Supplementary Material (ESI) for New Journal of Chemistry

A chemo-enzymatic synthesis of chiral secondary alcohols bearing sulfur-containing functionality

Qihui Chen , Ke Wang and Chengye Yuan*

Supplementary information

All reagents were used as purchased. Column chromatography was performed with silica gel (300-400 mesh). All yields given refer to isolated yields. IR spectra were obtained on a Shimadzu IR-440 spectrometer. ^{1}H NMR (300 MHz) was registered on 300 M spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. ^{13}C NMR (100 MHz) was recorded on 400 M spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. All reactions were monitored with the aid of TLC. The optical rotation values were determined by polarimeter (J-S P-1030). The enantiomeric excess value of product was determined by HPLC (Waters) with chiral column (CHIRALPAK OJ or CHIRALPAK AD-H or CHIRALPAK OD or CHIRALPAK AS).

General procedure for bioreduction of sulfur-containing alcohols by baker's yeast in diisopropyl ether/minor water solvent system

To a 25 mL round-bottomed flask equipped with a magnetic stir bar were added 1g baker's yeast, 10mL isopropyl ether and 0.7mL water. The solution was stirred 5 minutes, after which each β-keto sulfone **1a** (198mg, 1mmol) was placed in. The mixture was stirred at 30℃ and monitored by TLC. Four hours later, the mixture was filtered, the filtrate was removed under reduced pressure and residue was subjected to flash chromatography on silica gel (petroleum : EtOAc=1:1) to afford a colourless oil **2a,** 198mg, yield: 99%, ee: 99%.

(S)-1-phenylsulfonylpropan-2-ol, **2a** was obtained as a colourless oil, 198mg, yield: 99%, E.e = 99% (Using AD-H column, hexane/^{i}PrOH=80/20, 0.7mL/min,), $[\alpha]_D^{25}$= +20 (*c* 1.4, $CHCl_3$); Lit[1]: $[\alpha]_D^{20}$ = +15.7 (*c* 1.00, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.89-7.93 (2H, m), 7.54-7.69 (3H, m), 4.28-4.33 (1H, m), 3.45 (1H, s), 3.12-3.27 (2H, m), 1.22 (3H, d, *J*=6Hz).

(S)-1-(4-methylphenylulfonyl)propan-2-ol, **2b** was obtained as a colourless oil, 200mg, yield: 95%, E.e = 99% (Using AD-H column, hexane/^{i}PrOH=60/40, 0.7mL/min), $[\alpha]_D^{22}$= +18 (*c* 0.97, $CHCl_3$); Lit[2]: $[\alpha]_D^{20}$ = +10 (*c* 1.00, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.74 (2H, d, *J*=9 Hz), 7.32 (2H, d, *J*=9 Hz), 4.17-4.28 (1H, m), 3.04-3.19 (3H,m), 2.39 (3H, s), 1.16 (3H, d, *J*=6Hz).

(S)-1-(4-methoxyphenylsulfonyl)propan-2-ol, **2c** was obtained as a colourless oil, 182mg, yield: 85% , E.e = 99% (Using AD-H column, hexane/^{i}PrOH=80/20, 0.7mL/min, retention time: (S)-enantiomer, 21.85 min, (R)-enantiomer, 23.07 min), $[\alpha]_D^{21}$ = +15 (*c* 1.33, $CHCl_3$); Lit[3]: $[\alpha]_D$ = +4.8 (*c* 1.00, $CHCl_3$); δ_H(300 MHz, $CDCl_3$,

Me_4Si) 7.02 (2H, d, *J*=9 Hz), 7.83 (2H, d, *J*=9 Hz), 4.22-4.29 (1H, m), 3.86 (3H, s), 3.32 (1H, s), 3.08-3.23 (2H, m), 1.21 (3H, d, *J*=6Hz).

