Supporting Information

Cooperative Chiral Salen Ti^{IV} Catalysts with Built-in Phase-Transfer Capability Accelerated Asymmetric Sulfoxidation in Water

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General procedure for asymmetric oxidation of sulfides to sulfoxides

The selected catalyst (1.0 mol% of substrate, based on titanium content in the catalyst) and sulfides (1.0 mmol) were added into water (1 mL) under stirring. H_2O_2 (30 wt.%, 1.2 mmol) was then dropwise added within 15 min at room temperature. The oxidation progress was monitored constantly by TLC. After reaction, the reaction solution was extracted with CH_2Cl_2 for three times (3 × 3 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and 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 NMR spectra. Enantiomeric excess (ee value) of the corresponding chiral sulfoxides were determined by HPLC analysis using the Daicel chiralpak AD columns. The separated aqueous layer containing catalyst was treated with *n*-hexane (5 mL). Catalyst could be readily precipitated out from the aqueous phase. The recovered catalyst was washed with ether (3 × 5 mL), and dried in vacuo at 30 °C overnight for consecutive reuse.

Methyl phenyl sulfoxide: The product of asymmetric oxidation of methyl phenyl sulfide has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S1 and S2). 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 = 18.1 min and minor enantiomer t_S = 21.1 min (see Fig. S3, S4 and S5).

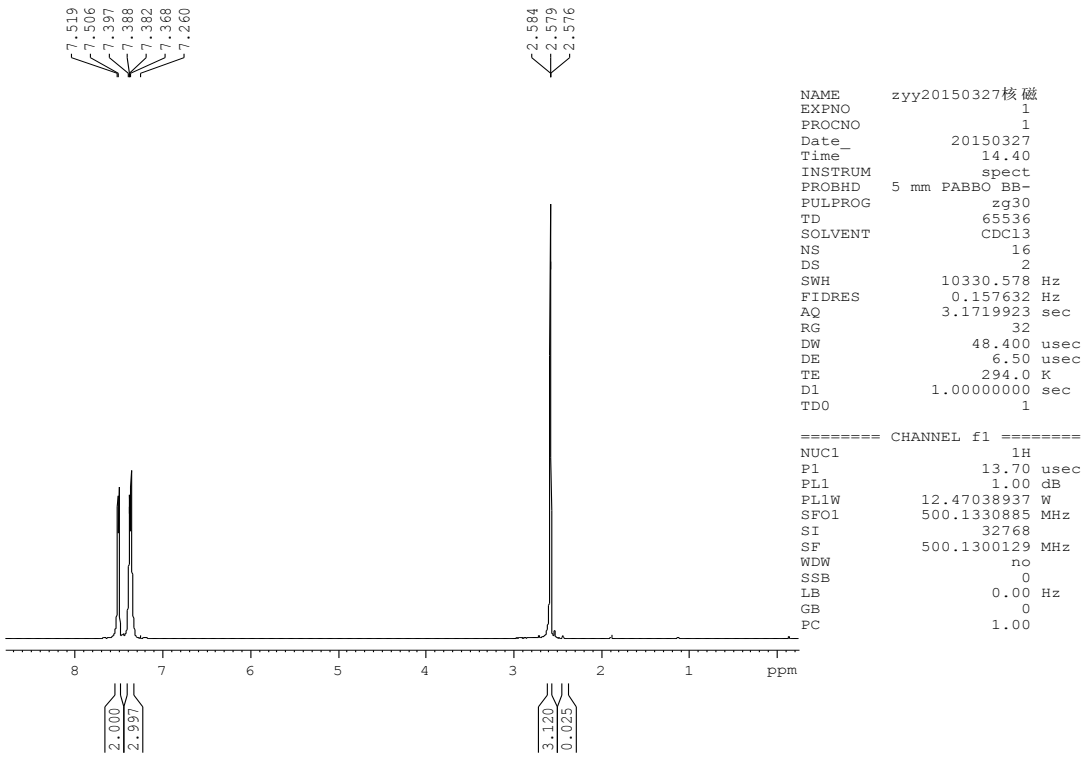


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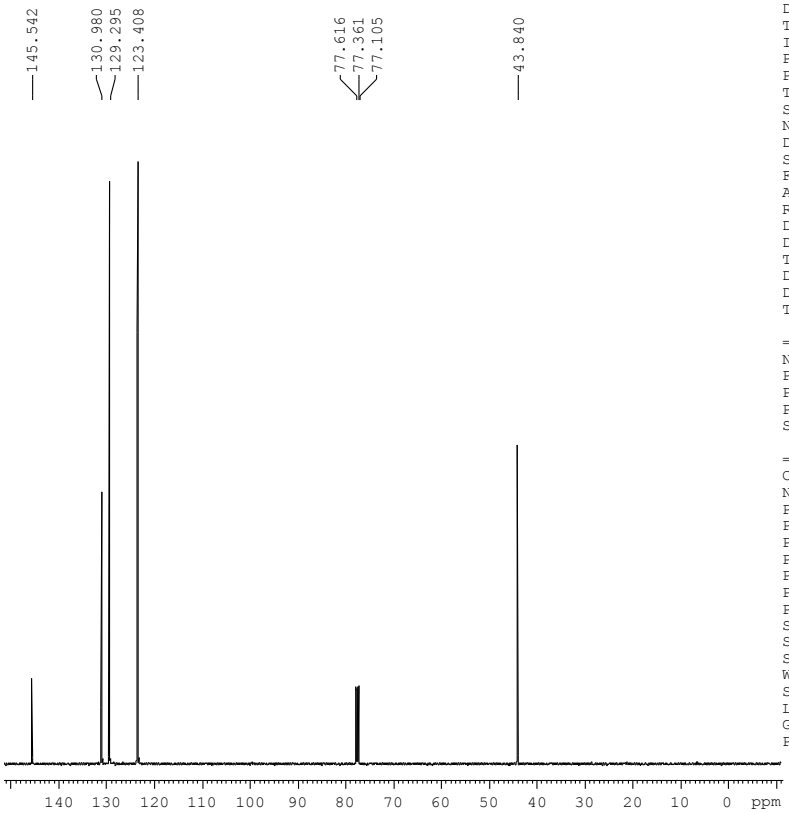
Fig. S1. ^{1}H NMR of methyl phenyl sulfoxide.

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PL13W         0.40075597 W
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Fig. S2. ^{13}C NMR of methyl phenyl sulfoxide.

