Supporting Information:

C₂ Symmetric Bicyclo[2.2.2]octadienes as Chiral Ligands: Their High Performance in Rhodium-Catalyzed Asymmetric Arylation of *N*-Tosylarylimines

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Supporting Data

General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ¹H, and 125 MHz for ¹³C). Chemical shifts are reported in δ ppm referenced to an internal SiMe₄ standard for ¹H NMR and chloroform-*d* (δ 77.05) for ¹³C NMR. Optical rotations were measured on a JASCO DIP-370 polarimeter.

Materials. THF, Et₂O, and 1,4-dioxane were distilled from benzophenone-ketyl under nitrogen prior to use. Diisopropylamine was distilled from CaH₂ under nitrogen prior to use. PdCl₂(dppf),¹ (2-pyridyl)triflimide,² [RhCl(C₂H₄)₂]₂,³ and (1*R*,4*R*)-2,5-dibenzylbicyclo[2.2.1]hepta-2,5-diene ((*R,R*)-Bn-nbd*)⁴ were prepared according to the reported procedures.

Preparation of Chiral 2,5-Disubstituted Bicyclo[2.2.2]octa-2,5-diene Ligands (Bn-bod* and Ph-bod*).

Racemic bicyclo[2.2.2]octan-2,5-dione was prepared according to the reported procedures.⁵

Resolution of Racemic Bicyclo[2.2.2]octan-2,5-dione with (*R*)-5-(1-Phenylethyl)semioxamazine. To a mixture of bicyclo[2.2.2]octan-2,5-dione (7.43 g, 53.8 mmol) and (*R*)-5-(1-phenylethyl)semioxamazine⁶ (22.3 g, 107.6 mmol) in 250 mL of ethanol was added a small amount of sodium acetate and acetic acid, and the mixture was heated to reflux for 3 h. The resulting precipitate was filtered and it was washed with ethanol. The solid product was recrystallized three times from methanol to give 3.34 g (12% yield) of the hydrazone. For hydrolysis of the hydrazone, a suspension of the hydrazone in an excess of 20% sulfuric acid was heated to reflux for 4 h. The reaction mixture was extracted with

CH₂Cl₂ four times. The combined organic layers were washed with 0.2 N NaOH twice and then dried over magnesium sulfate. Removal of the solvent gave the crude product which is 97.5% ee by HPLC analysis with chiral stationary phase column, Chiralcel OJ (hexane/2-PrOH = 1/1). The crude product was purified by recrystallization from ethanol to give 335 mg (4.5% yield) of (1*R*,4*R*)-bicyclo[2.2.2]octan-2,5-dione (**1**) as white solid which is >99% ee by the HPLC analysis. $[\alpha]^{20}_{\text{D}} -55$ (*c* 1.22, CHCl₃). (lit⁷ $[\alpha]^{20}_{\text{D}} +50$ (*c* 0.55, CHCl₃) for (*S,S*)-**1**).

(1*R*,4*R*)-2,5-Bis(trifluoromethanesulfonyloxy)bicyclo[2.2.2]octa-2,5-diene (2**).** LDA was generated by dropwise addition of a 1.59 M solution of *n*-BuLi (692 μ L, 1.10 mmol) in hexane to a -78 °C solution of diisopropylamine (154 μ L, 1.10 mmol) in 0.50 mL of THF. This solution was stirred for additional 20 minutes before a solution of (1*R*,4*R*)-bicyclo[2.2.2]octan-2,5-dione (50.0 mg, 0.362 mmol) in 1.0 mL of THF was slowly added at -78 °C. The resulting mixture was stirred at -78 °C for additional 1 h, before a solution of *N*-(2-pyridyl)triflimide (394 mg, 1.10 mmol) in 1.0 mL of THF was slowly added at -78 °C. This mixture was warmed to room temperature while stirred for 2 days. Ice water was added to quench the reaction and the organic solvent was removed *in vacuo*. The aqueous layer was extracted with Et₂O three times. The combined organic layers were washed with 10% NaOH and then dried over magnesium sulfate. Removal of the solvent gave the crude product, which was purified by chromatography on silica gel column (hexane/diethyl ether = 10/1) to give 102 mg (70% yield) of (1*R*,4*R*)-2,5-bis(trifluoromethanesulfonyloxy)bicyclo[2.2.2]octa-2,5-diene (**2**) as colorless oil. ¹H NMR (CDCl₃): δ 1.56-1.64 (m, 2H), 1.82-1.90 (m, 2H), 3.69-3.73 (m, 2H), 6.16 (dd, *J* = 7.2 and 2.9 Hz, 2H). ¹³C{¹H} NMR (CDCl₃): δ 24.67, 40.18, 118.59 (q, *J*_{C-F} = 320 Hz), 119.43, 155.14. Anal. Calcd for C₁₀H₈F₆O₆S₂: C, 29.86; H, 2.00. Found: C, 29.99; H, 2.13.

