Supporting Information

Light-controlled cooperative catalysis of asymmetric sulfoxidation based on azobenzene-bridged chiral salen Ti^{IV} catalysts
CONTENTS:

1. Synthetic details of azobenzene-bridged bimetallic chiral salenTiIV catalysts (denoted as ATGC-n, n= 0, 2, 3, 4).

2. Identification of catalysts (ATGC-n, n= 0, 2, 3, 4) and the intermediates.

3. Evaluation of catalytic activity of ATGC-n in asymmetric sulfoxidation.
1. Synthetic details of azobenzene-bridged bimetallic chiral salen Ti$^{IV}$ catalysts (denoted as ATGC-$n$, $n=0,2,3,4$)

1.1 Materials and reagents

4,4'-dihydroxyazobenzene, tert-butyl $N$-(2-bromoethyl)carbamate, tert-butyl $N$-(3-bromopropyl)carbamate and tert-butyl $N$-(4-bromopropyl)carbamate were purchased from Aldrich. The tetra-isopropyl titanate, phenyl methyl sulfide, phenyl ethyl sulfide, $p$-methoxyphenyl methyl sulfide, $o$-methoxyphenyl methyl sulfide, and $p$-bromophenyl methyl sulfide were obtained from J&K. 2-tert-Butyl phenol was purchased from Alfa Aesar. Other commercially available chemicals were laboratory grade reagents from local suppliers. ($R,R$)-$N,N'$-Bis(3,5-di-tert-butylsalicylidene)-$N$-(3-tert-butyl-5-chloro-methylsalicylidene)-1,2-cyclohexanediamine (denoted as CL) was synthesized as described procedure in corresponding reference.$^1$ [N,N'-Bis(3,5-di-tert-butyl salicylidene)-1,2-cyclohexanediaminato]titanium(IV) di-isopropyl (denoted as Neat-C, as shown in Chart S1) was prepared according to described procedures.$^2$ Phenyl $n$-butyl sulfide, and phenyl $n$-hexyl sulfide were synthesized according to Ref.$^3$

![Chart S1 The structure of Neat-C.](image)

1.2 Methods

FT-IR spectra were obtained from potassium bromide pellets with a resolution of 4 cm$^{-1}$ and 64 scans in the range 400–4000 cm$^{-1}$ using an AVATAR 370 Thermo Nicolet spectrophotometer. UV-visible absorption spectra were measured on a UV/Vis Agilent 8453 spectrophotometer using a 10
mm path length quartz cell. The irradiation lamp was a UV lamp with $\lambda_{\text{max}} = 365$ nm. Samples were exposed to air during irradiation. NMR was recorded at a BRUKER AVANCE-500 spectrometer with TMS as an internal standard. All irradiations were performed directly in the Quartz NMR tubes. The measurements were repeated for at least three times to ensure good reproducibility. Trans/cis isomers ratios were obtained from the integrations of the signals from aromatic protons in corresponding isomers. Elemental analyses of C, H and N were carried out on Vario EL III Elemental analyses made in Germany. Contents of titanium in the samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) on a NexION 300X analyzer (Perkin-Elmer Corp.). The optical rotation of samples was measured in dichloromethane on a WZZ-2A Automatic Polarimeter.

1.3 Preparation of azobenzene-bridged bimetallic chiral salenTi$^\text{IV}$ catalysts (denoted as ATGC-n, where n represented the repeated methylene units in aliphatic linkers, n= 0, 2, 3, 4).

1.3.1 Preparation of ATGC-n (n= 2, 3, 4).

ATGC-n (n= 2, 3, 4) with various length of alkyl-terminated azobenzene spacers were prepared according to the procedure in Scheme S1.

![Scheme S1 Synthesis of ATGC-n (n= 2, 3, 4)](image)
Synthesis of Azo-\text{C}_{(n)}\text{-NH-Boc} (n= 2, 3, 4). 4, 4'-Dihydroxyazobenzene (0.96 g, 4.5 mmol) was dissolved in anhydrous DMF (30 mL). A suspension of sodium hydride (0.48 g, 12 mmol) in anhydrous DMF (10 mL) was slowly added into above solution. The mixture was stirred at room temperature until no bubble was observed. \textit{N}-Benzyloxycarbonyl bromoalkylamines of \textit{Br}(\text{CH}_2)_n\text{NHBoc} (10 mmol, n= 2, 3, 4) was then added into the stirring mixture. After being stirred at 60 °C for 4 h, the resulted mixture was poured into ice water (50 mL) and extracted with ether (3 × 10 mL). Combined organic phase was concentrated under vacuum. The crude product was further purified by crystallization from cold ethanol, giving Azo-\text{C}_{(n)}\text{-NH-Boc} (n= 2, 3, 4) as the yellow powders.

Synthesis of alkyl-terminated azobenzene linkers of Azo-\text{C}_{(n)}\text{-NH}_2 (n= 2, 3, 4). Azo-\text{C}_{(n)}\text{-NH-Boc} (n= 2, 3, 4) (3.0 mmol) was dissolved in a saturated solution of dry hydrogen bromide in ether (15 mL, 0.43 M) at 0 °C. The action mixture was stirred at 0 °C for 3 h, and then at 25 °C overnight. After removal of solvent, the resulting dark red solid was dissolved in water (50 mL). Aqueous sodium hydroxide (2.5 M) was used to adjust their pH value to 7.5. Crude product was extracted from the aqueous solutions with ether. Combined organic phase was washed with deionized water (3 × 15 mL), and concentrated under vacuum to afford Azo-\text{C}_{(n)}\text{-NH}_2 (n= 2, 3, 4) as yellow powders.