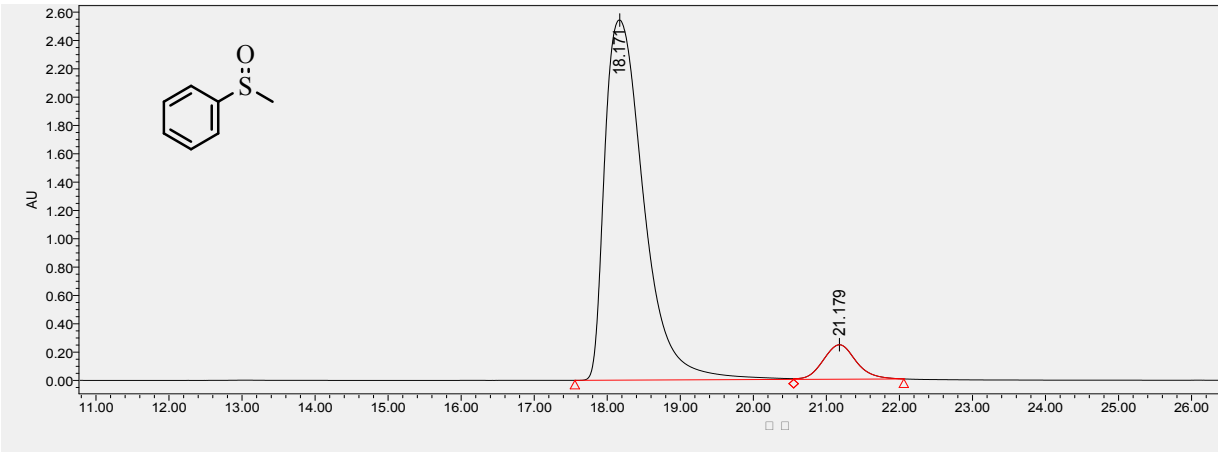

Fig. S3. HLPC of methyl phenyl sulfoxide obtained over **PIBC-8** (ee value = 85%).

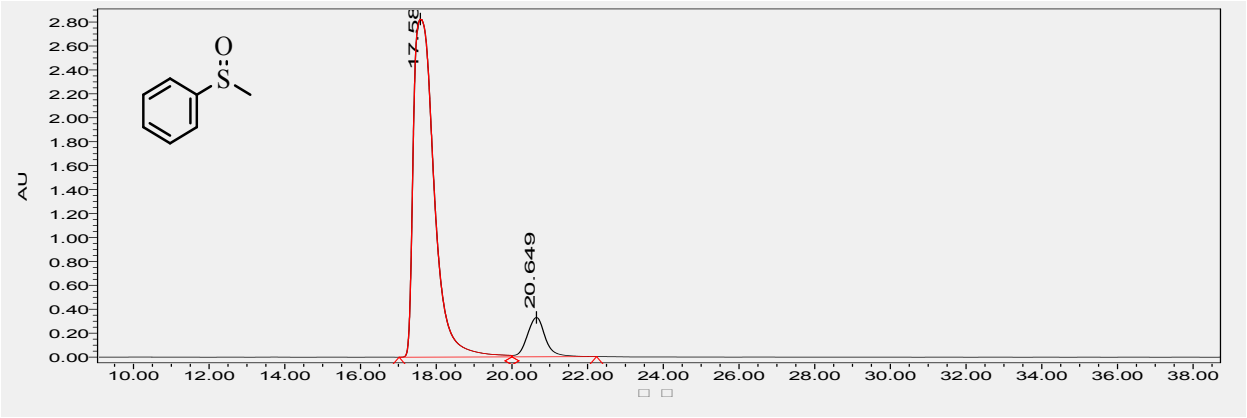

Fig. S4. HLPC of methyl phenyl sulfoxide obtained over IL-complex (ee value = 79%).

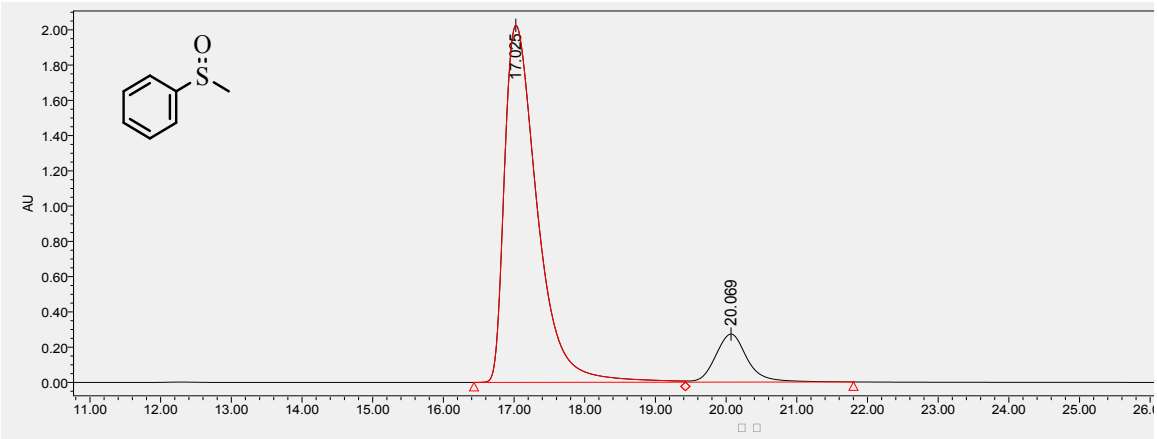

Fig. S5. HLPC of methyl phenyl sulfoxide obtained over neat complex (ee value = 77%).

Methyl *p*-methoxyphenyl sulfoxide: The product of asymmetric oxidation of methyl *p*-methoxyphenyl sulfide has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S6 and S7). 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 = 17.2 min (see Fig. S8, S9 and S10).

