.

1. Introduction

Lewis acid promoted ring opening of epoxides with amines or alcohols is important organic transformation for production of *β*-amino alcohols or *β*-alkoxy alcohols, which are versatile intermediates in synthesizing a vast range of biologically active products, unnatural amino acids and chiral auxiliaries.[1] And ring-opening reaction of epoxides have been applied in the manufacture of drugs and pharmaceuticals,[2] such as (-)-swainsonine, HBV inhibitor and lasalocid (Fig. **1**).

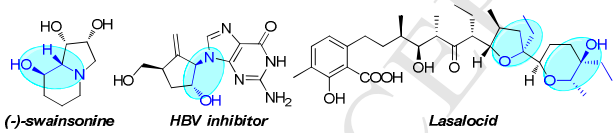


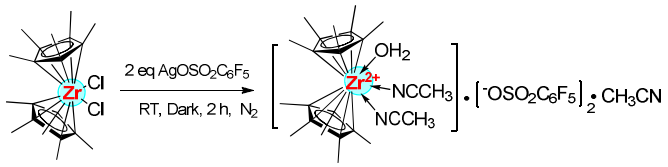
Fig. 1. Ring opening of epoxide applied in pharmaceuticals

The classical protocol for synthesis of *β*-amino alcohols is direct aminolysis of epoxides at elevated temperatures in an excess amount of amines.[3] Due to poor nucleophilicity of alcohols, alcoholysis of epoxides requires either strongly acidic or basic conditions.[4] To avoid drawbacks of classical aminolysis protocol and harsh conditions of alcoholysis, the various methods have been developed to open epoxide ring with amines or alcohols in the presence of Lewis acids catalysts such as $InCl_3$,[5] $ZrCl_4$,[6] $SbCl_3$,[7] $ZnCl_2$,[8] $BF_3\cdot OEt_2$,[9] Cp_2ZrCl_2,[10] $Al(OTf)_3$,[11] $Cu(BF_4)_2$.[12] Nonetheless, there are disadvantages with those methods, e.g. using air-sensitive catalysts, elevated temperature, long reaction time, moderate yields, poor regioselectivity, high catalyst loadings and poor recyclability of catalysts. Thus, there is ongoing activity aimed to establish a more simple and efficient catalytic protocol to accomplish this transformation.

It is well known that zirconocene compounds have attracted much attention due to their broad application in organic synthesis.[13] However, their potential as Lewis acid catalysts have rarely been reported, which may be resulted from the lower Lewis acidity of Cp_2ZrCl_2 and their derivatives.[14] In 2006, Otera group found that the perfluoroctanesulfonate groups could be used as effective counter anions to increase the acidity as well as the water-tolerant ability.[15] With this in mind, we have synthesized a series of air-stable zirconocene perfluoroalkyl(aryl)sulfonates complexes, which showed strong Lewis acidity and high catalytic activity in many organic reactions.[16] It should be noted that the remarkable air-stability and strong Lewis acidity of these complexes mainly hinges on the perfluoroalkyl(aryl)sulfonate groups. However, their relatively low solubility in organic solvents owing to the strong lipophobic nature of perfluorooctanesulfonate group possibly declined the catalytic efficiency. To address this problem, we found that alkyl group incorporated with Cp ring can increase the solubility, as well as the catalytic efficiency.[17] Also the lipophobicity of perfluorobenzenesulfonate group was weaker than that of the perfluorooctanesulfonate group, and the toxicity of was lower than that of PFOS.[18] Herein, we successfully synthesized and characterized bis(pentamethylcyclopentadienyl) zirconium pentafluorbezenesulfonate $[\{(CH_3)_5Cp\}_2Zr(CH_3CN)_2(H_2O)][OSO_2C_6F_5]_2\cdot CH_3CN$ (**1**). Moreover, we reported its catalytic application in epoxide ring-opening reactions by amines or alcohols in detail.

2. Results and discussion

Complex **1** was synthesized by treatment of $[(CH_3)_5Cp]_2ZrCl_2$ with $AgOSO_2C_6F_5$ (2 equiv) in CH_3CN solution, and the yield was 72% (Scheme 1).



Scheme **1.** The synthetic route of complex **1**

The crystal structure of **1** in the solid state was confirmed by X-ray analysis. An ORTEP representation of **1** and selected bonds and angles were shown in Fig. 2. The crystal structure of complex **1** shows it is uninuclear, which is different from the complex $[\{CpZr(OH_2)_3\}_2(\mu^2\text{-}OH)_2][SO_3C_6F_5]_4\cdot 6H_2O$, even though their synthetic procedures are identical.[16b] In the crystal structure of **1**, the zirconium atom is stabilized by one water and two CH_3CN molecules, which also lie on the plane that bisects the angle between the Cp ring planes. The Zr-O and Zr-N distances of **1** are 2.242(5), 2.303(6) and 2.297(6) Å, respectively. The $C_6F_5SO_3^-$ ions and the dissociated CH_3CN molecule are packed around the complex cation and the C_6F_5 sides of the anion are clustered together to produce hydrophobic domains.

