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Asymmetric borane reduction of prochiral ketones catalyzed by C_3-symmetric sulfonamide

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Abstract—A novel, recoverable, C_3-symmetric sulfonamide **L-1** has been developed for the asymmetric borane reduction of prochiral ketones in refluxing THF. The optically active secondary alcohols were obtained in excellent enantiometric excesses (up to 97% ee) and good yields. The C_3-symmetric sulfonamide **L-1** can be easily recovered and reused four times without any significant loss of catalytic activity.

1. Introduction

C_3 symmetry is an interesting subject in synthetic chemistry, with a number of C_3-symmetric chiral ligands and their applications in asymmetric catalysis being reported.[1] For example, C_3-symmetric tris(phospine) ligands have been reported to act as efficient catalysts in the enantioselective hydrogenation of various unsaturated substrates (up to 95% ee).[2] Chan et al. have synthesized the C_3-symmetric oxazolinyl ligands, which catalyzed the addition of diethylzinc to aromatic aldehydes to give secondary alcohols with high enantiomeric excesses (up to 90%).[3] Katsuki and coworkers have employed tridentate tris(oxazoline) ligands as chiral auxiliaries in copper-mediated asymmetric allylic oxidation of cycloalkenes to give the corresponding products with moderate to high enantioselectivities (up to 93% ee).[4] Tang et al. also developed pseudo-C_3-symmetric trisoxazolines, and successfully applied them into the copper-catalyzed indole alkylation (up to 93% ee), the kinugasa reaction (up to 85% ee), and copper-catalyzed Diels–Alder reaction (up to 82% ee).[5] Very recently, Du et al. synthesized a series of C_3-symmetric tripodal tris (β-hydroxyamide) ligands to the complete asymmetric borane reduction of prochiral ketones with excellent enantioselectivities (up to 98% ee).[6] Therefore, there is a need to synthesize the versatile C_3-symmetric ligands for asymmetric reactions.

On the other hand, the separation and recycling of chiral catalysts has attracted much attention.[7] The enantioselective reduction of prochiral ketones to the corresponding optically active secondary alcohols is still an important methodology. One of the most popular methods using chiral 1,3,2-oxazaborolidines as catalysts was firstly developed by Itsuno et al.[8] and further improved upon by Corey, Bakshi, and Shibata, known as the CBS catalyst.[9] Many applications of this homogeneous catalysts have been reported in the literature.[10] However, the development of efficient methods for recovering the catalysts remains a challenging target. In the recent years, chiral sulfonamides acting as robust catalysts for the reduction of ketones have been reported.[11] In our previous study, we have reported an imidazolium-tagged sulfonamide catalyst **L-2** for the enantioselective reduction of ketones in refluxing toluene.[12] Our ongoing interest is to explore and synthesize a new chiral sulfonamide catalyst with a C_3-symmetric structure. Herein, we report the synthesis of a novel, recoverable C_3-symmetric sulfonamide **L-1** and its application in the enantioselective borane reduction of prochiral ketones. Compared with the imidazolium-tagged sulfonamide **L-2** and the C_1-symmetric sulfonamide **L-3**, the present ligand **L-1** gives a better enantioselectivity (Fig. 1).

