Oxidation of sulfides to chiral sulfoxides using Schiff base-vanadium (IV) complexes

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Abstract
A library of Schiff base ligands was synthesized from salicylaldehyde by reaction with various β-amino alcohols. These ligands were used with vanadium (IV) to screen for the enantioselective oxidation of sulfides to chiral sulfoxides.

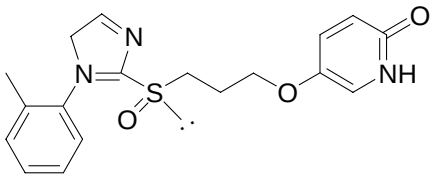
Keywords: Sulfide, chiral sulfoxide, Schiff base, vanadium (IV) catalyst

Introduction

An increasing number of chiral sulfoxides are becoming useful chiral auxiliaries in asymmetric synthesis.[1-6] Satoh and coworkers have reported the synthesis of chiral allenes by first coupling alkenyl aryl sulfoxides with aldehydes followed by alkyl anion induced elimination of the sulfur.[7] Toru has reported the enantioselective addition of Grignard reagents to 1-(arylsulfinyl)-2-naphthaldehyde, where a chiral sulfoxide conformer controls stereoselectivity of the addition.[8] Optically active β-(trimethylsilyl)ethyl sulfoxides supported on Merrifield resin undergo enantioselective Michael addition to α,β-unsturated esters, followed by removal of the sulfoxide group via thermal elimination.[9]

Recently a number of reports have appeared describing the use of chiral alkene and diene sulfoxides in synthetically-useful Diels-Alder reactions, where the chiral sulfoxide plays a major role in inducing chirality in the final product.[10-13] Yuste and Ellman have independently described the use of sulfoxides as chiral auxilaries in the asymmetric synthesis of β-amino alcohols which, in turn are synthetically-useful chiral building blocks. [14a, b, c, 15a, b] Toru has reported the elegant use of a chiral sulfoxide to synthesize an insecticidal chiral chrysanthamate.[16a] More recently, Colobert[16b] and Bravo[16c] have demonstrated the use of chiral sufoxides in the synthesis of *myo*-inositol, pyrrolidine and tetrahydroisoquinoline alkaloids, respectively. These examples clearly demonstrate the versatility of chiral sulfoxides as chiral auxilaries in asymmetric synthesis.

A number of sulfoxides are also finding application in the pharmaceutical industry. The chiral sulfoxide quinolone **1** is known to inhibit platelet adhesion by interfering with the release of 12(*S*)-hydroxyeicosatetraenoic acid from platelets.[17a, b, 18] Pyrazolotriazine **2** is a new drug developed to treat hyperuricemia and isochemic reperfusion injury. The drug inhibits the biosynthesis of uric acid by blocking xanthine oxidase.[19] Unge and co-workers have reported the asymmetric synthesis of esomeprazole, a drug containing a chiral sulfoxide group known to inhibit gastric acid secretion.[20a] Padmanahan and co-workers from Cambridge Neuro Science have reported the asymmetric synthesis of a sulfoxide containing a guanidine portion that is an active *N*-methyl-D-aspartate ion-channel blocker.[20b] These few examples clearly illustrate the growing importance of chiral sulfoxides in the pharmaceutical industry.



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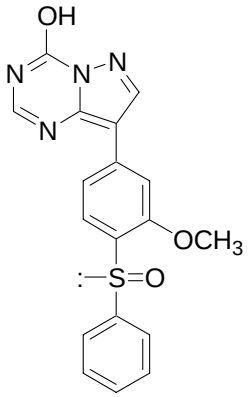
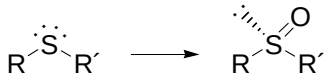


2

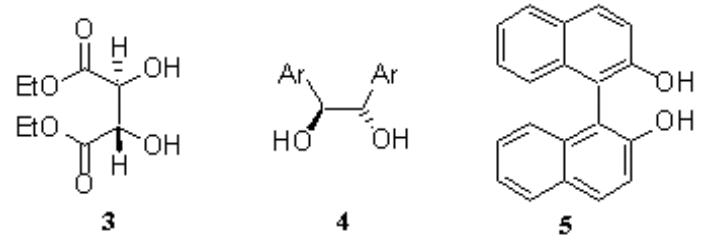
Since enantiomerically pure sulfoxides can play an important role as chiral auxilaries in organic synthesis, it is surprising that very few examples exist in which this ligand participates in homogeneous catalysis. Khiar used a Fe(III) complex of C_2-symmetric bis-sulfoxide as a catalyst in the asymmetric Diels-Alder reaction.[21] Shibasaki and Williams have independently used Pd-sulfoxide complexes in asymmetric allylic substitution.[22, 23] Bolm and Carreño have also attempted the use of chiral sulfoxides to catalyse the enantioselective addition of diethyl zinc to aromatic aldehydes; the products were obtained in moderate ee's. [24, 25]

These results have prompted researchers over the past two decades to develop new methods leading to asymmetric oxidation of a sulfide to a chiral sulfoxide (Equation 1).