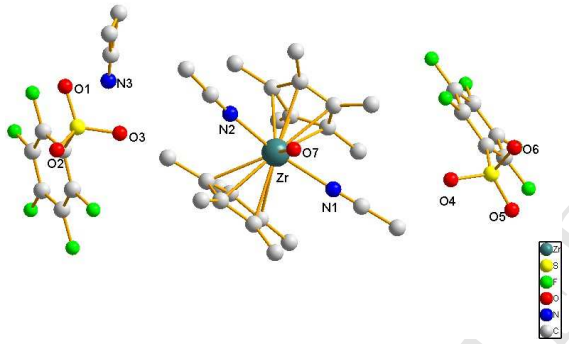


Fig. 2. The crystal structure of the complex **1** and selected bonds (A˚) and angles (deg): The Zr1-O7, 2.242(5); Zr1-N1, 2.303(6); Zr1-N2, 2.297(6); Zr1-C18, 2.570(7); Zr1-C19, 2.552(7); Zr1-C20, 2.546(6); Zr1-C21, 2.526(7); Zr1-C22, 2.515(7); O7-Zr-N1 70.87(18); O7-Zr-N2 71.30(18); N2-Zr-N1 142.2(2); O7-Zr-C21 90.21(19).

It is notable that the solid samples remained as dry crystals or powder after being kept in open air over three months. From the viewpoint of operation, such an excellent air-stable complex have great advantage over zirconocene bis(triflate) and the traditional Lewis-acid catalysts.[19]

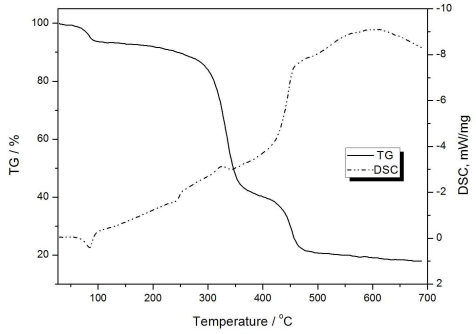


Fig. 3. TG-DSC curves of complex **1**.

The thermal behavior of complex **1** was investigated by TG-DSC under N_2 atmosphere (Fig. 3). The TG-DSC curves indicated three stages of weight loss. The endothermic step below 100 °C can be attributed to the removal of water and CH_3CN molecules. Complex **1** was stable up to about 260 °C. The weight loss of an exothermic nature at 300 °C is plausibly due to the oxidation of organic entities.

Conductivity measurement was applied to investigate its ionic dissociation behavior in CH_3CN (1.0 mmol·L^{-1}). The molar conductivity (Λ) of complex **1** thus measured at 20 °C was 137 μS·cm^{-1} (see Table S1 in ESI). The large molar conductivity value is consistent with the complete ionization into a 1:2 electrolyte,[20] implying that the complex is cationic in the solid as well as in the solution state. Another notable feature is the unusual solubility of **1** in Acetone, CH_3CN, THF, EtOAc and MeOH (Table 1). Actually, owing to the existence of ten methyl, one can see that complex **1** shows higher solubility in common polar organic solvents than the complex $[\{CpZr(OH_2)_3\}_2(\mu^2\text{-}OH)_2][SO_3C_6F_5]_4\cdot 6H_2O$.[16b]

Table 1 The solubility of complex **1** in organic solvents at 25 °C

Solvent	Solubility (g/L) of **1** [a]
Acetone	647
CH_3CN	842
THF	346
EtOAc	128
MeOH	384
Et_2O	16
CH_2Cl_2	0
n-Hexane	0
Toluene	0

