Tetrahedron: *Asymmetry* 20 (2009) 2639–2645

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

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

Enantioselective Rh-catalyzed transfer hydrogenation of α-sulfonyloxy heteroaryl ketones; asymmetric synthesis of (*S*)-bufuralol

Se Hun Kwak [a,b], Do-Min Lee [a], Kee-In Lee [a,b,*]

[a] *Bio-Organic Science Division, Korea Research Institute of Chemical Technology, PO Box 107, Yusong, Taejon 305-600, Republic of Korea*
[b] *Department of Medicinal and Pharmaceutical Chemistry, University of Science and Technology, Gwahangno 113, Yusong, Taejon 305-333, Republic of Korea*

ARTICLE INFO

Article history:
Received 21 September 2009
Accepted 4 November 2009
Available online 26 November 2009

ABSTRACT

Asymmetric transfer hydrogenation of α-sulfonyloxy heteroaryl ketones mediated by Cp*RhCl[(*S*,*S*)-TsDPEN] using an azeotropic mixture of formic acid/triethylamine afforded the corresponding diol-2-monosulfonates in excellent yield with high enantioselectivity. This led to the asymmetric synthesis of (*S*)-bufuralol.

1. Introduction

Amino alcohols have been identified as rich resources in organic and medicinal chemistry. Amino alcohols are often found not only in the structural units of many building blocks, chiral auxiliaries, and ligands in organic transformations,[1] but also in the structural motifs of many biologically active compounds. In particular, optically active alcohols or amines containing heteroaryl moieties are of great importance as key intermediates for the synthesis of biologically active compounds, such as bufuralol, duloxetine, zileuton, MK-0417, and L-770644.[2] Much attention has been paid to the enantioselective preparation of chiral precursors under asymmetric catalysis, classical/enzymatic resolution and biotransformative pathways. A number of studies have disclosed the methods comprising of the oxazaborolidine-catalyzed reduction of ketones,[3] asymmetric hydrogenation of aminoketones,[4] and asymmetric epoxidation of allylic alcohols.[5] Moreover, there have been many reports on the synthesis of such an important class of compounds; however, the application has been rather limited to aromatic and olefinic ketones. Recently, heteroaryl-containing alcohols and amines have been prepared through biotransformation; lipase-mediated resolution of β-cyano-, γ-chloro-, and γ-azidoalcohols[6a–d], and Baker's yeast-mediated reduction of α-hydroxyketone derivatives.[6e,f]

Asymmetric transfer hydrogenation (ATH) has had its applications broadened to the enantioselective hydrogenation of unsaturated carbonyl and imine groups.[7] In general, ATH offers an operational simplicity, since the reaction does not involve molecular hydrogen and is insensitive to air oxidation, hence it proves particularly valuable in the scale-up synthesis of active pharmaceutical ingredients.[8] However, this approach has only rarely been used for simple heteroaryl ketones, mostly as the 2-acetyl analogues of furan, thiophene, and benzofuran.[9] Previously, we reported the asymmetric transfer hydrogenation of 2-tosyloxy-1-phenylethanone derivatives with TsDPEN-Rh catalyst in formic acid/triethylamine and further applications to the synthesis of β-adrenergic agonists.[10] In continuation of our earlier efforts toward the preparation of biologically important compounds, particularly those possessing a chiral aminoalcohol unit, we herein report an enantioselective Rh-catalyzed transfer hydrogenation of α-sulfonyloxy heteroaryl ketones and further elaborate to access the facile synthesis of (*S*)-bufuralol,[9c,11] a non-selective β-adrenergic antagonist.

2. Results and discussion

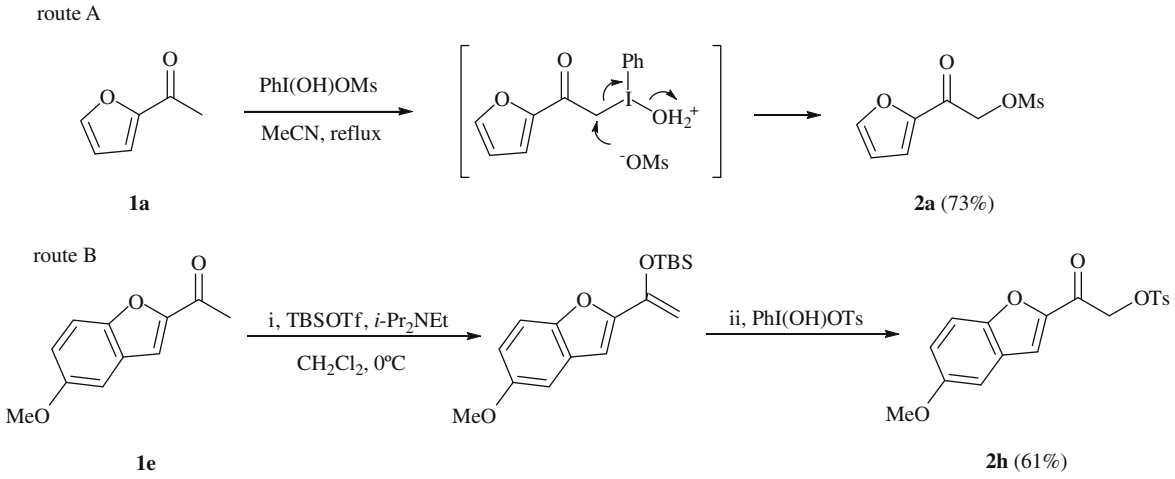
2.1. α-Sulfonyloxylation of heteroaryl ketones

The α-sulfonyloxy heteroaryl ketones were prepared by sulfonyloxylation of the corresponding ketones and their trimethylsilyl enol ethers with [hydroxy(tosyloxy)iodo]benzene (PhI(OH)OTs) or [hydroxy(mesyloxy)iodo]benzene (PhI(OH)OMs).[12] The starting ketones were either commercially available or easily accessible in a few steps.

Thus, 2-mesyloxy-1-(furan-2-yl)ethanone **2a** was conveniently prepared in 73% yield from the corresponding 2-acetylfuran **1a** with PhI(OH)OMs in refluxing acetonitrile (route A), as shown in Scheme 1. It is known that the α-mesyloxylation of methylketones is initiated by the electrophilic addition of $[PhI(OH)]^{+}OMs^{-}$ to enolizable ketones to give aldol adducts, followed by nucleophilic displacement by the nearby mesyloxy anion to result in the observed products. The above-mentioned procedure is quite general for the α-sulfonyloxylation of thiophene, benzofuran, and benzothiophene derivatives, however, the reaction of 1-(5-methoxybenzofuran-2-yl)ethanone **1e** with either PhI(OH)OTs or PhI(OH)OMs was problematic, resulting in very poor yield and several majorly decomposed products. A similar phenomenon was also observed

* Corresponding author. Tel.: +82 42 860 7186; fax: +82 42 860 7160.
E-mail address: kilee@krict.re.kr (K.-I. Lee).

