Supporting Information for

**Enantioselective Ring-Opening of meso-Epoxide by Aromatic Amines Catalysed by a Homochiral Metal-Organic Framework**

Sridhar Regati, Yabing He, Muralidhara Thimmaiah, Peng Li, Shengchang Xiang, Banglin Chen* and John Cong-Gui Zhao*

**General Information**

All reagents and solvents were used as received from commercial suppliers without further purification. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker AV400 or AV600 spectrometer. Tetramethylsilane (TMS) and deuterated solvents (CDCl$_3$, $\delta = 77.0$ ppm; DMSO-$d_6$, $\delta = 39.5$ ppm) were used as internal standards in $^1$H NMR and $^{13}$C NMR experiments, respectively. The coupling constants were reported in Hertz. Thermogravimetric analyses (TGA) were measured using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 3 °C min$^{-1}$. Powder X-ray diffraction (PXRD) patterns were recorded by a Rigaku Ultima IV diffractometer operated at 40 kV and 44 mA with a scan rate of 1.0 degmin$^{-1}$.

The cis-stilbene epoxides used in this study were synthesized according to the reported literature procedures. They were purified either by column chromatography or distillation. Aniline and aniline derivatives were purified by distillation and recrystallization before use.

**Crystal structure determination**

Intensity data for **UTSA-32** were collected at 185(2) K on a Bruker SMART Apex II CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 watts power (50 kV, 40 mA). The structure was solved by direct methods and subsequent difference Fourier syntheses, and refined using the SHELXTL software package. The H atoms on the ligands and coordinated H$_2$O were placed in idealized positions and refined using...
a riding model. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules and thereby, to produce a set of solvent-free diffraction intensities. Crystal data for UTSA-32: C_{40}H_{23}Cl_{12}O_{12}Zn_{2}, M = 897.22, monoclinic, space group P2_1, a = 10.1889(13) Å, b = 16.651(2) Å, c = 19.730(3) Å, β = 101.825(2)^o, V = 3276.4(7) Å^3, Z = 2, D_c = 0.909 g cm^{-3}, μ(Mo-Kα, λ = 0.71073 Å) = 0.851 mm^{-1}, F(000) = 906, 2θ_{max} = 50.1, 17147 reflections collected, 9823 independent reflections (R_{int} = 0.0702), which were used in all the calculations, Final R_1 = 0.0893 for I > 2σ(I), wR_2 = 0.2404 for all data, GOF = 0.943, Flack parameter = 0.10(3). CCDC 713157. See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF or other electronic format.

Synthesis of UTSA-32

A mixture of Zn(NO_3)_2·6H_2O (15.0 mg, 0.050 mmol) and organic linker H_4L (15.0 mg, 0.020 mmol) was dissolved into N,N’-dimethylacetamide (DMA) (2.0 mL)-ethanol (1.0 mL) mixed solvents in a crew-capped vial. The vial was then capped and heated to 110 °C in 2 hours, maintained at 110 °C for 48 hours and cooled to room temperature in 12 hours. Colorless rodlike crystals were obtained in 62% yield. UTSA-32 can be formulated as [Zn_2(L)(H_2O)_2]·(DMA)_4 on the basis of single crystal X-ray structure determination, TGA and microanalysis. TGA data: Calcd. weight loss for 4DMA and 2H_2O: 30.7%, Found: 30.1%; Anal. Calcd for C_{56}H_{64}N_4O_{16}Zn_2Cl_2: C, 53.77; H, 5.16%; N, 4.48, Found: C, 53.89%; H, 5.22; N, 4.57%

General Experimental Procedure for the meso-epoxide opening reaction with aniline derivatives

To a mixture of the epoxide (0.10 mmol) and aniline derivative (0.25 mmol) in a vial, 10 mol % of UTSA-32a catalyst was added followed by 1 mL of toluene (UTSA-32a was obtained by heating as-synthesized UTSA-32 under high vacuum at 150 °C for 24 hrs). The vial was heated at 50 °C for the indicated time. The reaction mixture was cooled and filtered to remove the catalyst, washed with ethanol. The filtrate was evaporated under reduced pressure (rotary evaporator), and the residue was purified by column chromatography to give the product amino alcohol.
Figure S1. PXRD patterns of (a) as-synthesized UTSA-32 and (c) activated UTSA-32a, along with the simulated PXRD pattern from single X-ray crystal structure.