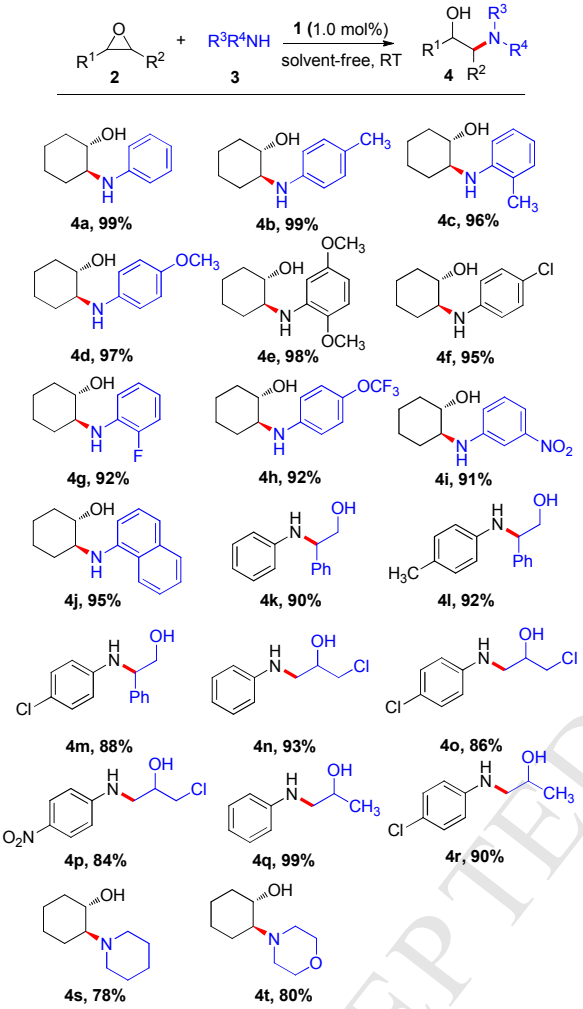
[a] The sample was freshly prepared and recrystallized in vacuum at toom temperature in a period of 2 hours.

In addition, we estimated the Lewis acidity of complex **1** by the red shift (λ_{em}) of Lewis acid metal ions (Zr^{2+}) with 10-methylacridone on the basis of fluorescence spectra.[21] The fluorescence maxima (λ_{em}) of complex **1** is 471 nm (see Fig. S1 in ESI). We also employed the Hammett indicator method to determine its acidity,[22] and found that it showed a relatively strong acidity with the acid strength of $0.8 < H_0 < 3.3$ (H_0 being the Hammett acidity function; see Fig. S2 in ESI). These features facilitate its catalytic performance in catalytic epoxide ring-opening reactions.

In view of the strongly acidic character of complex **1**, 1.0 mol % complex **1** was assessed as a catalyst for the ring opening reaction of epoxides with amines at room temperature under solvent-free conditions. As shown in Table 2, complex **1** shows high catalytic activity in the reaction of cyclohexene oxide with different aromatic amines, the yield of the product is excellent, i.e. from 91% to 99%. In all cases (**4a-4j**), only the major trans-β-amino-alcohol isomers can be isolated, illustrating the high diastereoselectivity of complex **1**. The aromatic amines with electron-donating groups (e.g., methyl and methoxyl, **4b-4e**) exhibit higher reaction activity than that with electron-withdrawing groups (e.g., F, Cl, OCF_3 and NO_2, **4f-4i**). Gratifyingly, 1-naphthylamine also shows high reaction activity with 95% yield (**4j**). Furthermore, high regio-selectivity is observed when styrene oxide is adopted. As expected in the case of styrene oxide α-amino was obtained as the major product (α/β = 95/5) due to the formation of the stabilized benzylic cation during the reaction (**4k**, 90%). The substituents in the phenyl group of phenyl amine show only slight effect on the activity (**4l**, **4m**, 92%, 88%). Different epoxides (e.g., epichlorohydrin, epoxypropane) also exhibit high reactivity and regioselectivity

(**4n-4r**, 84-93%), and *β*-aminoclcohols were obtained as the major product due to the predominant attack of amine on the less hindered carbon of the epoxide. In the cases of secondary amine such as piperidine, morpholine, satisfactory yields can be achieved (**4s**, **4t**, 80%, 85%). Thus, an efficient protocol for the aminolysis of epoxides has been developed.

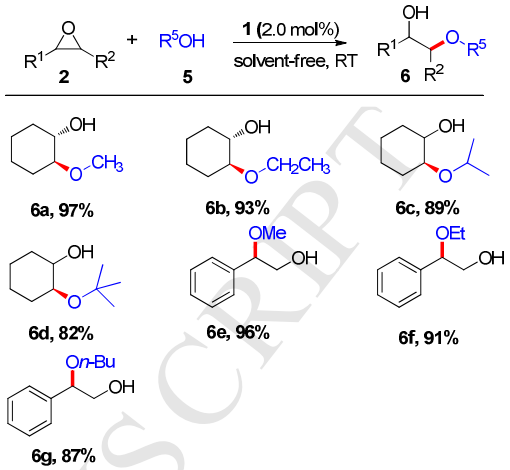
Table 2 Product yields of aminolysis reaction of epoxides with amines catalyzed by **1** [a]



[a] **1**, 0.01 mmol; epoxides **2**, 1.0 mmol; amines **3**, 1.0 mmol; solvent-free; Temp: RT; **4a-4e**, **4k-4l**, **4q**: 10 min; **4f-4g**, **4j**, **4m**, **4o**, **4r**: 15 min, **4h-4i**, **4p**: 25 min; **4s-4t**: 120 min; isolated yields.