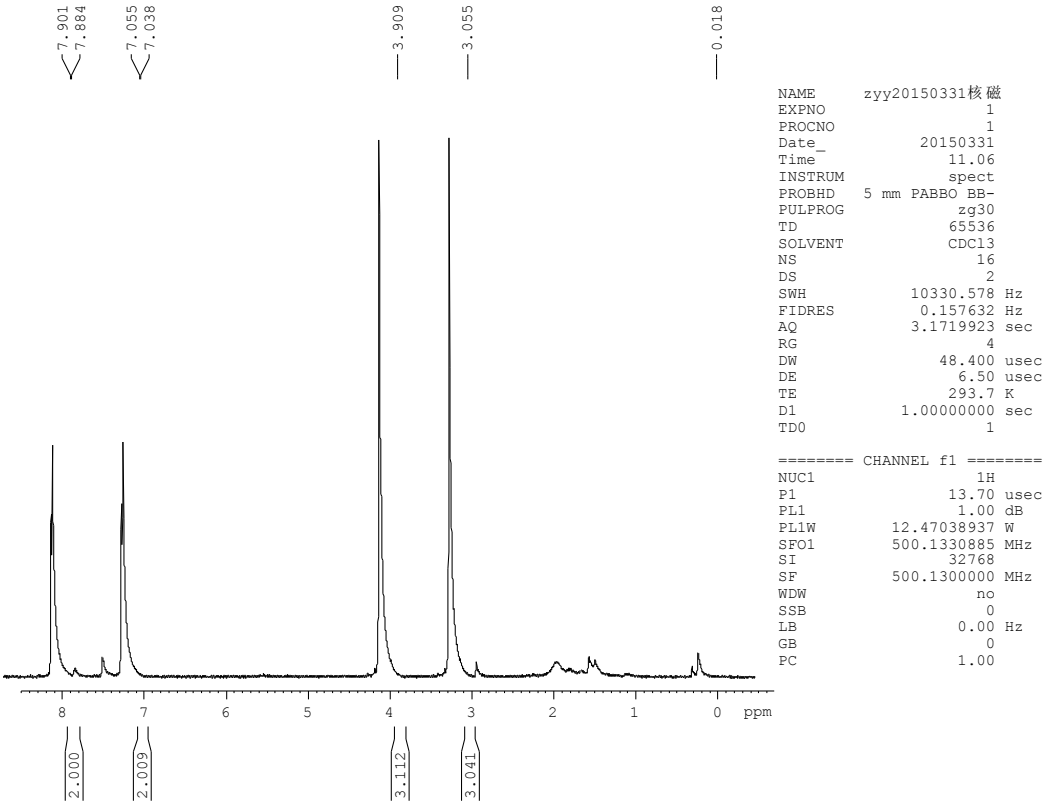

Fig. S6. ^{1}H NMR of methyl *p*-methoxyphenyl sulfoxide.

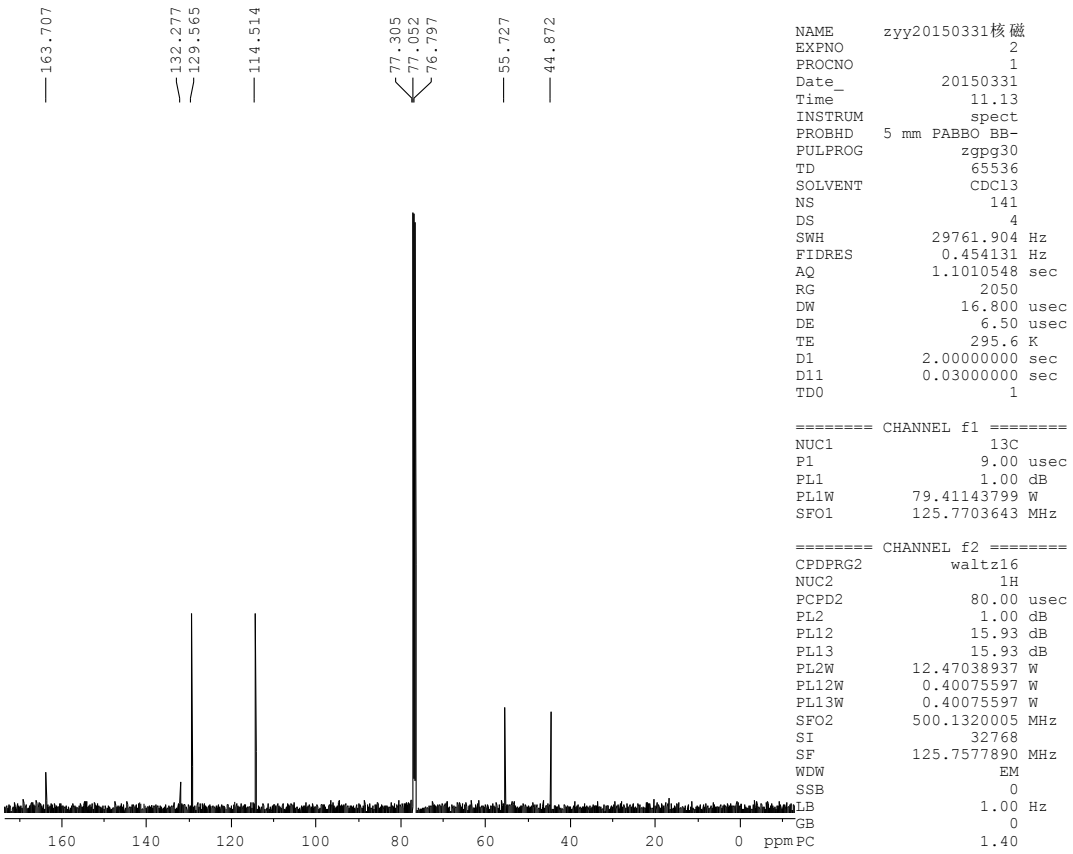

Fig. S7. ^{13}C NMR of methyl *p*-methoxyphenyl sulfoxide.

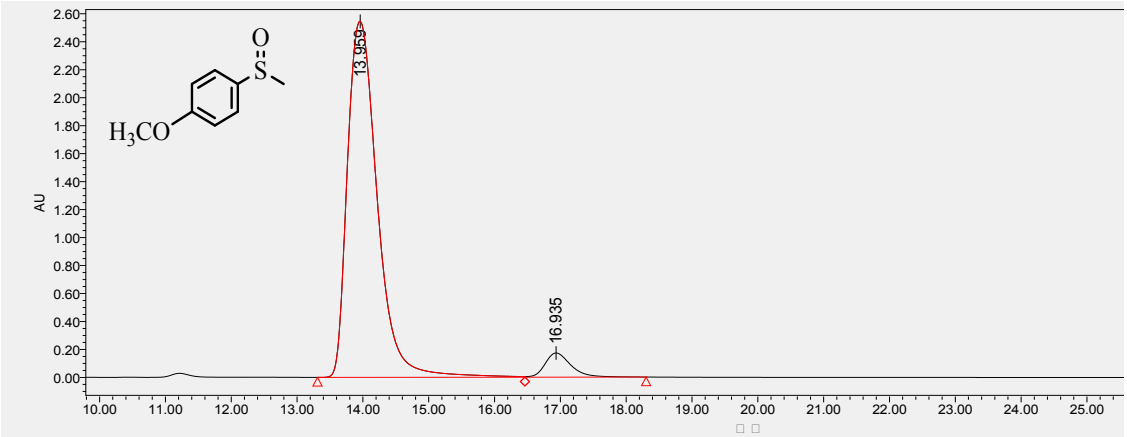

Fig. S8. HLPC of methyl *p*-methoxyphenyl sulfoxide obtained over **PIBC-8** (ee value = 90%).