0957-4166/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2009.11.002



Scheme 1. α-Sulfonyloxylation of heteroaryl ketones.

for substrates possessing an electron-donating group, such as **1g** and **1h**, and the reaction was not successful. Presumably, the electron-rich species hampered the initial formation of enol-tautomer, which is crucial for certain types of aldol condensation.

Alternatively, the reaction of PhI(OH)OMs with the TBS enolate of **1e** in dichloromethane furnished 2-mesyloxy-1-(5-methoxybenzofuran-2-yl)ethanone **2g** in 61% yield (route B). Thus, the limitation could be overcome indirectly by means of their silyl enolates, derived from the corresponding methylketones with TBSOTf, which were then trapped with either PhI(OH)OTs or PhI(OH)OMs to afford the desired α-sulfonyloxy ketones in moderate yields. Following the above-mentioned procedures, some heteroaryl ketones (Fig. 1) were prepared and readily used for the asymmetric transfer hydrogenation.

2.2. Asymmetric transfer hydrogenation of α-sulfonyloxy heteroaryl ketones

The Rh-catalyst, Cp*RhCl[(*S*,*S*)-TsDPEN], was prepared from the reaction of dichloro(pentamethylcyclopentadienyl)rhodium(III) dimer and (1*S*,2*S*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine in dichloromethane in the presence of triethylamine.[13] The formic acid/triethylamine (molar ratio = 5/2) azeotrope was prepared by double distillation of the mixtures.[14] Upon reduction of 1 mmol of **2a** with (*S*,*S*)-Rh (substrate/catalyst molar ratio = 500) and a formic acid/triethylamine mixture (molar ratio = 5/2, 0.2 mL), stirring in ethyl acetate (4 mL) for 1 h at ambient temperature resulted in (*R*)-**3a** in 92% yield with 98% enantiomeric excess (ee). It should be noted that the observed enantioselectivity was similar to that reported in the corresponding α-chloroketone.[9b] The ee values were measured by chiral HPLC analysis using a Daicel Chiralcel OD-H or OJ-H column. The racemic alcohols (±)-**3** were prepared by the sodium borohydride reduction of **2** in THF, and used as standards for ee determination.

We examined the 2- and 3-iomeric heterocyclic substrates differentiated by electronically demanding groups using the same protocol and the results are summarized in Table 1. For a given catalytic system, the value of enantioselectivity was not much sensitive to the structural patterns, although the yield did decrease in the cases of the 3-isomers. Only the reduction of 5-nitrobenzofuran **2f** showed a decrease in enantioselectivity when compared to those of the corresponding congeners **2h** and **2i**. This result indicates that an attractive interaction between arene ligand and heteroaryl substrate is still favorable, presumably due to the contribution of a relatively electron-rich substrate. The overall results again suggest that the reduction of heteroaryl ketones operates in the same way as that of aryl ketones. The Rh-catalyst performed effectively in the transfer hydrogenation of α-sulfonyloxy

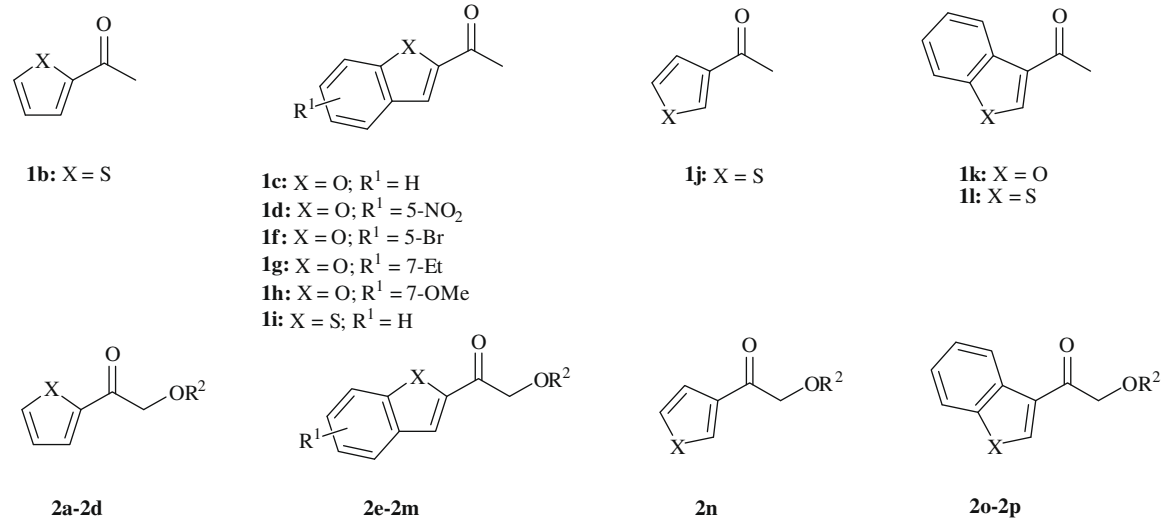
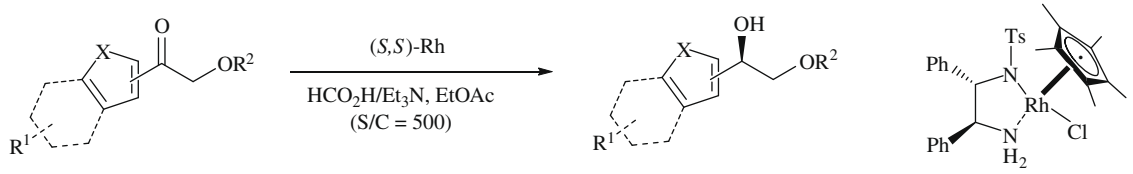


Figure 1. Substrates prepared for transfer hydrogenation. Route A: **2b** (72%), **2c** (81%), **2d** (87%), **2e** (69%), **2f** (66%), **2i** (62%), **2m** (60%), **2n** (58%), **2o** (62%), **2p** (64%). Route B: **2g** (61%); **2j** (52%); **2k** (54%); **2l** (53%); the structures of **2a**–**2p** are shown in Table 1.