(S)-1-(4-nitrophenylsulfonyl)propan-2-ol, **2d** was obtained as a light yellow liquid (Found: C, 44.58; H, 4.61; N, 5.38. $C_9H_{11}NO_5S$ requires: C, 44.08; H, 4.52; N, 5.71.), 60mg, yield: 47%, E.e = 96% (Using AD-H column, hexane/^{i}PrOH=60/40, 0.7mL/min, retention time: (S)-enantiomer, 15.82 min, (R)-enantiomer, 13.95 min), $[\alpha]_D^{21}$ = +13 (*c* 0.98, $CHCl_3$) ; δ_H(300 MHz, $CDCl_3$, Me_4Si) 8.42 (2H, d, *J*=9 Hz), 8.14 (2H, d, *J*=9 Hz), 4.38-4.43 (1H, m), 3.19-3.36 (2H,m), 2.66 (1H, s), 1.26 (3H, d, *J*=6Hz); δ_C(100 MHz, $CDCl_3$, Me_4Si) 150.10, 145.17, 129.58, 124.55, 63.51, 62.58, 22.93; ν_{max} /cm^{-1} 3537, 3398, 3115, 2979, 2930, 1608, 1535, 1351, 1299, 1143, 1083, 855, 742 ; m/z(EI) 246 (3, M^++1), 230 (10), 186 (22), 170 (5), 136 (11), 122(34), 106 (13), 75 (36), 59 (100), 50 (34), 45 (35), 41(43%).

(S)-1-(4-chlorophenylsulfonyl)propan-2-ol, **2e** was obtained as a colourless oil (Found: C, 46.02; H, 4.80. $C_9H_{11}ClO_3S$ requires: C, 46.06; H, 4.72.), 154mg, yield: 77%, E.e = 99% (Using AD-H column, hexane/^{i}PrOH=80/20, 0.7mL/min, retention time: (S)-enantiomer, 9.17 min, (R)-enantiomer, 8.18 min), $[\alpha]_D^{21}$ = +15 (*c* 1.1, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.85 (2H, d, *J*=9 Hz), 7.54 (2H, d, *J*=9 Hz), 4.27-4.34 (1H, m), 3.11-3.28 (3H, m), 1.24 (3H, d, *J*=6Hz); δ_C(100 MHz, $CDCl_3$, Me_4Si) 140.89, 137.86, 129.80, 129.48, 63.54, 62.46, 22.69; ν_{max} /cm^{-1} 3499, 2968, 2927, 2918, 1587, 1577, 1477, 1313, 1149, 1085, 822, 763, 749, 628; m/z(EI) 235 (2, M^++1), 217 (4), 190 (12), 175 (23), 159 (14), 125(34), 111 (60), 75 (61), 59 (100),50 (27), 41 (39%).

(S)-1-phenylsulfonylbutan-2-ol, **2f** was obtained as a colourless oil, 106mg, yield: 91%, E.e = 92% (Using AS column, hexane/^{i}PrOH=90/10, 0.7mL/min), $[\alpha]_D^{23}$ = +16 (*c*0.94, $CHCl_3$); Lit[4]: $[\alpha]_D$ = +1.2 (*c* 0.99, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.89-7.96 (2H, m), 7.57-7.71 (3H, m), 4.08-4.10 (1H, m), 3.44 (1H, s),3.17-3.30 (2H, m), 1.48-1.59 (2H, m), 0.92 (3H, t, *J*=6Hz).

(S)-1-phenylsulfonylpentan-2-ol, **2g** was obtained as a colourless oil (Found: C, 57.95; H, 7.14; $C_{11}H_{16}O_3S$ requires: C, 57.87; H, 7.06.), 80mg, yield: 74%, E.e = 70% (Using AS column, hexane/^{i}PrOH=70/30, 0.7mL/min, retention time: (S)-enantiomer, 18.81 min, (R)-enantiomer, 16.65 min), $[\alpha]_D^{25}$ = +11 (*c* 1.00, $CHCl_3$) ; δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.93-7.96(2H, m), 7.58-7.73 (3H, m), 4.18-4.20 (1H, m), 3.38(1H, s), 3.16-3.23 (2H, m), 1.32-1.44 (4H, m), 0.88 (3H, t, *J*=6Hz); δ_C(100 MHz, $CDCl_3$, Me_4Si) 139.42, 133.99, 129.45, 127.89, 65.72, 62.35, 38.54, 18.22, 13.69; ν_{max} /cm^{-1} 3507, 2963, 2934, 2875, 1448, 1304, 1145, 1086, 788, 750, 689; m/z(EI) 229 (13, M^++1), 211 (13), 185 (47), 141 (56), 125 (14), 77 (100), 69 (22), 51 (30), 41 (37%).