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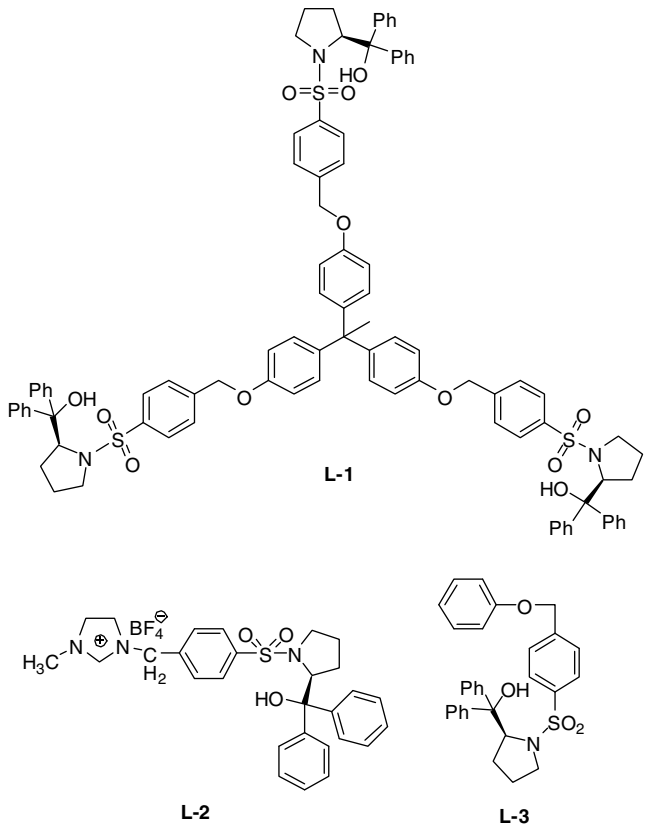
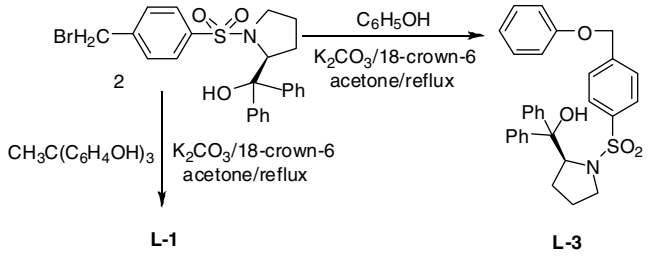


Figure 1.

2. Results and discussion

The synthetic procedure for the C_3-symmetric sulfonamide **L-1** and the C_1-symmetric sulfonamide **L-3** is shown in Scheme 1. Imidazolium-tagged sulfonamide **L-2** is prepared according to our previous work.[12] Compound **2** was directly grafted onto 1,1,1-tris(4-hydroxyphenyl)-ethane and phenol in refluxing acetone in the presence of K_2CO_3 and 18-crown-6 to give **L-1** as a white solid in 94% yield and **L-3** as a white solid in 96% yield, respectively.



Scheme 1. The synthesis of C_3-symmetric sulfonamide **L-1** and C_1-symmetric sulfonamide **L-3**.

It is well known that the enantioselectivity of borane reduction is greatly affected by solvent, temperature, and the amount of catalyst. In order to evaluate the above effects, we investigated the reduction of acetophenone with the C_3-symmetric ligand **L-1** under various reaction conditions and compared the catalytic activities and enantioselectivities of ligands **L-2** and **L-3**. The results are summarized in Table 1.

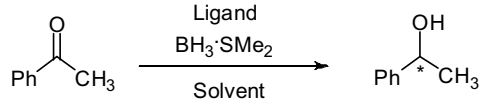
After being extensively reviewed, we chose the reaction media of toluene and THF to examine the solvent effects. At room temperature, the reduction was completed within 10 h in THF and 16 h in toluene with moderate ee values (entries 1 and 2). When the reaction temperature reached 50 °C, the ee values were 85% in THF and 76% in toluene (entries 3 and 4), respectively. By increasing the temperature to reflux, the reaction was completed within 4 h and 90% ee was obtained. The results showed that THF is a more effective solvent for the present reduction and the level of enantiometric excess is sensitive to the reaction temperature. Subsequently, the catalyst loading was investigated. It was observed that a decrease in the catalyst loading from 10 to 5 mol % at reflux temperature resulted in a slight decrease in the enantioselectivity and a slight loss of yield (entries 5 and 6). By further reducing the amount of catalyst to 3 mol %, a large decrease in the ee value was seen (entry 7). As a compromise between catalyst loading and the ee value, a ligand **L-1** loading of 5 mol % provided the optimum level of enantioselectivity, which is presumably because the rate of the catalyzed reaction in the presence of 5 mol % catalyst is sufficiently faster than the non-catalytic reduction with only $BH_3{\cdot}SMe_2$.[13] We also examined the effects of ligands **L-2** and **L-3** on the reduction of acetophenone, and lower enantiometric excesses were obtained. It was important to note that only 82% ee and 73% ee were obtained respectively, although 15 mol % of **L-3** and **L-2** was loaded (entries 8 and 11). These results indicate that the structural effect of C_3-symmetric sulfonamide **L-1** increases the enantioselectivity of the catalyst greatly.

