A Facile Synthesis of Optically Active Four Stereoisomers of 1-Aminobenz[*f*]indan-2-ol

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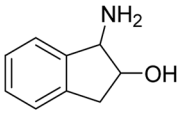
Optically active *cis*- or *trans*-1-aminoindan-2-ol (**1**) has been utilized as chiral auxiliaries and ligands[1] and as chiral resolving agent for racemic arylalkanoic acids.[2] As an effort to improve the chiral recognition ability of optically active *cis*- or *trans*-**1**, recently optically active *cis*- and *trans*-1-aminobenz[*f*]indan-2-ol (**2**) were prepared.[3,4] By enlarging the phenylene group of *cis*- or *trans*-**1** to the naphthalene group of *cis*- or *trans*-**2**, the chiral recognition ability was significantly improved because of the more effective CH/π interactions, which have been recognized to play a remarkable role in molecular arrangement in crystals,[5] in the less soluble diastereomeric salt crystals.



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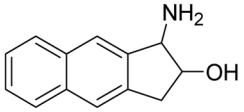

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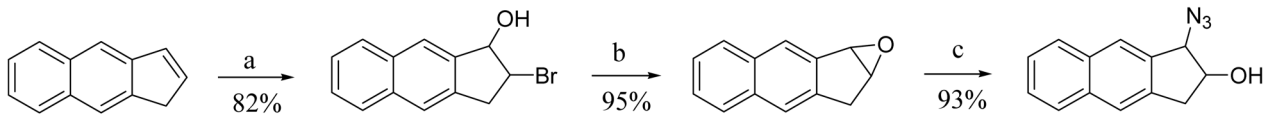
The method of preparing optically pure *cis*- and *trans*-**2** reported is based on the classical chemical resolution with the formation of enantioselective diastereomeric salt between racemic *cis*-**2** and (*R*)-2-naphthylglycolic acid[3] or with the formation of enantioselective diastereomeric salt between racemic *trans*-**2** and (+)-dibenzoyl-*D*-tartaric acid or (−)-dibenzoyl-*L*-tartaric acid.[4] However, the method reported is somewhat complicated. In this study, we wish to report a more efficient synthetic method based on the kinetic resolution with enzyme for the preparation of optically active four stereoisomers of **2** as shown in Schemes 1 and 2.

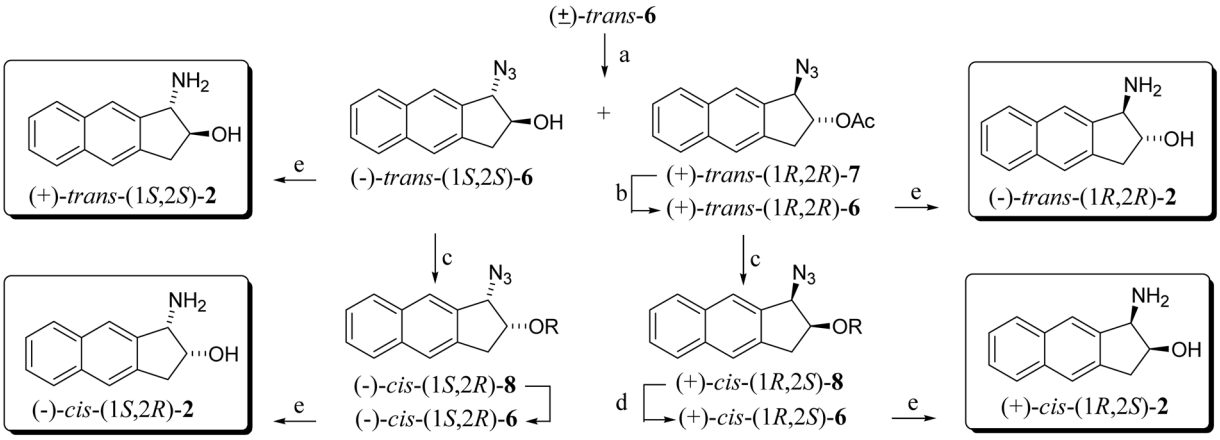
The starting material benz[*f*]indene (**3**) shown in Scheme 1 was prepared by the method reported.[6] Instead of the direct epoxidation, **3** was reacted with *N*-bromosuccinimide (NBS) in 50% aqueous THF at room temperature to afford 2-bromobenz[*f*]indan-2-ol (**4**) in 82% yield and then in the presence of NaOH, **4** was cyclized in methanol to afford 1,2-epoxybenz[*f*]indane (**5**) in 95% yield as shown in Scheme 1. The yield for the synthesis of **5** starting from **3** was overall 78%. The method for the synthesis of **5** shown in Scheme 1 was more efficient in terms of the chemical yield (78%) than the reported direct epoxidation (52%) of **3** with *meta*-chloroperoxybenzoic acid (MCPBA).[4] Compound **5** was converted to racemic *trans*-1-azidobenz[*f*]indan-2-ol [(±)-*trans*-**6**] by reacting with sodium azide in the presence of NH_4Cl in 93% yield. The overall yield (73%) for the preparation of (±)-*trans*-**6** from **3** via the method shown in Scheme 1 was improved about 30 % compared to that for the method described in the literature.[4]