Synthesis of ATGC-n (n=2, 3, 4). The obtained Azo-\text{C}_{(n)}\text{-NH}_2 (2.5 mmol) was mixed with asymmetric chiral salen ligand (CL, 3.23 g, 6.0 mmol) in dry toluene (15 mL) under room temperature. The mixture was refluxed for 72 h under argon and concentrated in vacuo. A residue was purified by column chromatography on silica gel using dichloromethane/methanol (4/1, v/v) as eluent. The resulting azobenzene-bridged chiral salen ligand was dissolved in dichloromethane, and followed by treatment with Ti(O\text{Pr})_4 (1.76 g, 6.2 mmol) for 3 h at room temperature. After removal
of solvent, the crude product was washed with \(n\)-hexane (3 × 25 mL). The resulting orange solid was dissolved in dichloromethane (10 mL), and treated with water (2 mL) to remove any traces of TiO\(_2\) by filtration. The filtrate was concentrated in vacuum and further dried in vacuum at 40 °C overnight, giving yellow powders of ATGC-\(n\) (\(n= 2, 3, 4\)).

1.3.2 Preparation of ATGC-0.

A control catalyst of ATGC-0, in which two Ti(salen) units was directly tethered with azobenzene, was prepared to evaluate the function of flexible alkyl spacer on cooperative catalysis. The preparation procedure was shown in Scheme S2. During the procedure, 4, 4’-dihydroxyazobenzene (0.54 g, 2.5 mmol) treated with sodium hydride (0.12 g, 5.1 mmol) was added into the CL (3.23 g, 6.0 mmol)-contained dimethyl formamide solution (30 mL). The mixture was stirred at 60 °C for 4 h under argon and concentrated in vacuo. The resulting azobenzene-bridged chiral salen ligand was dissolved in dichloromethane, and followed by treatment with Ti(O\text{iPr})\(_4\) (1.76 g, 6.2 mmol) for 3 h at room temperature. After removal of solvent, the crude product was washed with \(n\)-hexane (3 × 25 mL). The resulting orange solid was dissolved in dichloromethane (10 mL), and treated with water (2 mL) to remove any traces of TiO\(_2\) by filtration. The filtrate was concentrated in vacuum and further dried in vacuum at 40 °C overnight, giving yellow powders of ATGC-0.
2. Identification of the catalysts (ATGC-n, n=0, 2, 3, 4) and the intermediates.

2.1 Characterization of Azo-C_{10r}-NH-Boc (n=2, 3, 4).

**Azo-C_{10r}-NH-Boc**

Azo-C_{10r}-NH-Boc (1.98 g, yield of 88%): Calc. for (C_{26}H_{36}N_{4}O_{6}): C: 62.38, H: 7.25, N: 11.19%.

Found: C: 62.37, H: 7.24, N: 11.21%. FT-IR (KBr): \( \gamma_{\text{max}}/\text{cm}^{-1} \) 3284, 2979, 2930, 1719, 1688, 1596, 1544, 1497, 1461, 1365, 1301, 1276, 1255, 1183, 1145, 1108, 1064, 842, 668. The structure of Azo-C_{10r}-NH-Boc was further identified by \(^1\text{H} \text{NMR} \), see Figure S1. \(^1\text{H} \text{NMR} \) (500 MHz, CDCl\(_3\)): \( \delta \) (ppm): 7.85-7.83 (m, 4 H, ortho to -N=N- in azobenzene), 6.97-6.95 (m, 4 H, meta to -N=N- in azobenzene), 4.07 (m, 4 H, Ph-O-CH\(_2\)-), 3.54 (m, 4 H, -CH\(_2\)-NH-), 1.43 (m, 18 H, -OC(CH\(_3\))\(_3\) in Boc-group).
Azo-C(β)-NH-Boc

Azo-C(β)-NH-Boc (1.99 g, yield of 84%): Calc. for (C₂₈H₄₀N₄O₆): C: 63.62, H: 7.63, N: 10.6%. Found: C: 63.63, H: 7.61, N: 10.7%. FT-IR (KBr): \( \gamma_{\text{max}}/\text{cm}^{-1} \) 3395, 2980, 2926, 1693, 1601, 1580, 1524, 1500, 1468, 1392, 1297, 1269, 1240, 1171, 1149, 1069, 938, 841, 668. The structure of Azo-C(β)-NH-Boc was further identified by \(^1\)H NMR spectrum (see Figure S2). \(^1\)H NMR (500 MHz, CDCl₃): \( \delta \) (ppm): 7.84 (m, 4 H, ortho to -N=N- in azobenzene), 6.96 (m, 4 H, meta to -N=N- in azobenzene), 4.08 (m, 4 H, Ph-O-CH₂-), 3.33 (m, 4 H, -CH₂-CH₂-NH-), 2.00 (m, 4 H, -CH₂-CH₂-NH-), 1.43 (m, 18 H, -OC(CH₃)_₃ in Boc- group).
Figure S2 $^1$H NMR of Azo-C$_{4j}$-NH-Boc.

**Azo-C$_{4j}$-NH-Boc**

(Azo-C$_{4j}$-NH-Boc (2.25 g, yield of 90%): Calc. for (C$_{30}$H$_{44}$N$_4$O$_6$): C: 64.73, H: 7.97, N: 10.06%.

Found: C: 64.72, H: 7.98, N: 10.05%. FT-IR (KBr): $\gamma_{\text{max}}$/cm$^{-1}$ 3425, 2956, 2857, 1618, 1555, 1439, 1391, 1361, 1304, 1254, 1206, 1115, 1049, 846, 669. The structure of Azo-C$_{4j}$-NH-Boc was further identified by $^1$H NMR spectrum (see Figure S3). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.84 (m, 4 H, ortho to -N=N- in azobenzene), 6.98 (m, 4 H, meta to -N=N- in azobenzene), 4.04 (m, 4 H, Ph-O-CH$_2$-), 3.20 (m, 4 H, -CH$_2$-CH$_2$-NH-), 1.84 (m, 4 H, Ph-OCH$_2$-CH$_2$-), 1.69 (m, 4 H, -CH$_2$-CH$_2$-NH-), 1.44 (m, 18 H, -OC(CH$_3$)$_3$ in Boc-group).
2.2 Characterization of Azo-C_{10r}-NH\textsubscript{2} (n= 2, 3, 4).