(1*R*,4*R*)-2,5-Dibenzylbicyclo[2.2.2]octa-2,5-diene ((*R,R*)-Bn-bod*). To a mixture of (1*R*,4*R*)-2,5-bis(trifluoromethanesulfonyloxy)bicyclo[2.2.2]octa-2,5-diene (**2**) (78.9 mg, 0.20 mmol) and PdCl₂(dppf) (1.4 mg, 2.0 μ mol) in 1.5 mL of Et₂O was added benzylmagnesium bromide (3.33 mL, 0.36 M, 1.2 mmol) in Et₂O at room temperature, and the reaction mixture was heated to reflux for 24 h. After cooled to room temperature, the reaction mixture was quenched with water, and extracted with Et₂O. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 10/1) and GPC to give 33.8 mg (59% yield) of (1*R*,4*R*)-2,5-dibenzylbicyclo[2.2.2]octa-2,5-diene as white solid. ¹H NMR (CDCl₃): δ 1.07-1.15 (m, 2H), 1.18-1.26 (m, 2H), 3.22-3.28 (m, 2H), 3.43 (s, 4H), 5.82 (dd, *J* = 6.1 and 1.2 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 4H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 4H). ¹³C{¹H} NMR (CDCl₃): δ 26.05, 40.14, 41.13, 125.87, 128.15, 128.24, 129.01, 139.68, 147.15. Anal. Calcd for C₂₂H₂₂: C, 92.26; H, 7.74. Found: C, 92.17; H, 7.85. $[\alpha]^{20}_{\text{D}} +86$ (*c* 0.71, CHCl₃).

(1*R*,4*R*)-2,5-Diphenylbicyclo[2.2.2]octa-2,5-diene ((*R,R*)-Ph-bod*). To a mixture of (1*R*,4*R*)-2,5-bis(trifluoromethanesulfonyloxy)bicyclo[2.2.2]octa-2,5-diene (**2**) (78.9 mg, 0.20 mmol) and PdCl₂(dppf) (1.4 mg, 2.0 μmol) in 1.5 mL of Et₂O was added phenylmagnesium bromide (1.0 mL, 1.2 M, 1.2 mmol) in Et₂O at room temperature, and the reaction mixture was heated to reflux for 8 h. After cooled to room temperature, the reaction mixture was quenched with water, and extracted with Et₂O. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, hexane/benzene = 10/1) to give 39.5 mg (78% yield) of (1*R*,4*R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene as white solid. ¹H NMR (CDCl₃): δ 1.56 (s, 4H), 4.23 (d, *J* = 6.3 Hz, 2H), 6.63 (dd, *J* = 6.3 and 2.0 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 4H), 7.44 (d, *J* = 7.5 Hz, 4H). ¹³C{¹H} NMR (CDCl₃): δ 25.75, 40.03, 124.73, 126.76, 128.46, 129.13, 138.16, 146.77. Anal. Calcd for C₂₀H₁₈: C, 92.98; H, 7.02. Found: C, 93.03; H, 7.14. [α]_D²⁰ -30 (*c* 0.72, CHCl₃).