Figure S2. TGA curve of as-synthesized UTSA-32.
**Figure S3.** CO$_2$ sorption isotherm of UTSA-32a at 196 K.

**Additional References**

Compound Characterization Data

\((1\text{S,2\text{S}})-1,2\text{-Diphenyl-2-(phenylamino)ethanol}\):\(^1\)\(^2\) \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.31\text{-}7.10\) (m, 10H), 6.83-6.57 (m, 5H), 4.89 (d, \(J = 6.0\) Hz, 1H), 4.56 (d, \(J = 6.0\) Hz, 1H), 3.69 (brs, 1H). \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\)): \(\delta = 146.5, 140.9, 140.5, 129.3, 128.8, 128.5, 128.1, 127.7, 127.5, 126.8, 118.1, 114.3, 78.3, 64.9\). \([\alpha]_D^{24} = -31.9^\circ\) (c = 0.46, CH\(_2\)Cl\(_2\), 85% ee). HPLC (Daicel Chiralcel\(^\text{®}\) IB column, hexane/i-PrOH = 95/5, flow rate = 1 mL/min, 254 nm): \(t_R = 24.8\) min (minor), \(t_R = 29.3\) min (major).

\((1\text{S,2\text{S}})-1,2\text{-Diphenyl-2-(p-tolylamino)ethanol}\):\(^6\) \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.27\text{-}7.18\) (m, 10H), 6.90-6.87 (m, 4H), 4.83 (d, \(J = 6\) Hz, 1H), 4.48 (d, \(J = 6.3\) Hz, 1H), 2.73 (brs, 1H), 2.19 (s, 3H). \(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 147.4, 137.7, 137.5, 137.2, 137.0, 129.3, 129.1, 129.0, 127.2, 126.5, 117.8, 114.1, 78.0, 64.4, 21.4\). \([\alpha]_D^{24} = -37.9^\circ\) (c = 0.43, CH\(_2\)Cl\(_2\), 75% ee). HPLC (Daicel Chiralcel\(^\text{®}\) IB column, hexane/i-PrOH = 95/5, flow rate = 1 mL/min, 254 nm): \(t_R = 24.6\) min (major), 26.4 min (minor).

\((1\text{S,2\text{S}})-1,2\text{-Diphenyl-2-(p-methoxyphenylamino)ethanol}\):\(^5\) \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.25\text{-}7.14\) (m, 10H), 6.67-6.49 (m, 4H), 4.80 (d, \(J = 6.6\) Hz, 1H), 4.40 (d, \(J = 6.6\) Hz, 1H), 3.67 (s, 3H), 2.81 (brs, 1H). \(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 152.6, 141.4, 140.7, 140.3, 128.6, 128.3, 128.0, 127.6, 127.5, 126.8, 115.9, 114.8, 78.3, 66.4, 55.9\). \([\alpha]_D^{24} = -28.9^\circ\) (c = 0.39, CH\(_2\)Cl\(_2\), 62% ee). HPLC (Daicel Chiralcel\(^\text{®}\) AD-H column, hexane/i-PrOH = 82/20, flow rate = 0.5 mL/min, 247 nm): \(t_R = 37.1\) min (major), \(t_R = 45.2\) min (minor).