Table 1
Catalytic transfer hydrogenation of α-sulfonyloxy heteroaryl ketones



2 **3** Cp*RhCl[(*S*,*S*)-TsDPEN]

Entry[a]	X	R^1	R^2	Time (h)	Alcohol	Yield (%)	ee[b] (%)
2a	O	—	Ms	1	**3a**	92	98
2b		—	Ts	1	**3b**	98	99
2c	S	—	Ms	1	**3c**	95	95
2d		—	Ts	1	**3d**	97	96
2e	O	H	Ts	1	**3e**	96	—[c]
2f		5-NO_2	Ts	2	**3f**	90	88
2g		5-OMe	Ms	3	**3g**	90	96
2h		5-OMe	Ts	2	**3h**	99	96
2i		5-Br	Ts	1	**3i**	95	94
2j		7-Et	Ms	1	**3j**	97	97[d]
2k		7-Et	Ts	1	**3k**	94	95[d]
2l		7-OMe	Ts	2	**3l**	91	96
2m	S	H	Ts	2	**3m**	91	96
2n	S	—	Ts	4	**3n**	85	96
2o	O	—	Ts	2	**3o**	84	95
2p	S	—	Ts	2	**3p**	83	93

[a] Reaction conditions are as follows: ketone **2** (1 mmol), (*S*,*S*)-Rh (substrate/catalyst = 500), HCO_2H/Et_3N (molar ratio = 5/2, 0.2 mL), EtOAc (4 mL).
[b] The % ee values were determined by HPLC analysis using a Daicel Chiralcel OD-H column unless otherwise indicated.
[c] Separation failed.
[d] Chiralcel OJ-H column used.

heteroaryl ketones with an azeotropic mixture of formic acid/triethylamine to produce the corresponding 1,2-diol monosulfonates in excellent yield with high enantioselectivity. This represents a simple and highly efficient procedure for the preparation of chiral diols containing heteroaryl moieties, which could be used as precursors to access aminoalcohols.

2.3. Asymmetric synthesis of (*S*)-bufuralol[9c,11]

Bufuralol, 1-(7-ethylbezofuran-2-yl)-2-tert-butylamino-1-hydroxyethane, is a potent non-selective β-adrenoreceptor antagonist and administered as a racemic mixture. However, it is known that the β-blocking potency of (*S*)-bufuralol is approximately 100 times greater than that of the (*R*)-enantiomer.[15] With (*S*)-2-mesyloxyethanol **3j** in hand, we were able to access (*S*)-bufuralol as shown in Scheme 2. As already established, the reaction of (*S*)-**3j** with *tert*-butylamine in refluxing ethanol provided (*S*)-bufuralol **4**, $[\alpha]_D^{20} = -54.5$ (*c* 0.37, $CHCl_3$), with 99% ee in 45% yield.

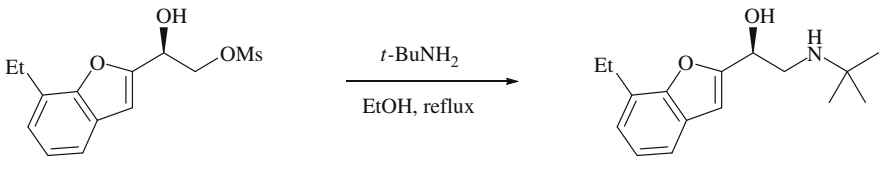
3. Conclusion

The α-sulfonyloxy heteroaryl ketones were prepared by the sulfonyloxylation of the corresponding ketones or trimethylsilyl enol ethers, depending on their electronic nature. The asymmetric transfer hydrogenation of α-sulfonyloxy heteroaryl ketones mediated by the Rh-catalyst using an azeotropic mixture of formic acid/triethylamine afforded the corresponding diol-2-monosulfonates in excellent yield with high enantioselectivity. The enantioselectivity appears to be little affected by the properties of the heteroaryl moiety. This represents a useful approach to the preparation of chiral alcohols from heteroaryl ketones, particularly those possessing a chiral aminoalcohol unit. This approach has led to the efficient synthesis of (*S*)-bufuralol.

4. Experimental

4.1. Preparation of α-sulfonyloxy heteroaryl ketones

According to the known procedure, α-sulfonyloxy heteroaryl ketones **2a**–**2p** were prepared by the sulfonyloxylation of the corresponding ketones or their trimethylsilyl enol ethers with [hydroxy(tosyloxy)iodo]benzene (PhI(OH)OTs) or [hydroxy(mesyloxy)iodo]benzene (PhI(OH)OMs),[12] where the starting ketones were either commercially available or easily accessible in a few steps. The 2-acetylbenzofuran derivatives **1e**[16] and **1g**[11b] were prepared, respectively, from the corresponding 2-hydroxybenzaldehyde



3j **4:** (*S*)-Bufuralol

Scheme 2. Asymmetric synthesis of (*S*)-bufuralol.

derivatives, and 3-acetylbenzofuran **1k**[17] from 1-(2-methoxyphenyl)-2-propanone with dimethylformamide dimethyl acetal, according to the known protocols.

4.1.1. α-Sulfonyloxylation of ketone (route A): representative procedure for the preparation of 2-mesyloxy-1-(2-furanyl)ethanone 2a[12c]

A mixture of [hydroxy(mesyloxy)iodo]benzene (4.31 g, 9.08 mmol) and **1a** (1 g, 9.1 mmol) in acetonitrile (25 mL) was stirred at reflux for 1 h. After cooling to rt, the reaction mixture was concentrated in vacuo. The resulting mixture was diluted with ethyl acetate (30 mL) and then was washed with saturated $NaHCO_3$ (2×10 mL) and brine (10 mL). The organic phase was dried over Na_2SO_4 and concentrated to give a residue. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 2/1) to give 1.36 g (73%) of **2a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.34 (dd, 1H, J = 3.6 and 0.6 Hz), 6.63 (dd, 1H, J = 3.6 and 1.6 Hz), 5.35 (s, 2H), 3.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.3, 149.8, 147.3, 118.6, 112.8, 69.4, 39.0; EIMS (70 eV) m/z (rel intensity) 204 (M^+, 88), 95 (M^+-CH_2OMs, 100).

4.1.2. 2-Tosyloxy-1-(2-furanyl)ethanone 2b[12c]

Yield = 72%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 1H, J = 3.0 Hz), 7.85 (d, 2H, J = 8.4 Hz), 7.51 (d, 1H, J = 5.1 Hz), 7.36–7.33 (m, 3H), 5.07 (s, 2H), 2.45 (s, 3H); EIMS (70 eV) m/z (rel intensity) 280 (M^+, 38), 95 (100), 65 (42).

4.1.3. 2-Mesyloxy-1-(2-thiophenyl)ethanone 2c[12a]

Yield = 81%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.75 (m, 2H), 7.21–7.18 (m, 1H), 5.38 (s, 2H), 3.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.2, 139.4, 135.2, 132.5, 128.6, 69.6, 39.1; EIMS (70 eV) m/z (rel intensity) 220 (M^+, 32), 124 (60), 111 (100), 83(49). Anal. Calcd for $C_7H_8O_4S_2$: C, 38.17; H, 3.66; S, 29.11. Found: C, 37.01; H, 3.63; S, 27.74.