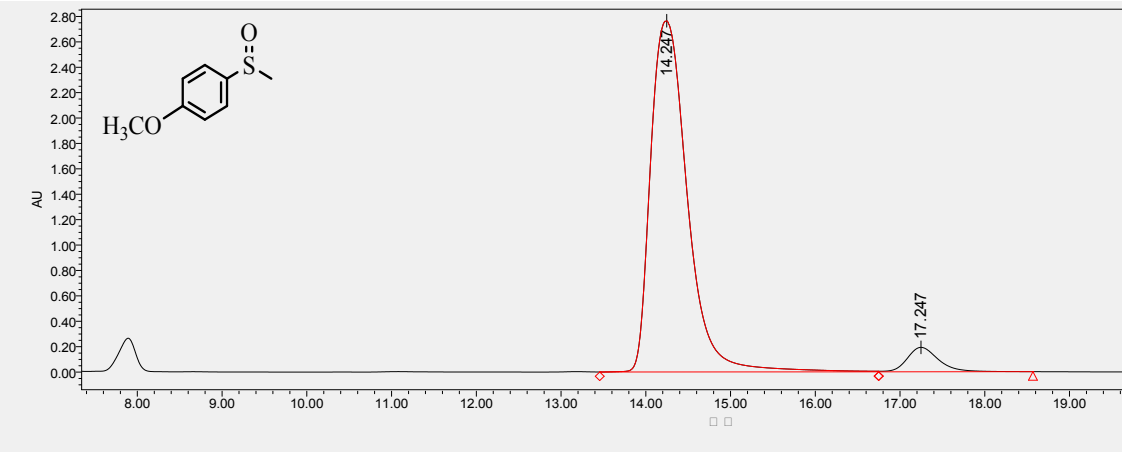

Fig. S9. HLPC of methyl *p*-methoxyphenyl sulfoxide obtained over IL-complex (ee value = 82%).

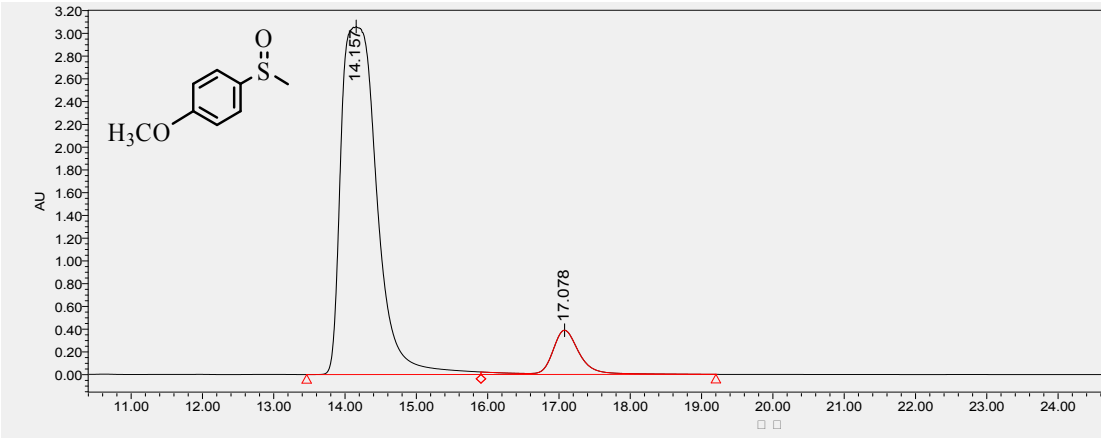

Fig. S10. HLPC of methyl *p*-methoxyphenyl sulfoxide obtained over neat complex (ee value = 77%).

Methyl *o*-methoxyphenyl sulfoxide: The product of asymmetric oxidation of methyl *o*-methoxyphenyl sulfide has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S11 and S12). 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 = 13.8 min and minor enantiomer t_S = 16.8 min (see Fig. S13, S14 and S15).

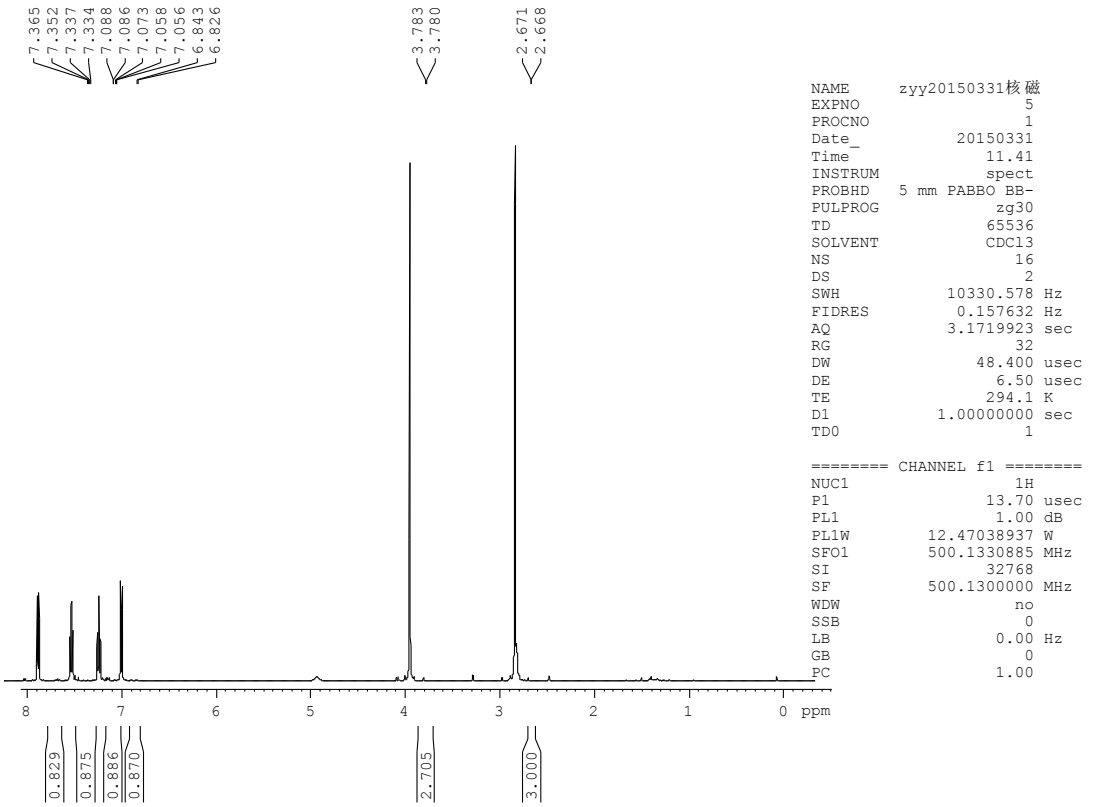

Fig. S11. ^{1}H NMR of methyl *o*-methoxyphenyl sulfoxide.