\((1\text{S,2\text{S}})-1,2\text{-Diphenyl-2-(p-fluorophenylamino)ethanol}\):\(^1\) \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.26\text{-}7.17\) (m, 10H), 6.79-6.43 (m, 4H), 4.82 (d, \(J = 6.3\) Hz, 1H), 4.60 (brs, 1H), 4.43 (d, \(J = 6.3\) Hz, 1H), 3.67 (s, 3H), 2.61 (brs, 1H). \(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 147.5, 140.8, 140.5, 129.2, 128.7, 128.4, 128.0, 127.7, 127.5, 126.8, 125.3, 115.3, 78.2, 64.9\). \([\alpha]_D^{24} = -43.5^\circ\) (c = 0.42, CH\(_2\)Cl\(_2\), 89% ee). HPLC (Daicel Chiralcel\(^\text{®}\) IB column, hexane/i-PrOH = 95/5, flow rate = 1 mL/min, 254 nm): \(t_R = 23.3\) min (major), \(t_R = 26.5\) min (minor).
(1S,2S)-1,2-Diphenyl-2-(p-chlorophenylamino)ethanol: \(^1\) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.32-7.23\) (m, 10H), 6.85-6.49 (m, 4H), 4.89 (d, \(J = 6.0\) Hz, 1H), 4.66 (brs, 1H), 4.49 (d, \(J = 6.0\) Hz, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 146.4, 140.8, 140.4, 129.2, 128.7, 128.4, 128.0, 127.6, 127.4, 126.7, 125.2, 115.3, 78.2, 64.8\). \([\alpha]_{D}^{24} = -22.1^\circ\) (\(c = 0.375,\) CH\(_2\)Cl\(_2\), 58% ee). HPLC (Daicel Chiralcel\(^\circledast\) AD-H column, hexane/i-PrOH = 95/5, flow rate = 1 mL/min, 247 nm): \(t_R = 35.2\) min (major), \(t_R = 43.1\) min (minor).

(1S,2S)-1,2-Diphenyl-2-(p-bromophenylamino)ethanol: \(^1\) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.24-7.14\) (m, 10H), 6.77-6.41 (m, 4H), 4.80 (d, \(J = 7.5\) Hz, 1H), 4.57 (brs, 1H), 4.41 (d, \(J = 6.0\) Hz, 1H), 2.59 (brs, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 147.7, 141.0, 140.7, 129.7, 128.9, 128.6, 128.2, 127.7, 126.9, 115.5, 114.5, 78.4, 65.1\). \([\alpha]_{D}^{24} = -41.4^\circ\) (\(c = 0.49,\) CH\(_2\)Cl\(_2\), 31% ee). HPLC (Daicel Chiralcel\(^\circledast\) IB column, hexane/i-PrOH = 90/10, flow rate = 1 mL/min, 254 nm): \(t_R = 21.8\) min (major), \(t_R = 28.4\) min (minor).

(1S,2S)-2-Phenylaminocyclopentanol: \(^7\) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.19-7.16\) (m, 2H), 6.72-6.66 (m, 2H), 4.08-4.06 (m, 1H), 3.61-3.56 (m, 1H), 2.30-2.17 (m, 1H), 2.01-1.95 (m, 1H), 1.84-1.64 (m, 3H), 1.43-1.38 (m, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 147.9, 129.4, 117.7, 113.4, 78.4, 62.2, 33.1, 31.4, 21.2.\) \([\alpha]_{D}^{24} = 14.6^\circ\) (\(c = 0.63,\) CH\(_2\)Cl\(_2\), 12% ee). HPLC (Daicel Chiralcel\(^\circledast\) IB column, hexane/i-PrOH = 95/5, flow rate = 1 ml/min, 254 nm): \(t_R = 26.3\) min (major), \(t_R = 29.4\) min (minor).

(1S,2S)-2-Phenylaminocyclohexanol: \(^5\) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.20-7.14\) (m, 2H), 6.76-6.71 (m, 2H), 3.35-3.33 (m, 1H), 3.16-3.14 (m, 1H), 2.75 (brs, 1H), 2.17-2.11 (m, 2H), 1.78-1.72 (m, 2H), 1.43-1.26 (m, 3H), 1.08-1.04 (m, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 147.9, 129.4, 117.7, 113.4, 78.4, 62.2, 33.1, 31.4, 21.2.\) \([\alpha]_{D}^{24} = 29.3^\circ\) (\(c = 0.48,\) CH\(_2\)Cl\(_2\), 15% ee). HPLC (Daicel Chiralcel\(^\circledast\) IB column, hexane/i-PrOH = 95/5, flow rate = 1 ml/min, 254 nm): \(t_R = 19.4\) min (major), \(t_R = 22.8\) min (minor).