Racemic (±)-*trans*-**6** is a significant intermediate, which is used as a starting material for the preparation of optically active four stereoisomers of **2** through the kinetic resolution and configuration inversion. Kinetic resolution of racemic (±)-*trans*-**6** was performed by reacting it with vinyl acetate in *tert*-butyl methyl ether in the presence of lipase PS (*Pseudomonas* sp., Amano), which has been successfully utilized for the resolution of *trans*-**1** through lipase-mediated kinetic transesterification.[7] The effect of the reaction time and the quantity of lipase PS on the resolution of 1 mmole of racemic (±)-*trans*-**6** in *tert*-butyl methyl ether containing 10 mmole of vinyl acetate was examined as a preliminary experiment. The result showed that the resolution was completed after 48 h. However, the resolution was not complete within 48 h regardless of the quantity of lipase PS used (10 ~100 mg/mmol). After 48 h, the use of a large quantity of lipase PS (>100 mg/mol) led to a partial racemization while a small quantity of lipase PS (10 mg/mmol) did not affect the resolution until 72 h. According to the preliminary experiment, resolution of 1 mmole of racemic (±)-*trans*-**6** was performed by reacting it with 10 mmole of vinyl acetate in the presence of 10 mg of lipase PS in *tert*-butyl methyl ether for 48 h. From this reaction, (+)-(1*R*,2*R*)-*trans*-2-acetoxy-1-azidobenz[*f*]indane [(+)-*trans*-(1*R*,2*R*)-**7**] was obtained in



3 **4** **5** (±)-*trans*-**6**

Scheme 1. (a) *N*-bromosuccinimide (NBS), room temperature. (b) NaOH, room temperature. (c) NaN_3, NH_4Cl, 80% aqueous ethanol, reflux.



Scheme 2. (a) lipase PS, vinyl acetate, *tert*-BuOMe, room temperature. (b) K_2CO_3, MeOH, room temperature, 97%. (c) 4-nitrobenzoic acid, triphenylphosphine, diethyl azodicarboxylate, THF, 0 °C to room temperature, 70%. (d) $NaOCH_3$, methanol and CH_2Cl_2, room temperature, 95%. (e) H_2, 10% Pd/C, methanol, 98%.

96% yield with 99% ee, leaving the unreacted (−)-*trans*-(1*S*,2*S*)-**6** with 98% recovery in optically pure state (99% ee). In each case, the optical purity was determined by chiral liquid chromatography on a CHIRALCEL OD chiral column. Optically active (+)-*trans*-(1*R*,2*R*)-**7** was converted into (+)-*trans*-(1*R*,2*R*)-**6** on methanolysis in the presence of potassium carbonate without the loss of the original chiral integrity in 97% yield with 99% ee. Optical purity of (+)-*trans*-(1*R*,2*R*)-**6** was also confirmed by chiral liquid chromatography on a CHIRALCEL OD chiral column.