(S)-1-phenylthiopropan-2-ol, **2i** was obtained as a colourless oil, 31mg, yield: 97%**,** E.e = 95% (Using AD column, hexane/^{i}PrOH=80/20, 0.7mL/min), $[\alpha]_D^{24}$ = +35 (*c* 1.03, $CHCl_3$); Lit[1]: $[\alpha]_D^{20}$ = +54.7 (*c* 1.00, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si)

7.19-7.41 (5H, m), 3.83-3.85 (1H, m), 3.10-3.16(1H, m), 2.80-2.88 (1H, m), 2.49 (1H, s), 1.27 (3H, d, *J*=6Hz).

(S)-1-(4-methylphenyl)thiopropan-2-ol, **2j** was obtained as a colourless oil, 31mg, yield: 96%, E.e = 99% (Using AD column, hexane/^{i}PrOH=90/10, 0.7mL/min), $[\alpha]_D^{24}$ = +60 (*c* 1.03, $CHCl_3$); Lit[5]: it's enantiomer, $[\alpha]_D$ =-60.1 (*c* 0.7, CH_2Cl_2); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.31(2H, d, *J*=8 Hz), 7.11 (2H, d, *J*=8 Hz), 3.78-3.81 (1H, m), 3.04-3.10 (1H,m), 2.74-2.81 (1H, m), 2.53 (1H, s), 2.33 (3H, s), 1.25 (3H, d, *J*=6Hz).

(S)-1-(4-methoxyphenyl)thiopropan-2-ol, **2k** was obtained as a colourless oil (Found: C, 60.39; H, 7.15; $C_{10}H_{14}O_2S$ requires: 60.57; H, 7.12.), 33mg, yield: 86%, E.e = 99% (Using AD column, hexane/^{i}PrOH=90/10, 0.7mL/min, retention time: (S)-enantiomer, 11.93 min, (R)-enantiomer, 14.78 min), $[\alpha]_D^{24}$ = +54 (*c* 1.07, $CHCl_3$) ; δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.36-7.40 (2H, m), 6.83-6.87 (2H, m), 3.74-3.80 (4H, m), 2.96-3.02 (1H,m), 2.68-2.75 (1H, m), 2.61 (1H, s), 1.23 (3H, d, *J*=6Hz); δ_C(100 MHz, $CDCl_3$, Me_4Si) 159.32, 133.78, 125.31, 114.78, 65.41, 55.36, 45.65, 21.78; ν_{max} /cm^{-1} 3401, 2970, 2837, 1594, 1495, 1286, 1246, 1033, 827 ; m/z(EI) 198 (13, M^+), 197 (70), 154 (47), 139 (79), 125 (22), 109 (41), 95 (16), 77 (18), 63 (20), 45(100%).

(S)-1-(4-chlorophenyl)thiopropan-2-ol, **2l** was obtained as a colourless oil, 29mg, yield: 67%, E.e = 98% (Using AD column, hexane/^{i}PrOH=90/10, 0.7mL/min), $[\alpha]_D^{24}$ = +34 (*c* 0.67, $CHCl_3$); Lit[6]; δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.32 (2H, d, *J*=9 Hz), 7.26 (2H, d, *J*=9 Hz), 3.80-3.88 (1H, m), 3.05-3.10 (1H, m), 2.81-2.88 (1H, m), 2.38 (1H, s), 1.27 (3H, d, *J*=6Hz).

(S)-1-(4-nitrophenyl)thiopropan-2-ol, **2m** was obtained as a light yellow liquid (C, 50.71; H, 5.15; N, 6.48; $C_9H_{11}NO_3S$ requires C, 50.69; H, 5.20; N, 6.57.), 36mg, yield: 92%, E.e = 96% (Using AD-H column, hexane/^{i}PrOH=80/20, 0.7mL/min, retention time: (S)-enantiomer, 13.35 min, (R)-enantiomer, 16.11 min), $[\alpha]_D^{25}$ = +21 (*c* 0.90, $CHCl_3$) ;δ_H(300 MHz, $CDCl_3$, Me_4Si) 8.14 (2H, d, *J*=9 Hz), 7.41 (2H, d, *J*=9 Hz), 4.03-4.05 (1H, m), 3.19-3.25 (1H,m), 3.01-3.09 (1H,m), 2.19 (1H, s), 1.37 (3H, d, *J*=6Hz); δ_C(100 MHz, $CDCl_3$, Me_4Si) 146.77, 145.35, 126.91, 123.98, 66.16, 41.22, 22.48; ν_{max} /cm^{-1} 3180, 2973, 2927, 1579, 1507, 1338, 1091, 854, 838, 741; m/z (EI) 213 (35, M^+), 169 (50), 152 (23), 139 (15), 122 (19), 78 (7), 45 (100%).

