Supporting Information

Bio-inspired single-chain polymeric nanoparticles containing chiral salen Ti^{IV} complex for highly enantioselective sulfoxidation in water

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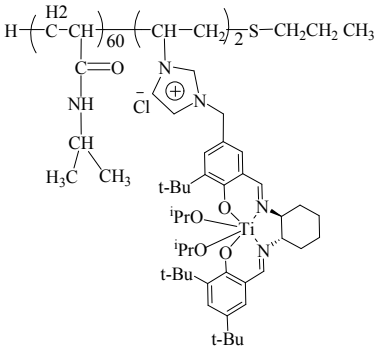
CONTENT:

1. Identification of the catalysts ($PN_{60}(IS)_2$, $PN_{68}(IS)_4$, $PN_{66}(IS)_6$, $PN_{64}(IS)_8$, and $PN_{64}S_8$)

$PN_{60}(IS)_2$



The structure and chemical composition of **$PN_{60}(IS)_2$** were identified by ^{1}H NMR spectrum (see Fig. S1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.24~6.89 (m, 60 H, HC-N*H*-C=O), 6.08 (m, 2 H, N-C*H*-CH_2- of N-vinyl), 4.18 (m, 2 H, C=NC*H*), 3.99 (m, 60 H, -C*H*-CH_2 in NIPAAm), 3.88 (m, 2 H, C=NC*H*), 3.67 (m, 8 H, -CH-CH_2- of N-vinyl in IL and -N-CH_2-N-), 3.45 (m, 60 H, CH_3-C*H*-CH_3 in NIPAAm), 3.06 (m, 12 H, -N-CH_2-CH_2-N- and -N-CH_2-Ph-), 2.84 (m, 2 H, SH-CH_2-CH_2-CH_3), 2.64~2.73 (m, 4 H, CH_3-C*H*-CH_3 of ^{i}PrO- in Ti(salen)), 2.38 (m, 2 H, SH-CH_2-CH_2-CH_3), 1.86~2.12 (m, 120 H, -CH_2-CH- in NIPAAm), 1.71(s, 3 H, SH-CH_2-CH_2-CH_3), 1.43 (16 H, cyclohexyl-*H*), 1.13~1.33 (54 H, *H*- in t-butyl), 1.09~1.16 (m, 384 H, CH_3-CH-CH_3 in ^{i}PrO- and NIPAAm). The degrees of polymerization of the individual NIPAAm and IL/Ti(salen) were determined using the ^{1}H NMR spectrum (see Fig. S1) by comparing the signals attributable to individual blocks (NIPAAm at *ca.* 3.45 ppm assigned to assigned to CH_3-C*H*-CH_3 and IL/Ti(salen) at *ca.* 6.08 ppm assigned to N-C*H*-CH_2- of N-vinyl) with that of end methyl group (-SH-CH_2-CH_2-CH_3) (at *ca*. 1.71 ppm).