**Azo-C_{10r}-NH\textsubscript{2}**

![NMR spectrum](image)

Figure S3 \textsuperscript{1}H NMR of Azo-C_{10r}-NH-Boc.

**Azo-C_{10r}-NH\textsubscript{2}** (0.82 g, yield of 91%): Calc. for (C\textsubscript{16}H\textsubscript{20}N\textsubscript{4}O\textsubscript{2}): C: 63.98, H: 6.71, N: 18.65%.

Found: C: 63.96, H: 6.72, N: 18.66%. FT-IR (KBr): \(\gamma_{\text{max}}/\text{cm}^{-1}\) 3428, 3336, 2931, 1598, 1581, 1497, 1460, 1388, 1360, 1314, 1298, 1253, 1148, 1109, 1064, 843, 557. The structure of Azo-C_{10r}-NH\textsubscript{2} was further identified by \textsuperscript{1}H NMR spectrum (see Figure S4). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm):

7.87-7.85 (m, 4 H, ortho to -N=N- in azobenzene), 7.01-6.99 (m, 4 H, meta to -N=N- in azobenzene), 4.06 (m, 4 H, Ph-O\textsubscript{1}CH\textsubscript{2}), 3.12 (m, 4 H, -CH\textsubscript{2}-NH\textsubscript{2}).
**Azo-C$_{10}$-NH$_2$**

![Azo-C$_{10}$-NH$_2$](image)

Azo-C$_{10}$-NH$_2$ (0.92 g, yield of 93%): Calc. for (C$_{18}$H$_{24}$N$_4$O$_2$): C: 65.83, H: 7.37, N: 17.06. Found: C: 65.82, H: 7.35, N: 17.08%. FT-IR (KBr): $\gamma_{max}$/cm$^{-1}$ 3449, 3339, 2929, 1601, 1598, 1495, 1470, 1387, 1357, 1311, 1296, 1242, 1151, 1108, 1055, 841, 556. The structure of **Azo-C$_{10}$-NH$_2$** was further identified by $^1$H NMR spectrum (see Figure S5). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ (ppm): 7.80 (m, 4 H, ortho to -N=N- in azobenzene), 7.10 (m, 4 H, meta to -N=N- in azobenzene), 4.12 (m, 4 H, Ph-O-CH$_2$-), 2.69 (m, 4 H, -CH$_2$-CH$_2$-NH$_2$), 1.80 (m, 4 H, -CH$_2$-CH$_2$-NH$_2$).
Figure S5 $^1$H NMR of Azo-$C_{4\beta}$-NH$_2$

Azo-$C_{4\beta}$-NH$_2$

Azo-$C_{4\beta}$-NH$_2$ (1.0 g, yield of 94%): Calc. for (C$_{20}$H$_{28}$N$_4$O$_2$): C: 67.39, H: 7.92, N: 15.72%.

Found: C: 67.38, H: 7.93, N: 15.71%. FT-IR (KBr): $\gamma_{\text{max}}$/cm$^{-1}$ 3421, 3337, 2925, 1600, 1500, 1462, 1384, 1358, 1256, 1148, 1099, 1063, 948, 857, 543. The structure of Azo-$C_{4\beta}$-NH$_2$ was further identified by $^1$H NMR spectrum (see Figure S6). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ (ppm): 7.84 (m, 4 H, ortho to -N=N- in azobenzene), 7.14 (m, 4 H, meta to -N=N- in azobenzene), 4.11 (m, 4 H, Ph-$O$-$CH_2$), 2.88 (m, 4 H, -CH$_2$-CH$_2$-CH$_2$-NH$_2$), 1.83-1.76 (m, 8 H, -CH$_2$-CH$_2$-CH$_2$-NH$_2$).
2.3 Characterization of ATGC-n (n= 0, 2, 3, 4).

**ATGC-0**

ATGC-0 (2.23 g, yield of 68%): Calc. for (C_{90}H_{126}N_{6}O_{10}Ti_{2}): C: 69.84, H: 8.21, N: 5.43%.

Found: C: 69.86, H: 8.20, N: 5.42%. FT-IR (KBr): $\gamma_{\text{max}}$/cm$^{-1}$ 2948, 2868, 2676, 2603, 2494, 1612, 1543, 1487, 1439, 1392, 1270, 1172, 1028, 767, 709, 552. The structure of ATGC-0 was further identified by $^1$H NMR (see Figure S7). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 8.29 (m, 4 H, Ph-HC=N-), 7.89 (m, 4 H, ortho to -N=N- in azobenzene), 7.59-7.04 (m, 8 H, Ph-H in Ti(salen)), 6.97 (m, 4 H, meta to -N=N- in azobenzene), 3.10-3.08 (m, 8 H, cyclohexyl-H and Ph-O-CH$_2$-Ti(salen)), 2.29 (m, 4 H, CH$_3$-CH-CH$_3$ of iPrO- in Ti(salen)), 1.44-1.41 (m, 16 H, cyclohexyl-H), 1.32-1.25 (m, 78 H, -CH$_3$ of t-Bu and t-PrO- in Ti(salen)). $\alpha_{25}^D = -20.1$ (c = 0.005 g. mL$^{-1}$, CH$_2$Cl$_2$), titanium content: 0.31 mmol.g$^{-1}$. 