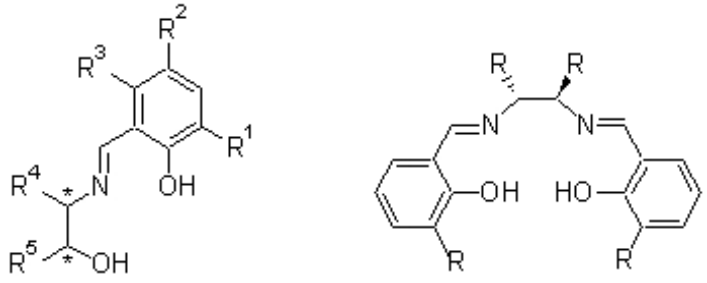


(1)

Numerous methodologies have been reported for the transformation of a prochiral sulfide to a chiral sulfoxide. Most of them involve use of a chiral ligand with a transition metal, such as titanium, vanadium or manganese, in the presence of hydrogen peroxide or an hydrogen peroxide adduct as the oxygen source. The chiral ligands that have been successfully used include: bidentate diethyl tartrate **3**,[26] diol **4**,[27] BINOL **5**,[28, 29] tridentate Schiff base ligands **6**[30-32] and tetradentate Salen type ligands **7**. [33-36]



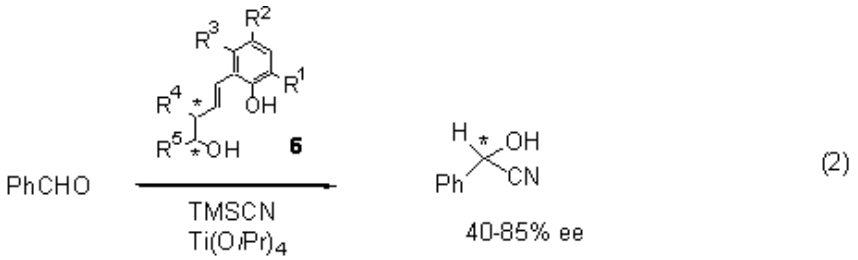
3 **4** **5**



6 **7**

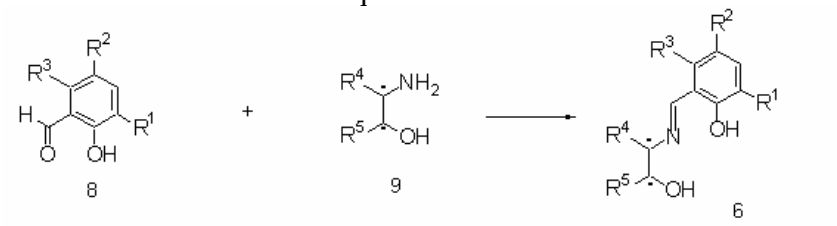
Results and Discussion

As part of a wider study of asymmetric transformations, we proposed the preparation of a large library of chiral Schiff base ligands of the -O---N---O- type **6**. Along with a transition metal ion, Ti(IV), V(IV), Cu(II) or Zn(II)), it would permit screening of the Schiff base ligands in various asymmetric chemical transformations. Recent application of this strategy in our laboratories to the addition of trimethylsilyl cyanide to benzaldehyde in the presence of Ti (IV) ion resulted in trimethylsilyl cyanohydrins in 40-85% enantioselectivity (Equation 2). [37, 38]



(2)

Vanadium (IV)-Schiff base complexes have been successfully used by Bolm, [31] Ellman [15] and Skarzewski [32] to oxidize different sulfide substrates to chiral sulfoxides. Based on these reports we have created a library of Schiff base ligands with subtle variations in the size of the substituents on the ligand. The library of ligands was derived from salicylaldehydes **8** and chiral β-amino alcohols **9** as shown in Equation 3.



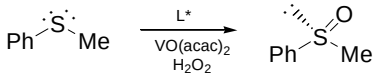
(3)

R^1= R^2= $C(CH_3)_3$, R^3= H
R^1= $C(CH_3)_3$, R^2= R^3= H
R^1=R^2= CH_3, R^3= H
R^1= Adamantyl, R^2= CH_3, R^3= H
R^1= R^2= $C(CH_3)_2Ph$, R^3= H
R^1= R^2= $C(CH_3)_2CH_2CH_3$, R^3= H
R^1= OCH_3, R^2= R^3=H
R^1= $C(CH_3)_3$, R^2= NO_2, R^3= H
R^1=H, R^2= NO_2, R^3= H
R^1= $C(CH_3)_3$, R^2= Br, R^3= H
R^1=R^2=Br, R^3= H
R^1=H, R^2= Br, R^3= H
R^1=H, R^2=R^3=Ph

R^4= R^5= $CH_2C_6H_4$
R^4= $C(CH_3)_3$, R^5= H
R^4= Ph, R^5= H
R^4 = R^5= Ph
R^4= $CH(CH_3)_2$, R^5= H
R^4= $CH_2CH(CH_3)_2$, R^5= H
R^4= CH_3, R^5= H
R^4=H, R^5=CH_3
R^4= CH_2CH_3, R^5= H
R^4= $CHCH_3CH_2CH_3$, R^5= H

The results of our screening are shown in Table 1. From our previous work with these ligands in the trimethylsilylcyanation of benzaldehyde catalyzed by Ti(IV)-Schiff base complexes, we discovered it was necessary to have a bulky substituent ortho to the phenol (R_1). [37] A similar trend was also observed in the sulfide oxidation; when R_1= H, OCH_3 or R_2, R_3= naphthyl, the observed ee's were low. Hence, we designed a number of Schiff bases with a bulky substituent at R_1, and then varied the size of substituents on R_2, R_4 and R_5. Initially, we incorporated a conformationally-rigid five membered ring at R_4 and R_5, derived from *cis*-1-amino-2-indanol. Our assumption here was that the bulky indanol ring would increase the energy difference between two diastereomeric transition structure orientations, thereby enhancing the resulting enantioselectivity. When R_1= *tert*-butyl or adamantyl, and R_4, R_5= *cis*-1-amino-2-indanyl, reasonably good enantioselectivities were observed (ligand **10**). However, when R_1 was replaced with 3,3-dimethyl propyl or 1,1-dimethylbenzyl, enantioselectivity was considerably lower (ligands **15** and **16**). This lowering of enantioselectivity probably came from steric overcrowding around the metal, thereby inhibiting the sulfide-metal coordination. Interestingly, when the rigid five-membered ring was replaced with a conformationally more flexible β-amino alcohol fragment (R_4), enantioselectivity was considerably improved, (ligands **42**, **43** and **44**). However, when both R_4 and R_5 were substituted, the enantioselectivity once again decreased (ligands **28-32**). Our results are in accordance with the recent report from Bergman and Ellman,[14a] who have