(S)-1-(4-bromophenyl)thiopropan-2-ol, **2n** was obtained as a light yellow liquid (C, 43.76; H, 4.45; $C_9H_{11}BrOS$ requires C, 43.74; H, 4.49.), 30mg, yield: 73%, E.e = 97% (Using AD column, hexane/^{i}PrOH=90/10, 0.7mL/min, retention time: (S)-enantiomer, 10.68 min, (R)-enantiomer, 12.13 min), $[\alpha]_D^{24}$ = +26 (*c* 1.00, $CHCl_3$) ; δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.41(2H, d, *J*=9 Hz), 7.25 (2H, d, *J*=9 Hz), 3.84-3.86 (1H, m), 3.06-3.12 (1H, m), 2.81-2.88 (1H, m), 2.36 (1H, s), 1.27 (3H, d, *J*=6Hz); δ_C(100 MHz, $CDCl_3$, Me_4Si) 134.68, 132.06, 131.42, 120.44, 65.67, 43.52, 22.01; ν_{max} /cm^{-1} 3387, 2972, 2926, 1475, 1092, 1070, 1008, 808; m/z (EI) 248 (14, M^+), 204 (41), 122 (20), 108 (20), 77 (9), 69(6), 45 (100%).

General procedure of preparation of four stereoisomers of substituted phenylsulfinylpropan-2-ol

To a 25 mL round-bottomed flask equipped with a magnetic stir bar were added 3g baker's yeast, 30ml isopropyl ether and 2.1 ml water, the solution was stirred 5 min, after which phenylsulfinlypropan-2-one **3a** (420mg, 2.3 m mol) was placed in. The mixture was stirred at 30℃; the reaction was monitored by TLC. 80 min later, the mixture was filtered, the solvent was removed under reduced pressure and residue was subjected to flash chromatography on silica gel (petroleum : EtOAc=1:1~1:2) to afford the desired product (Ss)-phenylsufinylpropan-2-one **4a** and (Rs, Sc)-phenylsulfinylpropan-2-ol **5a** respectively, oxidation by triacetoxyperiodinane, **5a** was converted to (Ss)-phenylsufinylpropan-2-one **6a**.
(Ss)-Phenylsulfinylpropan-2-ol **7a** was obtained by reducing (Ss)-phenylsulfinylpropan-2-one **4a** by NaBH4, followed by CALB catalyzed kinetic resolution of **7a** afforded acetate of **8a** and (Ss, Sc)-phenylsulfinylpropan-2-ol **9a**.(General procedures for kinetic resolution of phenylsulfinylpropan-2-ol: 100mg CALB, 5mL $^{i}Pr_2O$, 1mL $CH_3COOCHCH2$ were used for 1 m mol substrate, 24h later, the acetate of **8a** and remaining alcohol **9a** were obtained.) Transesterification of **8a** catalyzed by $BF3.Et_2O$ in methanol afforded (Ss, Rc)-phenylsulfinylpropan-2-ol **10a**, similarly, (Rs, Sc)-phenylsulfinylpropan-2-ol **13a** and (Rs, Rc)-phenylsulfinylpropan-2-ol **14a** were prepared.

(Ss)-Phenylsulfinylpropan-2-one, **4a** was obtained as a colourless solid, mp:61-63℃, 176mg, yield: 42%, $[\alpha]_D^{26}$= -211 (*c* 1.76, $CHCl_3$); Lit[1]: $[\alpha]_D^{20}$= -256 (*c* 1.5, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.54-7.68 (5H, m), 3.78-3.90 (2H, m), 2.25 (3H, s).

(Rs, Sc)-Phenylsulfinylpropan-2-ol **5a** was obtained as a colourless solid, mp:137-140 ℃, 160 mg, yield: 38%, $[\alpha]_D^{26}$=+295 (*c* 1.26, $CHCl_3$); Lit[1]: $[\alpha]_D^{20}$= +334 (*c* 1.33, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.54-7.65 (5H, m), 4.34-4.38 (1H, m), 3.98 (1H, s), 3.05-3.13 (1H, m), 2.64-2.69 (1H, m), 1.24-1.34 (3H, m).

(Rs)-Phenylsulfinylpropan-2-one **6a** was obtained as a colourless solid, mp:58-60℃, 147 mg, yield: 92%, $[\alpha]_D^{27}$=+194 (*c* 0.77, $CHCl_3$); Lit[3]: $[\alpha]_D^{22}$= +269 (*c* 0.8, CH_3OH); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.54-7.68 (5H, m), 3.78-3.90 (2H, m), 2.25 (3H, s).