Figure S6 $^1$H NMR of **Azo-C$_{4j}$-NH$_2$**.
ATGC-2

ATGC-2 (2.65 g, yield of 76%): Calc. for (C$_{94}$H$_{136}$N$_8$O$_{10}$Ti$_2$): C: 69.10, H: 8.39, N: 6.86%.

Found: C: 69.98, H: 8.40, N: 6.87%. FT-IR (KBr): $\gamma_{\max}$/cm$^{-1}$ 3446, 2951, 2864, 1623, 1555, 1438, 1388, 1361, 1272, 1206, 1173, 1117, 1029, 865, 847, 773, 758, 682, 668, 590. The structure of ATGC-2 was further identified by $^1$H NMR (see Figure S8). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 8.29 (m, 4 H, Ph-$\text{HC-N}$-), 7.69 (m, 4 H, ortho to -N=N- in azobenzene), 6.97-7.20 (m, 8 H, Ph-$H$ in salen), 6.97 (m, 4 H, meta to -N=N- in azobenzene), 4.32 (m, 4 H, Ph-$\text{O-CH}_2$-), 3.46 (m, 4 H, -CH$_2$-$\text{CH}_2$-$\text{NH}$-), 3.32-3.31 (m, 8 H, cyclohexyl-$H$ and -NH-$\text{CH}_2$-$\text{Ti(salen)}$),
2.22 (m, 4 H, CH\textsubscript{3}-CH\textsubscript{2}-CH\textsubscript{3} of i\textsuperscript{PrO-} in Ti(salen)), 1.69-1.43 (m, 16 H, cyclohexyl-\textit{H}), 1.35-1.28 (m, 78 H, -CH\textsubscript{3} of t-Bu and i\textsuperscript{PrO-} in Ti(salen)). \(\alpha_{25}^0 = -19.3\) (c = 0.005 g mL\textsuperscript{-1}, CH\textsubscript{2}Cl\textsubscript{2}), titanium content: 0.21 mmol g\textsuperscript{-1}.

Figure S8 \textsuperscript{1}H NMR of ATGC-2.

ATGC-3

ATGC-3 (2.6 g, yield of 73\%): Calc. for \((C\textsubscript{96}H\textsubscript{140}N\textsubscript{8}O\textsubscript{10}Ti\textsubscript{2})\): C: 69.38, H: 8.49, N: 6.74\%. Found: C: 69.37, H: 8.51, N: 6.73\%. FT-IR (KBr): \(\gamma_{\text{max}}\text{cm}^{-1}\) 3424, 2956, 2862, 1615, 1555, 1438, 1463, 1391, 1361, 1303, 1271, 1254, 1206, 1175, 1116, 1072, 1027, 866, 847, 773, 758, 712, 670, 649, 584. The structure of ATGC-3 was further identified by \textsuperscript{1}H NMR (see Figure S9). \textsuperscript{1}H NMR (500
MHz, CDCl$_3$): $\delta$ (ppm): 8.31 (m, 4 H, Ph-HC=N-), 7.86 (m, 4 H, ortho to -N=N- in azobenzene), 7.22-7.16 (m, 8 H, Ph-H in salen), 7.07 (m, 4 H, meta to -N=N- in azobenzene), 4.30 (m, 4 H, Ph-O-CH$_2$), 3.59 (m, 4 H, -CH$_2$-CH$_2$-NH-), 3.37 (m, 8 H, cyclohexyl-H and -NH-CH$_2$-Ti(salen)), 2.71 (m, 4 H, -CH$_2$-CH$_2$-NH-), 2.23 (m, 4 H, CH$_3$-CH-CH$_3$ of t-PrO- in Ti(salen)), 1.42-1.41 (m, 16 H, cyclohexyl-H), 1.33-1.29 (m, 78 H, -C$_3$H$_8$ of t-Bu and i-PrO- in Ti(salen)). $\alpha_{25}$D = -21.5 (c = 0.005 g. mL$^{-1}$, CH$_2$Cl$_2$), titanium content: 0.31 mmol. g$^{-1}$.

Figure S9 $^1$H NMR of ATGC-3.

ATGC-4

ATGC-4 (2.80 g, yield of 77%). Calc. for (C$_{98}$H$_{144}$N$_8$O$_{10}$Ti$_2$): C: 69.65, H: 8.59, N: 6.63%.

Found: C: 69.63, H: 8.61, N: 6.64%. FT-IR (KBr): $\gamma_{\text{max}}$/cm$^{-1}$ 3439, 2954, 2855, 1618, 1555, 1465,
The structure of ATGC-4 was further identified by $^1$H NMR (see Figure S10). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 8.41-8.34 (m, 4 H, Ph-HC=N-), 7.88 (m, 4 H, ortho to -N=N- in azobenzene), 7.25-7.08 (m, 8 H, Ph-H in salen), 7.01 (m, 4 H, meta to -N=N- in azobenzene), 4.12 (m, 4 H Ph-O-CH$_2$-), 3.38 (m, 8 H, cyclohexyl-H and -NH-CH$_2$-Ti(salen)), 3.24 (m, 4 H, -CH$_2$-CH$_2$-NH-), 2.78-2.72 (m, 8 H, -CH$_2$-CH$_2$-CH$_2$-NH-), 2.24 (m, 4 H, CH$_3$-CH$\cdot$CH$_3$ of iPrO- in Ti(salen)), 1.46 (m, 16 H, cyclohexyl-H), 1.31-1.28 (m, 78 H, -CH$_3$ of t-Bu and iPrO- in Ti(salen)). $\alpha$$_{25}^{D}$ = -24.2 (c = 0.005 g. mL$^{-1}$, CH$_2$Cl$_2$), titanium content: 0.15 mmol. g$^{-1}$.