Table 1. Enantioselective catalytic oxidation of sulfide to sulfoxides promoted by chiral Schiff base-vanadium(IV) complexes derived from β-aminoalcohols



Schiff Base	R^1	R^2	R^3	R^4	R^5	% Yield	% e.e. (Configuration)
10	Adamantyl	CH_3	H	$CH_2C_6H_4$		54	50 (*R*)
11	OCH_3	H	H	$CH_2C_6H_4$		56	38 (*R*)
12	H	NO_2	H	$CH_2C_6H_4$		88	24(*S*)
13	CH_3	CH_3	H	$CH_2C_6H_4$		61	38(*S*)
14	$C(CH_3)_3$	NO_2	H	$CH_2C_6H_4$		50	45 (*S*)
15	$C(CH_3)_2CH_2CH_3$	$C(CH_3)_2CH_2CH_3$	H	$CH_2C_6H_4$		90	22 (*S*)
16	$C(CH_3)_2Ph$	$C(CH_3)_2Ph$	H	$CH_2C_6H_4$		51	18 (*S*)
17	Br	Br	H	$CH_2C_6H_4$		88	61 (*R*)
18	$C(CH_3)_3$	Br	H	$CH_2C_6H_4$		83	51 (*R*)
19	$C(CH_3)_3$	H	H	$CH_2C_6H_4$		64	45(*R*)
20	Adamantyl	CH_3	H	Ph	H	63	42 (*R*)
21	$C(CH_3)_2CH_2CH_3$	$C(CH_3)_2CH_2CH_3$	H	Ph	H	62	44 (*R*)
22	$C(CH_3)_2Ph$	$C(CH_3)_2Ph$	H	Ph	H	66	28 (*R*)
23	$C(CH_3)_3$	$C(CH_3)_3$	H	Ph	H	42	35 (*R*)
24	H	Br	H	Ph	H	92	16(*R*)
25	Br	Br	H	Ph	H	48	36(*R*)
26	$C(CH_3)_3$	Br	H	Ph	H	76	29(*R*)
27	H	Ph		Ph	H	61	9(*R*)
28	$C(CH_3)_3$	Br	H	Ph	Ph	73	24(*R*)
29	Adamantyl	CH_3	H	Ph	Ph	66	35 (*R*)
30	$C(CH_3)_2CH_2CH_3$	$C(CH_3)_2CH_2CH_3$	H	Ph	Ph	80	38 (*R*)
31	$C(CH_3)_2Ph$	$C(CH_3)_2Ph$	H	Ph	Ph	91	15 (*R*)
32	$C(CH_3)_3$	$C(CH_3)_3$	H	Ph	Ph	64	28 (*R*)
33	Adamantyl	CH_3	H	$CH_2CH(CH_3)_2$	H	65	41 (*S*)
34	$C(CH_3)_2CH_2CH_3$	$C(CH_3)_2CH_2CH_3$	H	$CH_2CH(CH_3)_2$	H	66	24 (*S*)
35	$C(CH_3)_2Ph$	$C(CH_3)_2Ph$	H	$CH_2CH(CH_3)_2$	H	77	20(*S*)
36	$C(CH_3)_3$	$C(CH_3)_3$	H	$CHCH_3CH_2CH_3$	H	60	37 (*S*)
37	Adamantyl	CH_3	H	$CH(CH_3)_2$	H	56	43 (*S*)
38	$C(CH_3)_3$	$C(CH_3)_3$	H	$CH(CH_3)_2$	H	58	37 (*R*)
39	$C(CH_3)_2CH_2CH_3$	$C(CH_3)_2CH_2CH_3$	H	$C(CH_3)_3$	H	41	49 (*S*)
40	$C(CH_3)_2Ph$	$C(CH_3)_2Ph$	H	$C(CH_3)_3$	H	83	50 (*S*)
41	Adamantyl	CH_3	H	$C(CH_3)_3$	H	67	53 (*S*)

42	$C(CH_3)_3$	Br	H	$C(CH_3)_3$	H	98	58(*S*)

Table 1. Continued

43	Br	Br	H	$C(CH_3)_3$	H	44	57(*S*)
44	$C(CH_3)_3$	$C(CH_3)_3$	H	$C(CH_3)_3$	H	73	59(*S*)
45	$C(CH_3)_3$	$C(CH_3)_3$	H	CH_2CH_3	H	65	41 (*S*)
46	Br	Br	H	CH_2CH_3	H	82	49(*R*)
47	H	Br	H	CH_2CH_3	H	66	44(*R*)
48	H	Br	H	CH_3	H	83	31(*S*)
49	Br	Br	H	CH_3	H	78	48(*S*)
50	Br	Br	H	H	CH_3	82	42(*S*)

isolated the active intermediate in the Schiff base-vanadium catalyzed oxidation of sulfide to sulfoxide. The intermediate was found to be a 2:1 complex of Schiff base ligand to vanadium, which then reacts with hydrogen peroxide, eliminating one of the ligands to give a vanadium hydroperoxide complex, which then oxidizes the sulfide to sulfoxide. It is reasonable to assume that a certain amount of steric crowding around the metal in the transition state is essential in order to enhance the enantioselectivity of the sulfide oxidation. From our and previous works related to trimethylsilylcyanation of aldehyde and sulfide to sulfoxide oxidation using Schiff base ligands, it appears that a *tert*-butyl substituent provides the ideal steric size and gives good enantioselectivity in both types of reactions.

