Supporting Information

Cooperative chiral salen Ti\textsuperscript{IV} catalyst supported on ionic liquid-functionalized graphene oxide accelerated asymmetric sulfoxidation in water

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General procedure for asymmetric oxidation of sulfides to sulfoxides

The selected catalyst (1 mol% substrate, based on the titanium content in catalyst) and sulfides (1.0 mmol) were added into H$_2$O (1 mL) under stirring at 20 °C. H$_2$O$_2$ (30 wt%, 1.2 mmol) was then added dropwise over 15 min. The resulting mixture was stirred at 20 °C until the reaction was judged to be complete based on GC analysis. After the reaction, the heterogeneous catalyst was recovered by centrifugation, washed with dichloromethane, and successively reused for subsequent sulfoxidation. The reaction solution was extracted with dichloromethane (3 × 4 mL). Combined organic layer was dried over anhydrous sodium sulfate, and was concentrated in vacuo. Further purification of the residue by chromatography on silica gel (petroleum ether/ethyl acetate, 1.5:1) afforded pure sulfoxides. The products have been identified by $^1$H and $^{13}$C NMR spectra. Enantiomeric excess (ee value) of the corresponding chiral sulfoxides were determined by HPLC analysis using the Daicel chiralpak AD columns.
**Methyl phenyl sulfoxide:** The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig. S1 and S2). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.40-7.52 (m, 2 H, ArH), 7.38-7.39 (m, 3 H, ArH), 2.57-2.58 (s, 3 H, Me). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm): 145.5, 131.0, 129.3, 123.4, (ArC), 43.8 (SCH$_3$). Ee value of the obtained methyl phenyl sulfoxide was determined by HPLC with a Chiralpak AD column (i-PrOH/n-hexane = 1: 9 (v/v), UV 254 nm, flow rate 1.0 mL/min, major enantiomer $t_R = 17.7$ min and minor enantiomer $t_S = 20.3$ min (see Fig. S3, S4, S5 and S6).

![Fig. S1 $^1$H NMR of methyl phenyl sulfoxide.](image-url)
**Fig. S2** $^{13}$C NMR of methyl phenyl sulfoxide.

**Fig. S3** HLPC of methyl phenyl sulfoxide obtained over GO-IL-Ti(salen) (ee = 92%).
**Fig. S4** HLPC of methyl phenyl sulfoxide obtained over neat complex (ee = 74%).

**Fig. S5** HLPC of methyl phenyl sulfoxide obtained over *IL-Ti(salen)* (ee = 85%).

**Fig. S6** HLPC of methyl phenyl sulfoxide obtained over *GO-NH-Ti(salen)* (ee = 79%).

**Methyl o-methoxyphenyl sulfoxide:** The product has been identified by $^1$H and $^{13}$C NMR
spectra (see Fig. S7 and S8). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 6.83-7.73 (m, 4 H, ArH), 3.77-3.78 (s, 3 H, OCH$_3$), 2.66-2.67 (s, 3 H, SCH$_3$). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm): $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm): 154.7, 132.8, 132.0, 124.4, 121.5, 110.6, (ArC), 55.7 (OCH$_3$), 41.1 (SCH$_3$). Ee value of the obtained methyl o-methoxyphenyl sulfoxide was determined by HPLC with a Chiralpak AD column (i-PrOH/n-hexane = 2: 8 (v/v)), UV 254 nm, flow rate 1.0 mL/min, major enantiomer $t_R = 7.9$ min and minor enantiomer $t_S = 11.5$ min (see Fig. S9, S10, S11 and S12).

![Fig. S7 $^1$H NMR of methyl o-methoxyphenyl sulfoxide.](image-url)
---Fig. S8---

$^{13}$C NMR of methyl o-methoxyphenyl sulfoxide.

---Fig. S9---

HLPC of methyl o-methoxyphenyl sulfoxide obtained over GO-IL-Ti(salen) (ee = 87%).
**Fig. S10** HLPC of methyl o-methoxyphenyl sulfoxide obtained over neat complex (ee = 70%).

**Fig. S11** HLPC of methyl o-methoxyphenyl sulfoxide obtained over **IL-Ti(salen)** (ee = 82%).

**Fig. S12** HLPC of methyl o-methoxyphenyl sulfoxide obtained over **GO-NH-Ti(salen)** (ee = 71%).
**Methyl p-methoxyphenyl sulfoxide:** The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig. S13 and S14). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.88-7.90 (d, 2 H, ArH), 7.04-7.06 (d, 2 H, ArH), 3.91 (s, 3 H, OCH$_3$), 3.06 (s, 3 H, SCH$_3$). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm): 163.7, 132.3, 129.6, 114.5 (ArC), 55.7 (OCH$_3$), 44.9 (SCH$_3$). Ee value of the obtained methyl p-methoxyphenyl sulfoxide was determined by HPLC with a Chiralpak AD column (i-PrOH/n-hexane = 2: 8 (v/v)), UV 254 nm, flow rate 1.0 mL/min, major enantiomer $t_R$ = 14.2 min and minor enantiomer $t_S$ = 17.0 min (see Fig. S15, S16, S17 and S18).

![Fig. S13 $^1$H NMR of methyl p-methoxyphenyl sulfoxide.](image-url)
**Fig. S14** $^{13}$C NMR of methyl $p$-methoxyphenyl sulfoxide.