Preparation of *N*-Tosylarylimines.

N-Tosylarylimines (**3a-3h**) were prepared according to the reported procedures.⁸

***N*-(4-Chlorophenyl)methylidene-4-methylbenzenesulfonamide (3a)** [CAS:3175-65-1]: 98% yield. ¹H NMR (CDCl₃) δ 2.44 (s, 3H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 8.99 (s, 1H).

***N*-(4-Trifluoromethylphenyl)methylidene-4-methylbenzenesulfonamide (3b)** [CAS:198012-02-1]: 93% yield. ¹H NMR (CDCl₃) δ 2.45 (s, 3H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 2H), 8.05 (d, *J* = 8.3 Hz, 2H), 9.08 (s, 1H).

***N*-(4-Methoxyphenyl)methylidene-4-methylbenzenesulfonamide (3c)** [CAS:14674-38-5]: 94% yield. ¹H NMR (CDCl₃) δ 2.42 (s, 3H), 3.88 (s, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 8.9 Hz, 2H), 8.94 (s, 1H).

***N*-(4-dimethylaminophenyl)methylidene-4-methylbenzenesulfonamide (3d)** [CAS:14674-40-9]: 77% yield. ¹H NMR (CDCl₃) δ 2.40 (s, 3H), 3.08 (s, 6H), 6.65 (d, *J* = 8.9 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 8.81 (s, 1H).

***N*-(2-Methoxyphenyl)methylidene-4-methylbenzenesulfonamide (3e)** [CAS:100200-70-2]: 97% yield. ¹H NMR (CDCl₃) δ 2.43 (s, 3H), 3.92 (s, 3H), 6.96 (t, *J* = 8.8 Hz, 1H), 6.98 (t, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.55 (td, *J* = 7.8, 1.7 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 8.05 (td, *J* = 7.8, 1.7 Hz, 1H), 9.55 (s, 1H).

***N*-(1-Naphthyl)methylidene-4-methylbenzenesulfonamide (3f)** [CAS:36216-15-6]: 93% yield. ¹H NMR (CDCl₃) δ 2.43 (s, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* =

7.8 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.67 (t, J = 8.1 Hz, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.95 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 7.2 Hz, 1H), 8.98 (d, J = 8.2 Hz, 1H), 9.61 (s, 1H).

***N*-(2-Furyl)methylidene-4-methylbenzenesulfonamide (3g)** [CAS:135822-87-6]: 67% yield. ^1H NMR (CDCl_3) δ 2.43 (s, 3H), 6.64 (dd, J = 3.5, 1.7 Hz, 1H), 7.33-7.37 (m, 3H), 7.74 (dt, J = 1.7, 0.7 Hz, 1H), 7.87 (d, J = 8.3 Hz, 2H), 8.81 (s, 1H).

***N*-Phenylmethylidene-4-methylbenzenesulfonamide (3h)** [CAS:13707-41-0]: 95% yield. ^1H NMR (CDCl_3) δ 2.43 (s, 3H), 7.34 (d, J = 8.2 Hz, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.89 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 7.4 Hz, 2H), 9.03 (s, 1H).

General Procedure for the Rhodium-Catalyzed Asymmetric Arylation of Arylborexines ((ArBO)₃) to *N*-Tosylarylimines.

To the solution of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (0.58 mg, 0.0015 mmol, 3 mol % Rh) and (*R, R*)-Ph-bod* (0.85 mg, 0.0033 mmol, 1.1 eq to Rh) in 1,4-dioxane (0.3 mL) was added KOH aq (6.5 μL , 3.1 M, 20 mol % KOH, H_2O : 1 eq to boron) at room temperature for 5 min. This solution containing the catalyst was added to the solution of imine **3** (0.10 mmol) and arylborexine **4** (0.12 mmol, 1.2 eq to **3**) in 1,4-dioxane (0.5 mL) at the same temperature. After 6 h stirring at 60 °C, the mixture was passed through a short silica gel column (pretreated with methanol, eluent: ethyl acetate). The residue was chromatographed on silica gel (hexane/ethyl acetate = 2/1) to give the arylated product. The reaction conditions and results are summarized in Tables 1

