Supporting Information I

Lithium BINOL Phosphate Catalyzed Desymmetrization of *meso*-Epoxides with Aromatic Thiols

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Contents:

General Information: All reactions were carried out in flame-dried or oven-dried screw-cap test tubes and were allowed to proceed under a dry argon atmosphere with magnetic stirring. Anhydrous *p*-xylene was purchased from Aldrich, other solvents (toluene and dichloromethane) were purified by passing through a column of activated alumina under a dry argon atmosphere. Cyclohexene oxide **1a** and **1h** was purchased from commercially available sources. Epoxides **1b**[1], **1c**[2], **1d**[3], **1e**[3], **1f**[4], **1g**[4], and **1h**[3] were synthesized according to the literature procedures. Alkenes were purchased from commercial sources and used without further purification. Thiols were purchased from commercially available sources. Liquid thiols were distilled onto 4 Å molecular sieves directly before use. 2-Naphthalenethiol was purified by sublimation to a white solid. Chiral BINOL was purchased from commercial sources and used without further purification. Substituted BINOL phosphoric acids (*R*), **P1**[5], **P2**[6], **P3**[7], and **P4**[8] were synthesized according to the known literature procedures. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with Merck silica gel (230-400 mesh). Enantiomeric excess (ee) was determined using a Varian Prostar HPLC with a 210 binary pump and a 335 diode array detector. Optical rotations were performed on a Rudolph Research Analytical Autopol IV polarimeter (λ 589) using a 700-μL cell with a path length of 1-dm. ^{1}H NMR and ^{13}C NMR were recorded on a Varian Inova-400 spectrometer (400 MHz) with chemical shifts reported relative to tetramethylsilane (TMS). The HRMS data were measured on an Agilent 1100 LC/MS ESI/TOF mass spectrometer with electro-spray ionization. Compounds described in the literature were characterized by comparing their ^{1}H NMR, ^{13}C NMR.

General procedure for racemic reaction of thiophenol (2a) with epoxides (1a-h): To a flame-dried reaction tube with septa and stir bar was added epoxide, **1a-h** (0.1 mmol) and Li(O*i*Pr**)** (20

mol%). The tube was evacuated and filled with argon. Anhydrous toluene (2.0 mL) and MeOH (0.5 mL) were added to the mixture, followed by thiophenol, **2a** (0.12 mmol) *via* syringe. The reaction was stirred at room temperature for 24 h. The crude product was purified directly by flash column chromatography (hexane: ethyl acetate = 5:1) to give the corresponding β-hydroxy sulfide product. The ee values of the products were determined by chiral HPLC analysis after the products were purified.

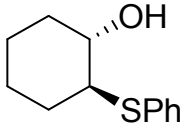
General Procedure for phosphate metal complexes M(P1)$_n$ – M(P4)$_n$: Catalysts M(**P1**)$_n$ – M(**P4**)$_n$ (20 mol% or 10 mol%, M = Ti, Sr, Li, Zn) were prepared in situ for each individual desymmetrization of meso-epoxides by thiols. To a flame dried test tube was added **P1** – **P4** (20 mol% or 10 mol%) and Ti(O*i*Pr)$_4$ (10 mol%), or Sr(O*t*Bu) (10 mol%), or Li(O*i*Pr) (20 mol%), or 10 mol%), or Zn(OMe)$_2$ (10 mol%). 1 mL each of CH_2Cl_2 and MeOH was added and reaction mixture was stirred for 2 h. After removal of solvent, 1 mL of CH_2Cl_2 was added and then removed under reduced pressure to obtain the catalyst as a white solid.

Li(**P4**) Characterization:

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.01 (s, 2H), 6.92 (s, 2H), 6.70(s, 2H), 3.02 – 2.97 (m, 1H), 2.89 – 2.78(m, 2H), 2.71 – 2.59(m, 4H), 2.14 - 2.05(m, 2H), 1.82 - 1.76(m, 5H), 1.62 – 1.56(m, 2H), 1.29 – 1.07(m, 33H), 0.84-0.82 (m, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 147.28, 146.42, 146.13, 134.34, 134.23, 134.15, 130.09, 129.04, 128.54, 120.38, 119.14, 109.54, 33.66, 30.14, 29.67, 28.58, 27.08, 26.08, 24.48, 24.13, 24.10, 23.57, 23.32, 22.64, 22.62. ^{31}P NMR (162 MHz, CDCl3) δ 3.88. HRMS (MALDI) Calcd for $C_{50}H_{65}LiO_4P$, $(M+H)^+$ m/z = 767. 478, found = 767.636. $(M+Na)^+$ m/z = 789. 478, found = 789.309.