To further explore the applicability of complex **1**, we assessed its catalytic activity towards the alcoholysis of epoxides with various primary, secondary, and tertiary alcohols. As illustrated in Table 3, in the presence of 2.0 mol% of complex **1**, both cyclohexyl epoxide and styrene epoxide show high reaction activity and regio-selectivity with different alcohols at room temperature under solvent-free conditions. First, we carried out the ring opening reactions on cyclohexyl epoxide with primary secondary, and tertiary alcohols, the reaction resulted in the exclusive formation of the trans-products in very good to excellent yields (**6a-6d**, 82-97%). Due to steric effect, isopropyl alcohol and tertiary butanol took a slightly longer time than primary alcohols but the regio-selectivity was not affected. Further, we investigated styrene epoxide incorporating more hindered hydroxyl functionality and the results showed high yields of *β*-alkoxy alcohol as the major product were obtained (**6e-6g**, 87-96%), which owing to opening of styrene epoxide at the benzylic position is favored due to the stable carbo-cation generated.

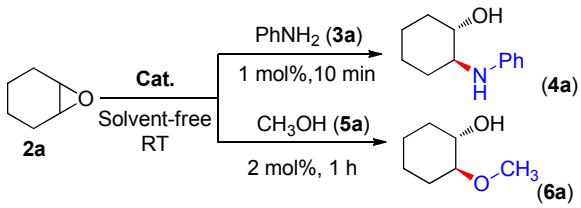
Table 3 Product yields of alcoholysis reaction of epoxides with alcohols catalyzed by **1** [a]



[a] **1**, 0.02 mmol; epoxides **2**, 1.0 mmol; alcohols **5**, 1.0 mmol; solvent-free; Temp: RT; **6a, 6b, 6e, 6f**: 1 h; **6c, 6g**: 3 h; **6d**: 8 h; isolated yields.

In addition, the activities of complex **1** and different zirconium compounds such as $ZrCl_4$, $(Me_5Cp)_2ZrCl_2$, $ZrO(OTf)_2$, $ZrO(NO_3)_2{\cdot}nH_2O$, $[\{CpZr(H_2O)_3\}_2(\mu^2OH)_2][OSO_2C_6F_5]_2{\cdot}6H_2O$ were estimated by the reaction of cyclohexyl epoxide with phenylamine or methyl alcohol (Table 4). As expected, no product was obtained without a catalyst being present (Entry 1). High yields were attained over complex **1** and zirconocene pentafluorbezenesulfonate (Entry 2, 7). While the other catalysts showed much lower yields, plausibly due to their moisture-sensitive properties or lower Lewis acidity or weak lipophilicity (Entry 3-6). However, It is noteworthy that the relatively lower catalytic efficiency of $[\{CpZr(H_2O)_3\}_2(\mu^2OH)_2][OSO_2C_6F_5]_2{\cdot}6H_2O$ may be owing to the low solubility and lipophilic property, which makes the substrates hard to approach the center metal atom for activating. Thus, the results illustrate the superiority of complex **1** in the ring opening reaction of epoxides.

Table 4 Catalyst comparison in the ring opening reaction of cyclohexyl epoxide with phenylamine or methyl alcohol



Entry	Catalyst[e]	4a[a]	6a[b]
1	No catalyst	0	0
2	Catalyst **1**	99	97
3	$ZrCl_4$	68	58
4	$(Me_5Cp)_2ZrCl_2$	32	42
5	$ZrO(OTf)_2$	63	60
6	$ZrO(NO_3)_2{\bullet}nH_2O$	51	57
7	$[\{CpZr(OH_2)_3\}_2(\mu^2OH)_2][SO_3C_6F_5]_4{\cdot}6H_2O$	90	87

[a] **Cat.**, 0.01 mmol; **2a** (1 mmol); **3a** (1 mmol); RT; 10 min; isolated yields. [b] **Cat.**, 0.02 mmol; **2a** (1 mmol); **5a** (1 mmol); RT; 1h; isolated yields.

To test the reusability of the catalyst and reproducibility of catalytic performance, the complex **1** was subject to cycles of the aminolysis reaction (**2a** + **3a** → **4a**) and the alcoholysis reaction (**2a** + **5a** → **6a**). In the five trials of the above model reaction catalyzed by complex **1**, the yield slightly declines, demonstrating the good recyclability of catalyst **1** (Table 5).

Table 5 Yields of the aminolysis reaction (**2a** + **3a** → **4a**) and the alcoholysis reaction (**2a** + **5a** → **6a**) catalyzed by recovered catalyst **1**.[a]

Cycle	Yield (%)[b] **2a** + **3a** → **4a**	Cat (%)[c]	Yield (%)[b] **2a** + **5a** → **6a**	Cat (%)[c]
1	99	98	97	95
2	98	97	96	96
3	99	98	97	97
4	99	98	96	95
5	98	96	97	95

[a] **1**, 0.01 mmol or 0.02 mmol; **2a**: 1.0 mmol; **3a**: 1.0 mmol; **5a**: 1.0 mmol; [b] Isolated yield of desired product. [c] Isolated yield of recovered catalyst.