Having investigated the size of substituents on the Schiff base ligands and their effects on the enantioselectivity, we next turned our attention to studying the electronic effects of these substituents in the sulfide to sulfoxide oxidation. Skarzewski and coworkers have reported that with the electron withdrawing nitro group *para* to the phenolic OH in the Schiff base-V(IV) complex(system) gives high enantioselectivity in the sulfide to sulfoxide oxidation.[32] However, in our hands R_2= NO_2 and R_1= *tert*-butyl led to low ee, which is also in agreement with Ellmann's observation.[14] When the strong electron withdrawing nitro was replaced with a less electron attractive bromine atom, along with sterically bulky substituents R_1, R_4 and R_5 on the Schiff base ligand, enantioselectivity was improved (ligand **18**). A similar trend was also seen in the trimethylsilylcyanation of benzalaldehyde catalyzed by Schiff base-Ti(IV) complex.[39]

In conclusion, the steric requirements of the Schiff base-vanadium (IV) complex-catalyzed oxidation of a sulfide to a chiral sulfoxide parallels the Ti(IV)-Schiff base catalyzed trimethylsilyl cyanation reactions.[38] Added to this, the presence of electron- withdrawing bromine at R_1 or R_2 along with appropriate bulky substituents on the ligand enhances the enantioselectivity in the sulfide to sulfoxide oxidation. Thus, in designing new chiral Schiff base ligand-vanadium complexes for the sulfide to sulfoxide oxidation, consideration has to be given to both steric and electronic factors.

Experimental Section

General procedure for the oxidation of methyl phenyl thio ether to sulfoxide

The enantiomeric excesses were determined using a Hewlett-Packard liquid chromatograph (detecting UV diodes at 254 nm), with a (*R,R*)-WHELK-01 chiral column.

In a 25 mL flask were placed vanadyl acetylacetonate (5.2 mg, 0.02 mmol), the ligand **10** (1*R*,2*S*)-(+)-1-[N-(3´-(1''-adamantyl)-5´-methylsalicylidene)amino]-2-indanol, (0.012g, 0.03 mmol) along with 4 mL CH_2Cl_2, and the solution was stirred for 5 min at room temperature. To the stirring solution methylphenylsulfide was added (0.240g, 2 mmol) and the mixture was then cooled to 0 ^oC, adding 30% H_2O_2 (0.124g, 1.1 mmol) slowly. The mixture was stirred for 20 h at 0 ^oC, after which a second portion of $[VO(acac)_2]$ (5.2 mg, 0.02 mmol) was added, more ligand **10** (12 mg, 0.03 mmol) and 30% H_2O_2 (124 mg, 1.1 mmol), stirring for an additional 20 h period at 0 ^oC. The mixture was then extracted with CH_2Cl_2 (2 x 5 mL), the organic extracts were combined and washed with H_2O, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to give a dark brown liquid. HPLC retention times for the methylphenyl sulfoxides (***R***) = 26.9 min and (***S***) = 29.2 min (hexane:2-propanol, 95:5).

Details of the general procedure for the synthesis and characterization of the Schiff base ligands **10, 11, 15-17**, **19-23**, **29-32**, **37-41** and **44** were reported in previous work.[37,38]

(1*R*,2*S*)-(+)-1-[*N*-(5'-Nitrosalicylidene)amino]-2-indanol (12). Orange solid (0.77 g, 86%); mp 216-218 ^oC; $[\alpha]^{25}_D$= +60.76^o (c=0.5, CH_2Cl_2). IR (KBr) 3214, 2939, 2898, 1655, 1610, 1545, 1329 and 749 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.68(s, 1H), 8.40(d, 1H, J= 2.9 Hz), 8.08(dd, 1H, J_1= 2.9 Hz and J_2= 9.6 Hz), 7.34-7.25(m, 4H), 6.68(d, 1H, J= 9.6 Hz), 5.08(d, 1H, J= 5.3 Hz), 4.70(q, 1H, J= 4.5 Hz), 3.20(dd, 2H, J_1= 5.3 Hz and J_2= 16.0 Hz) and 3.12(dd, 2H, J_1= 5.3 Hz and J_2= 16.0 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 174.71, 164.79, 140.47, 137.93, 135.06, 130.25, 128.17, 128.09, 126.23, 124.69, 123.96, 120.81, 113.87, 72.46, 69.24 and 39.03 ppm. EIMS (m/e): 298 [M^+] (48), 281(30), 149(40), 132(76), 104(100) and 77(65). Anal. calcd. for $C_{16}H_{14}N_2O_4$: C, 64.43; H, 4.70. Found: C, 64.50; H, 4.75.