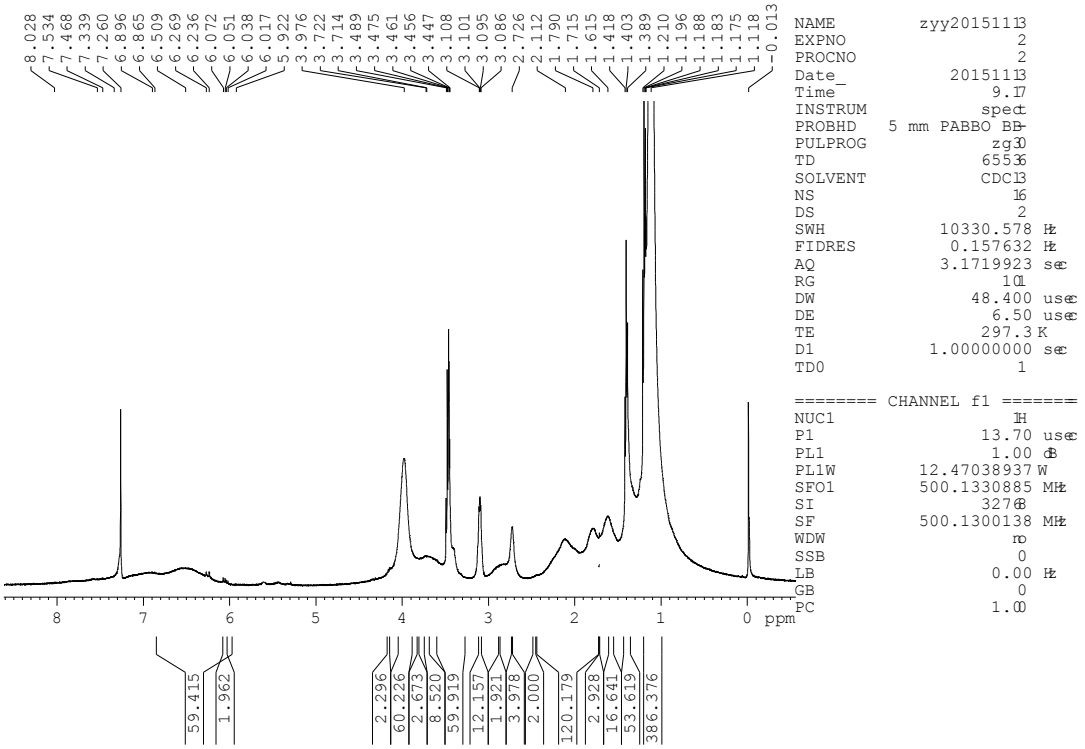
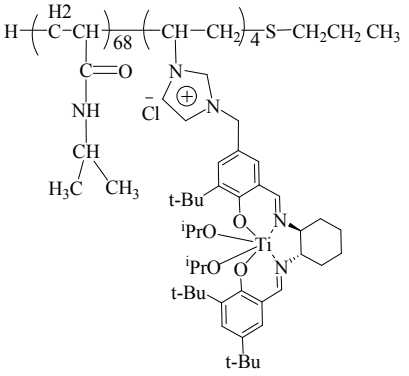


Fig. S1 ^{1}H NMR of the **$PN_{60}(IS)_2$**.

$PN_{68}(IS)_4$



The structure and chemical composition of **$PN_{68}(IS)_4$** were identified by ^{1}H NMR spectrum (see Fig. S2). ^{1}H NMR (500 MHz, CD_3Cl_3): δ 8.15~7.68 (m, 8 H, C*H*=N), 7.14~7.64 (m, 16 H, Ar*H*), 6.24~6.89 (m, 68 H, HC-N*H*-C=O), 6.05 (m, 4 H, N-C*H*-CH_2- of N-vinyl), 4.14 (m, 4 H, C=NC*H*), 3.99 (m, 68 H, -C*H*-CH_2- in NIPAAm), 3.85(m, 4 H, C=NC*H*), 3.58 (m, 16 H, -CH-CH_2- of N-vinyl in IL and -N-CH_2-N-), 3.26 (m, 68 H, CH_3-C*H*-CH_3 in NIPAAm), 2.90 (m, 24 H,

-N-CH_2-CH_2-N- and -N-CH_2-Ph-), 2.78(m, 2 H, SH-CH_2-CH_2-CH_3), 2.34~2.68 (m, 8 H, CH_3-C*H*-CH_3 of ^{i}PrO- in Ti(salen)), 2.10 (m, 2 H, SH-CH_2-CH_2-CH_3), 1.78~1.98 (m, 136 H, -CH-CH_2 in NIPAAm), 1.73 (s, 3 H, SH-CH_2-CH_2-CH_3), 1.47 (m, 32 H, cyclohexyl-*H*), 1.21~1.38 (m, 108 H, *H*- in t-butyl), 1.06~1.15 (m, 456 H, CH_3-CH-CH_3 in ^{i}PrO- and NIPAAm). The degrees of polymerization of the individual NIPAAm and IL/Ti(salen) were determined using the ^{1}H NMR spectrum (see Fig. S2) by comparing the signals attributable to individual blocks (NIPAAm at *ca.* 3.26 ppm assigned to CH_3-C*H*-CH_3 and IL/Ti(salen) at *ca.* 6.05 ppm assigned to N-C*H*-CH_2- of N-vinyl) with that of end methyl group (-SH-CH_2-CH_2-CH_3) (at *ca*. 1.73 ppm).