![Figure S10 $^1$H NMR of ATGC-4.](image)

2.4 FT-IR

Successful bridging Ti(salen) units with Azo-C$_{10}$-NH$_2$ was confirmed by FT-IR spectroscopy. ATGC-3 with a middling length of the aliphatic chain was chosen as the typical catalyst for the structural identification. Figure S11 showed the FT-IR spectra of ATGC-3, Azo-C$_{13}$-NH$_2$, as well
as Neat-C for comparison. Clearly, Azo-C₁₆-NH₂ showed characteristic N-H stretching of terminal primary amino (–NH₂) group (3449 and 3339 cm⁻¹), N=N stretching of azobenzene (1598 cm⁻¹), and C–O–C stretching of the aromatic ether group (1242 and 1108 cm⁻¹) in its FT-IR spectrum (Fig. S11-a). After Ti(salen) modification, the bands corresponding to the primary amino (–NH₂) group disappeared with the formation of a new band at around 3435 cm⁻¹, which was the characteristic stretching vibration of N-H in the second amine (–NH-) group (Figure S11-c vs. S11-a). It provided convincing proof that the terminated amino group underwent N-alkylation with chloromethyl (–CH₂Cl) groups of the asymmetric salen ligand during the modification. Ti(salen) units were thus bridged with the Azo-C₁₆-NH₂ linker, giving the azobenzene-bridged bimetallic Ti(salen) catalysts of ATGC-3. The successful linkage was also evident from the fact that ATGC-3 gave the characteristic bands assigned to the vibrations of C=N (1621 cm⁻¹), C-O (1547 cm⁻¹) and Ti-O (807 cm⁻¹) in Ti(salen) complex (Figure S11-c vs. S11-b). The characteristic bands were similar with that in Neat-C, suggesting the intact active site during the linkage.

Figure S11 FT-IR spectra of Azo-C₁₆-NH₂ (a), Neat-C (b) and ATGC-3 (c).
3. Evaluation of catalytic activity of ATGC-n in asymmetric sulfoxidation.

3.1 Catalytic performance

Before reaction, dark-adapted catalyst was exposed to UV light (λ = 365 nm) for 20 min to ensure the cis-state of azobenzene linker. The UV-treated catalyst (0.1 mol% of substrate, based on the titanium content in catalyst) was mixed with aryl alkyl sulfides (1.0 mmol) in ethanol (2 mL) under stirring at 25 °C. Aqueous hydrogen peroxide (aq. H$_2$O$_2$, 30 wt%, 1.2 mmol) was then dropwise added into the solution within 15 min. The resulting mixture was exposed to UV light and stirred at room temperature, until the reaction was judged to be complete based on GC analysis. And then, reaction mixture was extracted with ethyl acetate for five times (5×3 mL). The upper extracted solution was combined and concentrated in vacuo. Further purification of the residue by chromatography on silica gel (petroleum ether/ethyl acetate, 1.5/1) afforded pure chiral sulfoxides. The products have been identified by $^1$H NMR spectra. Conversion and chemoselectivity to the chiral sulfoxides were measured by a 6890N gas chromatograph (Agilent Co.) equipped with a capillary column (HP19091G-B213, 30 m×0.32 mm×0.25 mm) and a FID detector. Enantiomer excess (ee) values of chiral products were determined by HPLC analysis using the Daicel Chiralpak AD columns.

*Phenyl methyl sulfoxide:* The product has been identified by $^1$H NMR spectrum (see Figure S12).

$^1$H NMR (CDCl$_3$, 500 MHz): δ (ppm): 7.63-7.51 (m, 5 H, ArH), 2.72 (s, 3 H, -SCH$_3$).

Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL.min$^{-1}$, injector temperature and detector temperature were 250 °C, column temperature was 150 °C, $t_{Phenyl methyl sulfoxide} =$ 5.5 min. Ee value was determined by HPLC ($^i$PrOH/ n-hexane = 1: 9 (v/v));
flow rate = 1.0 mL.min\(^{-1}\); 25 °C; \(\lambda = 254\) nm; major enantiomer \(t_R = 5.5\) min, minor enantiomer \(t_S = 6.4\) min (see Figure S13-S21). \([\alpha]_D = +115.3\) (\(c = 0.4\) in acetone). lit: \([\alpha]_D = -130.1\) (\(c=1.7\) in acetone) for (S), 90% ee.\(^5\)

Figure S12 \(^1\)H NMR of phenyl methyl sulfoxide.

Figure S13 HLPC of phenyl methyl sulfoxide obtained over ATGC-0 under UV irradiation (ee value = 80%).
Figure S14 HLPC of phenyl methyl sulfoxide obtained over ATGC-0 in dark (ee value = 75%).

Figure S15 HLPC of phenyl methyl sulfoxide obtained over ATGC-2 under UV irradiation (ee value = 90%).

Figure S16 HLPC of phenyl methyl sulfoxide obtained over ATGC-2 in dark (ee value = 75%).
Figure S17 HLPC of phenyl methyl sulfoxide obtained over ATGC-3 under UV irradiation (ee value >99%).

Figure S18 HLPC of phenyl methyl sulfoxide obtained over ATGC-3 in dark (ee value = 78%).