(1*R*,2*S*)-(+)-1-[*N*-(3',5'-Di-methylsalicylidene)amino]-2-indanol (13). Yellow solid (0.86 g, 91.3%); mp 101-104 ^oC; $[\alpha]^{25}_D$= +42.66^o (c=0.50, CH_2Cl_2). IR (KBr) 3320, 2955, 1638 and 743 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.49(s, 1H), 7.27-7.15(m, 4H), 7.01(s, 1H), 6.95(s, 1H), 4.73(d, 1H, J= 5.2 Hz), 4.64(q, 1H, J= 5.4 Hz), 3.22(dd, 1H, J_1= 5.8 Hz and J_2= 15.8 Hz), 3.07(dd, 1H, J_1= 5.4 Hz and J_2= 15.8 Hz), 2.26(s, 3H) and 2.20(s, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.08, 157.18, 141.00, 140.80, 135.03, 129.55, 128.68, 127.49, 127.14, 125.93, 125.55, 124.95, 117.71, 75.70, 75.42, 39.77, 20.57 and 15.64 ppm. EIMS (m/e): 281[M^+] (82.90), 263(18.17), 149(100), 133(32.01), 91(29.61) and 77(44.45). Anal. calcd. for $C_{18}H_{19}NO_2$: C, 76.86; H, 6.76. Found: C, 76.90; H, 6.77.

(1*S*,2*R*)-(-)-1-[*N*-(3'-*tert*-Butyl-5'-nitrosalicilidene)amino]-2-indanol (14). Yellow solid (0.48 g, 40.0%); mp 72-78 ^oC; $[\alpha]^{25}_D$= -29.33^o (c=0.50, CH_2Cl_2). IR (KBr) 3419, 3108, 2952, 1638, 1600, 1557, 1316 y 748 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.53(s, 1H), 8.22(d, 1H, J=2.8 Hz), 8.16(d, 1H, J= 3.0 Hz), 7.36-7.20(m, 4H), 4.95(d, 1H, J_1= 5.2 Hz), 4.76(q, 1H, J= 5.4 Hz), 3.30(dd, 1H, J_1= 6.0 Hz, J_2= 16.0 Hz), 3.11(dd, 1H, J_1= 5.0 Hz, J_2= 16.0 Hz) y 1.42(s, 9H) ppm;

^{13}C NMR (50 MHz, $CDCl_3$) δ 165.04, 169.10, 140.37, 140.44, 139.24, 138.30, 129.24, 127.48, 127.21, 125.81, 125.54, 125.03, 116.70, 74.92, 73.45, 39.47, 35.21 and 28.89 ppm. EIMS (m/e): 354[M^+] (82), 337(18), 221(43), 207(37), 179(42), 133(100), 105(53), 91(31) y 77(39).

(1*R*,2*S*)-(+)-1-[*N*-(3'-*tert*-Butyl-5'-bromosalicylidene)amino]-2-indanol (18). Yellow oil (1.13 g, 87.4%) ; $[\alpha]^{25}_D$= +11.03^o (c=0.5, CH_2Cl_2). IR (neat) 3374, 2951, 1625, 749 and 600 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.47(s, 1H), 7.44(d, 1H, J= 2.6 Hz), 7.32(d, 1H, J= 2.6 Hz), 7.34-7.21(m, 4H), 4.73(d, 1H, J= 5.2 Hz), 4.61(q, 1H, J= 5.2 Hz), 3.18(dd, 1H, J_1= 5.6 Hz and J_2= 15.8 Hz), 3.05(dd, 1H, J_1= 5.2 Hz and J_2= 15.8 Hz) and 1.36(s, 9H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.56, 159.57, 140.42, 140.05, 139.98, 132.47, 131.69, 128.34, 126.75, 125.18, 124.57, 119.53, 109.54, 74.88, 74.78, 50.28, 39.26, 34.94, 29.22 and 29.00 ppm. EIMS (m/e): 387[M^+] (69), 240(24), 133(100), 103(77) and 77(77).

(*R*)-(+)-2-[*N*-(5'-Bromosalicylidene)amino]-2-phenyl-1-ethanol (24). Yellow solid (0.35 g, 98 %); mp 118-120 ^{o}C; $[\alpha]^{25}_D$= +34.0^o (c= 0.012, CH_2Cl_2). IR (KBr) 3406, 2909, 2861, 1623, 768 and 700cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.37(s, 1H), 7.41-7.25(m, 7H), 6.86(d, 1H, J= 8.0 Hz), 4.47(t, 1H, J= 6.4 Hz) and 3.93(d, 2H, J= 6.2 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.97, 160.05, 138.80, 135.32, 133.82, 128.94, 128.09, 127.09, 120.04, 119.04, 110.35, 75.74 and 67.58 ppm. Anal. calcd. for $C_{15}H_{14}NO_2Br$: C, 56.25; H, 4.37. Found: C, 56.30; H, 4.41.

(*R*)-(+)-2-[*N*-(3',5'-Dibromosalicylidene)amino]-2-phenyl-1-ethanol (25). Brown oil (0.23 g, 81%); $[\alpha]^{25}_D$= +106.0^o (c= 0.032, CH_2Cl_2). IR (neat) 3345, 2928, 2872, 1636, 736 and 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.30(s, 1H), 7.65(d, 1H, J= 2.4 Hz), 7.30(d, 1H, J= 2.4 Hz), 7.42-7.33(m, 5H), 4.55(t, 1H, J= 7.4 Hz), 3.96(d, 1H, J= 5.2 Hz), 3.93(d, 1H, J= 2.0 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.06, 160.50, 138.16, 137.11, 133.14, 128.94, 128.24, 126.75, 118.33, 113.47, 108.14, 73.34 and 67.0 ppm. Anal. calcd. for $C_{15}H_{131}NO_2Br_2$: C, 45.11; H, 3.26. Found: C, 45.14; H, 3.30.