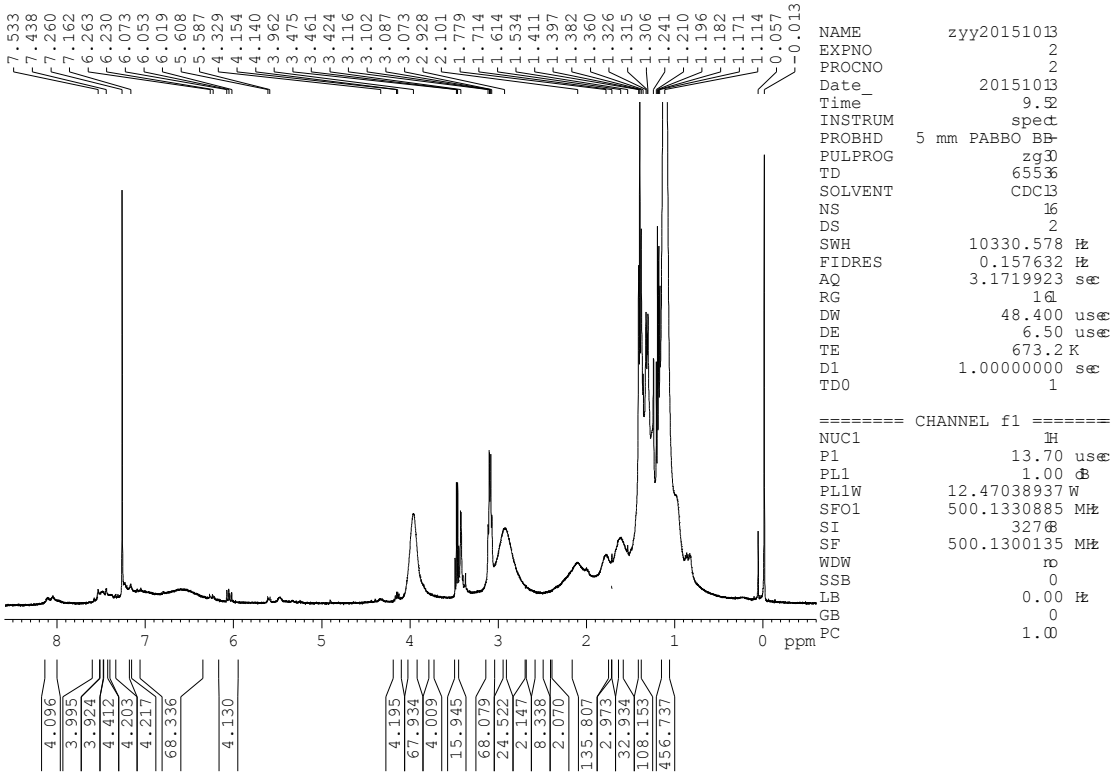
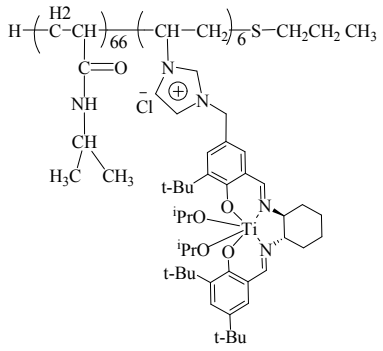