Under Mitsunobu condition (4-nitrobenzoic acid, triphenylphosphine, diethyl azodicarboxylate), (−)-*trans*-(1*S*,2*S*)-**6** and (+)-*trans*-(1*R*,2*R*)-**6** were converted into (−)-*cis*-(1*S*,2*R*)-1-azido-2-(4-nitrobenzoyloxy)benz[*f*]indane [(−)-*cis*-(1*S*,2*R*)-**8**] and (+)-*cis*-(1*R*,2*S*)-1-azido-2-(4-nitrobenzoyloxy)benz[*f*]indane [(+)-*cis*-(1*R*,2*S*)-**8**] in 70% yield without the loss of any optical purity respectively. As a consequent step, each of (−)-*cis*-(1*S*,2*R*)-**8** and (+)-*cis*-(1*R*,2*S*)-**8** was converted into corresponding (−)-*cis*-(1*S*,2*R*)-**6** and (+)-*cis*-(1*R*,2*S*)-**6** by treating with sodium methoxide in methanol in 95% yield in each case. The stereochemistry inversion of (−)-*trans*-(1*S*,2*S*)-**6** and (+)-*trans*-(1*R*,2*R*)-**6** into (−)-*cis*-(1*S*,2*R*)-**6** and (+)-*cis*-(1*R*,2*S*)-**6** was confirmed by the chiral liquid chromatography on a CHIRALCEL OD chiral column as shown in Figure 1.

Finally, each of (−)-*trans*-(1*S*,2*S*)-**6**, (+)-*trans*-(1*R*,2*R*)-**6**, (−)-*cis*-(1*S*,2*R*)-**6** and (+)-*cis*-(1*R*,2*S*)-**6** was hydrogenated on palladized carbon to give corresponding (+)-*trans*-(1*S*,2*S*)-**2**, (−)-*trans*-(1*R*,2*R*)-**2**, (−)-*cis*-(1*S*,2*R*)-**2** or (+)-*cis*-(1*R*,2*S*)-**2** in 98% yield without the loss of optical purity. The enantiomeric purity of the four stereoisomers of 1-aminobenz[*f*]indan-2-ol (**2**) thus prepared was determined to be 99% ee by HPLC on a chiral stationary phase, which was prepared by bonding (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid to aminopropyl silica gel as reported previously.[8]

Experimental Section

General. The NMR spectra were obtained with a Varian

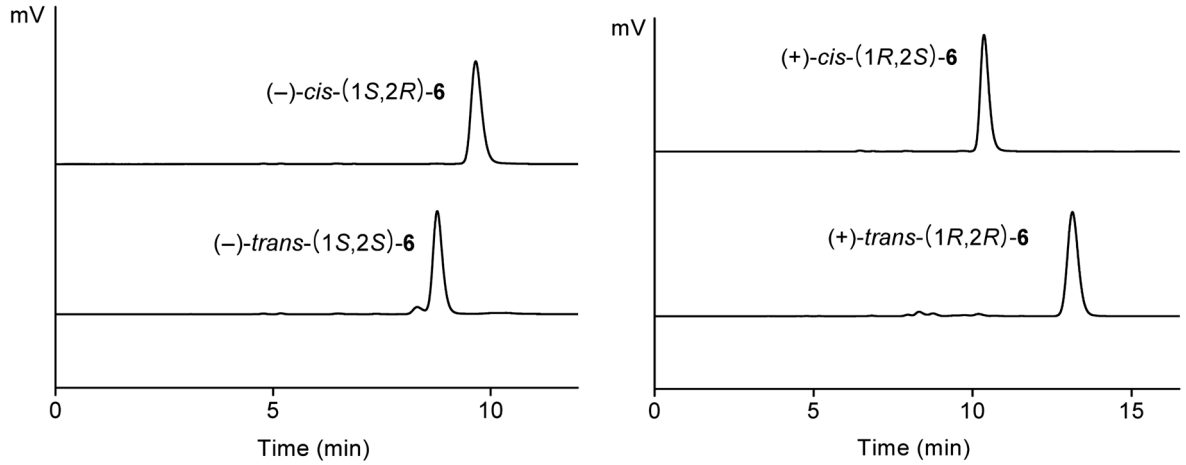


Figure 1. Chromatograms showing the results for the stereochemical inversion of optically active (−)-*trans*-(1*S*,2*S*)-**6** and (+)-*trans*-(1*R*,2*R*)-**6** into (−)-*cis*-(1*S*,2*R*)-**6** and (+)-*cis*-(1*R*,2*S*)-**6**. The chromatograms were obtained on a CHIRALCEL OD chiral column (2-propanol/hexane, 5 : 95).