Under the optimized reaction conditions, the C_3-symmetric sulfonamide **L-1** was applied to the asymmetric borane reduction of a variety of aromatic ketones (Table 2).

Compared to the reaction of **L-2**, ligand **L-1** provided good scope and generality of substrates. High yields and enantioselectivities were obtained not only for the prochiral ketones containing electron-withdrawing group (entries 2, 4–6) but also for those with a substitution at the *ortho*-position (entries 10 and 13), unlike ligand **L-2**, of which the enantioselectivity was highly dependent on steric effects. Slightly decreasing ee values were observed for prochiral ketones with electron-donating groups, and therefore electron-withdrawing groups are relatively beneficial for the enantioselectivity. We also extended the reaction to the reduction of α-haloacetophenone under the same conditions, which also gave the high yields and excellent ee values (entries 11–13). This indicated that the reactivity and enantioselectivity were not significantly affected by a halogen atom. However, moderate enantioselectivity was given for the reduction of cyclic aryl ketone and aryl ethyl ketone, which was presumably due to electronic effects (entries 15 and 16).

Meanwhile, it is worth noting that the C_3-symmetric sulfonamide **L-1** can be easily separated and recycled. After

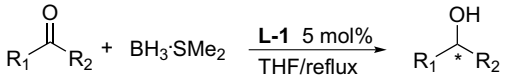
Table 1. Enantioselective borane reduction of acetophenone[a]



Entry	Solvent	Ligand (mol %)	Temperature (°C)	Yield[b] (%)	ee[c] (%)	Configuration[d]
1	THF	**L-1** (10)	rt	92	66	(*R*)
2	Toluene	**L-1** (10)	rt	90	55	(*R*)
3	THF	**L-1** (10)	50	93	85	(*R*)
4	Toluene	**L-1** (10)	50	90	76	(*R*)
5	THF	**L-1** (10)	Reflux	96	90	(*R*)
6	THF	**L-1** (5)	Reflux	95	88	(*R*)
7	THF	**L-1** (3)	Reflux	93	80	(*R*)
8	THF	**L-3** (15)	Reflux	95	82	(*R*)
9[e]	THF	**L-2** (10)	Reflux	94	52	(*R*)
10[e]	Toluene	**L-2** (10)	Reflux	95	65	(*R*)
11[e]	Toluene	**L-2** (15)	Reflux	95	73	(*R*)

[a] Reaction was carried out on a 1.0 mmol scale in 5 mL of solvent, molar ratio of $PhCOCH_3/BH_3{\cdot}SMe_2 = 1.0{:}1.1$.
[b] Isolated yield by column chromatography.
[c] Determined by HPLC analysis using a Daicel Chiralcel OJ column.
[d] The absolute configuration was determined by comparison with the literature.
[e] Obtained from the literature data.[12]

Table 2. Catalytic asymmetric reduction of ketones[a]



Entry	Ketone	Yield[b] (%)	ee[c] (%)	Configuration[d]
1	Acetophenone	95	88	(*R*)
2	1-(4-Chlorophenyl)ethanone	94	90	(*R*)
3	1-(4-Methoxyphenyl)ethanone	91	82	(*R*)
4	1-(4-Nitrophenyl)ethanone	95	90	(*R*)
5	1-(4-Bromophenyl)ethanone	95	92	(*R*)
6	1-(4-Fluorophenyl)ethanone	94	91	(*R*)
7	1-(3-Bromophenyl)ethanone	93	86	(*R*)
8	1-(3-Methoxylphenyl)ethanone	90	86	(*R*)
9	1-(3-Methylphenyl)ethanone	92	86	(*R*)
10	1-(2-Fluorophenyl)ethanone	90	97	(*R*)
11	2-Bromo-1-phenylethanone	94	89	(*S*)
12	2-Chloro-1-(4-methoxyphenyl)ethanone	92	81	(*S*)
13	2-Bromo-1-(2,4-dimethylphenyl)ethanone	94	92	(*S*)
14	β-Acetonaphthone	93	87	(*R*)
15	1-Tetralone	86	77	(*R*)
16	Propiophenone	80	73	(*R*)