(Ss)-Phenylsulfinylpropan-2-ol, **7a** was obtained as a colourless solid (C, 58.53; H, 6.37; $C_9H_{12}O_2S$ requires C, 58.67; H, 6.56.), mp:90-100℃, 150mg, yield: 92%, $[\alpha]_D^{26}$= -226 (*c* 1.04, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.54-7.68(5H, m), 4.36-4.52 (1H, m), 3.88-4.05 (1H, m), 2.96-3.11 (1H, m), 2.65-2.82 (1H, m), 1.24-1.33 (3H, m); δ_C(100 MHz, $CDCl_3$, Me_4Si) 143.90, 131.23(m), 129.43(m), 123.90(m), 64.43(m), 62.65(m), 23.28(m); ν_{max} /cm^{-1} 3328, 2969, 2926, 1445, 1121, 1086, 1043, 1015, 997, 750, 691, 485; m/z (ESI): 185($M+H^+$).

(Ss, Rc)-1-Phenylsulfinylmethylethyl acetate, **8a** was obtained as a colourless oil (C, 58.19; H, 6.35; $C_{11}H_{14}O_3S$ requires C, 58.38; H, 6.24.), 112mg, yield: 58%, $[\alpha]_D^{28}$=-168 (*c* 0.60, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.51-7.68 (5H, m), 5.36-5.39 (1H, m), 2.95-2.98 (2H, m), 2.08 (3H, s), 1.38-1.41 (3H, m); δ_C(100 MHz, $CDCl_3$, Me_4Si)169.96, 144.20, 131.20, 129.39, 123.86, 65.64, 64.12, 21.06, 20.24; ν_{max} /cm^{-1} 3463, 3058, 2982, 2936, 1750, 1444, 1373, 1230, 1128, 1091, 958, 752, 692; m/z (ESI): 227 (M^++H^+), 249 (M^++Na^+), 281 (M^++Na^++MeOH).

(Ss, Sc)-Phenylsulfinylpropan-2-ol, **9a** was obtained as a colourless oil, 52mg, yield: 35%, E.e>99%, syn/anti= 26:1, retention time: 22.99min, $[\alpha]_D^{28}$= -248 (*c* 1.04, $CHCl_3$); Lit[7]: $[\alpha]_D$= -260 (*c* 1.0, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.53-7.68 (5H, m), 4.39-4.46 (1H, m), 4.10 (1H, s), 3.00-3.08 (1H, m), 2.77-2.82 (1H, m), 1.33 (3H, d, *J*=6 Hz).

(Ss, Rc)-Phenylsulfinylpropan-2-ol, **10a** was obtained as a colourless solid, mp:135-137℃, 56mg, yield: 95%, E.e=99%, syn/anti= 1:38, retention time: 17.67min, $[\alpha]_D^{28}$= -217 (*c* 0.94, $CHCl_3$); Lit[3]: $[\alpha]_D^{22}$= -287 (*c* 1.6, CH_3OH); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.53-7.66(5H, m), 4.37-4.44 (1H, m), 3.91 (1H, s), 2.99-3.07 (1H, m), 2.70-2.75 (1H, m), 1.26 (3H, d, *J*=6 Hz).

(Rs)-Phenylsulfinylpropan-2-ol, **11a** was obtained as a colourless solid (C, 58.57; H, 6.58; $C_9H_{12}O_2S$ requires C, 58.67; H, 6.56.), mp:90-95℃, 40mg, yield: 92%, $[\alpha]_D^{27}$=+233 (*c* 1.10, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.54-7.68 (5H, m), 4.36-4.52 (1H, m), 3.88-4.05 (1H, m), 2.96-3.11 (1H, m), 2.65-2.82 (1H, m),1.24-1.33 (3H, m); δ_C(100 MHz, $CDCl_3$, Me_4Si) 143.92, 131.24(m), 129.45(m), 123.90(m), 64.45(m), 62.66(m), 23.31; ν_{max} /cm^{-1} 3327, 2969, 2926, 1445, 1121, 1086, 1043, 1015, 996, 749, 691, 484; m/z (ESI) 185 ($M+H^+$).