Fig. S2 ^{1}H NMR of the **$PN_{68}(IS)_4$**

$PN_{66}(IS)_6$



The structure and chemical composition of **$PN_{66}(IS)_6$** were identified by ^{1}H NMR spectrum (see Fig. S3). ^{1}H NMR (500 MHz, CD_3Cl_3): δ 8.13~7.72(m, 12 H, C*H*=N), 7.18~7.69 (m, 24 H, Ar*H*), 6.21~6.92 (m, 66 H, HC-N*H*-C=O), 6.16 (m, 6 H, N-C*H*-CH_2- of N-vinyl), 4.04 (m, 6 H, C=NC*H*), 3.97 (m, 66 H, -C*H*-CH_2- in NIPAAm), 3.81(m, 6 H, C=NC*H*), 3.56 (m, 24 H, -CH-CH_2- of N-vinyl in IL and -N-CH_2-N-), 3.23 (m, 66 H, CH_3-C*H*-CH_3 in NIPAAm), 3.09 (m, 36 H, -N-CH_2-CH_2-N- and -N-CH_2-Ph-), 2.75(m, 2 H, SH-CH_2-CH_2-CH_3), 2.41~2.61 (m, 12 H, CH_3-C*H*-CH_3 of ^{i}PrO- in Ti(salen)), 2.23 (m, 2 H, SH-CH_2-CH_2-CH_3), 1.76~1.82 (m, 132 H, -CH-CH_2 in NIPAAm), 1.75 (s, 3 H, SH-CH_2-CH_2-CH_3), 1.41(m, 48 H, cyclohexyl-*H*), 1.22~1.31(m, 162 H, *H*- in t-butyl), 1.01~1.12 (m, 469 H, CH_3-CH-CH_3 in ^{i}PrO- and NIPAAm). The degrees of polymerization of the individual NIPAAm and IL/Ti(salen) were determined using the ^{1}H NMR spectrum (see Fig. S3) by comparing the signals attributable to individual blocks (NIPAAm at *ca.* 3.23 ppm assigned to CH_3-C*H*-CH_3 and IL/Ti(salen) at *ca.* 6.16 ppm assigned to N-C*H*-CH_2- of N-vinyl) with that of end methyl group (-SH-CH_2-CH_2-CH_3) (at *ca*. 1.75 ppm).

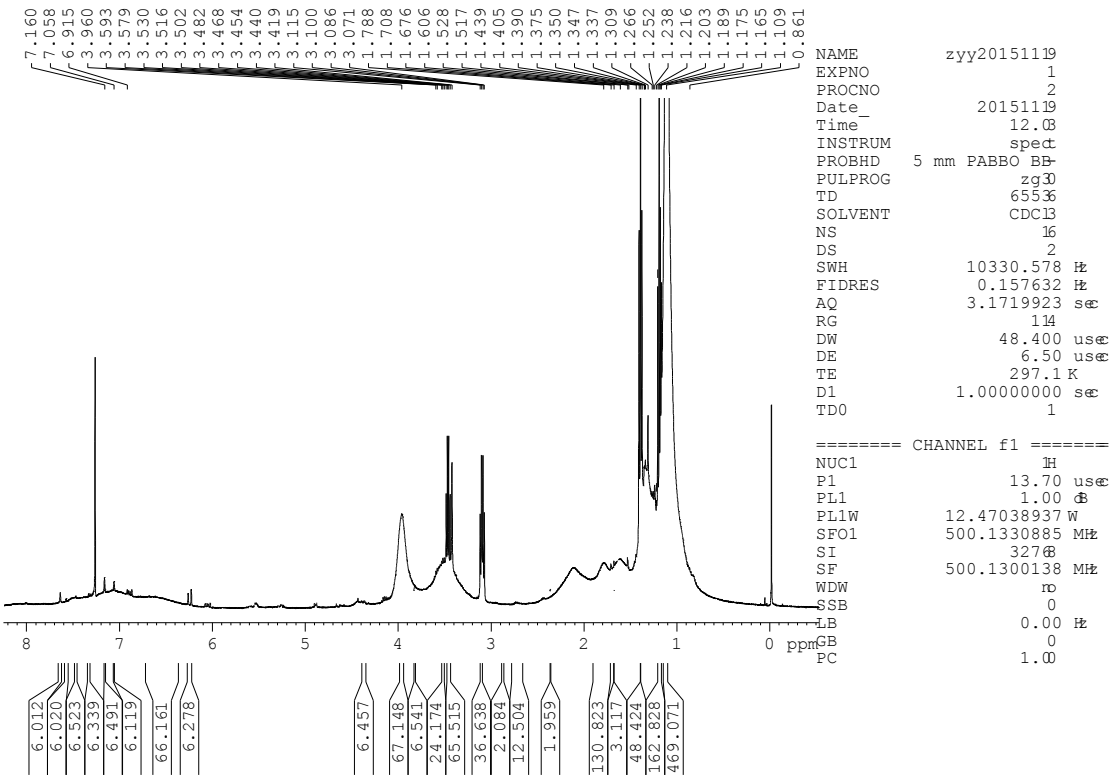
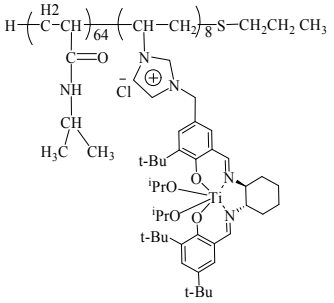


Fig. S3 ^{1}H NMR of the **$PN_{66}(IS)_6$**.