[a] Reaction was carried out with 1.0 mmol scale in 5 mL of solvent, molar ratio of ketone/$BH_3{\cdot}SMe_2 = 1.0{:}1.1$.
[b] Isolated yield by column chromatography.
[c] Determined by HPLC analysis using a Daicel Chiralcel OJ column.
[d] The absolute configuration was determined by comparison with the literature.

the reduction was completed, the reaction was quenched with water and extracted. After evaporating the solvent, the product was isolated by being redissolved in diethyl ether resulting in the precipitate ligand **L-1** being obtained. Next, the C_3-symmetric sulfonamide **L-1** was washed several times with diethyl ether and dried. Recycling of the C_3-symmetric sulfonamide **L-1** was tested by the reduction of acetophenone (Table 3). The results show that ligand **L-1** could be reused at least four times with little or no loss of performance.

Table 3. Recycling of C_3-symmetric sulfonamide **L-1** (reduction of acetophenone)

Cycle	1	2	3	4
Ligand[a] (%)	94	90	92	96
Yield[b] (%)	93	90	89	91
ee[c] (%)	85	87	87	84

[a] Isolated yield by precipitation.
[b] Isolated yield by column chromatography.
[c] Determined by HPLC analysis using a Daicel Chiralcel OJ column.

3. Conclusion

In conclusion, a novel, recoverable, C_3-symmetric sulfonamide **L-1** has been synthesized, which was used as an efficient catalyst in the enantioselective borane reduction of prochiral ketones with good to excellent enantioselectivities have been obtained (up to 97% ee). The reduction permits extensive recycling of the C_3-symmetric sulfonamide catalyst without substantial loss in the activity within four cycles.

4. Experimental

All the reactions were carried out under a dry argon atmosphere. THF was freshly distilled over sodium before use. All the ketones were prepared according to the reported procedure and further purified by crystallization or distillation. Borane-dimethyl sulfide was obtained from Aldrich Chemical Co. The purity of all reagents was checked by NMR spectroscopy.

Melting points were determined on a microscopic apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz and 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ using TMS as an internal standard. IR spectra were obtained using a Nicolet NEXUS 670 FT-IR spectrometer and only major peaks are reported in cm^{-1}. HRMS spectra were performed on a Bruker APEX instrument. Elemental analyses were performed on Perkin–Elmer 240-C. Optical rotation value was measured on a Perkin–Elmer 341MC polarimeter. Enantiometric excesses were determined by HPLC with a Chiralcel OJ column.

4.1. Synthesis of ligands

4.1.1. Synthesis of C_3-symmetric sulfonamide L-1. To a stirred solution of **2**[12] (4.85 g, 10 mmol) and 1,1,1-tris(4-hydroxyphenyl)-ethane (1.01 g, 3.3 mmol) in acetone (20 mL) were added potassium carbonate (1.52 g, 11 mmol) and 18-crown-6 (10 mg, 0.04 mmol). The reaction mixture was heated at reflux for 24 h under argon. After cooling to room temperature, the reaction was quenched with water (15 mL) and extracted with CH_2Cl_2 (3×15 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. After evaporating the solvent under reduced pressure, the residue was purified by flash column chromatography on a silica gel (methanol/dichloromethane = 1:20 as eluent) to give the C_3-symmetric sulfonamide **L-1** as a white solid. Yield: 4.72 g (94%). Mp: 132–134 °C; $[\alpha]_D^{20} = -54.8$ (c 2.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, $J = 8.0$ Hz, 6H), 7.55 (d, $J = 8.4$ Hz, 6H), 7.37–7.43 (m, 12H), 7.21–7.32 (m, 18H), 7.02 (d, $J = 8.8$ Hz, 6H), 6.86 (d, $J = 8.8$ Hz, 6H), 5.09 (s, 6H), 4.86–4.89 (m, 3H), 4.47 (d, $J = 2.8$ Hz, 3H), 3.25–3.32 (m, 3H), 2.80–2.87 (m, 3H), 1.78–1.87 (m, 6H), 1.17–1.25 (m, 3H), 0.76–0.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.2, 145.4, 143.5, 142.6, 142.2, 137.3, 129.6, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 113.9, 79.8, 68.7, 67.3, 50.6, 49.8, 30.6, 29.4, 23.7. IR (KBr): 3465, 2975, 1506, 1334, 1245, 1155, 701 cm^{-1}. Anal. Calcd for $C_{92}H_{87}N_3O_{12}S_3$: C, 72.56; H, 5.76; N, 2.76. Found: C, 72.08, H, 5.73, N, 2.75.