(Rs, Sc)-1-Phenylsulfinylmethylethyl acetate, **12a** was obtained as a colourless oil (C, 58.30; H, 6.42; $C_{11}H_{14}O_3S$ requires C, 58.38; H, 6.24.), 32mg, yield: 41%, $[\alpha]_D^{27}$=+102 (*c* 0.58, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.51-7.67 (5H, m), 5.16-5.23 (1H, m), 3.16-3.23 (1H, m), 2.93-3.11 (1H, m), 2.08 (3H, s), 1.39 (3H, d, *J*=6 Hz); δ_C(100 MHz, $CDCl_3$, Me_4Si) 169.94, 143.56, 131.21(m), 129.36(m), 124.02(m), 65.46(m), 63.29(m), 21.07(m), 20.21; ν_{max} /cm^{-1} 3059, 2981, 2935, 1739, 1445, 1374, 1238, 1090, 1044, 958, 751, 692, 545; m/z (ESI) 227 ($M+H^+$).

(Rs, Sc)-Phenylsulfinylpropan-2-ol, **13a** was obtained as a colourless solid, mp:137-140℃, 20mg, yield: 56%, E.e=99%, syn/anti= 1:29, retention time: 13.52min, $[\alpha]_D^{27}$=+317 (*c* 0.64, $CHCl_3$); Lit[3]: $[\alpha]_D^{20}$= +334 (*c* 1.33, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.54-7.65 (5H, m), 4.32-4.39 (1H, m), 4.02 (1H, s), 3.05-3.12 (1H, m), 2.65-2.70 (1H, m), 1.24-1.33 (3H, m).

(Rs, Rc)-Phenylsulfinylpropan-2-ol, **14a** was obtained as a colourless oil (C, 58.35; H, 6.53; $C_9H_{12}O_2S$ requires C, 58.67; H, 6.56.), 13mg, yield: 95, E.e>99%, syn/anti= 12:1, retention time: 20.09min, $[\alpha]_D^{28}$=+204 (*c* 0.22, $CHCl_3$); δ_H(300 MHz, $CDCl_3$,

Me_4Si) 7.54-7.68 (5H, m), 4.49-4.53 (1H, m), 3.85 (1H, s), 2.96-3.04 (1H, m), 2.77-2.83 (1H, m), 1.24-1.34 (3H, m); δ_C(100 MHz, $CDCl_3$, Me_4Si) 143.90, 131.43, 129.50, 123.82, 65.23, 63.63, 23.31; ν_{max} /cm^{-1} 3369, 2971, 1445, 1126, 1087, 1019, 997, 751, 692; m/z (ESI) 207 ($M+Na^+$).

(Ss)-4-Chlorophenylsulfinylpropan-2-one, **4b** was obtained as a colourless solid, mp:76-78℃, 207mg, yield: 39%, $[\alpha]_D^{27}$= -207 (*c* 1.04, $CHCl_3$); Lit[8]: $[\alpha]_D^{23}$= -231 (*c* 1.16, CH_3OH); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.51-7.63 (4H, m), 3.80-3.90 (2H, m), 2.26 (3H, s).

(Rs, Sc)-4-Chlorophenylsulfinylpropan-2-ol, **5b** was obtained as a colourless solid, mp:95-110℃, 206mg, yield: 41%, $[\alpha]_D^{27}$=+219 (*c* 0.30, $CHCl_3$); Lit[8]; δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.52-7.62 (4H, m), 4.34-4.40 (1H, m), 3.90 (1H, s), 3.00-3.08 (1H, m), 2.65-2.70 (1H, m), 1.27 (3H, d, *J*=6 Hz).

(Rs)-4-Chlorophenylsulfinylpropan-2-one, **6b** was obtained as a colourless solid (C, 49.61; H, 4.25; $C_9H_9ClO_2S$ requires C, 49.89; H, 4.19.), mp:78-80℃, 163mg, yield: 87%, $[\alpha]_D^{26}$=+157 (*c* 0.60, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.61 (2H, d, *J*=9 Hz), 7.53 (2H, d, *J*=9 Hz), 3.79-3.89 (2H, m), 2.26 (3H, s); δ_C(100 MHz, $CDCl_3$, Me_4Si) 199.10, 141.41, 137.87, 129.74, 125.48, 68.47, 31.99; ν_{max} /cm^{-1} 2959, 2909, 1701, 1477, 1351, 1287, 1162, 1087, 1054, 1014, 813, 743, 493, 442; (m/z (ESI) 216 (M).