Zn(**P3**)$_2$ Characterization: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.03 (t, *J* = 8.0 Hz, 8H), 7.49 – 7.44 (m, 8H), 7.32 (t, *J* = 8.0 Hz 4H), 7.23 (d, *J* = 8.0 Hz, 4H). ^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 149.52, 149.45, 131.84, 130.47, 129.93, 128.42, 124.67, 122.35, 121.56, 121.55 ^{31}P NMR (162 MHz, CDCl3) δ 4.71. HRMS (MALDI) Calcd for $C_{40}H_{25}O_8P_2Zn$, $(M+H)^+$ m/z = 759. 032, found = 759.346.

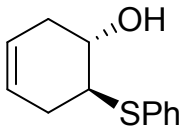
General procedure for asymmetric reaction of thiophenol (2a) with epoxides (1a-h): To a flame-dried reaction tube with septa and stir bar was added epoxide, **1a-g** (0.1 mmol), Li(**P4)** (20 or 10 mol %), and flame-dried 4Å molecular sieves (40.0 mg). The tube was evacuated and filled with argon. Anhydrous *p*-xylene (0.5 mL) was added to the mixture, followed by thiophenol, **2a** (0.12 mmol) *via* syringe. The reaction was stirred at room temperature for 48 h. The crude product was purified directly by flash column chromatography (hexane: ethyl acetate = 5:1 to 1: 1 solvent mixture) to give the corresponding chiral β-hydroxy sulfide product. The ee values of the products were determined by chiral HPLC analysis after the products were purified.



2-(Phenylthio)cyclohexanol (3a)

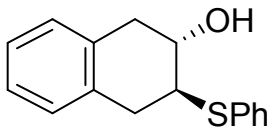
The reaction was performed according to the general procedure to obtain a 20.2 mg, 97% yield, 91% ee (20 mol% catalyst used), 17.1 mg, 82% yield, 88% ee (10 mol% catalyst used). HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 95/5, 0.5 mL/min), $t_{\text{r-major}}$ 21.00 min, $t_{\text{r-minor}}$ 13.76 min. $[\alpha]^{20}_D$ = +56.2° (c = 1.55, $CHCl_3$) for the product with 88% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.31 – 7.26 (m, 3H), 3.31 (td, *J* = 10.0 Hz, *J* = 4.4 Hz, 1H), 2.97 (s, 1H), 2.76 (ddd, *J* = 11.8 Hz, *J* = 9.9 Hz, *J* = 4.0 Hz, 1H), 2.13 – 2.05 (m, 2H), 1.72 – 1.65 (m, 2H),

1.33 – 1.21 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 133.95, 132.79, 129.09, 127.93, 72.24, 56.69, 34.01, 32.89, 26.35, 24.48. HRMS (ESI) calcd for $C_{12}H_{16}OS$ ($[M+Na]^+$) m/z 231.0814, found 231.0818. $[M+H-H_2O]^+$, found m/z 191.0888.



6-(Phenylthio)cyclohex-3-enol (3b)

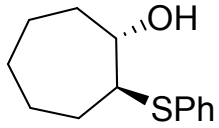
The reaction was performed according to the general procedure to obtain a 17.5 mg, 85% yield, 96% ee (20 mol% catalyst was used) 16.9 mg, 82% yield, 94% ee (10 mol% catalyst was used). HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 7.93 min, $t_{\text{r-minor}}$ 6.47 min. $[\alpha]^{20}_D$ = +132.5° (c = 0.84, $CHCl_3$) for the product with 96% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.19 – 7.11 (m, 3H), 5.47 – 5.40 (m, 2H), 3.63 – 3.57 (m, 1H), 3.20 (d, J = 2.4 Hz, 1H), 3.06 (td, J = 10.0 Hz, J = 5.6 Hz, 1H), 2.50 – 2.38 (m, 2H), 2.10 – 1.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.16, 132.85, 128.91, 127.55, 125.30, 124.47, 68.64, 51.49, 33.18, 31.77. HRMS (ESI) calcd for $C_{12}H_{14}OS$ ($[M+H]^+$) m/z 207.0838, found 207.0841. ($[M+Na]^+$) m/z 229.0658, found 229.0651.