4.1.4. 2-Tosyloxy-1-(2-thiophenyl)ethanone 2d[12b,c]

Yield = 87%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, 2H, J = 8.1 Hz), 7.79 (d, 1H, J = 3.9 Hz), 7.73 (d, 1H, J = 4.8 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.15 (t, 1H, J = 4.5 Hz), 5.08 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.7, 145.4, 140.4, 135.1, 133.2, 132.4, 130.0, 128.5, 128.2, 69.9, 21.7; EIMS (70 eV) m/z (rel intensity) 296 (M^+, 8), 111 (100). Anal. Calcd for $C_{13}H_{12}O_4S_2$: C, 52.69; H, 4.08; S, 21.64. Found: C, 52.99; H, 4.14; S, 21.84.

4.1.5. 2-Tosyloxy-1-(2-benzofuranyl)ethanone 2e

Yield = 69%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, 2H, J = 8.4 Hz), 7.73 (d, 1H, J = 7.8 Hz), 7.64 (s, 1H), 7.55–7.51 (m, 2H), 7.37–7.31 (m, 3H), 5.22 (s, 2H), 2.45 (s, 3H); EIMS (70 eV) m/z (rel intensity) 330 (M^+, 100), 252 (5), 145 (55), 89 (25). Anal. Calcd for $C_{17}H_{14}O_5S$: C, 61.81; H, 4.27; S, 9.71. Found: C, 62.27; H, 4.61; S, 8.16.

4.1.6. 2-Tosyloxy-1-(5-nitrobenzofuran-2-yl)ethanone 2f

Yield = 66%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (d, 1H, J = 2.3 Hz), 8.44 (dd, 1H, J = 9.1 and 2.3 Hz), 7.88 (d, 2H, J = 8.4 Hz), 7.79 (m, 1H), 7.70 (d, 1H, J = 9.3 Hz), 7.39 (d, 2H, J = 8.3 Hz), 5.22 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.5, 157.8, 152.2, 145.7, 145.1, 132.3, 130.1, 128.2, 126.9, 124.2, 120.3, 114.8, 113.2, 69.7, 21.7; EIMS (70 eV) m/z (rel intensity) 375 (M^+, 37), 297 (7), 190 (100), 154 (88), 143 (29), 91 (46).

4.1.7. 2-Tosyloxy-1-(5-bromobenzofuran-2-yl)ethanone 2i

Yield = 62%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (m, 3H), 7.60 (m, 2H), 7.45 (d, 1H, J = 8.6 Hz), 7.37 (d, 2H, J = 7.8 Hz), 5.21 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.5, 154.3, 150.6, 145.5, 132.5, 132.1, 130.0, 128.5, 128.2, 126.1, 117.5, 114.0, 113.6, 69.7, 21.7; EIMS (70 eV) m/z (rel intensity) 410 (M^+, 39), 408 (M^+, 35), 223 (100), 167 (17), 155 (34), 91 (28).

4.1.8. 2-Tosyloxy-1-(2-benzothiophenyl)ethanone 2m

Yield = 60%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.88 (m, 4H), 7.47 (m, 2H), 7.35 (d, 2H, J = 8.2 Hz), 5.19 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.5, 145.4, 139.3, 138.0, 136.4, 132.5, 131.6, 129.9, 128.2, 126.1, 125.9,125.3, 122.2, 70.4, 21.6; EIMS (70 eV) m/z (rel intensity) 346 (M^+, 9), 161 (100), 147 (5), 133 (15), 89 (28).

4.1.9. 2-Tosyloxy-1-(3-thiophenyl)ethanone 2n[18]

Yield = 58%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 1H, J = 4.2 Hz), 7.85 (d, 2H, J = 8.4 Hz), 7.51 (d, 1H, J = 6.3 Hz), 7.36–7.33 (m, 3H), 5.07 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.9, 145.4, 138.2, 133.4, 132.5, 129.9, 128.2, 126.9, 126.7, 70.3, 21.7; EIMS (70 eV) m/z (rel intensity) 296 (M^+, 3), 218 (3), 141 (6), 111 (100), 91 (18). Anal. Calcd for $C_{13}H_{14}O_4S_2$: C, 52.69; H, 4.08; S, 21.64. Found: C, 52.01; H, 4.47; S, 22.26.

4.1.10. 2-Tosyloxy-1-(3-benzofuranyl)ethanone 2o

Yield = 62%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47(s, 1H), 8.15 (m, 1H), 7.84 (d, 2H, J = 8.7 Hz), 7.54 (m, 1H), 7.37 (m, 4H), 4.95 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.0, 155.0, 152.2, 145.7, 132.2, 130.1, 128.1, 126.1, 124.9, 123.9, 122.7, 119.1, 111.5, 71.0, 21.7; EIMS (70 eV) m/z (rel intensity) 330 (M^+, 16), 175 (9), 145 (100), 89 (35).

4.1.11. 2-Tosyloxy-1-(3-benzothiophenyl)ethanone 2p

Yield = 64%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (d, 1H, J = 7.5 Hz), 8.34 (s, 1H), 7.85(m, 3H), 7.46 (m, 2H), 7.30 (d, 2H, J = 7.8 Hz), 5.16 (s, 2H), 2.39 (s, 3H); EIMS (70 eV) m/z (rel intensity) 346 (M^+, 13), 161 (100), 147 (5), 133 (14), 89 (29).

4.1.12. α-Sulfonyloxylation of silyl enol ether (route B): representative procedure for the preparation of 2-tosyloxy-1-(5-methoxybenzofuran-2-yl)ethanone 2h

To a solution of **1e** (750 mg, 3.94 mmol) in anhydrous dichloromethane (4 mL) in an ice-bath was added DIPEA (1.03 mL, 5.92 mmol) via a syringe. To this solution, TBSOTf (0.83 mL, 4.73 mmol) was slowly added via a syringe. The resulting mixture was stirred for 30 min at 0 °C and then allowed to warm to room temperature. To this mixture was added [hydroxy(tosyloxy)iodo]benzene (2.32 g, 5.92 mmol) and the resulting mixture was stirred for 1 h. The resulting mixture was diluted with ethyl acetate (10 mL) and then washed with brine (10 mL). The organic phase was dried over Na_2SO_4 and concentrated to give a residue. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 2/1) to give 867 mg (61%) of **2h**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 2H, J = 8.1 Hz), 7.58 (s, 1H), 7.44 (d, 1H, J = 9.0 Hz), 7.37 (d, 2H, J = 8.1 Hz), 7.14–7.08 (m, 2H), 5.21 (s, 2H), 3.86 (s, 3H), 2.45 (s, 3H); EIMS (70 eV) m/z (rel intensity) 360 (M^+, 9), 175 (100), 119 (19), 91 (12).

4.1.13. 2-Mesyloxy-1-(5-methoxybenzofuran-2-yl)ethanone 2g

Yield = 61%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.47 (d, 1H, J = 9.1 Hz), 7.17–7.10 (m, 2H), 5.47 (s, 2H), 3.86 (s, 3H), 3.30 (s, 3H); EIMS (70 eV) m/z (rel intensity) 284 (M^+, 17), 209 (13), 175 (100), 119 (45).