4.1.2. Synthesis of C_1-symmetric sulfonamide L-3. To a stirred solution of **2** (4.85 g, 10 mmol) and phenol (0.93 g, 9.9 mmol) in acetone (20 mL) were added potassium carbonate (1.52 g, 11 mmol) and 18-crown-6 (10 mg, 0.04 mmol). The reaction mixture was heated at reflux for 24 h under argon. After cooling to room temperature, the reaction was quenched with water (15 mL) and extracted with CH_2Cl_2 (3×15 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. After evaporating the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 2:1 as eluent) to give the product as a white solid. Yield: 4.74 g (96%). Mp: 135–137 °C; $[\alpha]_D^{20} = -66.5$ (c 2.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, $J = 8$ Hz, 2H), 7.55 (d, $J = 8$ Hz, 2H), 7.19–7.43 (m, 13H), 6.95–6.99 (m, 2H), 5.01 (s, 2H), 4.85–4.88 (m, 1H), 4.44 (s, 1H), 3.25–3.32 (m, 1H), 2.78–2.85 (m, 1H), 1.74–1.88 (m, 2H), 1.15–1.26 (m, 1H), 0.76–0.88 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 145.9, 143.9, 143.0, 137.7, 129.9, 128.4, 128.3, 128.1, 127.9 (two peaks), 127.8, 127.7, 127.6, 121.7, 115.1, 80.2, 69.1, 67.8, 50.3, 29.9, 24.2. IR (KBr): 3463, 2929, 1494, 1343, 1237, 1155, 758, 686, 619 cm^{-1}. Anal. Calcd for $C_{30}H_{29}NO_4S$: C, 72.12; H, 5.85; N, 2.80. Found: C, 72.46; H, 5.88; N, 2.79. HRMS-FAB: m/z calcd for $C_{30}H_{29}NO_4SNa$: 522.1710. Found: 522.1704.

4.2. General procedure for the asymmetric reduction of prochiral ketones

Under an argon atmosphere, $BH_3{\cdot}SMe_2$ (1.1 mmol) was added to a suspension of C_3-symmetric sulfonamide **L-1** (0.05 mmol) in THF (5 mL) at room temperature. The mixture was heated at reflux and stirred for 1 h. Then a THF (5 mL) solution of ketone (1.0 mmol) was added dropwise over a period of 2 h by a syringe pump, and the mixture was stirred for another 1 h. The reaction mixture was quenched by the dropwise addition of water (5 mL) and extracted with CH_2Cl_2 (3×5 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. After evaporating the solvent under reduced pressure, the alcohol was redissolved in the diethyl ether, and the ligand **L-1** was precipitated. The ether phase was removed, and the C_3-symmetric sulfonamide **L-1** was further washed several times with diethyl ether and dried. The combined diethyl ether was concentrated by rotatory evaporation, and the product was purified by flash column chromatography on a silica gel to afford the corresponding secondary alcohol. The ee value was determined by HPLC with a Chiralcel OJ column. The absolute configuration of the product was determined by the comparison of the specific rotation with the literature data.[6b,14–17]

4.2.1. (*R*)-1-Phenyl-ethanol.[6b] Colorless oil. 95% Yield; 88% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 15.202 min [minor (*S*)-enantiomer], 16.615 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} =$

+38.2 (c 1.0, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.22–7.35 (m, 5H), 4.83 (q, $J = 6.6$ Hz, 1H), 2.35 (s, 1H), 1.45 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7, 128.4, 127.3, 125.3, 70.2, 25.0.

4.2.2. (*R*)-1-(4-Chlorophenyl)-ethanol.[6b] Colorless oil. 94% Yield; 90% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 13.775 min (minor *S*-enantiomer), 14.794 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +45.8$ (c 1.1, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.26–7.32 (m, 4H), 4.85 (q, $J = 6.8$ Hz, 1H), 2.10 (s, 1H), 1.45 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.5, 133.3, 128.8, 127.0, 69.9, 25.5.