3. Conclusions

In summary, we have synthesized and characterized mononuclear bis(pentamethylcyclopentadienyl) zirconium pentafluorbezenesulfonate. This complex is air-stable and strongly acidic, and shows high catalytic efficiency and regioselectivity in the aminolysis and alcoholysis of epoxides. Moreover, the complex possesses good reusability. On account of its stability, storability, as well as catalytic efficiency, the complex should find a broad range of utility.

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 ℃ 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 a HCT-1 (HENVEN, Beijing, China) instrument. IR spectra were recorded on NICOLET 6700 FTR spectrophotometer (Thermo Electron Corporation). Conductivity was measured on REX conductivity meter DDS-307. X-ray single crystal diffraction analysis was performed with SMART-APEX and RASA-7A by Shanghai Institute Organic Chemistry, China Academy of Science. Fluorescence spectroscopy (HITACHI F-4600) was measured in State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University (China). The acidity was measured by Hammett indicator method as described previously.[18a] Acid strength was expressed in terms of Hammett acidity function (H_o) as scaled by *pK*a value of the indicators.

4.1.1 Preparation of complex 1:

To a solution of $[(CH_3)_5Cp]_2ZrCl_2$ (0.432 g, 1.0 mmol) in 10 mL CH_3CN, a solution of $AgOSO_2C_6F_5$ (0.724g, 2 mmol) in 5 mL CH_3CN was added. After the mixture was stirred in the absence of light at room temperature for 2 hours, it was filtrated and evaporated in the vacuum and the surplus concentrates were maintained in the refrigerator for 24 hours, and the colorless crystals were obtained (0.718 g, 72%). Mp: 251-253 °C, ^{1}H NMR (400MHz, [d_6] acetone) δ: 2.97 (s, 12H, CH_3), 2.72 (s, 6H, CH_3), 2.52 (s, 12H, CH_3), 2.13 (s, *n*H, *CH*$_3$CN). ^{19}F NMR (376M, [d_6] acetone): δ: -138.84 to -138.95 (m, 2F; ArF), 153.80 (s, 1F; ArF), -163.15 to -163.32 (m, 2F; ArF); IR(KBr): v = 3378, 3228, 2909, 1643, 1531, 1503, 1381, 1230, 1110, 1044, 988, 936, 631, 537 cm^{-1}; Anal. Calc'd for $C_{38}H_{41}F_{10}N_3O_7S_2Zr$: C, 45.77; H, 4.14; found: C, 45.71; H, 4.19.

Crystal data for **1**: $C_{38}H_{41}F_{10}N_3O_7S_2Zr$; *Mr* = 997.08, Monoclinic, space group *P 21/n*, *a* = 11.6502(6) Å, *b* = 29.4744 (14) Å, *c* = 12.8100 (7) Å; *V* = 4171.2(4) Å ^{3}; *T* = 293(2) K; *Z* = 4; Reflections collected/unique, 82001/7346, R_{int} = 0.1120, R_1 = 0.0815, wR_2 = 0.2456. *GOF* = 1.059; CCDC No. 1565685.

4.1.2 Typical procedure for solubility of complex 1: Acetone (0.5 mL) was placed in a test tube; the complex **1** was added gradually at room temperature. When the amount of added **1** exceeds 323.5 mg, insoluble **1** appeared. Based on this data, solubility of **1** was determined to be 647 g·L^{-1}.

4.1.3 General procedure for the aminolysis and alcoholysis of epoxides: A mixture of cyclohexyl epoxide (98 mg, 1.0 mmol) and aniline (methyl alcohol) (93 mg, 1.0 mmol) and catalyst **1** (46 mg, 1.0 mol %) was stirred at room temperature for the appropriate reaction time and monitored by TLC. Then the mixture was diluted with CH_2Cl_2 (10 mL × 3). By means of filtration, the catalyst was separated and used for the next cycle, To the filtrate, after evaporation of the solvent, an oil mixture was obtained. The residue was purified by a short column chromatography eluted with ethyl acetate/petroleum ether (80/20).

4.2. Characterization data

4.2.1 4a-4t are known compounds, and ^{1}H NMR, ^{13}C NMR and Ms spectral data are summarized as follows:

*2-Anilino-1-cyclohexanol (**4a**)*:[6] white solid, M.p.: 58-59 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.21-7.17 (m, 2H), 6.77-6.71 (m, 3H), 3.38-3.32 (m, 1H), 3.17-3.12 (m, 1H), 2.84 (br.s, 1H), 2.14-2.11 (m, 2H), 1.80-1.69 (m, 2H), 1.41-1.28 (m, 3H), 1.10-0.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 146.65, 129.36, 123.08, 115.64, 74.77, 60.59, 33.44, 31.75, 25.16, 24.45; Ms (EI) *m/z* = 191.1 $[M]^+$.