Gemini 300 spectrometer. Chemical shifts were reported in parts per million (ppm) relative to tetramethyl silane as an internal standard. Melting points were taken on an Electrothermal Capillary Melting Point Apparatus and reported without correction. Optical purities were determined with an HPLC system consisting of a Waters Model 510 pump and a Youglin M720 detector. The UV detection was set at 254 nm.

***trans*-2-Bromobenz[*f*]indan-1-ol (4).** To a stirred solution of benz[*f*]indene (**3**) (1 g, 6.02 mmol) in 50% aqueous THF (100 mL) was added *N*-bromosuccinimide (1.18 g, 6.62 mmol) slowly at room temperature. After 12 h, the organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with 5% $Na_2S_2O_3$ and brine, and then dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to leave a crystalline material. The crystalline material was recrystallized from ethanol to give **4** (1.30 g, 82%). ^{1}H NMR ($CDCl_3$) δ (ppm) 7.78 (m, 3H), 7.63 (s, 1H), 7.41 (m, 2H), 5.39 (d, J = 5.7 Hz, 1H), 4.35 (m, 1H), 3.66 (dd, J = 6.9 Hz and 16.2 Hz, 1H), 3.36 (dd, J = 7.8 Hz and 16.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) 137.8, 136.4, 134.3, 133.4, 128.5, 128.0, 126.5, 126.0, 123.3, 123.3, 82.8, 54.8, 40.2.

1,2-Epoxybenz[*f*]indane (5). To a stirred solution of **4** (1.3 g, 4.95 mmol) in 20 mL of diethyl ether was added powdered NaOH (0.5 g, 12.5 mmol) at room temperature. After stirring for 4 h, water (15 mL) was added to the reaction mixture, and the organic layer was separated, and aqueous layer was additionally extracted with diethyl ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to afford **5** (0.86 g, 95%) as a crystalline material. mp 149-150 °C (lit[4] mp 148-150 °C); ^{1}H NMR ($CDCl_3$) δ (ppm) 7.95-7.33 (m, 6H), 4.41 (d, J = 2.7 Hz, 1H), 4.21 (t, J = 2.7 Hz, 1H), 3.39 (d, J = 18.3 Hz, 1H), 3.17 (d, J = 18.3 Hz, 1H); ^{13}C NMR ($CHCl_3$) δ (ppm) 141.0, 139.2, 134.1, 132.6, 128.2, 127.8, 126.3, 125.8, 124.9, 124.5, 59.0, 58.4, 34.3.

Racemic *trans*-1-azidobenz[*f*]indan-2-ol [(±)-*trans*-6]. A mixture of **5** (0.8 g, 4.40 mmol), NH_4Cl (0.37 g, 6.92 mmol) and NaN_3 (0.45 g, 6.92 mmol) in 80% aqueous ethanol (15 mL) was refluxed for 2 h. After cooling, water (10 mL) was added to the mixture, and the mixture was extracted with diethyl acetate. The extract was washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to afford (±)-*trans*-**6** as an analytically pure product (0.92 g, 93%). mp 103-105 °C (lit[4] mp 103-105 °C); ^{1}H NMR ($CHCl_3$) δ (ppm) 7.87-7.43 (m, 6H), 4.85 (d, J = 5.4 Hz, 1H), 4.53 (m, 1H), 3.45 (dd, J = 6.3 Hz and 16.2 Hz, 1H), 3.01 (dd, J = 6.0 Hz and 16.2 Hz, 1H), 2.36 (d, J = 3.9 Hz, 1H); ^{13}C NMR ($CHCl_3$) δ (ppm) 137.7, 137.4, 137.0, 133.2, 128.4, 127.9, 126.5, 125.9, 124.1, 78.9, 71.4, 38.7.