1,2,3,4-Tetrahydro-3-(phenylthio)naphthalen-2-ol (3c)

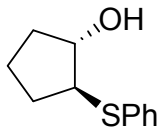
The reaction was performed according to the general procedure to obtain a 24.6 mg, 96% yield, 88% ee (20 mol% catalyst used), 19.5 mg, 76% yield, 87% ee (10 mol% catalyst used). HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 10.09 min, $t_{\text{r-minor}}$ 8.68

min. $[\alpha]^{20}_D$ = +87.0° (c = 1.41, $CHCl_3$) for the product with 88% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.9 Hz, *J* = 1.5 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.15 – 7.09 (m, 3H), 7.06 – 7.03 (m, 1H), 3.90 (td, *J* = 9.2 Hz, *J* = 6.0 Hz, 1H), 3.37 – 3.25 (m, 3H), 3.20 (s, 1H), 2.94 – 2.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.55, 133.95, 133.67, 132.34, 129.21, 129.20, 128.35, 128.04, 126.44, 126.33, 69.15, 52.29, 37.10, 35.42. HRMS (ESI) calcd for $C_{16}H_{16}OS$ ($[M+Na]^+$) m/z 279.0814, found 279.0834. $[M+H-H_2O]^+$, m/z 239.0893



2-(Phenylthio)cycloheptanol (3d)

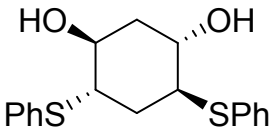
The reaction was performed according to the general procedure to obtain a 10.0 mg, 45% yield, 84% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 7.37 min, $t_{\text{r-minor}}$ 5.03 min. $[\alpha]^{20}_D$ = +34.7° (c = 0.63, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.25 – 7.16 (m, 3H), 3.49 (td, *J* = 9.2 Hz, 3.6 Hz, 1H), 2.94 (td, *J* = 9.6 Hz, J = 3.2 Hz, 1H), 2.83 (s, 1H), 2.02 – 1.95 (m, 1H), 1.92 – 1.85 (m, 1H), 1.68 – 1.47 (m, 5H), 1.42 – 1.33 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.85, 132.83, 129.11, 127.55, 74.77, 59.08, 33.75, 32.00, 27.76, 25.99, 22.13. HRMS (ESI) calcd for $C_{13}H_{18}OS$ ($[M+H]^+$) m/z 223.1151, found 223.1141. ($[M+Na]^+$) m/z 245.0971, found 245.0974.



2-(Phenylthio)cyclopentanol (3e)

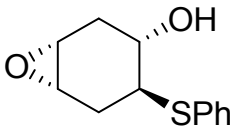
The reaction was performed according to the general procedure to obtain a 17.3 mg, 89% yield, 75% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{\text{r-major}}$ 13.00 min, $t_{\text{r-minor}}$ 8.03 min. $[\alpha]^{20}_D$ = +13.8° (c = 0.78, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* =

7.6 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 4.01 (d, *J* = 4.8 Hz, 1H), 3.31 (dd, *J* = 12.0 Hz, *J* = 8.0 Hz, 1H), 2.23 (s, 1H), 2.20 – 2.11 (m, 1H), 2.00 – 1.92 (m, 1H), 1.73 – 1.59 (m, 2H), 1.55 – 1.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.83, 130.72, 129.06, 126.61, 78.55, 54.02, 33.30, 31.07, 21.97. HRMS (ESI) calcd for $C_{11}H_{14}OS$ ($[M+Na]^+$) m/z 217.0658, found 217.0661. $[M+H-H_2O]^+$, m/z 177.0737.