Figure S19 HLPC of phenyl methyl sulfoxide obtained over ATGC-4 under UV irradiation (ee value > 99%).
Phenyl ethyl sulfoxide: The product has been identified by $^1$H NMR spectrum (see Figure S22).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.58-7.49 (m, 5 H, ArH), 2.88-2.76 (m, 2 H, -CH$_2$-CH$_3$), 1.18 (m, 3 H, -CH$_2$-CH$_3$). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL min$^{-1}$, injector temperature and detector temperature were 250 °C, column temperature was 150 °C, $t_{Phenyl ethyl sulfoxide}$ = 6.6 min; ee value was determined by HPLC ($^i$PrOH/ $n$-hexane = 1: 9 (v/v)); flow rate = 1.2 mL min$^{-1}$; 25 °C; $\lambda = 254$ nm; major enantiomer $t_R = 10.3$ min
and minor enantiomer $t_5 = 12.4$ min (see Figure S23-S25). $[\alpha]_D = +178.3 \ (c = 1.4 \text{ in EtOH});$ lit: $[\alpha]_D = -169.1 \ (c = 1.4 \text{ in EtOH})$ for $(S), 82\% \text{ ee}.$

Figure S22 $^1\text{H} \text{NMR}$ of phenyl ethyl sulfoxide.

Figure S23 $\text{HLPC}$ of phenyl ethyl sulfoxide obtained over ATGC-3 under UV irradiation (ee value $>99\%$).
Figure S24 HLPC of phenyl ethyl sulfoxide obtained over ATGC-3 in dark (ee value > 99%).

*Phenyl n-butyl sulfoxide:* The product has been identified by $^1$H NMR spectrum (see Figure S25).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.35-7.17 (m, 5 H, ArH), 2.96-2.93 (m, 2 H, CH$_3$-CH$_2$-CH$_2$-CH$_2$-S-), 1.68-1.64 (m, 2 H, CH$_3$-CH$_2$-CH$_2$-CH$_2$-S-), 1.49-1.46 (m, 2 H, CH$_3$-CH$_2$-CH$_2$-CH$_2$-S-), 0.96-0.93 (m, 3 H, CH$_3$-CH$_2$-CH$_2$-CH$_2$-S-). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL min$^{-1}$, injector temperature and detector temperature were 250 $^\circ$C, column temperature was 180 $^\circ$C, $t_{Phenyl \ n\-butyl \ sulfoxide} = 3.2$ min; ee value was determined by HPLC ($^i$PrOH/ n-hexane = 1: 9 (v/v)); flow rate = 1.2 mL.min$^{-1}$; 25 $^\circ$C; $\lambda = 254$ nm; major enantiomer $t_R = 5.44$ min and minor enantiomer $t_S = 5.93$ min (see Figure S26 and S27). $[\alpha]_D = +69.2$ (c =1.8 in ethanol); lit: $[\alpha]_D = +64.4$ (c =2.0 in ethanol) for (R), 90% ee.$^6$
Figure S25 $^1$H NMR of phenyl n-butyl sulfoxide.

Figure S26 HPLC of phenyl n-butyl sulfoxide obtained over ATGC-3 under UV irradiation (ee value = 97%).

Figure S27 HPLC of phenyl n-butyl sulfoxide obtained over ATGC-3 in dark (ee value = 85%).
Phenyl n-hexyl sulfide: The product has been identified by $^1$H NMR spectrum (see Figure S28).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.36-7.18 (m, 5 H, ArH), 2.97-2.94 (m, 2 H, -CH$_2$-CH$_2$-CH$_2$-S-), 1.71-1.64 (m, 2 H, -CH$_2$-CH$_2$-CH$_2$-S-), 1.49-1.43 (m, 2 H, -CH$_2$-CH$_2$-CH$_2$-S-), 1.37-1.35 (m, 4 H, CH$_3$-CH$_2$-CH$_2$-), 1.33-1.32 (m, 3 H, CH$_3$-CH$_2$-CH$_2$-). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL min$^{-1}$, injector temperature and detector temperature were 250 °C, column temperature was 180 °C, $t_{\text{Phenyl n-hexyl sulfoxide}} = 4.5$ min; ee value was determined by HPLC ([PrOH/ n-hexane = 1: 9 (v/v)); flow rate = 1.2 mL min$^{-1}$; 25 °C; $\lambda$ = 254 nm; major enantiomer $t_R = 5.23$ min and minor enantiomer $t_S = 6.12$ min (see Figure S29 and S30).

$[a]_D = +98.3$ (c =1.8 in ethanol).
Figure S29 HLPC of phenyl n-hexyl sulfoxide obtained over ATGC-3 under UV irradiation (ee value = 94%).

Figure S30 HLPC of phenyl n-hexyl sulfoxide obtained over ATGC-3 in dark (ee value = 83%).

**o-Methoxyphenyl methyl sulfoxide**: The product has been identified by $^1$H NMR spectrum (see Figure S31). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.81-6.94 (m, 4 H, ArH), 3.89 (s, 3 H, -OCH$_3$), 2.78 (s, 3 H, -SCH$_3$). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL.min$^{-1}$, injector temperature and detector temperature were 250 °C, column temperature was 150 °C, $t_{o\text{-methoxyphenyl methyl sulfoxide}}$ = 8.1 min; ee value was determined by HPLC ($^t$PrOH/ n-hexane = 2: 8 (v/v)); flow rate = 1.2 mL.min$^{-1}$; 25 °C; $\lambda$ = 254 nm; major enantiomer $t_R$ = 5.9 min and minor enantiomer $t_S$ = 7.0 min (see Figure S32 and S33). [a]$_D$= +321.3 (c=1.0 in acetone); lit: [a]$_D$= +318.6 (c=1.0 in acetone) for (R), 98% ee.\(^7\)
Figure S31 $^1$H NMR of o-methoxyphenyl methyl sulfoxide.

Figure S32 HPLC of o-methoxyphenyl methyl sulfoxide obtained over ATGC-3 under UV irradiation (ee value > 99%).