*2-(4-Methylphenylamino)cyclohexanol (**4b**)*:[6] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.99 (d, *J* = 8.0Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.78 (s, 1H), 3.36-3.30 (m, 1H), 3.11-3.05 (m, 1H), 2.57 (br.s, 1H), 2.24 (s, 3H), 2.12-2.09 (m, 2H), 1.78-1.69 (m, 2H), 1.40-1.26 (m, 3H), 1.07-0.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.58, 130.03, 128.07, 115.04, 74.74, 60.96, 33.31, 31.79, 25.30, 24.50, 20.58; Ms (EI) *m/z* = 205.1 $[M]^+$.

*2-(2-Methylphenylamino)cyclohexanol (**4c**)*:[6] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.26-7.06 (m, 2H), 6.80-6.68 (m, 2H), 3.46-3.40 (m, 1H), 3.24-3.18 (m, 1H), 2.74 (br.s, 1H), 2.16 (s, 3H), 2.13 (s, 2H), 1.79-1.72 (m, 2H), 1.45-1.29 (m, 3H), 1.09-1.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.90, 130.66, 127.39, 123.35, 118.14, 111.85, 74.96, 60.12, 33.43, 32.09, 25.27, 24.51, 17.90; Ms (EI) *m/z* = 205.1 $[M]^+$.

*2-(4-Methoxyphenylamino)cyclohexanol (**4d**)*:[23a] White solid, M.p.: 58-59 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.79-6.73 (m, 2H), 6.70-6.64 (m, 2H), 3.75 (s, 3H), 3.34-3.29 (m, 1H), 3.02-2.97 (m, 1H), 2.53 (br.s, 1H), 2.15-2.08 (m, 2H), 1.76-1.69 (m, 2H), 1.39-1.26 (m, 3H), 1.07-0.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.26, 141.69, 116.71, 115.11, 74.64, 62.02, 55.98, 33.32, 31.74, 25.32, 24.51; Ms (EI) *m/z* = 221.1 $[M]^+$.

*2-(4-(2,5-Dimethoxy)phenylamino)cyclohexanol (**4e**)*:[23c] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.69 (d, *J* =

8.8Hz, 1H), 6.39 (d, *J* = 2.8Hz, 1H), 6.22-6.19 (m, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.46-3.40 (m,1H), 3.15-3.09 (m,1H), 2.74 (br.s, 1H), 2.15-2.09 (m, 2H), 1.78-1.72 (m, 2H), 1.43-1.26 (m, 4H), 1.13-1.04 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ ppm 154.95, 142.40, 138.90, 110.55, 100.02, 99.71, 74.73, 59.85, 56.27, 55.81, 33.37, 31.73, 25.29, 24.51; Ms (EI) *m/z* = 251.1 $[M]^+$.

*2-(4-Chlorophenylamino)cyclohexanol(**4f**):*[6] White solid, M.p.: 99-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.12 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 3.38-3.33 (m, 1H), 3.11-3.05 (m, 1H), 2.82 (br.s, 1H), 2.13-2.07 (m, 2H), 1.78-1.72 (m, 2H), 1.44-1.25 (m, 3H), 1.09-1.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 146.62, 129.33, 123.03, 115.61, 74.73, 60.54, 33.41, 31.71, 25.14, 24.43; Ms (EI) *m/z* = 225.1 $[M]^+$.

*2-(2-fluorophenylamino)cyclohexanol(**4g**):*[23c] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 6.97-6.93 (m, 2H), 6.87 (t, *J* = 8.2 Hz, 1H), 6.67-6.64 (m, 1H), 3.45-3.39 (m, 1H), 3.15-3.12 (m, 1H), 2.71 (br.s, 1H), 2.15-2.04 (m, 2H), 1.78-1.72 (m, 2H), 1.43-1.24 (m, 3H), 1.17-1.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.70, 136.34, 124.84, 124.80, 117.91, 117.84, 115.04, 114.85, 114.07, 74.75, 60.13, 33.35, 31.90, 25.22, 24.43; Ms (EI) *m/z* = 209.1 $[M]^+$.

*2-(4-Trifluoromethyloxyphenylamino)cyclohexanol (**4h**):* [6] White solid, M.p.: 71-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.03 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 9.2 Hz, 2H), 3.40-3.34 (m, 1H), 3.09-3.06 (m, 2H), 2.65 (br.s, 1H), 2.12 (t, *J* = 9.2 Hz, 2H), 1.79-1.72 (m, 2H), 1.41-1.26 (m, 3H), 1.12-1.01 (m, 1H); Ms (EI) *m/z* = 275.1 $[M]^+$.