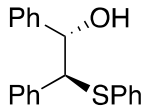
4,6-Bis(phenylthio)cyclohexane-1,3-diol (3f)

The reaction was performed according to the general procedure; the crude product was purified directly by flash column chromatography (hexane: ethyl acetate = 1:1) to obtain a 22.3 mg, 67% yield, 93% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-major}}$ 13.20 min, $t_{\text{r-minor}}$ 8.07 min. $[\alpha]^{20}_D$ = +60.5° (c = 0.47, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 4H), 7.29 – 7.26 (m, 6H), 3.95 (dd, *J* = 11.6 Hz, *J* = 5.6 Hz, 2H), 3.34 (dd, *J* = 12.0 Hz, *J* = 6.0 Hz 2H), 2.16 (t, *J* = 5.6 Hz, 3H), 2.08 (t, *J* = 5.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.50, 132.77, 129.33, 127.81, 68.96, 51.07, 36.18, 31.81. HRMS (ESI) calcd for $C_{18}H_{20}O_2S_2$ ($[M+Na]^+$) m/z 355.0797, found 355.0809. $[M+H-H_2O]^+$, m/z 315.0880



4-(Phenylthio)-epoxycyclohexan-5-ol (3g)

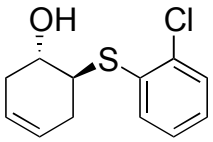
The reaction was performed according to the general procedure; the crude product was purified directly by flash column chromatography (CH_2Cl_2) to obtain a 19.1 mg, 86% yield, 91% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-major}}$ 7.91 min, $t_{\text{r-minor}}$ 7.12 min. $[\alpha]^{20}_D$ = +66.4° (c = 1.72, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.31 – 7.26 (m, 3H), 3.51 – 3.44 (m, 1H), 3.19 – 3.11 (m, 4H), 2.57 (dd, *J* = 15.6 Hz, *J* = 5.2 Hz, 1H), 2.45 (ddd, *J* = 15.6 Hz, *J* = 6.0 Hz, *J* = 3.8 Hz, 1H), 2.01 (dd, *J* = 15.6 Hz, *J* = 7.6 Hz, 1H), 1.89 (ddd, *J* = 15.6 Hz, *J* = 8.7 Hz, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.40, 132.36, 129.29, 128.09, 67.67, 52.51, 51.82, 47.50, 30.61, 29.75. HRMS (ESI) calcd for $C_{12}H_{14}O_2S$ ($[M+H]^+$) m/z 223.0787, found 223.0793. $[M+H-H_2O]^+$, m/z 205.0685.



3h

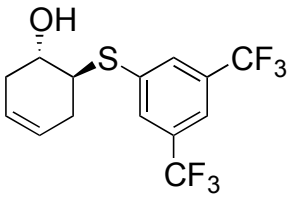
1,2-diphenyl-2-(phenylthio)ethanol (3h): The reaction was performed according to the general procedure to obtain a 30.0 mg, 98% yield, 87% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 13.96 min, $t_{\text{r-minor}}$ 10.23 min. $[\alpha]^{20}_D$ = +134.8° (c = 0.94, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.20 – 7.12 (m, 11H), 7.03 – 7.01 (m, 2H), 4.93 (d, *J* = 8.0 Hz, 1H), 4.35 (d, *J* = 8.0 Hz, 1H), 3.31 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.58, 139.40, 134.33, 132.57, 129.06, 128.74, 128.30, 128.16, 127.96, 127.62, 127.45, 127.07, 77.06, 64.13. HRMS (ESI) calcd for $C_{20}H_{18}OSNa$ ($[M+Na]^+$) m/z 329.0971, found 329.0967. $[M+H-H_2O]^+$, m/z 289.1046.

General procedure for reaction of thiols (2b-k) with 1,4-cyclohexadiene oxide (2a): To a flame-dried reaction tube with septa and stir bar was added epoxide, **2a** (0.1 mmol) and Li(**P4)** (10 mol %) and flame-dried 4Å molecular sieves (40.0 mg). The tube was evacuated and filled with argon. Anhydrous *p*-xylene (0.5 mL) was added to the mixture, followed by thiophenol, **2a** (0.12 mmol) *via* syringe. The reaction was stirred at room temperature for 48 h. The crude product was purified directly by flash column chromatography (hexane: ethyl acetate = 5:1) to give the corresponding chiral β-hydroxy sulfide product. The ee values of the products were determined by chiral HPLC analysis after the products were purified.