(Ss)-4-Chlorophenylsulfinylpropan-2-ol, **7b** was obtained as a colourless oil (C, 49.20; H, 5.32; $C_9H_{11}ClO_2S$ requires C, 49.43; H, 5.07.), 93mg, yield: 85%, $[\alpha]_D^{26}$=-254 (*c* 0.93, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.52-7.63 (4H, m), 4.34-4.49 (1H, m), 3.63 (1H, s), 2.96-3.09 (1H, m), 2.64-2.95 (1H, m), 1.25-1.34 (3H, m); δ_C(100 MHz, $CDCl_3$, Me_4Si) 141.78 (m), 137.38 (m), 129.65, 125.38, 64.44, 62.24, 23.12; ν_{max} /cm^{-1} 3325, 3086, 2976, 2934, 1477, 1391, 1371, 1189, 1125, 1087, 1019, 1010, 816, 743, 496; m/z (ESI) 241($M+Na^+$).

(Ss, Rc)-1-(4-Chlorophenyl)sulfinylmethylehtyl acetate, **8b** was obtained as a colourless oil, 39mg, yield: 36%, $[\alpha]_D^{27}$=-137 (*c* 0.98, $CHCl_3$); δ_H(300 MHz, CDCl3, Me4Si) 7.51-7.62 (4H, m), 5.35-5.39 (1H, m), 2.94-2.96 (2H, m), 2.09 (3H, s), 1.39 (3H, d, *J*=6 Hz); δ_C(100 MHz, $CDCl_3$, Me_4Si) 169.93, 142.71, 137.46, 129.69, 125.30, 65.51, 64.17, 21.04, 20.03; ν_{max} /cm^{-1} 3465，3083，2982，2936，1741，1477，1391，1374，1228，1129，1086，1049，1012，827，742; (m/z (ESI) 261 (M^++H^+), 283 (M^++Na^+), 315 (M^++Na^++MeOH); HRMS (MALDI): 261.03467; $C_{11}H_{14}O_3SCl$ (M^++1) requires 261.0355.

(Ss, Sc)-4-Chlorophenylsulfinylpropan-2-ol, **9b** was obtained as a colourless oil (C, 49.11; H, 5.00; $C_9H_{11}ClO_2S$ requires C, 49.43; H, 5.07.), 58mg, yield: 62, E.e>99%, syn/anti= 53:1, retention time: 61.50min, $[\alpha]_D^{27}$=-219 (*c* 0.97, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.51-7.63 (4H, m), 4.42-4.48 (1H, m), 3.73 (1H, s), 2.96-3.04 (1H, m), 2.76-2.82 (1H, m), 1.33 (3H, d, *J*=6 Hz); δ_C(100 MHz, $CDCl_3$, Me_4Si) 142.22, 137.62,

129.74, 125.34, 64.75, 64.16, 23.24; ν_{max} /cm^{-1} 3369, 2972, 1477, 1392, 1091, 1023, 1010, 820, 743, 505; m/z (ESI) 219 (M^++H^+), 459 ($2M^+$+Na^+).

(Ss, Rc)-4-Chlorophenylsulfinylpropan-2-ol, **10b** was obtained as a colourless solid (C, 49.15; H, 5.09; $C_9H_{11}ClO_2S$ requires C, 49.43; H, 5.07.), mp:100-108℃, 12mg, yield: 95, E.e>99%, syn/anti= 1:19, retention time: 38.61min, $[\alpha]_D^{26}$=-268 (*c* 0.60, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.52-7.61 (4H, m), 4.35-4.39 (1H, m), 3.90 (1H, s), 3.01-3.10 (1H, m), 2.64-2.71 (1H, m), 1.25-1.28 (3H, m); δ_C(100 MHz, $CDCl_3$, Me_4Si) 141.42, 137.41, 129.72, 125.43, 62.96, 62.85, 23.26; ν_{max} /cm^{-1} 3327, 2972, 1900, 1475, 1390, 1376, 1314, 1119, 1084, 1049, 1020, 1007, 814, 742, 500; m/z (ESI) 241 (M^++Na^+).