$PN_{64}(IS)_8$



The structure and chemical composition of **$PN_{64}(IS)_8$** were identified by ^{1}H NMR spectrum (see Fig. S4). ^{1}H NMR (500 MHz, CD_3Cl_3): δ 8.11~7.62 (m, 16 H, C*H*=N), 7.13~7.67 (m, 32 H, Ar*H*), 6.24~6.87 (m, 64 H, HC-N*H*-C=O), 6.22 (m, 8 H, N-C*H*-CH_2- of N-vinyl), 4.46 (m, 8 H, C=NC*H*), 4.05 (m, 64 H, -C*H*-CH_2- in NIPAAm), 3.78 (m, 8 H, C=NC*H*), 3.58 (m, 32 H, -CH-CH_2- of N-vinyl in IL and -N-CH_2-N-), 3.18 (m, 64 H, CH_3-C*H*-CH_3 in NIPAAm), 2.86 (m, 48 H, -N-CH_2-CH_2-N- and -N-CH_2-Ph-), 2.75(m, 2 H, SH-CH_2-CH_2-CH_3), 2.45~2.63 (m, 16 H, CH_3-

C*H*-CH_3 of ^{i}PrO- in Ti(salen)), 2.12 (m, 2 H, SH-CH_2-CH_2-CH_3), 1.75~1.87 (m, 128 H, -CH-CH_2- in NIPAAm), 1.73(s, 3 H, SH-CH_2-CH_2-CH_3), 1.41 (m, 64 H, cyclohexyl-*H*), 1.22~1.31 (m, 216 H, *H*- in t-butyl), 1.01~1.12 (m, 480 H, CH_3-CH-CH_3 in ^{i}PrO- and NIPAAm). The degrees of polymerization of the individual NIPAAm and IL/Ti(salen) were determined using the ^{1}H NMR spectrum (see Fig. S4) by comparing the signals attributable to individual blocks (NIPAAm at *ca.* 3.18 ppm assigned to CH_3-C*H*-CH_3 and IL/Ti(salen) at *ca.* 6.22 ppm assigned to N-C*H*-CH_2- of N-vinyl) with that of end methyl group (-SH-CH_2-CH_2-CH_3) (at *ca*. 1.73 ppm).