(*S*)-*N*-[(4-Chlorophenyl)phenylmethyl]-4-methylbenzenesulfonamide (5am) [CAS:258277-20-2]: Table 1 entry 1 ((*R, R*)-Ph-bod*); 96% yield (white solid), 98% ee. Table 1 entry 2 ((*R, R*)-Bn-bod*); 98% yield, 94% ee. Table 1 entry 3 ((*R, R*)-Bn-nbd*); 98% yield, 92% ee. Table 1 entry 4 ($[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ /(*R*)-binap/KOH); 28% yield, 31% ee. Table 1 entry 5 ((*R*)-segphos); 30% yield, 70% ee. Table 1 entry 6 ((*S*)-phosphoramidite); 44% yield, 6% ee. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min, wavelength = 230 nm. Retention times: 15.9 min [(*S*)-enantiomer], 20.2 min [(*R*)-enantiomer]. $[\alpha]^{20}_{\text{D}} -7.4$ (c 1.30, CHCl_3) for 98% ee. ^1H NMR (CDCl_3) δ 2.39 (s, 3H), 5.17 (broad s, 1H), 5.54 (d, J = 7.1 Hz, 1H), 7.01-7.09 (m, 4H), 7.12-7.24 (m, 7H), 7.55 (d, J = 8.3 Hz, 2H).

(*S*)-*N*-[(4-Trifluoromethylphenyl)phenylmethyl]-4-methylbenzenesulfonamide (5bm) [CAS:260997-42-0]: 97% yield (white solid), 95% ee. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min, wavelength = 230 nm. Retention times: 15.4 min [(*S*)-enantiomer], 22.5 min [(*R*)-enantiomer]. $[\alpha]^{20}_{\text{D}} +7.6$ (c 1.03, CHCl_3) for 95% ee. ^1H NMR (CDCl_3) δ 2.37 (s,

3H), 5.29 (broad s, 1H), 5.62 (d, $J = 7.1$ Hz, 1H), 7.03-7.07 (m, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 7.20-7.25 (m, 3H), 7.26 (d, $J = 8.3$ Hz, 2H), 7.44 (d, $J = 8.1$ Hz, 2H), 7.53 (d, $J = 8.3$ Hz, 2H).

(S)-N-[(4-Methoxyphenyl)phenylmethyl]-4-methylbenzenesulfonamide

(5cm) [CAS:258277-16-6]: 96% yield (pale yellow solid), 99% ee. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min, wavelength = 230 nm. Retention times: 18.9 min [(S)-enantiomer], 28.4 min [(R)-enantiomer]. $[\alpha]^{20}_{\text{D}} -19.7$ (c 1.03, CHCl_3) for 99% ee. ^1H NMR (CDCl_3) δ 2.38 (s, 3H), 3.75 (s, 3H), 4.97 (d, $J = 6.8$ Hz, 1H), 5.52 (d, $J = 6.8$ Hz, 1H), 6.73 (d, $J = 8.8$ Hz, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.07-7.12 (m, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 7.16-7.25 (m, 3H), 7.56 (d, $J = 8.3$ Hz, 2H).

(S)-N-[(4-Dimethylaminophenyl)phenylmethyl]-4-

methylbenzenesulfonamide (5dm) [CAS:258277-18-8]: 94% yield (white solid), 98% ee. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min, wavelength = 230 nm. Retention times: 20.7 min [(S)-enantiomer], 33.5 min [(R)-enantiomer]. $[\alpha]^{20}_{\text{D}} -57.1$ (c 1.05, CHCl_3) for 98% ee. ^1H NMR (CDCl_3) δ 2.38 (s, 3H), 2.89 (s, 6H), 4.92 (d, $J = 6.6$ Hz, 1H), 5.48 (d, $J = 6.6$ Hz, 1H), 6.54 (d, $J = 8.7$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 7.12-7.23 (m, 7H), 7.56 (d, $J = 8.1$ Hz, 2H).