4.1.14. 2-Mesyloxy-1-(7-ethylbenzofuran-2-yl)ethanone 2j

Yield = 52%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.57 (d, 1H, J = 8.0 Hz), 7.31 (m, 2H), 5.51 (s, 2H), 3.31 (s, 3H), 2.98 (q, 2H, J = 7.5 Hz), 1.37 (t, 3H, J = 7.5 Hz); EIMS (70 eV) m/z (rel intensity) 282 (M^+, 11), 186 (10), 173 (100), 115 (13).

4.1.15. 2-Tosyloxy-1-(7-ethylbenzofuran-2-yl)ethanone 2k

Yield = 54%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, 2H, J = 8.4 Hz), 7.63 (s, 1H), 7.55 (d, 1H, J = 7.2 Hz), 7.38–7.24 (m, 4H), 5.25 (s, 2H), 2.96 (q, 2H, J = 7.72 Hz), 2.45 (s, 3H), 1.35 (t, 3H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.4, 154.4, 149.5, 145.4, 132.6, 129.9, 129.0, 128.2, 128.0, 126.3, 124.5, 121.0, 115.0, 69.6, 22.6, 21.7, 13.9; EIMS (70 eV) m/z (rel intensity) 358 (M^+, 14), 203 (14), 186 (23), 173 (100), 115 (34), 91 (53).

4.1.16. 2-Tosyloxy-1-(7-methoxybenzofuran-2-yl)ethanone 2l

Yield = 53%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, 2H, J = 9.1 Hz), 7.62 (s, 1H), 7.36 (d, 2H, J = 7.7 Hz), 7.27 (m, 2H), 6.97 (dd, 1H, J = 7.27 and 1.6 Hz), 5.29 (s, 2H), 4.02 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.4, 150.1, 146.0, 145.5, 145.3, 132.6, 129.9, 128.3, 128.2, 128.5, 115.3, 114.6, 110.0, 69.8, 56.1, 21.7; EIMS (70 eV) m/z (rel intensity) 360 (M^+, 81), 175 (100), 155 (20), 119 (27), 91 (49).

4.2. Asymmetric transfer hydrogenation of α-sulfonyloxy heteroaryl ketones

General. The catalyst, Cp*RhCl[(*S*,*S*)-TsDPEN] was prepared from the reaction of dichloro(pentamethylcyclopentadienyl)rhodium(III) dimer and (1*S*,2*S*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine in dichloromethane in the presence of triethylamine, according to the literature procedure.[13] It should be noted that the catalyst was used without any purification, so the catalyst includes an equal molar of hydrochloride/triethylamine salt. This catalyst mixture is very stable and insensitive to atmospheric manipulations, and does not show any deterioration in the catalytic activity compared to that prepared from recrystalization.[10b] The formic acid/triethylamine (molar ratio = 5/2) azeotrope was prepared by the double distillation of the mixtures, according to the literature procedure.[14] The absolute configuration was determined by comparing the sign of the specific rotation with the literature data or chemical modification to the known compounds. Unless otherwise indicated, the absolute stereochemistry was assigned from the same sign of rotation of the isolated product.

4.2.1. Representative procedure for the synthesis of (*S*)-2-mesyloxy-1-(2-furanyl)ethanol 3a

Into a two-neck flask, were added (*S*,*S*)-Rh (1.6 mg, equivalent to 0.002 mmol) and **2a** (204 mg, 1 mmol) under a slight stream of argon. To this mixture, ethyl acetate (2 mL) and then an azeotropic mixture of HCO_2H/Et_3N (molar ratio = 5/2, 0.2 mL) were added via a syringe. The combined contents were stirred for 0.5 h. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (3 × 5 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated and then the residue was purified by column chromatography on silica gel (chloroform/ethyl acetate = 10/1) to give 190 mg (92%) of (*S*)-**3a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 1H), 6.38–6.37 (m, 2H), 5.03 (t, 1H, J = 5.5 Hz), 4.47–4.45 (m, 2H), 3.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3, 142.7, 110.5, 107.9, 71.1, 66.0, 37.5; EIMS (70 eV) m/z (rel intensity) 206 (M^+, 1), 110 (22), 97 ((M^+-CH_2OMs, 100); $[\alpha]_D^{27} = -30.7$ (c 1.01, $CHCl_3$); 98.42% ee.

4.2.2. (*S*)-2-Tosyloxy-1-(2-furanyl)ethanol 3b[19a,b]

Yield = 98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.4 Hz), 7.36–7.34 (m, 3H), 6.33 (s, 2H), 5.00–4.53 (m, 1H), 4.30 (dd, 1H, J = 10.4 and 4.3 Hz), 4.24 (dd, 1H, 10.4 and 7.1 Hz), 2.45 (s, 3H), 2.41 (d, 1H, J = 5.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3, 145.0, 142.6, 132.4, 129.9, 127.9, 110.3, 107.9, 71.4, 65.8, 21.6; EIMS (70 eV) m/z (rel intensity) 97 ((M^+-CH_2OTs, 100), 110 (100), 91 (75); $[\alpha]_D^{27} = -25.5$ (c 1.63, $CHCl_3$); lit.[19a] for (*R*)-**3b**, $[\alpha]_D^{20} = +36.7$ (c 4.01, Et_2O); 98.7% ee.; lit.[19b] for (*S*)-**3b**, $[\alpha]_D^{21} = -24.6$ (c 1.35, $CHCl_3$).

4.2.3. (*S*)-2-Mesyloxy-1-(2-thiophenyl)ethanol 3c

Yield = 95%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, 1H, J = 5.0 Hz), 7.07 (d, 1H, J = 3.3 Hz), 7.02 (dd, 1H, J = 5.0 and 3.5 Hz), 5.32–5.27 (m, 1H), 4.42 (dd, 1H, J = 10.9 and 4.0 Hz), 4.36 (dd, 1H, J = 10.9 and 7.4 Hz), 3.06 (s, 3H), 2.89 (d, 1H, J = 4.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 127.0, 125.7, 125.1, 73.2, 68.3, 37.6; EIMS (70 eV) m/z (rel intensity) 222 (M^+, 1), 113 ((M^+-OMs, 100), 85 (34); $[\alpha]_D^{27} = -33.2$ (c 0.56 $CHCl_3$); 94.7% ee.