(*R*)-(+)-2-[*N*-(3'-*tert*-Butyl-5-bromosalicylidene)amino]-2-phenyl-1-ethanol (26). Yellow oil (0.15 g, 79 %); $[\alpha]^{25}_D$= +78.00^o (c= 0.0238, CH_2Cl_2). IR (neat) 3365, 2952, 2870, 1628 and 750 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.32(s, 1H), 7.38 (d, 1H, J= 2.4 Hz), 7.35-7.26(m, 5H), 7.20(d, 1H, J= 2.4 Hz) 4.39(t, 1H, J= 6.0 Hz), 3.84(d, 2H, J= 6.0 Hz), 1.40(s, 9H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.97, 159.68, 140.35, 139.19, 132.90, 132.16, 129.10, 128.20, 127.38, 120.10, 110.20, 75.76, 67.55, 35.17 and 29.26 ppm. Anal. calcd. for $C_{19}H_{22}NO_2Br$: C, 60.63; H, 5.85. Found: C, 60.67; H, 5.88.

(*R*)-(+)-2-[*N*-(2'-Hydroxy-1-(*N*-naphthalidene)amino]-2-phenyl-1-ethanol (27). Yellow solid (0.052 g, 98 %); mp 179-181 ^{o}C; $[\alpha]^{25}_D$= +191.38^o (c=0.02, CH_2Cl_2). IR (KBr) 3222, 2930, 1630, 1060 and 754 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.89(s, 1H), 7.77(d, 1H, J= 9.0 Hz), 7.47(d, 1H, J= 9.0 Hz), 7.43-7.32(m, 7H), 7.16(t, 1H, J= 7.0 Hz), 6.83(d, 1H, J= 9.0 Hz), 4.67(dd, 1H, J_1= 3.5 Hz and J_2= 7.9 Hz), 4.04-3.96(m, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.87, 159.48, 138.06, 137.21, 133.61, 129.38, 129.30, 128.48, 128.08, 127.04, 126.67, 123.43, 123.05, 118.39, 107.39, 71.41 and 67.53 ppm. Anal. calcd. for $C_{19}H_{17}NO_2$: C,78.35; H, 5.84. Found: C, 78.40; H, 5.88.

(1*S*,2*R*)-(-)-2-[*N*-(3'-*tert*-Butyl-5-bromosalicylidene)amino]-1,2-diphenylethanol (28). Yellow solid (0.25 g, 93 %); mp 56-58 ^{o}C; $[\alpha]^{25}_D$= -33.0^o (c= 0.105, CH_2Cl_2). IR (KBr) 3424, 2952, 2878, 1631, 1045

and 705 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.0(s, 1H), 7.35-7.29(m, 11H), 7.00(d, 1H, J= 3.0 Hz), 5.00(d, 1H, J= 7.0 Hz), 4.47(d, 1H, J= 7.0 Hz), 1.41(s, 9H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.59, 159.66, 140.29, 132.78, 132.06, 129.04, 128.38, 127.42, 120.08, 109.97, 80.27, 78.48, 35.23 and 29.26 ppm. Anal. calcd. for $C_{25}H_{26}$ Br NO_2: C, 66.37; H, 5.75. Found: C, 66.40; H, 5.77.

(*S*)-(-)-2-[3'-Adamantyl-5-methylsalicylidene)amino]-4methyl-1-pentanol (33). Yellow solid (0.58 g, 83 %); mp 78-80 ^oC $[\alpha]^{25}_D$= -58.04^o (c=0.0026, CH_2Cl_2). IR (KBr) 3357, 2899, 1628, 1022 and 651 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.32(s, 1H), 7.08(d, 1H, J= 2.2 Hz), 6.91(d, 1H, J= 1.6 Hz), 3.64(d, 1H, J_1= 7.0 Hz), 3.40-3.27(m, 1H), 2.28 (s, 3H), 2.16(s, 6H), 2.07(s, 3H), 1.79(s, 6H), 1.61-1.52(m, 1H), 1.40-1.22(m, 2H), 0.91(d, 3H, J= 6.2 Hz). 0.86(d, 3H, J=6.2 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.43, 158.38, 137.40, 130.63, 129.62, 126.83, 118.18, 70.02, 66.53, 40.87, 40.30, 37.13, 36.90, 29.05, 24.37, 23.53, 21.50 and 20.67 ppm. Anal. calcd. for $C_{24}H_{35}NO_2$: C, 78.04; H, 9.48. Found: C, 78.05; H, 9.49.

(*S*)-(-)-2-[*N*-(3',5'-Di-*tert*-amylsalicylidene)amino]-4-methyl-1-pentanol (34). Yellow liquid (0.58 g, 93%); $[\alpha]^{25}_D$= -54.5^o (c=0.020, CH_2Cl_2). IR (neat) 3397, 2956, 2880, 1628, 1061 and 733 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.39(s, 1H), 7.26(d, 1H, J= 2.3 Hz), 7.05(d, 1H, J= 2.3 Hz), 3.75-3.60(m, 2H), 3.44-3.31(m, 1H), 1.92(q, 1H, J= 7.4 Hz, 1.67-1.49(m, 4H), 1.39(s, 6H), 1.27(s, 6H), 0.93(d, 3H, J=6.4 Hz), 0.89(d, 3H, J=6.6 Hz), 0.69(t, 3H, J= 7.4 Hz), 0.67(t, 3H, J= 7.4 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.17, 158.35, 138.59, 135.29, 129.39, 127.20, 117.86, 70.21, 66.88, 41.24, 38.78, 37.45, 37.03, 32.87, 28.65, 27.60, 24.58, 23.66, 21.83, 9.63 and 9.29 ppm. Anal. calcd. for $C_{23}H_{39}NO_2$: C, 76.45; H, 10.80. Found: C, 76.48; H, 10.84.