*2-(3-Nitrophenylamino)cyclohexanol (**4i**):*[23a] White solid, M.p.: 77-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.55-7.50 (m, 2H), 7.30-7.27 (m, 1H), 6.98-6.96 (m, 1H), 3.85 (br.s, 1H), 3.45-3.40 (m, 1H), 3.25-3.19 (m, 1H), 2.37 (s, 1H), 2.13 (t, *J* = 7.2 Hz, 2H), 1.82-1.74 (m, 2H), 1.46-1.28 (m, 3H), 1.17-1.08 (m, 1H); Ms (EI) *m/z* = 236.1 $[M]^+$.

*2-(naphthalen-1-yl-amino) cyclohexanol(**4j**):*[5] Brown solid, M.p.: 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.88-7.80 (m, 2H), 7.47-7.32 (m, 4H), 6.90-6.88 (m, 1H), 3.64-3.58 (m, 1H), 3.41-3.35 (m, 1H), 2.94 (s, 1H), 2.25-2.16 (m, 2H), 1.80-1.75 (m, 2H), 1.47-1.30 (m, 1H), 1.26-1.20 (m, 1H), Ms (EI) *m/z* = 241.2 $[M]^+$.

*2-phenyl-2-(phenylamino)ethanol(**4k**):*[6] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.42-7.36 (m, 4H), 7.33-7.30 (m, 1H), 7.18-7.13 (m, 2H), 6.73 (t, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.53 (q, *J* = 7.2 Hz, 1H), 3.95 (dd, *J* = 11.2 Hz, 4.0 Hz, 1H), 3.76 (dd, *J* = 11.2 Hz, 4.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ ppm 147.26, 140.18, 129.19, 128.84, 127.62, 126.78, 117.95, 113.94, 67.33, 59.96; Ms (EI) *m/z* = 213.1 $[M]^+$.

*2-phenyl-2-(p-tolylamino)ethanol(**4l**):*[6] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.41-7.27 (m, 5H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 4.53 (q, *J* = 7.2 Hz, 1H), 3.95 (dd, *J* = 11.2 Hz, 4.4 Hz, 1H), 3.75 (dd, *J* = 11.2 Hz, 4.0 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ ppm 144.91, 140.32, 129.66, 128.79, 127.55, 127.17, 126.75, 114.10, 67.35, 60.25, 20.36; Ms (EI) *m/z* = 227.1 $[M]^+$.

*2-((4-chlorophenyl)amino)-2-phenylethanol(**4m**):*[6] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.37-7.27 (m, 5H), 7.05 (d, *J* = 9.2 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 4.67 (dd, *J* = 6.8 Hz, 4.0 Hz, 1H), 3.96 (dd, *J* = 11.2 Hz, 4.0 Hz, 1H), 3.76 (dd, *J* = 11.2 Hz, 4.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ ppm 147.79, 139.66, 128.97, 128.90, 127.76, 126.74, 126.69, 122.49, 114.96, 67.27, 60.02; Ms (EI) *m/z* = 247.1 $[M]^+$.

*3-Chloro-2-phenylaminopropanol(**4n**):*[6] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.23-7.19 (m, 2H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 4.09-4.04 (m, 2H), 3.39-3.34 (m, 1H), 3.24-3.19 (m, 2H); Ms (EI) *m/z* = 185.1 $[M]^+$.

*3-Chloro-2-(4-choloroanilino)propanol(**4o**):*[23a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.13 (d, *J* = 9.2 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.19-4.03 (m, 1H), 3.65-3.59 (m, 2H), 3.36-3.32 (m, 1H), 3.21-3.17 (m, 2H); Ms (EI) *m/z* = 219.1 $[M]^+$.

*3-Chloro-2-(3-nitroanilino)propanol(**4p**):*[23a] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.55-7.54 (m, 1H), 7.44-7.43 (m, 1H), 7.31-7.26 (m, 1H), 6.94-6.91 (m, 1H), 4.42 (s, 1H), 4.15-4.10 (m, 1H), 3.74-3.64 (m, 2H), 3.46-3.42 (m, 1H), 3.31-3.26 (m, 1H), 2.51 (d, *J* = 5.2 Hz, 1H); Ms (EI) *m/z* = 230.1 $[M]^+$.

*1-(phenylamino)propan-2-ol (**4q**):*[6] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.12 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 4.04-3.99 (m, 1H), 3.21-3.17 (m, 1H), 2.97-2.94 (m, 1H), 2.64 (s, 1H), 1.27-1.18 (m, 3H); Ms (EI) *m/z* = 151.1 $[M]^+$.

*1-((4-chlorophenyl)amino)propan-2-ol (**4r**):*[6] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.26-7.16 (m, 2H), 6.76-6.65 (m, 3H), 4.05-4.00 (m, 1H), 3.26-3.22 (m, 1H), 3.03-2.98 (m, 1H), 2.68 (s, 1H), 1.27-1.18 (m, 3H); Ms (EI) *m/z* = 185.1 $[M]^+$.