(S)-N-[(2-Methoxyphenyl)phenylmethyl]-4-methylbenzenesulfonamide

(5em) [CAS:258277-17-7]: 98% yield (white solid), 99% ee. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min, wavelength = 230 nm. Retention times: 14.8 min [(R)-enantiomer], 17.0 min [(S)-enantiomer]. $[\alpha]^{20}_{\text{D}} -30.6$ (c 1.08, CHCl_3) for 99% ee. ^1H NMR (CDCl_3) δ 2.32 (s, 3H), 3.59 (s, 3H), 5.66 (d, $J = 9.1$ Hz, 1H), 5.76 (d, $J = 9.1$ Hz, 1H), 6.67 (d, $J = 8.0$ Hz, 1H), 6.78 (dd, $J = 7.5, 1.0$ Hz, 1H), 6.98 (dd, $J = 7.5, 1.0$ Hz, 1H), 7.04 (d, $J = 8.4$ Hz, 2H), 7.13-7.24 (m, 6H), 7.51 (d, $J = 8.4$ Hz, 2H).

(S)-N-[(1-Naphthyl)phenylmethyl]-4-methylbenzenesulfonamide (5fm)

[CAS:66558-07-4]: 95% yield (white solid), 98% ee. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min, wavelength = 230 nm. Retention times: 22.6 min [(R)-enantiomer], 30.2 min [(S)-enantiomer]. $[\alpha]^{20}_{\text{D}} -9.2$ (c 0.97, CHCl_3) for 98% ee. ^1H NMR (CDCl_3) δ 2.35 (s, 3H), 5.08-5.10 (m, 1H), 6.31 (d, $J = 6.6$ Hz, 1H), 7.06 (d, $J = 8.1$ Hz, 2H), 7.13-7.17 (m, 2H), 7.18-7.22 (m, 3H), 7.23-7.31 (m, 2H), 7.38 (ddd, $J = 8.4, 6.8, 1.3$ Hz, 1H), 7.44 (ddd, $J = 8.4, 6.8, 1.3$ Hz, 1H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.73 (d, $J = 7.9$ Hz, 1H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.82 (d, $J = 7.2$ Hz, 1H).

(S)-N-[(2-Furyl)phenylmethyl]-4-methylbenzenesulfonamide (5gm)

[CAS:158471-23-9]: 99% yield (pale yellow solid), 99% ee. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.5 mL/min, wavelength =

230 nm. Retention times: 22.1 min [(*S*)-enantiomer], 23.7 min [(*R*)-enantiomer]. $[\alpha]^{20}_{\text{D}} -21.6$ (*c* 1.03, CHCl_3) for 99% ee. ^1H NMR (CDCl_3) δ 2.38 (s, 3H), 5.15 (d, $J = 7.5$ Hz, 1H), 5.62 (d, $J = 7.5$ Hz, 1H), 5.99 (dt, $J = 3.3, 0.7$ Hz, 1H), 6.19 (dd, $J = 3.3, 1.8$ Hz, 1H), 7.12-7.20 (m, 4H), 7.21-7.27 (m, 4H), 7.58 (d, $J = 8.3$ Hz, 2H).

(*R*)-*N*-[(4-Chlorophenyl)phenylmethyl]-4-methylbenzenesulfonamide

(5hn) [CAS:258277-20-2]: 99% yield, 99% ee. the enantiomer of **3am**. $[\alpha]^{20}_{\text{D}} +6.1$ (*c* 1.27, CHCl_3) for 99% ee.

(*R*)-*N*-[(4-Methoxyphenyl)phenylmethyl]-4-methylbenzenesulfonamide

(5ho) [CAS:258277-16-6]: 97% yield, 96% ee. the enantiomer of **3cm**.