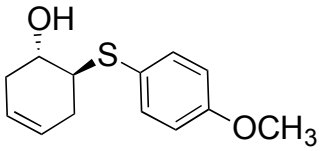
6-(2-Chlorophenylthio)cyclohex-3-enol (4b)

The reaction was performed according to the general procedure to obtain a 19.0 mg, 79% yield, 97% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 14.73 min, $t_{\text{r-minor}}$ 7.85 min. $[\alpha]^{20}_{D}$ = +91.7° (c = 0.71, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.53 (m, 1H), 7.41 – 7.39 (m, 1H), 7.21 – 7.17 (m, 2H), 5.59 – 5.57 (m, 2H), 3.81 – 3.75 (m, 1H), 3.28 (td, *J* = 10.0 Hz, *J* = 5.6 Hz, 1H), 2.82 (s, 1H), 2.64 – 2.56 (m, 2H), 2.25 – 2.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.83, 133.90, 133.30, 130.24, 128.70, 127.41, 125.40, 124.82, 69.77, 51.61, 33.41, 32.03. HRMS (ESI) calcd for $C_{12}H_{13}ClOS$ ($[M+H]^+$) m/z 241.0448, found 241.0448. ($[M+Na^+]$) m/z 263.0268, Found 263.0270



6-(3,5-Bis(trifluoromethyl)phenylthio)cyclohex-3-enol (4c)

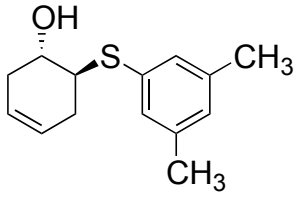
The reaction was performed according to the general procedure to obtain a 30.8 mg, 90% yield, 88% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 23.19 min, $t_{\text{r-minor}}$ 19.01 min. $[\alpha]^{20}_{D}$ = +30.3° (c = 1.22, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.68 (s, 1H), 5.63 – 5.55 (m, 2H), 3.82 – 3.77 (m, 1H), 3.34 (td, *J* = 9.6 Hz, *J* = 5.6 Hz, 1H), 2.69 (s, 1H), 2.62 – 2.57 (m, 2H), 2.25 – 2.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.80, 132.37 (q, $^2J_{C\text{-}F}$ = 33.3 Hz) 132.54 (s), 130.90, (m, for a carbon orthro to both CF_3 groups), 125.01, 124.90, 123.17 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 120.70 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 69.82, 51.57, 33.60, 32.13. HRMS (ESI) calcd for $C_{14}H_{12}F_6OS$ $[M+H-H_2O]^+$ m/z 325.0480, found 325.0486.



6-(4-Methoxyphenylthio)cyclohex-3-enol (4d)

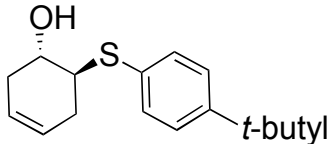
The reaction was performed according to the general procedure to obtain a 22.2 mg, 94% yield, 95% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 98/2 0.5 mL/min), $t_{\text{r-major}}$ 29.51 min, $t_{\text{r-minor}}$ 27.17 min. $[\alpha]^{20}_{D}$ = +144.6° (c = 1.37, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 6.83 – 6.79 (m, 2H), 5.52 – 5.48 (m, 2H), 3.75 (s, 3H), 3.58 (m,1H), 3.23 (s, 1H), 2.92 (td, *J* = 10.4 Hz, *J* = 5.6 Hz, 1H), 2.56 – 2.40 (m, 2H), 2.12 – 2.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.12, 136.90, 125.64, 124.55, 121.70, 114.66, 68.17, 55.43, 52.50, 33.40, 31.69.

HRMS (ESI) calcd for $C_{13}H_{16}O_2S$ ($[M+Na]^+$) m/z 259.0763, found 259.0759. $[M+H-H_2O]^+$, m/z 219.0838.