*2-(piperidin-1-yl)cyclohexanol(**4s**):*[6] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 3.37 (s, 3H), 2.91-2.87 (m, 1H), 2.69 (s, 1H), 2.12-2.05 (m, 1H), 1.98-1.94 (m, 1H), 1.71-1.65 (m, 2H), 1.27-1.18 (m, 3H), 1.09-0.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* ppm70.99, 68.54, 32.26, 26.72, 25.62, 24.83, 24.11, 22.15; Ms (EI) *m/z* = 183.1 $[M]^+$.

*2-morpholinocyclohexanol(**4t**):*[6] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 3.81 (s, 1H), 3.64-3.58 (m, 4H), 3.32-3.27 (m, 1H), 2.67-2.62 (m, 2H), 2.35-2.30 (m, 2H), 2.32-2.03 (m, 2H), 1.76-1.63 (m, 3H), 1.61-1.04 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* ppm 70.46, 68.33, 67.44, 33.13, 25.40, 23.97, 22.18; Ms (EI) *m/z* = 185.1 $[M]^+$.

4.2.2 6a-6g are known compounds, and the ^{1}H NMR, ^{13}C NMR spectral data are summarized as follows:

*2-methoxycyclohexanol (**6a**):*[12] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 3.37 (s, 3H), 2.91-2.87 (m, 1H), 2.69 (s, 1H), 2.12-2.05 (m, 1H), 1.98-1.94 (m, 1H), 1.71-1.65 (m, 2H), 1.27-1.18 (m, 3H), 1.09-0.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* ppm 84.98, 73.71, 56.29, 32.09, 28.35, 24.12, 23.95; Ms (EI) *m/z* = 130.1 $[M]^+$.

*2-ethoxycyclohexanol (**6b**):*[10] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 3.72-3.66 (m, 1H), 3.43-3.35 (m, 2H), 3.02-2.96 (m, 1H), 2.70 (s, 1H), 2.08-1.95 (m, 3H), 1.75-1.64 (m, 3H), 1.43-1.33 (m, 2H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* ppm 83.45, 73.72, 64.01, 32.98, 29.22, 24.25, 23.96, 15.61; Ms (EI) *m/z* = 144.1 $[M]^+$.

*2-isopropoxycyclohexanol (**6c**):*[12] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 3.67-3.60 (m, 1H), 3.41-3.33 (m, 1H), 3.11-3.04 (m, 1H), 2.77 (d, *J* = 10.4 Hz, 1H), 2.02-1.97 (m, 3H), 1.74-1.65 (m, 3H), 1.41-1.34 (m, 2H), 1.18-1.16 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* ppm 81.35, 73.76, 70.33, 33.11, 28.69, 24.38, 23.76, 23.75, 22.24; Ms (EI) *m/z* = 158.1 $[M]^+$.

*2-(tert-butoxy)cyclohexanol (**6d**):*[12] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 3.83 (s, 1H), 2.49-2.43 (m, 1H), 3.22-3.15 (m, 1H), 2.12-1.84 (m, 4H), 1.72-1.65 (m, 4H), 1.19 (s, 9H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ ppm 85.90, 75.22, 72.77, 33.25, 32.80, 29.70, 24.60, 24.08; Ms (EI) *m/z* = 172.1 $[M]^+$.

*2-methoxy-2-phenylethanol (**6e**):*[23b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.39-7.32 (m, 5H), 4.32 (q, *J* = 8.4 Hz, 1H), 3.72-3.63 (m, 2H), 3.33 (s, 3H), 2.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.39, 128.53, 128.12, 126.90, 84.80, 67.31, 56.88; Ms (EI) *m/z* = 152.1 $[M]^+$

*2-ethoxy-2-phenylethanol (**6f**):*[23b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.39-7.30 (m, 5H), 4.43 (q, *J* = 8.4 Hz, 1H), 3.70-3.51 (m, 2H), 3.48-3.40 (m, 2H), 2.75 (s, 1H), 1.24 (t, *J* = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.39, 128.53, 128.12, 126.90, 84.80, 67.31, 56.88; Ms (EI) *m/z* = 166.1 $[M]^+$

*2-butoxy-2-phenylethanol (**6g**):*[23b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.40-7.28 (m, 5H), 4.41 (q, *J* = 8.4 Hz, 1H), 3.68-3.61 (m, 2H), 3.48-3.34 (m, 2H), 2.53 (s, 1H), 1.61-1.57 (m, 2H), 1.44-1.35 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 139.07, 128.47, 127.98, 126.80, 82.92, 68.97, 67.46, 31.95, 19.36, 13.88; Ms (EI) *m/z* = 194.1 $[M]^+$.

Supporting Information: The crystal data of complex, copies of the ^{1}H NMR and ^{13}C NMR of all the products.

CCDC No. 1565685 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/ata_request/cif.

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