Figure S33 HPLC of o-methoxyphenyl methyl sulfoxide obtained over ATGC-3 in dark (ee value = 93%).
**p-Methoxyphenyl methyl sulfoxide:** The product has been identified by \(^1\)H NMR spectrum (see Figure S34). \(^1\)H NMR (CDCl\(_3\), 500 MHz): δ (ppm): 7.88-7.06 (m, 4 H, ArH), 3.91 (s, 3 H, -OCH\(_3\)), 3.05 (s, 3 H, -SCH\(_3\)). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL·min\(^{-1}\), injector temperature and detector temperature were 250 °C, column temperature was 150 °C, \(t_{p\text{-methoxyphenyl methyl sulfoxide}} = 6.01\) min; ee value was determined by HPLC (iPrOH/\(n\)-hexane = 2:8 (v/v)); flow rate = 1.2 mL·min\(^{-1}\); \(\lambda = 254\) nm; major enantiomer \(t_R = 6.8\) min and minor enantiomer \(t_S = 7.9\) min (see Figure S35 and S36). \([\alpha]D^\circ = +141.2\) (c =2.0 in CHCl\(_3\)); lit: \([\alpha]D^\circ = -129.7\) (c =2.0 in CHCl\(_3\)) for \((S), 86\%\) ee.\(^5\)

![Figure S34 \(^1\)H NMR of p-methoxyphenyl methyl sulfoxide.](image)

![Figure S35 HPLC of p-methoxyphenyl methyl sulfoxide obtained over ATGC-3 under UV irradiation (ee value = 92%).](image)
Figure S36: HLPC of methyl p-methoxyphenyl sulfoxide obtained over ATGC-3 in dark (ee value = 82%).

*p-Bromophenyl methyl sulfoxide*: The product has been identified by $^1$H NMR spectrum (see Figure S37). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.65-7.52 (m, 4 H, Ar H), 2.70 (s, 3 H, -SCH$_3$). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL.min$^{-1}$, injector temperature and detector temperature were 250 °C, column temperature was 150 °C, $t_{p-bromophenyl methyl sulfoxide}$ = 12 min; ee value was determined by HPLC (PrOH/ n-hexane = 1: 9 (v/v)); flow rate = 1.2 mL.min$^{-1}$; 25 °C; $\lambda$ = 254 nm; major enantiomer $t_R$ = 12.2 min and minor enantiomer $t_S$ = 16.0 min (see Figure S38 and S39). [a]$_D^\circ$ = +103.2 (c =1.0 in acetone); lit: [a]$_D^\circ$ = -97.5 (c=1.8 in acetone) for (S), 94% ee.$^5$

Figure S37: $^1$H NMR of p-bromophenyl methyl sulfoxide.
Figure S38 HLPC of $\rho$-bromophenyl methyl sulfoxide obtained over ATGC-3 under UV irradiation (ee value >99%).

Figure S39 HLPC of $\rho$-bromophenyl methyl sulfoxide obtained over ATGC-3 in dark (ee value =77%).

3.2 Proposed mechanism for the ATGC-n-catalyzed asymmetric sulfoxidation with $\text{H}_2\text{O}_2$ in ethanol upon UV irradiation

The UV-enforced synergistic effect of ATGC-n accorded with our hypothesis that the asymmetric sulfoxidation proceed through a bimetallic, cooperative mechanism, where di-$\mu$-oxo Ti(salen) complex of $\left[\{(\text{salen})\text{Ti}(\mu-O)\}_2\right]$ I was the real active catalyst for the transformation. As shown in Scheme S3, upon UV irradiation, the azobenzene linker was in cis-state. It located the two Ti(salen) units in proximity to each other, which was favorable for the formation of di-$\mu$-oxo
Ti(salen) complex 1. In the methanolic solution, di-μ-oxo Ti(salen) complex 1 was rapidly transformed to a monomeric Ti(salen) species 2 through rapid alkoxide exchange. Hydrogen peroxide was then reacted with the monomeric species 2, giving the corresponding peroxo species 3 to oxidize the sulfides. Monomeric Ti(salen) species 2 was thus recovered, and it was readily changeable to the di-μ-oxo Ti(salen) complex 1 for catalyst recycle. Similar report has been made by B. Saito and co-worker. 8

Scheme S3 Proposed mechanism for di-μ-oxo Ti(salen) complex mediated asymmetric sulfoxidation with H2O2 in ethanol.

3.3 Kinetic studies

Kinetic studies were used to further investigate the light-controlled cooperative catalysis over ATGC-n. The ATGC-3 with different loadings (0.05, 0.07, 0.1 and 0.15 mol% of substrate) was stirred with phenyl methyl sulfide (1.0 mmol) in ethanol (2.0 mL) at 25 °C with/without UV irradiation. H2O2 (30 wt%, 1.2 mmol) was added at one time. Conversion of phenyl methyl sulfide was determined by GC. The values for the initial reaction rates at different catalyst loading were derived from the conversion plots (Table S1 and S2). Initial rate plots for the asymmetric oxidation of phenyl methyl sulfide catalyzed by ATGC-3 with or without UV treatment were shown in Fig. S40.
The rate equation was considered as the sum of first- (intramolecular) and second- order (intermolecular) contributions and as a function of the total concentration of titanium ([Ti]):

\[ \text{rate} = k_{\text{intra}}[\text{Ti}] + k_{\text{inter}}[\text{Ti}]^2. \]

When the initial reaction rate is measured at different titanium concentrations [Ti], plots of the rate/[Ti] versus [Ti] should give linear correlations in which the y intercept is equal to the intramolecular rate coefficient (\(k_{\text{intra}}\)) and the slope corresponds to the intermolecular rate constant (\(k_{\text{inter}}\)). Contribution of intra- and intermolecular reactions can be thus assessed quantitatively. As expected, for ATGC-3 either UV-treated or in dark, the plots revealed linear correlations with positive slopes and non-zero y-intercepts (Fig. S40), which suggested the participation of both inter- and intramolecular pathways in sulfoxidation. Notably, the UV-treated ATGC-3 displayed a larger intramolecular rate component (\(k_{\text{intra}}=8.67 \text{ min}^{-1}\)) than ATGC-3 in dark (\(k_{\text{intra}}=2.46 \text{ min}^{-1}\)), consistent with UV-enforced intramolecular cooperative mode. While intermolecular reaction rate (\(k_{\text{inter}}\), slope of plots) was decreased slightly when ATGC-3 was treated with UV light, probably due to the steric hindrance of cis-ATGC-3, which reduced the stacking of neighbouring ATGC-3 for intermolecular cooperative function.