4.2.3. (*R*)-1-(4-Methoxylphenyl)-ethanol.[6b] Colorless oil. 91% Yield; 82% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 30.212 min [minor (*S*)-enantiomer], 32.074 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +46.5$ (c 1.0, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, $J = 8.1$ Hz, 2H), 6.85–6.87 (m, 2H), 4.81 (q, $J = 6.6$ Hz, 1H), 3.78 (s, 3H), 2.16 (s, 1H), 1.45 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 138.0, 126.6, 113.7, 69.8, 55.2, 24.9.

4.2.4. (*R*)-1-(4-Nitrophenyl)-ethanol.[6b] Colorless oil. 95% Yield; 90% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 34.650 min [minor (*S*)-enantiomer], 37.942 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +26.5$ (c 1.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, $J = 8.8$ Hz, 2H), 7.54 (d, $J = 8.8$ Hz, 2H), 5.01 (q, $J = 6.4$ Hz, 1H), 2.36 (s, 1H), 1.51–1.52 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.1, 147.1, 126.1, 123.7, 69.4, 25.4.

4.2.5. (*R*)-1-(4-Bromophenyl)-ethanol.[6b] Colorless oil. 95% Yield; 92% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 14.705 min [minor (*S*)-enantiomer], 15.748 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +31.5$ (c 1.0, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.43–7.46 (m, 2H), 7.20–7.26 (m, 2H), 4.81 (q, $J = 6.6$ Hz, 1H), 2.20 (s, 1H), 1.42–1.45 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.7, 131.5, 127.1, 121.1, 69.7, 25.2.

4.2.6. (*R*)-1-(4-Fluorophenyl)-ethanol.[6b] Colorless oil. 94% Yield; 91% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 95:5, 0.5 mL/min, 254 nm). Retention times: 14.961 min [minor (*S*)-enantiomer], 15.697 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +34.5$ (c 2.0, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.26–7.36 (m, 2H), 7.00–7.06 (m, 2H), 4.88 (q, $J = 6.6$ Hz, 1H), 1.84 (s, 1H), 1.48 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.4, 160.9, 142.3, 127.0, 115.4, 115.1, 69.8, 25.3.

4.2.7. (*R*)-1-(3-Bromophenyl)-ethanol.[14] Colorless oil. 93% Yield; 86% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254nm). Retention times: 13.432 min [minor (*S*)-enantiomer], 14.958 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +37.5$ (c 1.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.49 (s, 1H), 7.36 (d, $J = 7.8$ Hz, 1H), 7.16–7.25 (m, 2H), 4.79 (q, $J = 6.3$ Hz, 1H), 2.47 (s, 1H), 1.43 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.1, 130.3, 130.0, 128.5, 124.0, 122.5, 69.6, 25.1.

4.2.8. (*R*)-1-(3-Methoxylphenyl)-ethanol.[15] Colorless oil. 90% Yield; 86% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 20.647 min [minor (*S*)-enantiomer], 22.378 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +32.8$ (c 1.0, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.21–7.26 (m, 1H), 6.90–6.92 (m, 2H), 6.76–6.80 (m, 1H), 4.81 (q, $J = 6.6$ Hz, 1H), 3.78 (s, 3H), 2.35 (s, 1H), 1.45 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.6, 147.6, 129.4, 117.6, 112.7, 110.8, 70.1, 55.1, 25.0.

4.2.9. (*R*)-1-(3-Methylphenyl)-ethanol.[16] Colorless oil. 92% Yield; 86% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 13.099 [minor (*S*)-enantiomer], 13.775 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +45.8$ (c 1.0, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.06–7.25 (m, 4H), 4.82 (q, $J = 6.6$ Hz, 1H), 2.35 (s, 3H), 2.06 (s, 1H), 1.46 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.8, 138.1, 128.3, 128.1, 126.0, 122.4, 70.3, 25.0, 21.4.