(1S,2S)-1,2-bis(4-chlorophenyl)-2-(phenylamino)ethanol: \(^3\) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.28-7.05\) (m, 10H), 6.70-6.41 (m, 3H), 4.79-4.77 (d, \(J = 6.0\) Hz, 1H), 4.45-4.29 (d, \(J = 6.3\) Hz, 1H), 2.63 (brs, 1H). \(^{13}\)C NMR (75 MHz,
CDCl₃: δ = 147.5, 137.8, 137.6, 137.4, 137.2, 129.4, 129.2, 129.1, 127.3, 126.6, 117.9, 114.2, 78.1, 64.5. [α]D²⁴ = -19.2° (c = 0.68, CH₂Cl₂, 34% ee). HPLC (Daicel Chiralcel® IB column, hexane/i-PrOH = 95/5, flow rate = 1 ml/min, 254 nm): tR = 50.5 min (major), tR = 65.2 min (minor).

(1s,2s)-1,2-bis(p-tolyl)-2-(phenylamino)ethanol:¹ ¹H NMR (500 MHz, CDCl₃): δ = 7.26-7.04 (m, 10H), 6.67-6.62 (m, 1H), 6.55-6.51 (m, 2H), 4.84 (d, J = 5.4 Hz, 1H), 4.64 (brs, 1H), 4.50 (d, J = 5.4 Hz, 1H), 2.49 (brs, 1H), 2.34 (s, 3H), 2.32 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 147.1, 137.4, 137.2, 137.0, 136.8, 129.1, 128.8, 128.7, 126.9, 126.2, 117.5, 113.8, 77.7, 64.1, 21.2, 21.1. [α]D²⁴ = -31.9° (c = 0.41, CH₂Cl₂, 17% ee). HPLC (Daicel Chiralcel® AD-H column, hexane/i-PrOH = 90/10, flow rate = 1 mL/min, 254 nm): tR = 23.3 min (major), tR = 27.1 min (minor).

1s,2s)-1,2-di(naphthalen-2-yl)-2-(phenylamino)ethanol:² ¹H NMR (500 MHz, CDCl₃): δ = 7.28-7.04 (m, 14H), 6.77-6.63 (m, 3H), 6.52-6.54 (m, 2H), 4.88 (d, J = 6.0 Hz, 1H), 4.53 (d, J = 5.5 Hz, 1H), 3.74 (brs, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 147.2, 140.5, 140.1, 131.3, 129.7, 129.2, 129.1, 129.0, 128.9, 128.7, 128.5, 128.3, 128.2, 127.8, 127.4, 127.2, 126.5, 125.9, 117.8, 114.1, 78.0, 64.7. [α]D²⁴ = -116.4° (c = 0.31, CH₂Cl₂, 32% ee). HPLC (Daicel Chiralcel® AD-H column, hexane/i-PrOH = 90/10, flow rate = 1 mL/min, 254 nm): tR = 23.5 min (major), tR = 30.5 min (minor).
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![Chemical Structure](image-url)

**Relevant Chemical Reaction**

- **Formula:** HO- \(\text{C}_6\text{H}_5\text{NH}-\text{C}_6\text{H}_4\text{F}\)
- **Description:** This diagram illustrates the chemical structure of the compound, highlighting the various functional groups and their spatial arrangements.

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**Graph Attributes**

- **Y-Axis:** Retention Time
- **X-Axis:** Minutes
- **Graph Legend:** SPD-HVWp Ch1, 254nm
- **Data Points:** Each peak corresponds to a specific retention time and area, indicating the relative abundance of each component in the sample.

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This page contains electronic supplementary material (ESI) that is relevant to the main content of the article. The data presented here includes chromatographic analysis and chemical structure information, providing additional insights into the chemical composition and properties of the subject under study.
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Chemical Structure: HO\textsuperscript{2} Cyclic Ring NH Bonds

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