6-(3,5-Dimethylphenylthio)cyclohex-3-enol (4e)

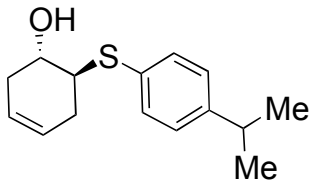
The reaction was performed according to the general procedure to obtain a 10.1 mg, 87% yield, 92% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 6.43 min, $t_{\text{r-minor}}$ 5.40 min. $[\alpha]^{20}_D$ = +85.6° (c = 0.44, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 2H), 6.89 (s, 1H), 5.55 (s, 2H), 3.68 (dd, *J* = 12.0 Hz, *J* = 8.0 Hz, 1H), 3.14 – 3.08 (m, 2H), 2.60 – 2.50 (m, 2H), 2.28 (s, 6H), 2.19 – 2.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.75, 132.07, 131.24, 129.80, 125.66, 124.66, 68.89, 52.07, 33.34, 32.18, 21.32. HRMS (ESI) calcd for $C_{14}H_{18}OS$ ($[M+Na]^+$) m/z 257.0971, found 257.0968. $[M+H-H_2O]^+$, m/z 217. 1044



6-(4-Tert-butylphenylthio)cyclohex-3-enol (4f)

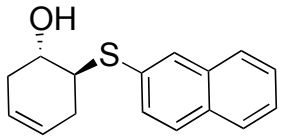
The reaction was performed according to the general procedure to obtain a 24.9 mg, 95% yield, 96% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 5.83 min, $t_{\text{r-minor}}$ 6.49 min. $[\alpha]^{20}_D$ = +107.5° (c = 1.72, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.32 – 7.29 (m, 2H), 5.55 – 5.54 (m, 2H), 3.69 – 3.63 (m, 1H), 3.10 – 3.03 (m, 2H),

2.60 – 2.48 (m, 2H), 2.20 – 2.08 (m, 2H), 1.34 – 1.24 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.43, 133.94, 128.73, 126.25, 125.73, 124.73, 68.76, 52.38, 34.78, 33.43, 32.16, 31.43. HRMS (ESI) calcd for $C_{16}H_{22}OS$ ($[M+H]^+$) m/z 263.1464, found 263.1464. ($[M+Na]^+$) m/z 285.1284, found 285.1285.



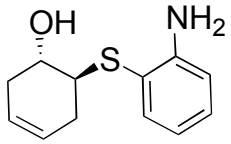
6-(4-Isopropylphenylthio)cyclohex-3-enol (4g)

The reaction was performed according to the general procedure to obtain a 16.6 mg, 67% yield, 91% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 96/4, 0.5 mL/min), $t_{\text{r-major}}$ 16.73 min, $t_{\text{r-minor}}$ 17.79 min. $[\alpha]^{20}_D$ = +110.8° (c = 0.83, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.53 (s, 2H), 3.68 – 3.62 (m, 1H), 3.12 (bs, 1H), 3.06 (td, *J* = 10.4 Hz, *J* = 5.6 Hz, 1H), 2.90 – 2.83 (m, 1H), 2.59 – 2.48 (m, 2H), 2.19 – 2.07 (m, 2H), 1.21 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.16, 134.32, 128.91, 127.33, 125.70, 124.69, 68.68, 52.38, 33.94, 33.41, 32.06, 24.03 HRMS (ESI) calcd for $C_{15}H_{20}OS$ ($[M+Na]^+$) m/z 271.1127, found 271.1124. $[M+H-H_2O]^+$, m/z 231.1198



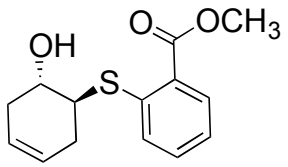
6-(Naphthalen-3-ylthio)cyclohex-3-enol (4h)

The reaction was performed according to the general procedure to obtain a 22.6 mg, 88% yield, 94% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 8.31 min, $t_{\text{r-minor}}$ 9.87 min. $[\alpha]^{20}_{D}$ = +101.1° (c = 1.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.81 – 7.75 (m, 3H), 7.54 – 7.44 (m, 3H), 5.59 – 5.52 (m, 2H), 3.77 (td, *J* = 8.8 Hz, *J* = 5.6 Hz, 1H), 3.27 (td, *J* = 10.0 Hz, *J* = 5.6 Hz, 1H), 3.10 (s, 1H), 2.64 – 2.56 (m, 2H), 2.26 – 2.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.70, 132.65, 132.38, 130.61, 130.21, 128.68, 127.82, 127.60, 126.77, 126.57, 125.53, 124.68, 68.99, 52.07, 33.40, 32.10. HRMS (ESI) calcd for $C_{16}H_{16}OS$ ($[M+H]^+$) m/z 257.0995, found 257.0989. ($[M+Na]^+$) m/z 279.0814, found 279.0823.