4.2.4. (*S*)-2-Tosyloxy-1-(2-thiophenyl)ethanol 3d[20]

Yield = 97%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, 2H, J = 8.4 Hz), 7.35 (d, 2H, J = 8.1 Hz), 7.28–7.26 (m, 1H), 6.98–6.95 (m, 2H), 5.25–5.20 (m, 1H), 4.23 (dd, 1H, J = 10.2 and 3.6 Hz), 4.17–4.08 (m, 1H), 2.67 (s, 1H, J = 3.9 Hz), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 141.5, 132.6, 130.0, 128.0, 127.0, 125.6, 125.0, 73.7, 68.3, 21.7; EIMS (70 eV) m/z (rel intensity) 172 (100), 113 ((M^+-CH_2OTs, 5), 91 (100). Anal. Calcd for $C_{13}H_{14}O_4S_2$: C, 52.33; H, 4.73; S, 21.49. Found: C, 51.97; H, 4.69; S, 22.14; $[\alpha]_D^{27} = -31.3$ (c 1.12, $CHCl_3$); lit.[20] for (*R*)-**3d**, $[\alpha]_D^{22} = +34.2$ (c 1.05, $CHCl_3$); 95.9% ee.

4.2.5. (*S*)-2-Tosyloxy-1-(2-benzofuranyl)ethanol 3e

Yield = 96%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.4 Hz), 7.54–7.51 (m, 1H), 7.38 (d, 1H, J = 8.1 Hz), 7.30–7.21 (m, 4H), 6.70 (s, 1H), 5.10 (dd, 1H, J = 10.5 and 5.7 Hz), 4.42 (dd, 1H, J = 10.5 and 3.9 Hz), 4.34 (dd, 1H, J = 10.5 and 6.6 Hz), 2.66 (d, 1H, J = 5.4 Hz), 2.41 (s, 3H); EIMS (70 eV) m/z (rel intensity) 332 (M^+, 100), 161 (84), 146 (96), 118 (84), 102 (61), 89 (89); $[\alpha]_D^{27} = -28.98$ (c 0.98, $CHCl_3$).

4.2.6. (*S*)-2-Tosyloxy-1-(5-nitrobenzofuran-2-yl)ethanol 3f

Yield = 90%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, 1H, J = 2.1 Hz), 8.22 (d, 1H, J = 9.0 and 2.3 Hz), 7.77–7.75 (m, 2H), 7.48 (d, 1H, J = 9.0 Hz), 7.32–7.26 (m, 2H), 6.88–6.87 (m, 1H), 5.19–5.13 (m, 1H), 4.45 (dd, 1H, J = 10.6 and 3.7 Hz), 4.35 (dd, 1H, J = 10.6 and 6.4 Hz), 2.92 (d, 1H, J = 5.8 Hz), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 157.5, 145.4, 144.3, 132.1, 130.0, 128.1, 127.9, 120.5, 117.8, 111.7, 105.5, 70.8, 66.5, 21.7; EIMS (70 eV) m/z (rel intensity) 377 (M^+, 2), 360 (6), 205 (24), 192 (100), 176 (30), 155 (99), 146(74). Anal. Calcd for $C_{17}H_{15}NO_7S$: C, 54.11; H, 4.01; N, 3.71; S, 8.50. Found: C, 54.25; H, 4.11; N, 3.67; S, 8.16; $[\alpha]_D^{20} = -18.0$ (c 0.6, $CHCl_3$); 88.02% ee.

4.2.7. (*S*)-2-Mesyloxy-1-(5-methoxybenzofuran-2-yl)ethanol 3g

Yield = 90%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, 1H, J = 8.9 Hz), 7.01–7.00 (m, 1H), 6.90 (dd, 1H, J = 8.9 and 2.5 Hz), 6.71 (s, 1H), 5.16–5.12 (m, 1H), 4.62–4.51 (m, 2H), 3.93 (s, 3H), 3.06 (s, 3H), 2.87 (d, 1H, J = 5.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 154.7, 149.9, 128.3, 113.6, 111.8, 104.9, 103.7, 71.1, 66.8, 55.9, 37.7; EIMS (70 eV) m/z (rel intensity) 286 (M^+, 10), 190 (26), 177 (100), 161 (10), 121 (15), 91 (12). Anal. Calcd for $C_{12}H_{14}O_6S$: C, 50.34; H, 4.93; S, 11.20. Found: C, 50.43; H, 5.53; S, 10.81; $[\alpha]_D^{30} = -32.0$ (c 1.0, $CHCl_3$); 96.38% ee.

4.2.8. (*S*)-2-Tosyloxy-1-(5-methoxybenzofuran-2-yl)ethanol 3h

Yield = 99%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.3 Hz), 7.28–7.24 (m, 3H), 6.98 (d, 1H, J = 2.3 Hz), 6.87 (dd, 1H, J = 8.9 and 2.5 Hz), 6.64 (s, 1H), 5.07 (dd, 1H, J = 5.9 and 4.0 Hz), 4.40 (dd, 1H, J = 10.4 and 4.0 Hz), 4.31 (dd, 1H, J = 10.4 and 6.8 Hz), 3.83 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ; EIMS (70 eV) m/z (rel intensity) 362 (M^+, 3), 190 (59), 177 (100), 161 (11), 121 (9), 91 (23); $[\alpha]_D^{27} = -23.15$ (c 0.97, $CHCl_3$); 96.28% ee.

4.2.9. (*S*)-2-Tosyloxy-1-(5-bromobenzofuran-2-yl)ethanol 3i

Yield = 95%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, 2H, J = 8.2 Hz), 7.65 (d, 1H, J = 1.5 Hz), 7.37 (dd, 1H, J = 6.75 and 1.98 Hz), 7.28–7.23 (m, 3H), 6.65 (s, 1H), 5.11–5.07 (m, 1H), 4.41 (dd, 1H,

J = 10.5 and 3.9 Hz), 4.32 (dd, 1H, J = 10.5 and 6.51 Hz), 2.42 (s, 3H), 2.36 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 153.5, 145.2, 132.2, 129.9, 129.6, 127.9, 127.5, 123.9, 116.1, 112.7, 104.2, 71.1, 66.5, 21.6; EIMS (70 eV) m/z (rel intensity) 412 (M^+, 1), 410 (M^+, 1), 238 (100), 227 (87), 209 (8), 126 (17); $[\alpha]_D^{20} = -18.8$ (c 0.91, $CHCl_3$); 93.64% ee.

4.2.10. (*S*)-2-Mesyloxy-1-(7-ethylbenzofuran-2-yl)ethanol 3j

Yield = 97%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.37 (m, 1H), 7.19–7.11 (m, 2H), 6.76 (d, 1H, J = 0.8 Hz), 5.20–5.17 (m, 1H), 4.64–4.53 (m, 2H), 3.06 (s, 3H), 2.92 (q, 2H, J = 7.3 Hz), 1.33 (t, 3H, J = 7.6 Hz); EIMS (70 eV) m/z (rel intensity) 284 (M^+, 10), 188 (26), 175 (100), 91 (23); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 153.5, 127.8, 127.3, 123.9, 123.3, 118.8, 105.0, 71.2, 66.8, 37.7, 22.7, 14.1; $[\alpha]_D^{20} = -45.15$ (c 1.11, $CHCl_3$); 97.32% ee.