(+)-*trans*-(1*R*,2*R*)-2-Acetoxy-1-azidobenz[*f*]indane [(+)-*trans*-(1*R*,2*R*)-7] and (−)-*trans*-(1*S*,2*S*)-1-azidobenz[*f*]-indan-2-ol [(−)-*trans*-(1*S*,2*S*)-6]. A suspension of (±)-*trans*-**6** (1 g, 4.44 mmol), vinyl acetate (2.5 mL, 26.30 mmol), and lipase PS (Pseudomonas sp, Amano; 44.58 mg) in *tert*-BuOMe (50 mL) was stirred at room temperature for 48h. The mixture was filtered through a *Celite* pad and the filtrate was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (ethyl acetate/hexane, 1 : 5) to give (+)-*trans*-(1*R*,2*R*)-**7** as a white solid and (−)-*trans*-(1*S*,2*S*)-**6** as a white solid.

(+)-*trans*-(1*R*,2*R*)-2-Acetoxy-1-azidobenz[*f*]indane [(+)-*trans*-(1*R*,2*R*)-7]. Yield: 0.57 g (96%); mp 98-99 °C; $[\alpha]_D^{21}$ +8.7 (*c* 1.0 $CHCl_3$). Optical purity was determined to be 99% ee by HPLC on a CHIRALCEL OD chiral column (2-propanol/hexane, 5 : 95). ^{1}H NMR ($CHCl_3$) δ (ppm) 7.88-7.39 (m, 6H), 5.41 (m, 1H), 5.01 (d, J = 4.5 Hz, 1H), 3.66 (dd, J = 6.6 Hz and 16.0 Hz, 1H), 3.79 (dd, J = 4.8 Hz and 16.0 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR ($CHCl_3$) δ (ppm) 170.8, 137.7, 136.3, 134.5, 133.2, 128.5, 127.9, 126.7, 126.1, 124.2, 124.1, 79.7, 68.8, 36.5, 21.3.

(−)-*trans*-(1*S*,2*S*)-1-Azidobenz[*f*]indan-2-ol [(−)-*trans*-(1*S*,2*S*)-6]. Yield: 0.49 g (98%); mp 102-104 °C; $[\alpha]_D^{23}$ −14.5 (*c* 1.0 $CHCl_3$). Optical purity was determined to be 99% ee by HPLC on a CHIRALCEL OD chiral column (2-propanol/hexane, 5 : 95).

(+)-*trans*-(1*R*,2*R*)-1-Azidobenz[*f*]indan-2-ol [(+)-*trans*-(1*R*,2*R*)-6]. To a stirred solution of (+)-*trans*-(1*R*,2*R*)-**7** (1 g, 3.74 mmol) in MeOH (30 mL) was added K_2CO_3 (1.6 g) at room temperature. After stirring for 1 h, the mixture was filtered through a *Celite* pad and the filtrate was evaporated under reduced pressure. The residue was dissolved in H_2O (15 mL) and the solution was extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous Na_2SO_4, evaporated under pressure and purified by flash chromatography on silica gel (ethyl acetate/hexane, 1 : 5) to give (+)-*trans*-(1*R*,2*R*)-**6** as a white solid. Yield: 0.82 g (97%); mp 103-104 °C; $[\alpha]_D^{22}$ +14.8 (*c* 1.0 $CHCl_3$). Optical purity was determined to be 99% ee by HPLC on a CHIRALCEL OD chiral column (2-propanol/hexane, 5 : 95).