Table S1 Kinetics measurement of ATGC-3 in asymmetric oxidation of phenyl methyl sulfide with H\(_2\)O\(_2\) in ethanol under UV irradiation

<table>
<thead>
<tr>
<th>Catalyst loading [M]</th>
<th>Reaction time (min)</th>
<th>Conversion (%)</th>
<th>Initial rate constants ((K_{\text{obs}}))</th>
<th>(K_{\text{obs}}[/\text{M}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>10</td>
<td>16</td>
<td>1.46</td>
<td>11.73</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>65</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.07</td>
<td>10</td>
<td>24</td>
<td>2.43</td>
<td>13.90</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>58</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* a
\begin{table}
\centering
\begin{tabular}{cccc}
\hline
Catalyst loading $^b$ & Reaction time (min) & Conversion $^c$ & Initial rate constants $^d$ ($K_{\text{obs}}$)\tabularnewline
[M] & & (%) & $K_{\text{obs}}$/[M] \tabularnewline
\hline
0.05 & 10 & 9 & 1.00 & 8.03 \tabularnewline
 & 20 & 16 & & \tabularnewline
 & 30 & 22 & & \tabularnewline
 & 40 & 26 & & \tabularnewline
 & 50 & 29 & & \tabularnewline
 & 60 & 32 & & \tabularnewline

0.07 & 10 & 18 & 2.07 & 11.85 \tabularnewline
 & 20 & 29 & & \tabularnewline
 & 30 & 35 & & \tabularnewline
 & 40 & 39 & & \tabularnewline
 & 50 & 44 & & \tabularnewline
 & 60 & 47 & & \tabularnewline

0.1 & 10 & 30 & 3.78 & 15.13 \tabularnewline
 & 20 & 46 & & \tabularnewline
 & 30 & 55 & & \tabularnewline
 & 40 & 60 & 35 & \tabularnewline
\hline
\end{tabular}
\end{table}

\textsuperscript{a} phenyl methyl sulfide (1.0 mmol), H$_2$O$_2$ (30 wt\%, 1.2 mmol, added at one portion), ethanol (2.0 mL), 60 min, 25 $^\circ$C, UV irradiation. \textsuperscript{b} 0.05, 0.07, 0.10, or 0.15 mol% of substrate, based on titanium content. \textsuperscript{c} Determined by GC.

Table S2 Kinetics measurement of \textbf{ATGC-3} in asymmetric oxidation of phenyl methyl sulfide with H$_2$O$_2$ in ethanol in dark $^a$
Phenyl methyl sulfide (1.0 mmol), H₂O₂ (30 wt%, 1.2 mmol, added at one portion), ethanol (2.0 mL), 60 min, 25 °C, in dark. b 0.05, 0.07, 0.10, or 0.15 mol% of substrate, based on titanium content.

c Determined by GC. d The initial rate constants (K_{obs}) were obtained by calculation of the tangent in t=0 for the conversion plots obtained by GC.

3.4 Computational Studies

Density functional theory (DFT) was employed to optimize the structures of bimetallic ATGC-n (n=0, 2, 3, and 4). The simulated structures were performed with B3LYP hybrid functional, where Ti, O, and N used 6-31 g* basis set, C used 3-21 g* basis set. For all DFT calculations, a convergence
criterion of $1.0 \times 10^{-6}$ a.u. was adopted for changes in energy and density matrix elements. The optimized three-dimensional structure modes of the bimetallic catalysts were showed in Figure S41, and the corresponding Ti$^{IV}$-Ti$^{IV}$ distance were listed in Table S3. Indeed, cis-azobenzene linker located two Ti(salen) units in proximity to each other. Two metallosalen units in cis-ATGC-3 were aligned face to face in a head-to-tail orientation with a minimum Ti$^{IV}$-Ti$^{IV}$ distance of 6.42 Å, as shown by the optimized, computed structure (Table S3). Such a spatial arrangement of two active centers was obviously favourable for cooperative function and thereby enforced a subsequent intramolecular, cooperative reaction pathway to realize high catalytic activity and selectivity. Further increasing the spacer length of ATGC-n (n= 4) was detrimental to the intramolecular bimetallic cooperation due to the long metal-metal distance (6.48 Å). Furthermore, the enlarged linker allowed for back-folding to give the “head-to-head” orientation, which might be also unfavourable for the cooperative effect.

Figure S41 The optimized molecular structure of the trans-ATGC-0 (a), cis-ATGC-0 (b), cis-ATGC-2 (c), cis-ATGC-3 (d), and cis-ATGC-4 (e)

<table>
<thead>
<tr>
<th>Modes</th>
<th>trans-ATGC-0</th>
<th>cis-ATGC-0</th>
<th>cis-ATGC-2</th>
<th>cis-ATGC-3</th>
<th>cis-ATGC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{IV}$-Ti$^{IV}$ distance</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti^{IV}-Ti^{IV} distance (Å)</td>
<td>26.9</td>
<td>19.6</td>
<td>7.05</td>
<td>6.42</td>
<td>6.48</td>
</tr>
</tbody>
</table>

References