(*R*)-*N*-[(2-Methylphenyl)phenylmethyl]-4-methylbenzenesulfonamide

(5hp): 96% yield (pale orange solid), 99% ee. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min, wavelength = 230 nm. Retention times: 12.0 min [(*R*)-enantiomer], 13.8 min [(*S*)-enantiomer]. $[\alpha]^{20}_{\text{D}} -14.1$ (*c* 1.05, CHCl_3) for 99% ee. ^1H NMR (CDCl_3) δ 2.16 (s, 3H), 2.37 (s, 3H), 4.99 (d, $J = 6.9$ Hz, 1H), 5.80 (d, $J = 6.9$ Hz, 1H), 7.04-7.08 (m, 4H), 7.10 (d, $J = 7.7$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.18-7.23 (m, 3H), 7.55 (d, $J = 8.4$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 19.36, 21.47, 58.10, 126.18, 127.13, 127.25, 127.53, 127.55, 128.55, 129.31, 130.66, 135.47, 137.51, 138.29, 140.04, 143.14. Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_2\text{S}$: C, 71.76; H, 6.02. Found: C, 71.74; H, 6.03.

(*R*)-*N*-[(4-Chlorophenyl)(4-methoxyphenyl)methyl]-4-

methylbenzenesulfonamide (5cn): 98% yield (white solid), 99% ee. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min, wavelength = 230 nm. Retention times: 25.4 min [(*R*)-enantiomer], 34.0 min [(*S*)-enantiomer]. $[\alpha]^{20}_{\text{D}} -14.9$ (*c* 1.04, CHCl_3) for 99% ee. ^1H NMR (CDCl_3) δ 2.40 (s, 3H), 3.75 (s, 3H), 4.94-5.03 (m, 1H), 5.49 (d, $J = 6.8$ Hz, 1H), 6.74 (d, $J = 8.8$ Hz, 2H), 6.94 (d, $J = 8.8$ Hz, 2H), 7.06 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 8.5$ Hz, 2H), 7.17 (d, $J = 8.2$ Hz, 2H), 7.55 (d, $J = 8.2$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 21.51, 55.31, 60.30, 114.12, 127.24, 128.59, 128.61, 128.74, 129.45, 132.32, 133.39, 137.32, 139.27, 143.42, 159.25. Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{ClINO}_3\text{S}$: C, 62.76; H, 5.02. Found: C, 62.79; H, 4.96.

Deprotection of 4-Methylbenzenesulfonyl Group with SmI_2/HMPA (for Sulfonamide **5am)**

A 0.1 M solution of SmI_2 in THF (5.1 mL, 0.51 mmol), prepared according to the reported procedure,⁹ and HMPA (0.40 mL, 2.32 mmol) were added to sulfonamide **5am** (37.5 mg, 0.101 mmol, 98% ee) at room temperature. After refluxing for 30 min, to this solution was added 0.1 M solution of SmI_2 in THF (5.1 mL, 0.51 mmol). After refluxing for 45 min, the reaction mixture was quenched with 10% HCl and washed with Et_2O . To the water

layer was added 2 N NaOH until pH 14 and the basic aqueous solution was extracted with Et₂O. The organic layer was dried over K₂CO₃ and concentrated under reduced pressure to give a mixture of (*S*)-(4-chlorophenyl)phenylmethanamine (**6am**) (14.2 mg, 0.065 mmol, 64% yield) and diphenylmethanamine (14% yield). The mixture was treated with formic acid and acetic anhydride to give a mixture of formamides of **6am** and diphenylmethanamine. A pure sample of the formamide of **6am** was obtained by separation of the mixture by GPC. Acidic hydrolysis of the formamide **6am** in methanol gave free amine (*S*)-(4-chlorophenyl)phenylmethanamine (**6am**) as colorless oil: ([α]²⁰_D +10.6 (c 1.1, EtOH) for (*S*)) (lit.¹⁰ [α]²⁰_D +10.8 (c 2.18, EtOH) for (*S*) isomer))

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