(−)-*cis*-(1*S*,2*R*)-1-Azido-2-(4-nitrobenzoyloxy)benz[*f*]-indane [(−)-*cis*-(1*S*,2*R*)-8]. To a stirred solution of (−)-*trans*-(1*S*,2*S*)-**6** (1.5 g, 6.66 mmol) and 4-nitrobenzoic acid (2.23 g, 13.32 mmol) in THF (50 mL) was added dropwise Ph_3P (3.49 g, 13.32 mmol) in 20 mL of THF at 0 °C during 20 min and then diethylazodicarboxylate (2.33 g, 13.32 mmol) in 20 mL of THF at the same temperature during 20 min. The mixture was stirred at 0 °C for 30 min, and then at room temperature for 2.5 h. The mixture was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane, 1 : 8) to give (−)-*cis*-(1*S*,2*R*)-**8** as a white solid (1.75 g, 70%). mp 182-183 °C; $[\alpha]_D^{23}$ –84.6 (*c* 0.13 THF); ^{1}H NMR ($CHCl_3$) δ (ppm) 8.29 (d, J = 10.5 Hz, 2H), 8.23 (d, J = 10.5 Hz, 2H), 7.92-7.50 (m, 6H), 5.90 (q, J = 5.4 Hz, 1H), 5.17 (d, J = 5.4 Hz, 1H), 3.56 (dd, J = 6.8 Hz and 16.8 Hz, 1H), 3.47 (dd, J = 5.2 Hz and 16.8 Hz, 1H); ^{13}C NMR ($CHCl_3$) δ (ppm) 164.6, 151.0, 136.9, 136.0, 135.1, 134.6, 133.3, 131.3, 128.6, 128.0, 126.9, 126.3, 124.4, 124.3, 123.8, 77.5, 65.5, 36.3.

(+)-*cis*-(1*R*,2*S*)-1-Azido-2-(4-nitrobenzoyloxy)benz[*f*]-indane [(+)-*cis*-(1*R*,2*S*)-8]. *Via* the exactly identical method

for the preparation of (−)-*cis*-(1*S*,2*R*)-**8**, (+)-*trans*-(1*R*,2*R*)-**6** afforded (+)-*cis*-(1*R*,2*S*)-**8** in 70%. mp 182-183 °C; $[\alpha]_D^{24}$ +86.3 (*c* 0.55 THF). Spectral data were identical to those of (−)-*cis*-(1*S*,2*R*)-**8**.

(−)-*cis*-(1*S*,2*R*)-1-Azidobenz[*f*]indan-2-ol [(−)-*cis*-(1*S*, 2*R*)-6]. To a stirred solution of NaOMe in MeOH (30 mL) was added dropwise a solution of (−)-*cis*-(1*S*,2*R*)-**8** (1 g, 2.67 mmol) in CH_2Cl_2 (20 mL) at room temperature. The mixture was stirred for 5 h and then evaporated under reduced pressure. The residue, after addition of brine, was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane, 1 : 5) to give (−)-*cis*-(1*S*,2*R*)-**6** (0.57 g, 95% yield). mp 100-101 °C; $[\alpha]_D^{23}$ −30.7 (*c* 0.43 $CHCl_3$). Optical purity was determined to be 99% ee by HPLC on a CHIRALCEL OD chiral column (2-propanol/hexane, 5 : 95). ^{1}H NMR ($CHCl_3$) δ (ppm) 7.88-7.44 (m, 6H), 4.96 (d, *J* = 5.4 Hz, 1H), 4.70 (m, 1H), 3.35 (dd, *J* = 6.3 Hz and 15.9 Hz, 1H), 3.13 (dd, *J* = 15.9 Hz and 6.3 Hz, 1H), 2.38 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR ($CHCl_3$) δ (ppm) 138.4, 136.9, 134.6, 133.2, 128.5, 127.9, 126.7, 126.0, 124.5, 74.8, 67.8, 38.8.

(+)-*cis*-(1*R*,2*S*)-1-Azidobenz[*f*]indan-2-ol [(+)-*cis*-(1*R*, 2*S*)-6]. *Via* the exactly identical procedure for the preparation of (−)-*cis*-(1*S*,2*R*)-**6**, (+)-*cis*-(1*R*,2*S*)-**6** was prepared (95%). mp 99-101 °C; $[\alpha]_D^{23}$ +31.5 (*c* 0.6 $CHCl_3$). Optical purity was determined to be 99% ee by HPLC on a CHIRALCEL OD chiral column (2-propanol/hexane, 5 : 95). NMR data were identical to those of (−)-*cis*-(1*S*,2*R*)-**6**.