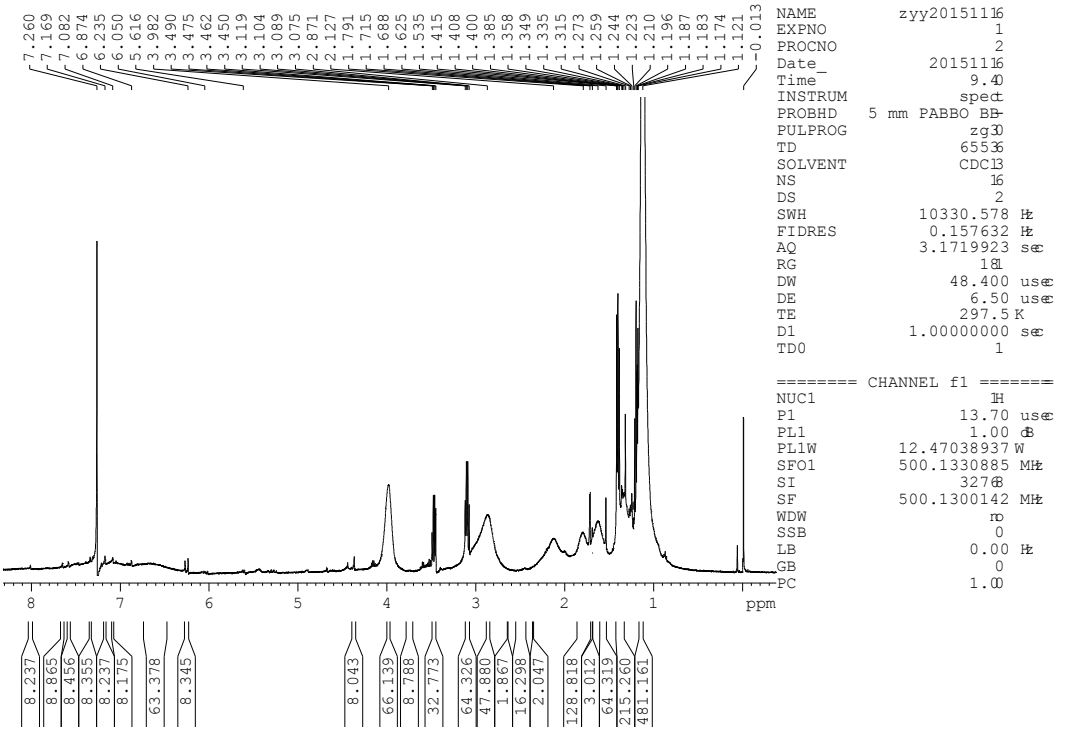
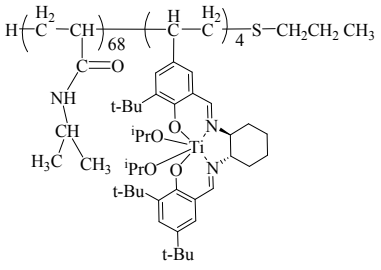


Fig. S4 ^{1}H NMR of the **$PN_{64}(IS)_8$.**

$PN_{68}S_4$



The structure and chemical composition of **$PN_{68}S_4$** were identified by ^{1}H NMR spectrum (see Fig. S5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31~7.78 (m, 8 H, C*H*=N), 7.11~7.72 (m, 16 H, Ar*H*), 6.06~6.78 (s, 68 H, HC-N*H*-C=O), 4.76 (s, 4 H, C=NC*H*), 4.09 (s, 68 H, -C*H*-CH_2- in NIPAAm), 3.48 (s, 4 H, C=NC*H*), 3.41 (m, 8 H, -CH-CH_2-Ph- in Ti(salen)), 3.19 (m, 68 H, CH_3-C*H*-CH_3 in NIPAAm), 2.91 (s, 2 H, SH-CH_2-CH_2-CH_3), 2.72~2.84 (s, 8 H, CH_3-C*H*-CH_3 of ^{i}PrO- in Ti(salen)), 2.63 (m, 2 H, SH-CH_2-CH_2-CH_3), 1.73~2.11 (s, 136 H,-CH-CH_2- in NIPAAm), 1.72 (s, 3 H, SH-CH_2-CH_2-CH_3), 1.59~1.67 (s, 32 H, cyclohexyl-*H*), 1.37~1.51 (108 H, *H*- in t-butyl), 1.07~1.32 (456 H, CH_3-CH-CH_3 in ^{i}PrO- and NIPAAm). The degrees of polymerization of the individual NIPAAm and Ti(salen) were determined using the ^{1}H NMR spectrum (see Fig. S5) by comparing the signals attributable to individual blocks (NIPAAm at *ca.* 3.19 ppm assigned to CH_3-C*H*-CH_3 and Ti(salen) at *ca.* 3.41 ppm assigned to -CH-CH_2-Ph-) with that of end methyl group (-SH-CH_2-CH_2-CH_3) (at *ca*. 1.72 ppm).