(*S*)-(-)-2-{*N*-[3',5'-Bis(α,α-dimethylbencyl)salicylidene]amino}-4-methyl-1-pentanol (35). Yellow liquid (0.84 g, 98%); $[\alpha]^{25}_D$= -37.98^o (c=0.0021, CH_2Cl_2). IR (neat) 3397, 2956, 1623, 1028 and 695 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.23(s, 1H), 7.36-7.06(m, 12H), 3.60-3.28(m, 2H), 3.38-3.10(m, 1H), 1.71(s, 9H), 1.61(s, 3H), 1.60-1.10(m, 3H), 0.85(d, 3H, J= 5.6 Hz), 0.82(d, 3H, J= 5.2 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.50, 165.93, 158.41, 150.98, 139.95, 136.54, 129.74, 129.25, 128.67, 128.51, 128.09, 128.02, 127.30, 127.03, 126.76, 126.26, 126.16, 125.62, 118.16, 42.75, 42.41, 41.07, 31.51, 31.02, 30.57, 28.89, 24.79, 23.86, 23.66, 22.06 and 21.88 ppm. Anal. calcd. for $C_{31}H_{31}NO_2$: C, 81.40; H, 8.53. Found: C, 81.44; H, 8.55.

(*S*)-(-)-2-[*N*-(3',5'-Di-*tert*-butylsalicylidene)amino]-3-methyl-1-pentanol (36). Yellow liquid (0.295 g, 85 %); $[\alpha]^{25}_D$= -39.26 (c=0.027g, CH_2Cl_2); IR(neat) 3372, 2959, 2875 1631 and 704 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.37(s, 1H), 7.39(d, 1H, J= 2.3 Hz), 7.12(d, 1H, J= 2.3 Hz), 3.80-3.73 (m, 2H), 3.18-3.05(m, 1H), 1.80-1.54(m, 1H), 1.45(s, 9H), 1.31(s, 9H), 1.26-1.12(m, 2H), 0.96-0.82(m, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.17, 158.44, 140.43, 136.99, 127.35, 126.40, 118.00, 77.23, 64.54, 37.17, 35.30, 34.40, 31.77, 29.72, 25.70, 16.13 and 11.63 ppm.

(*S*)-(-)-2-[*N*-(3'-*tert*-Butyl-5-bromosalicylidene)amino]-3,3-dimethyl-1-butanol (42). Yellow solid (0.37 g, 89 %); mp 141-143 ^oC; $[\alpha]^{25}_D$= -37.0^o (c=0.030, CH_2Cl_2); IR (KBr) 3441, 2962 and 1626 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 13.95(s, 1H), 8.22(s, 1H), 7.30 (d, 1H, J= 2.4 Hz), 7.22(d, 1H, J= 2.4 Hz), 3.92(dd, 1H, J_1= 2.56 Hz and J_2= 11.1 Hz) 3.72(t, 1H, J= 9.65 Hz), 2.93(dd, 1H, J= 2.8 Hz, J= 9.52 Hz), 1.40(s, 9H), 1.00(s, 9H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.60, 159.88, 140.35, 132.58, 131.99, 120.01, 110.01, 81.49, 62.62, 35.32, 33.44, 29.40 and 27.27 ppm. Anal. calcd. for $C_{17}H_{26}$ Br NO_2: C, 57.30; H, 7.30. Found: C, 57.33; H, 7.34.

(*S*)-(-)-2-[*N*-(3',5'-Dibromosalicylidene)amino]-3,3-dimethyl-1-butanol (43). Yellow solid (0.28 g, 98 %); mp 138-140 ^{o}C $[\alpha]^{25}_{D}$= -34.28 (c=0.00245g, CH_2Cl_2); IR (KBr) 3365, 2959, 2878, 1638, 1085, 857 y 753 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.083(s, 1H), 7.54 (d, 1H, J= 2.4 Hz), 7.20(d, 1H, J= 2.4 Hz), 4.039-3.96(dd, 1H, J_1= 3.0 Hz, J_2= 11.2 Hz), 3.73-3.62(dd, 1H, J_1= 9.6 Hz, J_2= 11.5 Hz), 3.13-3.08(dd, 1H, J_1= 2.4 Hz, J_2= 9.2 Hz), 1.00(s, 9H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.87, 164.65, 139.14, 133.70, 116.86, 115.51, 106.37, 77.98, 61.64, 32.84 and 26.84 ppm. Anal. calcd. for $C_{13}H_{17}NO_2Br_2$: C, 41.16; H, 4.48, Found: C, 41.46; H, 4.78.

(*S*)-(-)-2-[*N*-(3',5'-Di-*tert*-butylsalicylidene)amino]-1-butanol (45). Yellow solid (1.40 g, 92 %); mp 78-80 ^{0}C $[\alpha]^{25}_{D}$= -22.46^{o} (c=0.00276, CH_2Cl_2). IR (KBr) 3285, 2955, 2872, 1632, 1062, 831 and 687 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.40(s, 1H), 7.40(d, 1H, J= 2.4 Hz), 7.13(d, 1H, J= 2.2 Hz), 3.77-3.64(m, 1H, Hz), 3.24-3.11(m, 1H), 1.76-1.51(m, 2H), 1.45(s, 9H), 1.31(s, 9H), 0.91(t, 3H, J= 7.4 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.87, 158.07, 140.20, 136.70, 127.10, 126.10, 117.67, 73.64, 66.16, 35.01, 34.13, 31.84, 29.44, 25.16 and 10.67 ppm. Anal. calcd. for $C_{19}H_{31}NO_2$: C, 74.75; H, 10.16. Found: C, 74.79; H, 10.19.