4.2.10. (*R*)-1-(2-Fluorophenyl)-ethanol.[15] Colorless oil. 90% Yield; 97% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 95:5, 0.5 mL/min, 254 nm). Retention times: 10.184 min [minor (*S*)-enantiomer], 11.424 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +34.1$ (c 2.0, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.45–7.50 (m, 1H), 7.20–7.26 (m, 1H), 7.11–7.16 (m, 1H), 6.97–7.04 (m, 1H), 5.18 (q, $J = 6.6$ Hz, 1H), 2.13 (s, 1H), 1.50 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.8, 128.7, 126.6, 124.2, 115.4, 115.1, 64.5, 24.0.

4.2.11. (*S*)-2-Bromo-1-phenylethanol.[6b] Colorless oil. 94% Yield; 89% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 30.005 min [minor (*R*)-enantiomer], 32.256 min [major (*S*)-enantiomer]. $[\alpha]_D^{20} = +34.9$ (c 1.7, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.40 (m, 5H), 4.91 (dd, $J = 3.2$, 8.8 Hz, 1H), 3.51–3.64 (m, 2H), 2.72 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.9, 141.5, 130.1, 126.9, 126.4, 21.7.

4.2.12. (*S*)-2-Chloro-1-(4-methoxyphenyl)-ethanol.[12] Colorless oil. 92% Yield; 81% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 13.766 min [minor (*R*)-enantiomer], 15.761 min [major (*S*)-enantiomer]. $[\alpha]_D^{20} = +32.5$ (c 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.29 (m, 2H), 6.85–6.90 (m, 2H), 4.80 (dd, $J = 5.6$, 11.2 Hz, 1H), 3.78 (s, 3H), 3.56–3.69 (m, 2H), 2.83 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.5, 132.1, 127.2, 113.9, 73.6, 55.2, 50.6.

4.2.13. (*S*)-2-Bromo-1-(2,4-dimethylphenyl)-ethanol.[12] White solid. 94% Yield; 92% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 16.647 min [minor (*R*)-enantiomer], 18.059 min [major (*S*)-enantiomer]. $[\alpha]_D^{20} = +37.4$ (c 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, $J = 8.7$ Hz, 1H), 7.04 (d, $J = 8.8$ Hz, 1H), 6.97 (s, 1H), 5.07 (d, $J = 8.7$ Hz, 1H), 3.42–3.56 (m, 2H), 2.68 (s, 1H), 2.29 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 135.3, 134.5, 131.3, 127.1, 125.3, 70.6, 39.1, 21.0, 18.9.

4.2.14. (*R*)-1-(2-Naphthyl)-ethanol.[6b] White solid. 93% yield; 87% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 22.904 min [minor (*S*)-enantiomer], 27.917 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +36.5$ (c 2.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.83 (m, 4H), 7.43–7.50 (m, 3H), 5.04 (q, $J = 6.8$ Hz, 1H), 2.07 (s, 1H), 1.56 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 133.5, 133.2, 128.5, 128.2, 127.9, 126.4, 126.0, 124.0, 70.7, 29.9, 25.3.

4.2.15. (*R*)-1,2,3,4-Tetrahydronaphthalen-1-ol.[17] Colorless oil. 86% Yield; 77% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm). Retention times: 13.169 min [minor (*S*)-enantiomer], 15.630 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = -21.3$ (c 1.5, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.43 (m, 1H), 7.16–7.24 (m, 2H), 7.08–7.10 (m, 1H), 4.76 (br s, 1H), 2.66–2.86 (m, 2H), 1.71–1.99 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.7, 137.0, 128.9, 128.6, 127.5, 126.1, 68.0, 32.2, 29.2, 18.7.

4.2.16. (*R*)-1-Phenyl-propanol.[17] Colorless oil. 80% Yield; 73% ee determined by HPLC analysis (Daicel Chiralcel OJ column, hexane/2-propanol = 95:5, 0.5 mL/min, 254 nm). Retention times: 14.578 min [minor (*S*)-enantiomer], 16.285 min [major (*R*)-enantiomer]. $[\alpha]_D^{20} = +24.6$ (c 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24–7.34 (m, 5H), 4.57 (t, $J = 6.9$ Hz, 1H), 2.01 (s, 1H), 1.70–1.84 (m, 2H), 0.90 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.5, 128.3, 127.4, 125.9, 75.9, 31.8, 10.1.

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