4.2.11. (*S*)-2-Tosyloxy-1-(7-ethylbenzofuran-2-yl)ethanol 3k

Yield = 94%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, 2H, J = 8.3 Hz), 7.35 (dd, 1H, J = 7.4 and 1.2 Hz), 7.24 (d, 2H, J = 8.6 Hz), 7.17–7.08 (m, 2H), 6.68 (d, 1H, J = 0.7 Hz), 5.13–5.08 (m, 1H), 4.42 (dd, 1H, J = 10.3 and 4.0), 4.33 (dd, 1H, J = 10.3 and 6.6 Hz), 2.83 (q, 2H, J = 7.5 Hz), 2.72 (d, 1H, J = 5.4 Hz), 2.39 (s, 3H), 1.28 (t, 3H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 153.3, 145.1, 132.3, 129.8, 127.8, 127.7, 127.3, 123.7, 123.1, 118.7, 104.8, 71.3, 66.6, 22.6, 21.6, 14.0; EIMS (70 eV) m/z (rel intensity) 360 (M^+, 6), 188 (98), 175 (100); $[\alpha]_D^{20} = -33.1$ (c 0.66, $CHCl_3$); 94.67% ee.

4.2.12. (*S*)-2-Tosyloxy-1-(7-methoxybenzofuran-2-yl)ethanol 3l

Yield = 91%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75–7.72 (m, 2H), 7.28–7.25 (m, 2H), 7.18–7.11 (m, 2H), 6.79 (dd, 1H, J = 6.6 and 2.2 Hz), 6.71 (d, 1H, J = 0.8 Hz), 5.14–5.08 (m, 1H), 4.41 (dd, 1H, J = 10.4 and 3.9 Hz), 4.32 (dd, 1H, J = 10.4 and 6.7 Hz), 3.97 (s, 3H), 2.67 (d, 1H, J = 5.7 Hz), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 145.2, 145.1, 144.0, 132.2, 129.8, 129.3, 127.9, 123.7, 113.5, 106.5, 105.0, 71.3, 66.6, 55.9, 21.6; EIMS (70 eV) m/z (rel intensity) 362 (M^+, 11), 190 (76), 177 (100). Anal. Calcd for $C_{18}H_{18}O_6S$: C, 59.66; H, 5.01; S, 8.85. Found: C, 58.76; H, 4.87; S, 8.44; $[\alpha]_D^{20} = -29.6$ (c 0.52, $CHCl_3$); 96.49% ee.

4.2.13. (*S*)-2-Tosyloxy-1-(2-benzothiophenyl)ethanol 3m

Yield = 91%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.68 (m, 4H), 7.37–7.25 (m, 4H), 7.19 (s, 1H), 5.28 (m, 1H), 4.28 (dd, 1H, J = 10.3 and 3.9 Hz), 4.21 (dd, 1H, J = 10.3 and 7.41 Hz), 2.85 (d, 1H, J = 4.1 Hz), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 142.2, 139.3, 139.2, 132.2, 129.9, 127.9, 124.6, 124.5, 123.7, 122.4, 121.6, 73.3, 68.7, 21.7; EIMS (70 eV) m/z (rel intensity) 348 (M^+, 8), 175 (56), 162 (100). Anal. Calcd for $C_{17}H_{16}O_4S_2$: C, 58.60; H, 4.63; S, 18.41. Found: C, 57.78; H, 4.86; S, 18.53; $[\alpha]_D^{20} = -45.0$ (c 0.56, $CHCl_3$); 96.08% ee.

4.2.14. (*R*)-2-Tosyloxy-1-(3-thiophenyl)ethanol 3n

Yield = 85%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, 2H, J = 8.4 Hz), 7.35 (d, 2H, J = 9.1 Hz), 7.31–7.25 (m, 2H), 7.01 (dd, 1H, J = 5.0 and 1.4 Hz), 5.08–5.06 (m, 1H), 4.20 (dd, 1H, J = 10.3 and 3.4 Hz), 4.08 (dd, 1H, J = 10.3 and 8.1 Hz), 2.52 (d, 1H, J = 3.8 Hz), 2.45 (s, 3H); EIMS (70 eV) m/z (rel intensity) 298 (M^+, 2), 281 (50), 221 (13), 172 (17), 155 (81), 113 (46), 91 (100); $[\alpha]_D^{27} = -33.7$ (c 1.28, $CHCl_3$); 95.7% ee.

4.2.15. (*R*)-2-Tosyloxy-1-(3-benzofuranyl)ethanol 3o

Yield = 84%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77–7.75 (m, 2H), 7.60 (d, 1H, J = 0.7 Hz), 7.54–7.46 (m, 2H), 7.34–7.19 (m, 4H), 5.28–5.22 (m, 1H), 4.34 (dd, 1H, J = 10.5 and 3.5 Hz), 4.24 (dd, 1H, J = 10.5 and 7.6 Hz), 2.59 (d, 1H, J = 3.9 Hz), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 145.2, 142.5, 132.3,129.9, 127.9, 125.3, 124.8, 122.9, 119.9, 118.4, 111.7, 72.8, 65.6, 21.6; EIMS (70 eV) m/z (rel intensity) 332 (M^+, 2), 160 (24), 147 (100); $[\alpha]_D^{20} = -40.2$ (c 0.51, $CHCl_3$); 94.65% ee.

4.2.16. (*R*)-2-Tosyloxy-1-(3-benzothiophenyl)ethanol 3p

Yield = 83%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86–7.82 (m, 1H), 7.75 (d, 2H, J = 8.2 Hz), 7.71–7.67 (m, 1H), 7.47 (d, 1H, J = 0.5 Hz), 7.38–7.26 (m, 4H), 5.42–5.37 (m, 1H), 4.35 (dd, 1H, J = 10.6 and 3.1 Hz), 4.18 (dd, 1H, J = 10.6 and 8.1 Hz), 2.70 (d, 1H, J = 3.6 Hz), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 140.7, 136.6, 133.2, 132.5, 129.9, 127.9, 124.6, 124.3, 122.9, 121.5, 73.0, 68.1, 21.6; EIMS (70 eV) m/z (rel intensity) 348 (M^+, 10), 176 (25), 162 (100). Anal. Calcd for $C_{17}H_{16}O_4S_2$: C, 58.60; H, 4.63; S, 18.41. Found: C, 58.49; H, 4.76; S, 18.06; $[\alpha]_D^{20} = -77.05$ (c 0.51, $CHCl_3$); 92.72% ee.