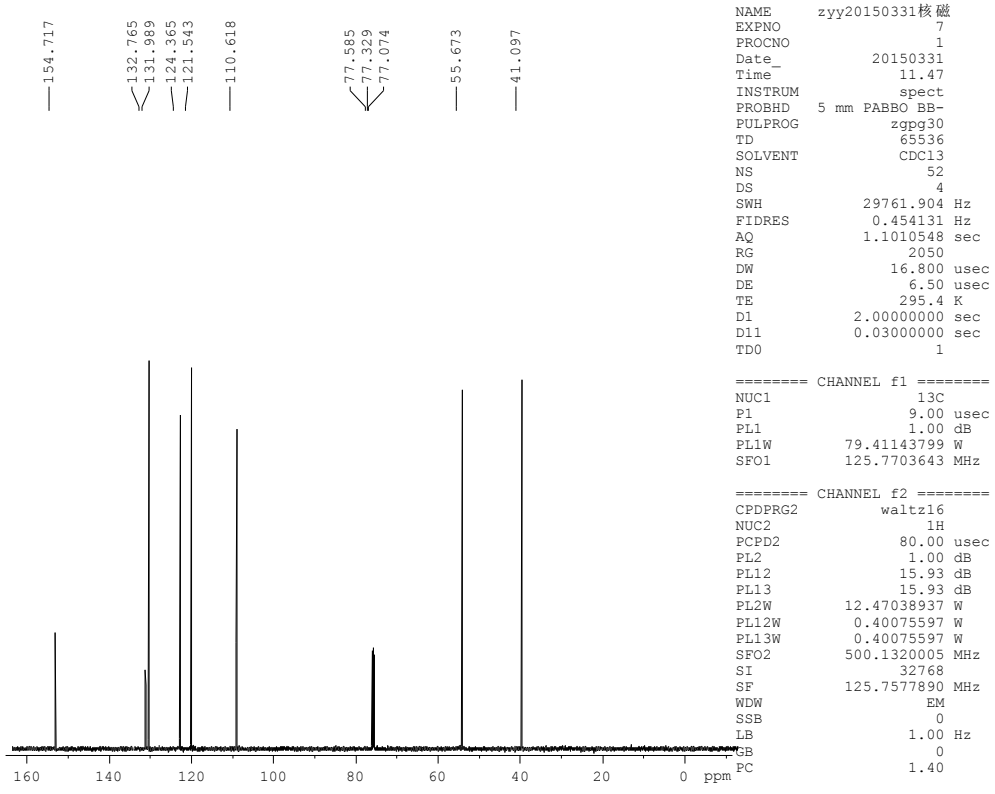

Fig. S12. ^{13}C NMR of methyl *o*-methoxyphenyl sulfoxide.

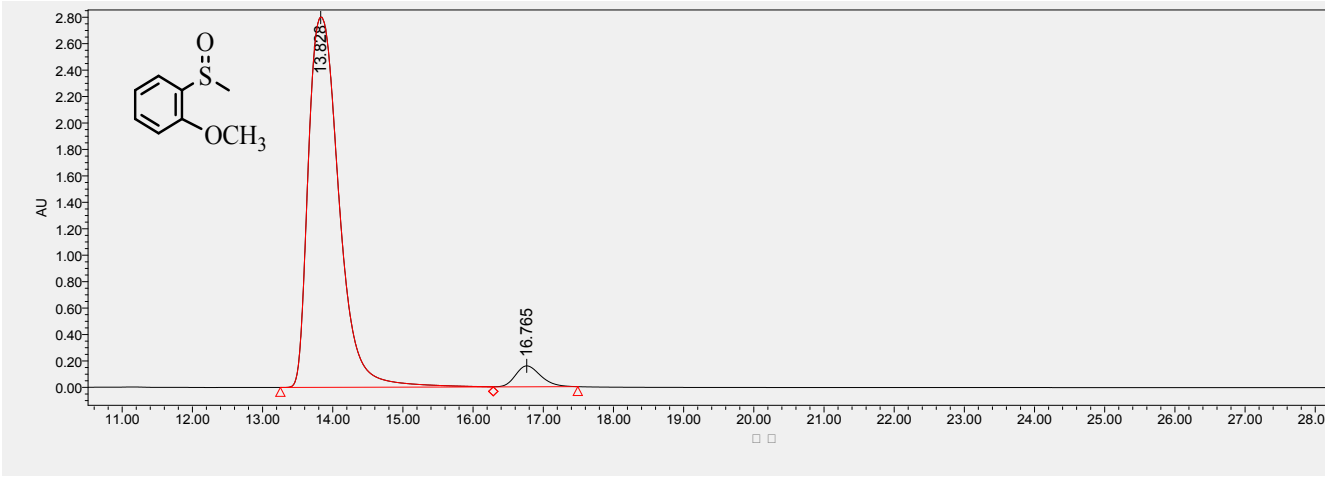

Fig. S13. HLPC of methyl *o*-methoxyphenyl sulfoxide obtained over **PIBC-8** (ee value = 91%).

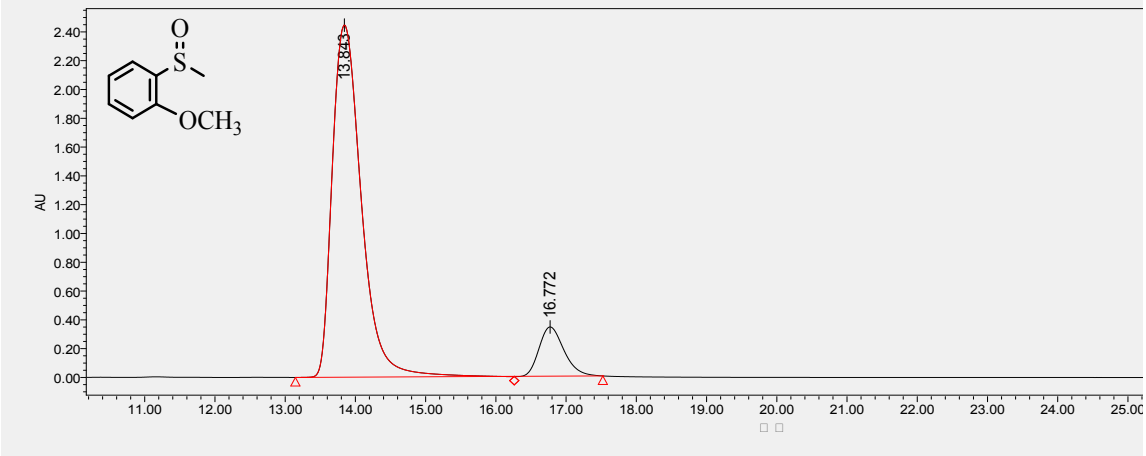

Fig. S14. HLPC of methyl *o*-methoxyphenyl sulfoxide obtained over IL-complex (ee value = 71%).