**Fig. S15** HPLC of methyl $p$-methoxyphenyl sulfoxide obtained over GO-IL-Ti(salen) (ee = 79%).

**Fig. S16** HPLC of methyl $p$-methoxyphenyl sulfoxide obtained over neat complex (ee = 64%).
Fig. S17 HLPC of methyl \( p \)-methoxyphenyl sulfoxide obtained over \textit{IL-Ti(salen)} (ee = 75%).

Fig. S18 HLPC of methyl \( p \)-methoxyphenyl sulfoxide obtained over \textit{GO-NH-Ti(salen)} (ee = 68%).

\textbf{Methyl \( p \)-nitrophenyl sulfoxide}: The product has been identified by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra (see Fig. S19 and S20). \(^1\text{H}\) NMR (CDCl\(_3\), 500 MHz): \(\delta\) (ppm): 2.59 (s, 3 H, SCH\(_3\)), 7.27-7.42 (d, 2 H, Ar\(H\)), 8.09-8.20 (d, 2 H, Ar\(H\)). \(^{13}\text{C}\) NMR (CDCl\(_3\), 125 MHz): \(\delta\) (ppm): 43.8 (SCH\(_3\)), 123.9, 124.9, 144.7, 148.8 (Ar\(C\)). Ee value of the obtained methyl \( p \)-nitrophenyl sulfoxide was determined by HPLC with a Chiralpak AD column (i-PrOH/\(n\)-hexane = 3: 7 (v/v)), UV 254 nm, flow rate 1.0 mL/min, major enantiomer \(t_r\) = 11.5 min and minor enantiomer \(t_s\) = 21.5 min (see Fig. S21, S22, S23 and S24).
**Fig. S19** $^1$H NMR of methyl $p$-nitrophenyl sulfoxide.

**Fig. S20** $^1$C NMR of methyl $p$-nitrophenyl sulfoxide.
**Fig. S21** HLPC of methyl p-nitrophenyl sulfoxide obtained over GO-IL-Ti(salen) (ee =75%).

**Fig. S22** HLPC of methyl p-nitrophenyl sulfoxide obtained over neat complex (ee =41%).

**Fig. S23** HLPC of methyl p-nitrophenyl sulfoxide obtained over IL-Ti(salen)  (ee =56%)
Fig. S24 HPLC of methyl p-nitrophenyl sulfoxide obtained over GO-NH-Ti(salen) (ee = 44%)

**Methyl p-bromophenyl sulfoxide:** The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig. S25 and S26). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 3.01 (s, 3 H, SCH$_3$), 7.13-7.83 (m, 4 H, ArH). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm): 44.53 (SCH$_3$), 125.1, 129.0, 132.7, 139.5 (ArC). Ee value of the obtained methyl p-bromophenyl sulfoxide was determined by HPLC with a Chiralpak AD column (i-PrOH/n-hexane = 5: 5 (v/v)), UV 254 nm, flow rate 1.0 mL/min, major enantiomer $t_R$ = 8.4 min and minor enantiomer $t_S$ = 9.9 min (see Fig. S27, S28, S29 and S30).

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**Fig. S25.** $^1$H NMR of methyl p-bromophenyl sulfoxide.
**Fig. S26** $^{13}$C NMR of methyl $p$-bromophenyl sulfoxide.

**Fig. S27** HLPC of methyl $p$-bromophenyl sulfoxide obtained over **GO-JL-Ti(salen)** (ee = 95%).
**Fig. S28** HLPC of methyl $p$-bromophenyl sulfoxide obtained over neat complex (ee = 89%).

**Fig. S29** HLPC of methyl $p$-bromophenyl sulfoxide obtained over $IL$-Ti(salen) (ee = 94%).

**Fig. S30** HLPC of methyl $p$-bromophenyl sulfoxide obtained over $GO$-NH-Ti(salen) (ee = 91%).
**Ethyl phenyl sulfoxide:** The product has been identified by $^1$H NMR and $^{13}$C NMR spectra (see Fig. S31 and S32). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 1.16-1.19 (m, 3 H, Me), 2.71-2.90 (m, 2 H, -CH$_2$), 7.49-7.60 (m, 5 H, ArH). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm): 5.95 (CH$_3$), 50.29 (SCH$_2$), 124.12, 129.12, 130.92, 143.33 (ArC). Ee value of the obtained ethyl phenyl sulfoxide was determined by HPLC with a Chiralpak AD column (i-PrOH/$n$-hexane = 1:9 (v/v)), UV 254 nm, flow rate 1.0 mL/min, major enantiomer $t_R = 8.35$ min and minor enantiomer $t_S = 10.21$ min (see Fig. S33, S34, S35 and S36).

**Fig. S31** $^1$H NMR of ethyl phenyl sulfoxide
Fig. S32 $^{13}$C NMR of ethyl phenyl sulfoxide.

Fig. S33 HPLC of ethyl phenyl sulfoxide obtained over GO-IL-Ti(salen) (ee = 98%).
Fig. S34 HLPC of ethyl phenyl sulfoxide obtained over neat complex (ee = 91%).

Fig. S35 HLPC of ethyl phenyl sulfoxide obtained over \textit{IL-Ti(salen)} (ee = 97%).
Fig. S36 HLPC of ethyl phenyl sulfoxide obtained over GO-NH-Ti(salen) (ee = 93%).