4.3. Asymmetric synthesis of (*S*)-bufuralol 4

To a solution of (*S*)-**3j** (145 mg, 0.5 mmol) in absolute ethanol (5 mL) was added *t*-butylamine (111.5 mg, 1.52 mmol) and the mixture refluxed for 15 h. The volatile materials were removed under vacuum and diethyl ether (10 mL) was added. The solution was washed with 10% sodium hydroxide (2.5 mL), water (3 mL), and dried with anhydrous magnesium sulfate. The solvent was removed and the product isolated by column chromatography on silica gel (petroleum ether/ethyl acetate/diethyl ether/methanol/triethylamine = 6:4:1:0.5:0.2) to give 59 mg (45%) of **4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, 1H, J = 7.5 Hz), 7.16–7.06 (m, 2H), 6.65 (s, 1H), 4.81 (t, 1H, J = 5.4 Hz), 3.05–2.98 (m, 2H), 2.96–2.88 (q, 2H, J = 7.6 Hz), 1.33 (t, 3H, J = 7.6 Hz), 1.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 153.4, 127.8, 127.6, 123.1, 122.8, 118.4, 103.2, 66.4, 50.4, 46.2, 29.1, 22.8, 14.1; $[\alpha]_D^{20} = -54.5$ (c 0.37, $CHCl_3$); 99.1% ee.

Acknowledgment

This work was supported by a grant for Industrial Technology Development Programs from the Korea Research Institute of Chemical Technology (BS.F-0801).

References

1. For reviews, see: (a) Fache, F.; Schulz, E.; Tommasino, L. M.; Lemaire, M. *Chem. Rev.* **2000**, *100*, 2159; (b) Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835; (c) Cardillo, G.; Tomasini, C. *Chem. Soc. Rev.* **1996**, *25*, 117; (d) Juraristi, E.; Quintana, D.; Escalante, J. *Aldrichim. Acta* **1994**, *27*, 3; (e) Cole, D. C. *Tetrahedron* **1994**, *50*, 9517.
2. (a) Ohkuma, T.; Koizumi, M.; Yoshida, M.; Noyori, R. *Org. Lett.* **2000**, *2*, 1749; (b) Deeter, J.; Frazier, J.; Staten, G.; Staszak, M.; Weigel, L. *Tetrahedron Lett.* **1990**, *31*, 7101; (c) Laczkowski, K. Z.; Pakulski, M. M.; Krzeminski, M. P.; Jaisankar, P.; Zaidlewicz, M. *Tetrahedron: Asymmetry* **2008**, *19*, 788; (d) Jones, T. K.; Mohan, J. J.; Xnvier, L. C.; Blacklock, T. J.; Mnthre, D. J.; Sohar, P.; Jones, E. T. T.; Reamer, R. A.; Roberta, F. E.; Grabowski, E. J. J. *J. Org. Chem.* **1991**, *56*, 763; (e) Shih, T. L.; Candelore, M. R.; Cascieri, M. A.; Chiu, S. H.; Colwell, L. F.; Deng, L.; Feeney, W. P. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 1251.
3. Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1986.
4. Ohkuma, T.; Ishii, D.; Takeno, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 6510.
5. Gao, Y.; Sharpless, K. B. *J. Org. Chem.* **1988**, *53*, 4081.
6. (a) Liu, H.; Hoff, B. H.; Anthonsen, T. *Chirality* **2000**, *12*, 26; (b) Kamal, A.; Khanna, G. B. R.; Ramu, R.; Krishnaji, T. *Tetrahedron Lett.* **2003**, *44*, 4783; (c) Kamal, A.; Malik, M. S.; Shaik, A. A.; Azeeza, S. *Tetrahedron: Asymmetry* **2008**, *19*, 1078; (d) Kamal, A.; Malik, M. S.; Shaik, A. A.; Azeeza, S. *J. Mol. Catal. B: Enzym.* **2009**, *58*, 132; (e) Paizs, C.; Tosa, M.; Majdik, C.; Moldovan, P.; Novak, L.; Kolonits, P.; Marcovici, A.; Irimie, F. D.; Poppe, L. *Tetrahedron: Asymmetry* **2003**, *14*, 1495; (f) Podea, P. V.; Paizs, C.; Tosa, M. I.; Irimie, F. D. *Tetrahedron: Asymmetry* **2008**, *19*, 1959.
7. (a) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97; (b) Palmer, M. J.; Wills, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2045; (c) Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226; (d) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393.
8. Farina, V.; Reeves, J. T.; Senanayake, C. H.; Song, J. *J. Chem. Rev.* **2006**, *106*, 2734.
9. (a) Okano, K.; Muratab, K.; Ikariya, T. *Tetrahedron Lett.* **2000**, *41*, 9277; (b) Hamada, T.; Torii, T.; Izawa, K.; Ikariya, T. *Tetrahedron* **2004**, *60*, 7411; (c) Zaidlewicz, M.; Tafelska-Kaczmarek, A.; Prewysz-Kwinto, A. *Tetrahedron:*

Asymmetry **2005**, *16*, 3205; (d) Kosmalski, T.; Wojtczak, A.; Zaidlewicz, M. *Tetrahedron: Asymmetry* **2009**, *20*, 1138.
10. Lee, D.-M.; Lee, J.-C.; Jeong, N.; Lee, K.-I. *Tetrahedron: Asymmetry* **2007**, *18*, 2662; (b) Lee, D.-M.; Kwak, S. H.; Lee, K.-I. *Bull. Korean Chem. Soc.* **2009**, *30*, 1317.
11. (a) Hull, J. D.; Scheinmanna, F.; Turner, N. J. *Tetrahedron: Asymmetry* **2003**, *14*, 567; (b) Zaidlewicz, M.; Tafelska-Kaczmarek, A.; Prewysz-Kwinto, A.; Chechłowska, A. *Tetrahedron: Asymmetry* **2003**, *14*, 1659.
12. (a) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 210; (b) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487; (c) Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Epa, W. R.; Prakash, I. *J. Org. Chem.* **1989**, *54*, 1101.
13. (a) Mashima, K.; Abe, T.; Tani, K. *Chem. Lett.* **1998**, 1199; (b) Murata, K.; Ikariya, T.; Noyori, R. *J. Org. Chem.* **1999**, *64*, 2186.
14. Narita, K.; Sekiya, M. *Chem. Pharm. Bull.* **1977**, *25*, 135.
15. Ariëns, E. J. *Eur. J. Clin. Pharmacol.* **1984**, *26*, 663.
16. Inoue, M.; Carson, M. W.; Frontier, A. J.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 1878.
17. Haefliger, W.; Hauser, D. *Synthesis* **1980**, 236.
18. Sakurai, N.; Mukaiyama, T. *Chem. Lett.* **2008**, *37*, 388.
19. (a) Porzelle, A.; Gordon, V. A.; Williams, C. A. *Synlett* **2007**, 1619; (b) Paolucci, C.; Rosini, G. *Tetrahedron: Asymmetry* **2007**, *18*, 2923.
20. Cho, B. T.; Yang, W. K.; Choi, O. K. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1204.