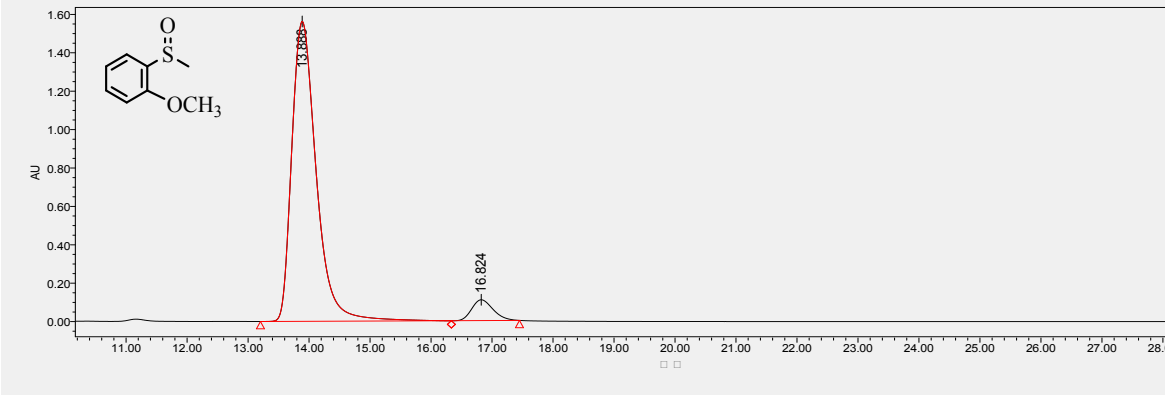

Fig. S15. HLPC of methyl *o*-methoxyphenyl sulfoxide obtained over neat complex (ee value = 79%).

Methyl *p*-nitrophenyl sulfoxide: The product of asymmetric oxidation of methyl *p*-nitrophenyl sulfide has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S16 and S17). 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 = 10.8 min and minor enantiomer t_S =20.1 min (see Fig. S18 and S19).

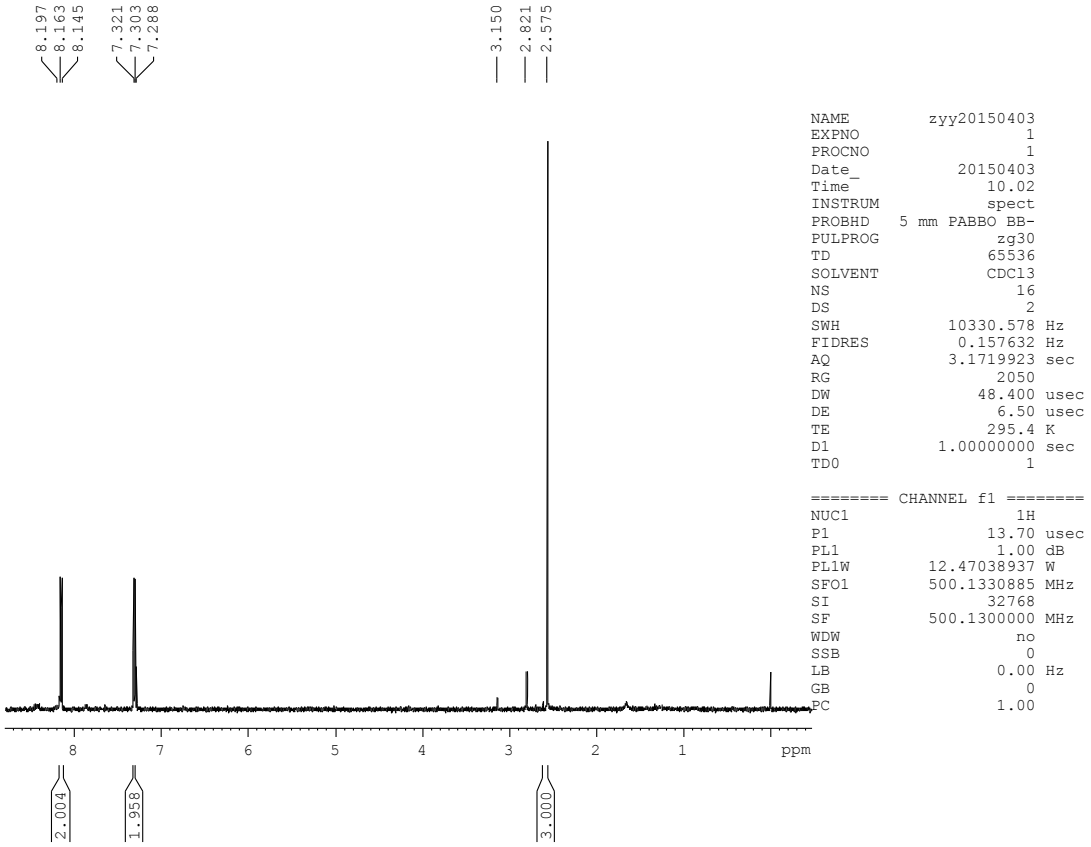

Fig. S16. ^{1}H NMR of methyl *p*-nitrophenyl sulfoxide.