(*R*)-(+)-2-[*N*-(3',5'-Dibromosalicylidene)amino]-1-butanol (46). Yellow solid (0.52 g, 81%); mp 137-139 ^{o}C; $[\alpha]^{25}_{D}$= +20.00^{o} (c= 0.035, CH_2Cl_2). IR (KBr) 3264, 2968, 2853, 1648, 1068, 756 and 691 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.17(s, 1H), 7.62(d, 1H, J= 2.1 Hz), 7.26(d, 1H, J= 2.1 Hz), 3.84(dd, 1H, J_1 = 3.8 Hz and J_2 = 11.4 Hz), 3.67(dd, 1H, J_1 = 8.4 Hz and J_2 = 11.2 Hz), 3.41-3.28(m, 1H), 1.80-1.50(m, 2H), 0.95(t, 3H, J= 7.6 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.91, 142.36, 137.00, 81.29, 80.66, 73.77, 68.93, 28.13 and 14.23 ppm. Anal. calcd. for $C_{11}H_{13}NO_2Br_2$: C, 37.60; H, 3.70. Found: C, 37.65; H, 3.74.

(*R*)-(+)-2-[*N*-(5'-Bromosalicylidene)amino]-1-butanol (47). Yellow solid (0.49 g, 99 %); mp 57-59 ^{0}C; $[\alpha]^{25}_{D}$= +22.65^{o} (c= 0.064, CH_2Cl_2). IR (KBr) 3284, 2925, 2872, 1633, 765 and 627 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.26(s, 1H), 7.39-7.32(m, 2H), 6.81(dd, 1H, J_1= 2.6 Hz, J_2= 6.8 Hz), 3.80-3.60 (m, 2H), 3.26-3.12(m, 1H), 1.72-1.48 (m, 2H), 0.89(t, 3H, J= 7.4 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.58, 160.94, 135.35, 133.83, 120.08, 119.40, 110.19, 73.34, 65.90, 25.14 and 10.58 ppm. Anal. calcd. for $C_{11}H_{14}NO_2Br$: C, 48.52; H, 5.14. Found: C, 48.58; H, 5.18.

(*S*)-(+)-2-[5'-Bromosalicylidene)amino]-1-propanol (48). Yellow solid (0.32 g, 56%); mp 49-51 ^{o}C; $[\alpha]^{25}_{D}$= +19.00^{o} (c= 0.051, CH_2Cl_2). IR (KBr) 3380, 2930, 2870, 1633 and 625 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.29(s, 1H), 7.40-7.30(m, 2H), 6.82(d, 1H, J= 7.8 Hz), 3.76-3.40(m, 3H), 1.25(d, 3H, J= 6.4 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.30, 160.41, 134.78, 133.23, 119.50, 118.91, 109.58, 66.71, 66.09 and 18.03 ppm. Anal. calcd. for $C_{10}H_{12}NO_2Br$: C,46.51; H, 4.65. Found: C, 46.54; H, 4.67.

(*R*)-(+)-2-[*N*-(3',5'-Di-bromosalicylidene)amino]-1-propanol (49). Yellow solid (0.25 g, 81%); mp 138-140 ^{o}C; $[\alpha]^{25}_{D}$= +29.70^{o} (c=0.00303, CH_2Cl_2). IR (KBr) 3274, 2963, 2847, 1650, 754 and 692 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.19(s, 1H), 7.66(d, 1H, J= 2.4 Hz), 7.30(d, 1H, J= 2.4 Hz), 4.16-3.99(tq, 1H, J_1= 3.8 Hz and J_2= 6.8 Hz), 3.72(dd, 1H, J_1= 15.1 Hz and J_2= 3.6 Hz), 3.52(dd, 1H, J_1= 12.4 Hz and J_2= 7.2 Hz), 1.28(d, 3H, J= 6.2 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.11, 161.92, 138.33, 133.25, 118.66, 114.23, 107.42, 66.20, 63.70, 39.98, 39.56 and 20.90 ppm. Anal. calcd. for $C_{10}H_{11}NO_2Br_2$: C, 35.60; H, 3.26. Found: C, 35.64; H, 3.30.

(*R*)-(-)-2-[*N*-(3',5'-Dibromosalicylidene)amino]-2-propanol (50). Yellow solid (0.57 g, 98%); mp 125-127 ^{o}C; $[\alpha]^{25}_{D}$= -30.88^{o} (c=0.0014, CH_2Cl_2). IR (KBr) 3350, 2980, 1658, 1143, 1046, 870 and 695 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.85(s, 1H), 7.30(d, 1H, J= 2.2 Hz), 7.00(d, 1H, J= 2.2 Hz), 3.70-3.56(m, 1H), 3.33(dd, 1H, J_1= 3.6 Hz and J_2= 12.2 Hz), 3.15(dd, 1H, J_1= 7.0 Hz and J_2= 12.4 Hz), 0.90(d, 3H, J= 2.0 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.90, 162.60, 137.92, 133.17, 118.08, 114.43, 106.15, 65.59, 62.73 and 20.92 ppm. Anal. calcd. for $C_{10}H_{11}NO_2Br_2$: C, 35.60; H, 3.26. Found: C, 35.62; H, 3.29.

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