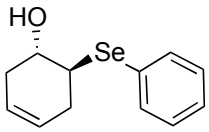
6-(2-Aminophenylthio)cyclohex-3-enol (4i)

The reaction was performed according to the general procedure to obtain a 19.9 mg, 90% yield, 94% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 23.09 min, $t_{\text{r-minor}}$ 16.05 min. $[\alpha]^{20}_{D}$ = +166.7° (c = 1.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.14 (td, *J* = 8.8 Hz, *J* = 1.6 Hz, 1H), 6.75 - 6.68 (m, 2H), 5.52 (s, 2H), 4.43 (bs, 2H), 3.59 (td, *J* = 10.0 Hz, *J* = 6.0 Hz, 1H), 2.96 (td, *J* = 10.0 Hz, *J* = 5.2 Hz, 1H), 2.53 – 2.48 (m, 2H), 2.24 – 2.02 (m, 2H), (OH- peak not seen in 1H NMR). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.35, 138.27, 130.79, 125.67, 124.80, 119.38, 115.79, 155.47, 69.19, 52.79, 33.87, 32.37 HRMS (ESI) calcd for $C_{12}H_{15}NOS$ ($[M+H]^+$) m/z 222.0947, found 222.0949



Methyl 2-(6-hydroxycyclohex-3-enylthio)benzoate (4j)

The reaction was performed according to the general procedure; the crude product was purified directly by flash column chromatography (hexane: ethyl acetate = 1:1) to obtain a 21.4 mg, 90% yield, 97% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-major}}$ 13.60 min, $t_{\text{r-minor}}$ 8.65 min. $[\alpha]^{20}_{D}$ = +36.2° (c = 2.05, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.41 (td, *J* = 7.7 Hz, *J* = 1.6 Hz, 1H), 7.21 (dd, *J* = 7.6, 1.0 Hz, 1H), 5.63 – 5.55 (m, 2H), 3.91 (s, 3H), 3.82 (td, *J* = 9.2 Hz, *J* = 5.6 Hz, 1H), 3.39 – 3.32 (m, 2H), 2.66 – 2.55 (m, 2H), 2.30 – 2.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.98, 137.94, 132.20, 131.45, 131.12, 130.82, 126.06, 125.44, 125.07, 70.47, 52.61, 51.62, 33.61, 32.58. HRMS (ESI) calcd for $C_{14}H_{16}O_3S$, ($[M+Na]^+$) m/z 287.0712, found 287.0714 ($[M+Na]^+$) m/z 287.0712, found 287.0714. $[M+H-H_2O]^+$, m/z 247.0787.



6-(phenylselanyl)cyclohex-3-enol (4k)

The reaction was performed according to the general procedure to obtain a 24.2 mg, 96% yield, 94% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 6.96 min, $t_{\text{r-minor}}$ 5.96 min. $[\alpha]^{20}_{D}$ = +108.1° (c = 1.05, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 2H), 7.31 – 7. 24 (m, 3H), 5.58- 5.49 (m, 2H), 3.72- 3.66 (m, 1H)3.24 (td, J = 5.6 Hz, J

= 10. 4Hz, 1H), 3.06 (s, 1H), 2.63- 2.54 (m, 2H), 2.29 – 2.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.93, 129.22, 128.27, 126.78, 126.03, 124.82, 68.84, 48.99, 33.31, 32.70. HRMS (ESI) calcd for $C_{12}H_{14}OSe$, ($[M+Na]^+$) m/z 277.0102, found 277.0098 ($[M+Na]^+$), $[M+H-H_2O]^+$, m/z 237.0177.

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