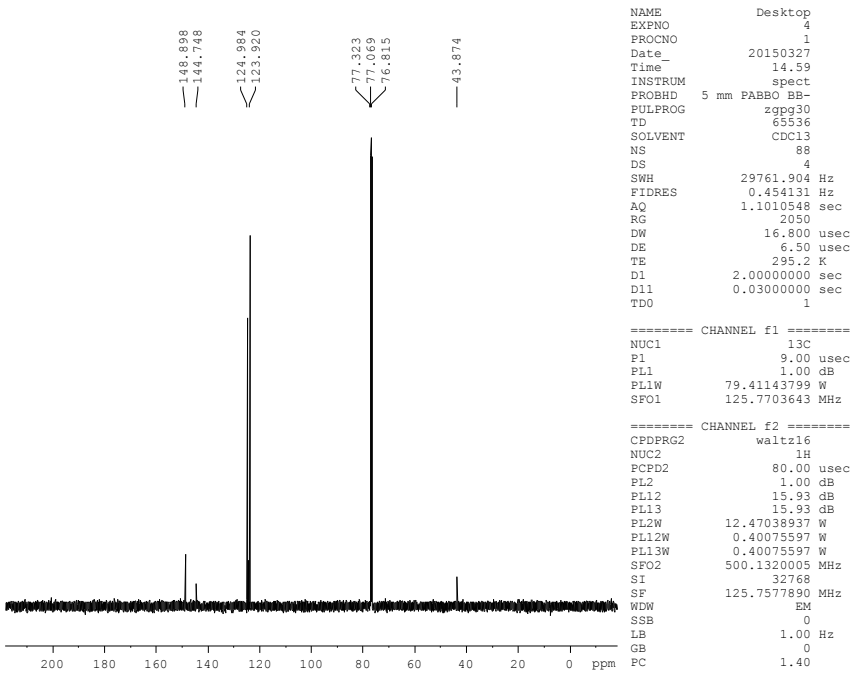

Fig. S17. ^{13}C NMR of methyl *p*-nitrophenyl sulfoxide.

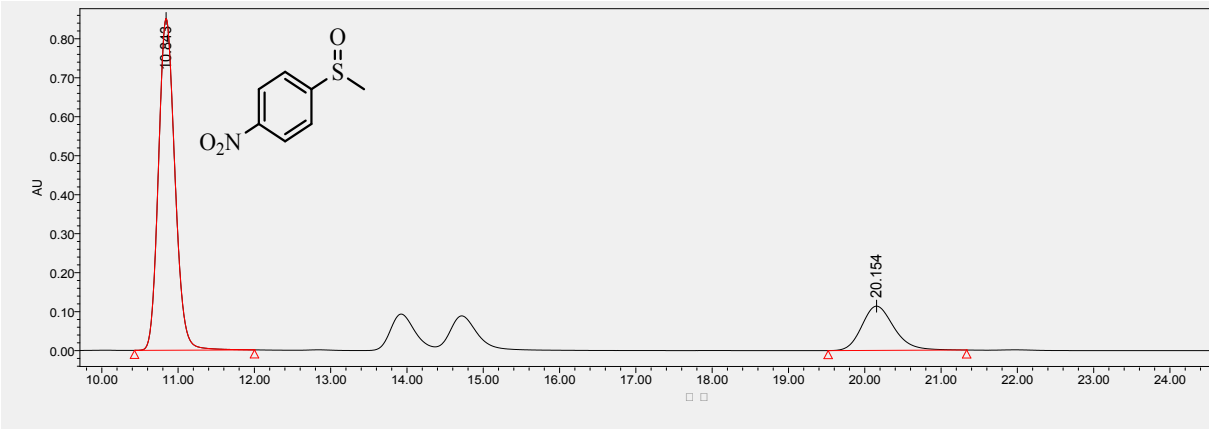

Fig. S18. HLPC of methyl *p*-nitrophenyl sulfoxide obtained over **PIBC-8** (ee value = 63%).

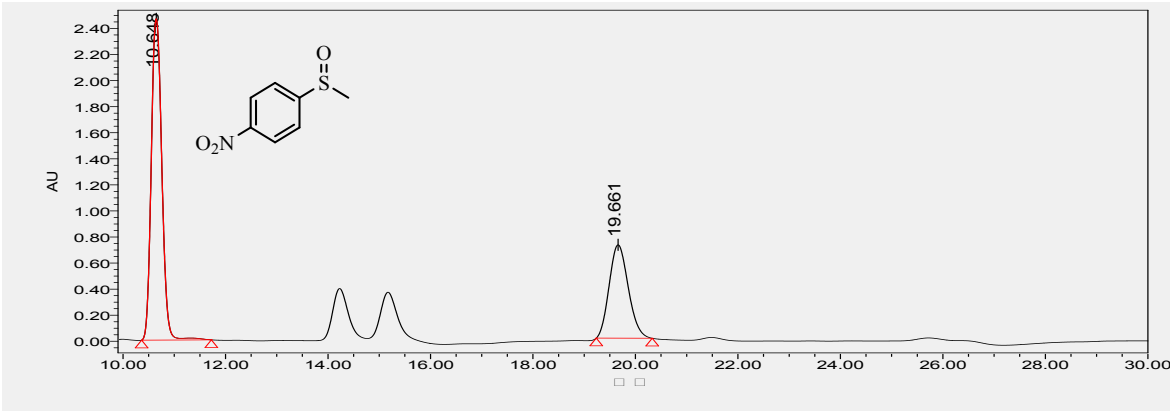

Fig. S19. HLPC of methyl *p*-nitrophenyl sulfoxide obtained over IL-complex (ee value = 31%).

Methyl *p*-bromophenyl sulfoxide: The product of asymmetric oxidation of methyl *p*-bromophenyl sulfide has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S20 and S21). 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. S22 and S23).