(Rs)-4-Chlorophenylsulfinylpropan-2-ol, **11b** was obtained as a colourless oil (C, 49.01; H, 4.98; $C_9H_{11}ClO_2S$ requires C, 49.43; H, 5.07.), 115mg, yield: 92%, $[\alpha]_D^{28}$=+225(*c* 1.00, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.52-7.62 (4H, m), 4.38-4.46 (1H, m), 3.86-4.15 (1H, m), 2.98-3.05 (1H, m), 2.68-2.82 (1H,m), 1.26-1.41 (3H, m); δ_C(100 MHz, $CDCl_3$, Me_4Si) 141.72(m), 137.35(m), 129.60(m), 125.34, 64.43(m), 62.18, 23.15(m); ν_{max} /cm^{-1} 3325, 3086, 2976, 2934, 1477, 1391, 1371, 1189, 1125, 1087, 1019, 1010, 816, 743, 496; m/z(ESI) 219 (M+H^+).

(Rs, Rc)-1-(4-Chlorophenyl)sulfinylmethylehtyl acetate, **12b** was obtained as a colourless oil, 79mg, yield: 57%, $[\alpha]_D^{27}$=+110 (*c* 1.00, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.50-7.62 (4H, m), 5.17-5.19 (1H, m), 3.14-3.22 (1H, m),2.92-2.98 2.09 (1H, m), 1.95-1.96 (3H, m), 1.37-1.40 (3H, m); δ_C(100 MHz, $CDCl_3$, Me_4Si) 169.93, 142.08, 137.52, 129.64(m), 125.62, 65.10, 62.53, 20.93, 20.21; ν_{max} /cm^{-1} 2967, 2943, 1739, 1477, 1373, 1238, 1091, 1045, 1012, 823, 742, 504; m/z (ESI) 261 (M+H^+); HRMS (MALDI): 283.01662; $C_{11}H_{13}O_3SClNa$ (M^++23) requires 283.01762.

(Rs, Sc)-4-Chlorophenylsulfinylpropan-2-ol, **13b** was obtained as a colourless solid, mp:95-110℃, 38mg, yield: 33, E.e=93%, syn/anti= 1:8915, retention time: 42.69min, $[\alpha]_D^{27}$= +245 (*c* 0.73, $CHCl_3$); Lit[8]; δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.52-7.62 (4H, m), 4.33-4.38 (1H, m), 3.75 (1H, s), 3.03-3.11 (1H, m), 2.63-2.68 (1H, m), 1.26 (3H, d, *J*=6 Hz).

(Rs, Rc)-4-Chlorophenylsulfinylpropan-2-ol, **14b** was obtained as a colourless oil (C, 49.22; H, 4.95; $C_9H_{11}ClO_2S$ requires C, 49.43; H, 5.07.), 42mg, yield: 95, E.e=98%, syn/anti= 12:1, retention time: 69.91min, $[\alpha]_D^{26}$=+196 (*c* 0.80, $CHCl_3$); δ_H(300 MHz, $CDCl_3$, Me_4Si) 7.51-7.63 (4H, m), 4.39-4.43 (1H, m), 3.83 (1H, s), 2.98-3.06 (1H, m), 2.76-2.82 (1H, m), 1.32-1.34 (3H, m); δ_C(100 MHz, $CDCl_3$, Me_4Si) 142.17, 137.61, 129.72, 125.35, 64.65, 64.26, 23.21; ν_{max} /cm^{-1} 3363, 2972, 1576, 1477, 1392, 1091, 1080, 1045, 1024, 1010, 820, 744, 504; m/z (ESI) 219 (M^++H^+), 459 ($2M^+$+Na^+).

References:

1 R. L. Crumble, B. S. Deol, J. E. Nemorin, D. D. Ridley, *Aust. J. Chem.* 1978, **31**, 1965;

2 P. Kielbasinski, M. Rachwalski, M. Mikolajczyk, M. A. H. Moelands, B. Zwanenburg, F. P. J. T. Rutjes, *Tetrahedron: Asymmetry,* 2005, **16**, 2157;

3 H. Ohta, Y. kato, G. Tsuchihashi, *J. Org. Chem*. 1987, **52**, 2735;

4 J. Hachtel, H-J. Gais, *Eur. J. Org. Chem.* 2000**,** 1457.

5 S. Singh, S. Kumar, S. S. Chimni, *Tetrahendron: Asymmetry* 2001, **12**, 2457;

6 S. Satwinder, K. Subodh, C. S. Singh, *Enantiomer* 2002**,** 231.

7 H.L. Holland, N. Ihasz, B.J. Lounsbery, *Can. J. Chem.* 2002, **80**, 640.

8 T. Fujitsawa, A. Fujimura, T. Sato, *Bull. Chem. Soc.* 1988, **61**, 1273.