(+)-*trans*-(1*S*,2*S*)-1-Aminobenz[*f*]indan-2-ol [(+)-*trans*-(1*S*,2*S*)-2]. A solution of (−)-*trans*-(1*S*,2*S*)-**6** (1 g, 4.44 mmol) in MeOH (30 mL) was hydrogenated on 10% Pd-C (50 mg) with 4 bar H_2 for 1h. After removal of the catalyst by filtration, the solvent was evaporated under reduced pressure to afford (+)-*trans*-(1*S*,2*S*)-**2** as a white solid, (0.87 g, 98% yield). mp 160 °C (decomposition); $[\alpha]_D^{22}$ +41.6 (*c* 0.3 MeOH). [lit.[4] mp 162 °C (decomposition), $[\alpha]_D^{19}$ +43 (*c* 0.25, $CHCl_3$)]. Optical purity was determined to be 99% ee by HPLC on a chiral stationary phase, which was prepared by bonding (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid to aminopropyl silica gel as reported previously[8] (chromatographic condition; mobile phase: 80% methanol in water + 10 mM acetic acid + 0.1 mM ammonium acetate. flow rate: 0.5 mL/min. detection: 254 nm UV. temperature: 20 °C). ^{1}H NMR (Acetone-d_6) δ (ppm) 7.82-7.40 (m, 6H), 4.98 (d, *J* = 6.6 Hz, 1H), 4.45 (m, 1H), 3.40 (dd, *J* = 7.2 Hz and 16.0 Hz, 1H), 3.03 (dd, *J* = 8.8 Hz and 16.0 Hz, 1H), 2.88 (bs, 1H), 2.01 (s, 2H); ^{13}C NMR (CD_3OD) δ (ppm) 141.0, 139.4, 134.0, 133.5, 127.7, 127.3, 125.2, 124.9, 123.1, 122.5, 74.6, 59.2, 38.6.

(−)-*trans*-(1*R*,2*R*)-1-Aminobenz[*f*]indan-2-ol [(−)-*trans*-(1*R*,2*R*)-2]. Yield 98% (99% ee). mp 160 °C (decomposition); $[\alpha]_D^{21}$ −40.3 (*c* 0.5 MeOH) [lit.[4] mp 162 °C (decomposition); $[\alpha]_D^{19}$ −39.9 (*c* 0.25, $CHCl_3$)]. NMR data were identical to those of (+)-*trans*-(1*S*,2*S*)-**2**.

(+)-*cis*-(1*R*,2*S*)-1-Aminobenz[*f*]indan-2-ol [(+)-*cis*-(1*R*, 2*S*)-2]. Yield 98% (99% ee). mp 167 °C (decomposition); $[\alpha]_D^{22}$ +87.5 (*c* 0.5 MeOH). [lit.[3] m.p 169 °C (decomposition); $[\alpha]_D$ +89 (*c* 0.2, $CHCl_3$)]. ^{1}H NMR (Acetone-d_6) δ (ppm) 7.88-7.40 (m, 6H), 5.03 (d, *J* = 6.0 Hz, 1H), 4.84 (m, 1H), 3.34 (dd, *J* = 6.0 Hz and 17.7 Hz, 1H), 3.32 (d, 17.7 Hz, 1H), 2.92 (bs, 1H), 2.01 (s, 2H); ^{13}C NMR (Acetone-d_6) δ (ppm) 143.9, 141.1, 134.3, 133.6, 128.1, 127.7, 125.6, 125.2, 124.2, 123.2, 81.0, 68.3, 38.5.

(−)-*cis*-(1*S*,2*R*)-1-Aminobenz[*f*]indan-2-ol [(−)-*cis*-(1*S*, 2*R*)-2]. Yield 98% (99% ee); mp 167 °C (decomposition); $[\alpha]_D^{22}$ −86.9 (*c* 0.5 MeOH). NMR data were identical to those of (+)-*cis*-(1*R*,2*S*)-**2**.

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