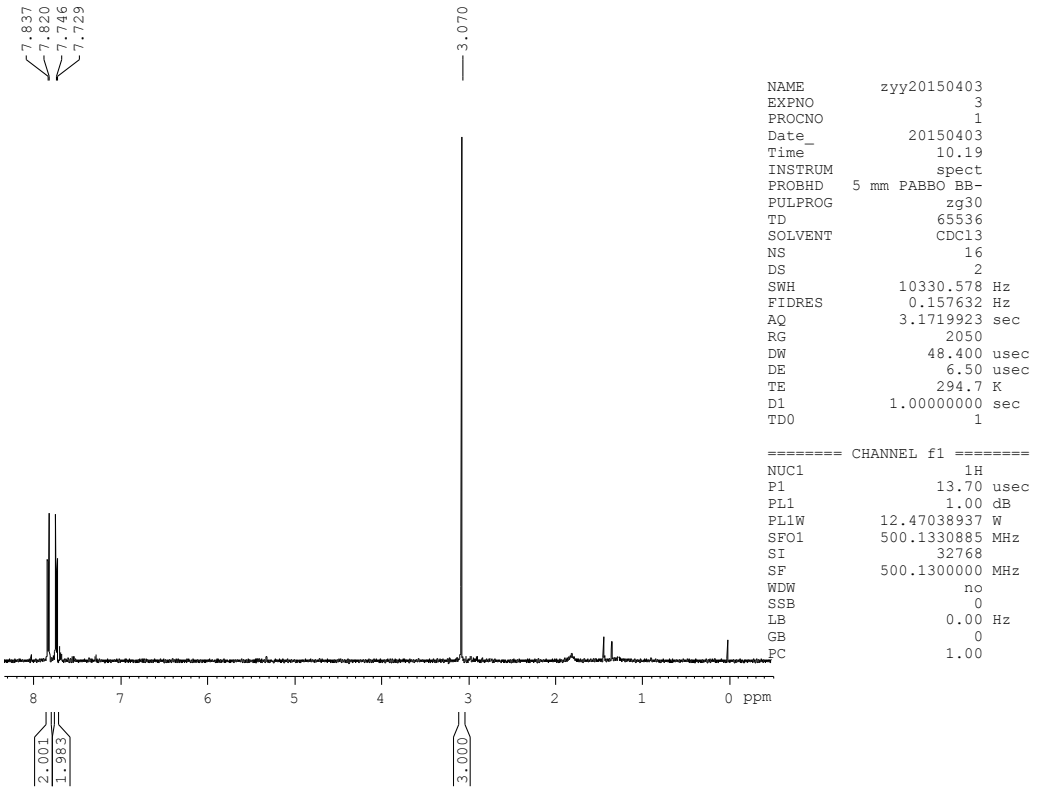

Fig. S20. ^{1}H NMR of methyl *p*-bromophenyl sulfoxide.

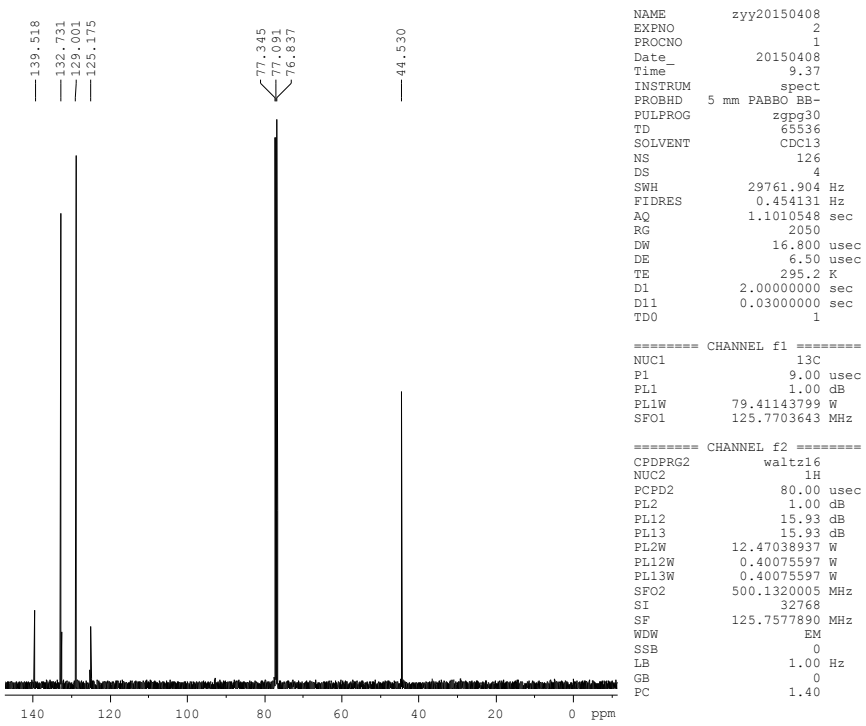

Fig. S21. ^{13}C NMR of methyl *p*-bromophenyl sulfoxide.

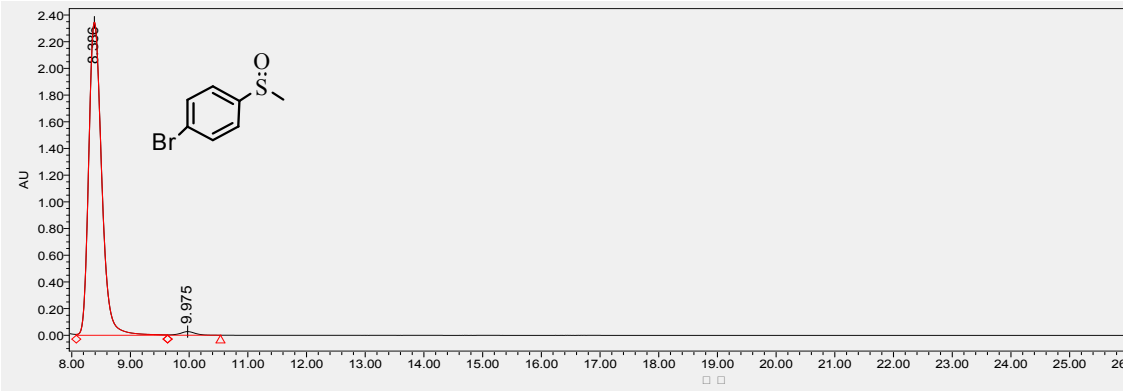

Fig. S22. HLPC of methyl *p*-bromophenyl sulfoxide obtained over **PIBC-8** (ee value = 98%).

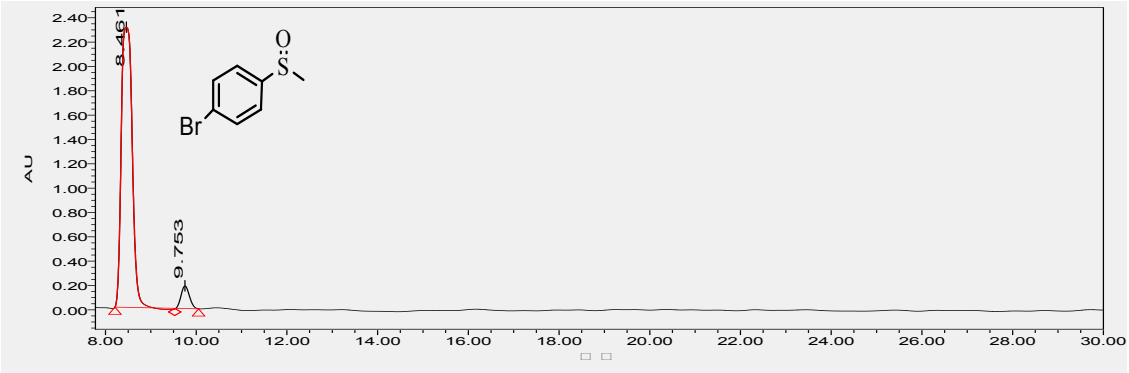

Fig. S23. HLPC of methyl *p*-bromophenyl sulfoxide obtained over IL-complex (ee value = 88%).