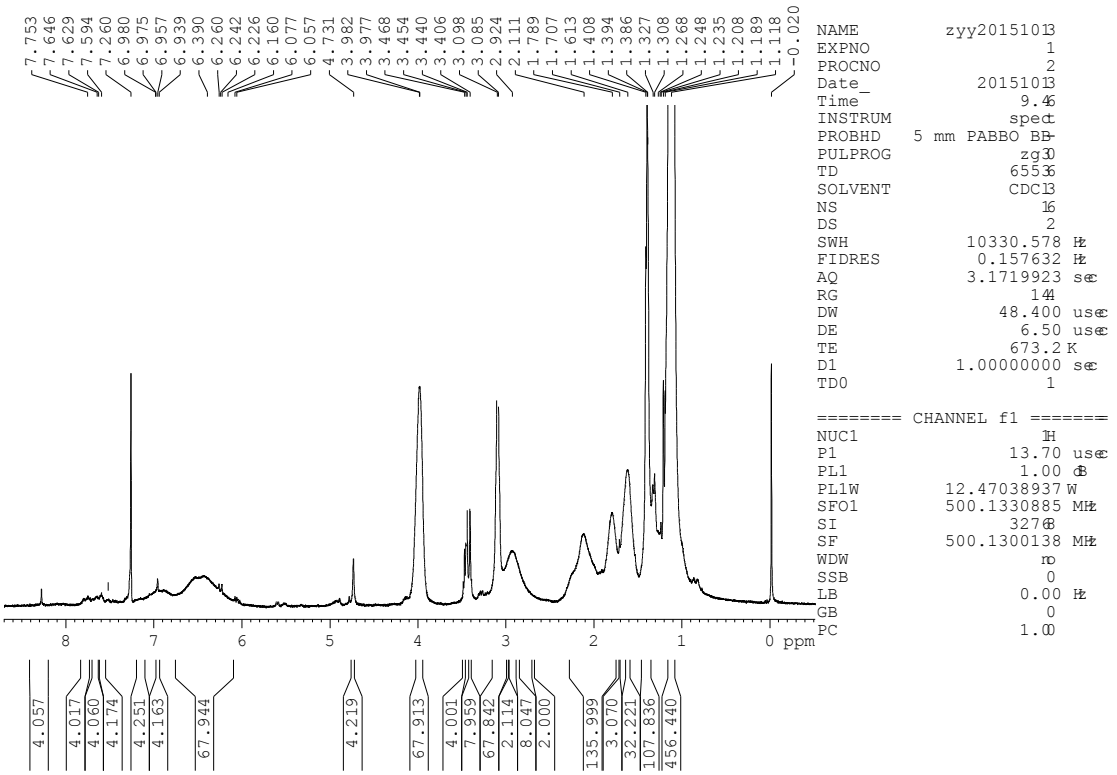


Fig. S5 ^{1}H NMR of the **$PN_{64}S_8$**.

2. The synthesis and identification of alkyl phenyl sulfides (ethyl phenyl sulfide, *n*-butyl phenyl sulfide, and *n*-hexyl phenyl sulfide).

2.1 Synthesis of alkyl phenyl sulfides

The alkyl phenyl sulfides were synthesized according to reference[1]. 1-Bromoalkane (1-bromoethane for ethyl phenyl sulfide, 1-bromo-*n*-butane for *n*-butyl phenyl sulfide, or 1-bromo-*n*-hexane for *n*-hexyl phenyl sulfide, 10 mmol) was dissolved in anhydrous ethanol at 40 ^{o}C, and then heated to 80 ^{o}C. Aqueous sodium (30 *wt*.%, 10 mmol) was dropwise added into this solution within 1.5 h. The resulting mixture was stirred at 80 ^{o}C for 4 h. After being cooled to room temperature, the lower alkyl phenyl sulfides were separated by using separatory funnel. The upper aqueous phase was extracted with $CHCl_3$ for several times. The extract was combined with the organic phase, and dried over anhydrous sodium sulfate. After the evaporation of $CHCl_3$, the alkyl phenyl sulfides were further purified by column chromatography on silica gel. The phenyl alkyl sulfides were identified by ^{1}H NMR and ^{13}C NMR.

Ethyl phenyl sulfide: The product has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S6 and S7). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 1.29 (m, 3 H, Me), 2.92-2.93 (m, 2 H, -C*H*$_2$-), 7.15-7.17 (m, 1 H, Ar*H*), 7.25-7.27 (m, 2 H, Ar*H*), 7.30-7.32 (m, 2 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 14.31 (*C*H$_3$), 27.56 (S*C*H$_2$), 125.68, 128.76, 128.99, 136.58 (Ar*C*).

[1] S. colonna, R. fornasier. *Synthesis*, 1975, **8**, 531

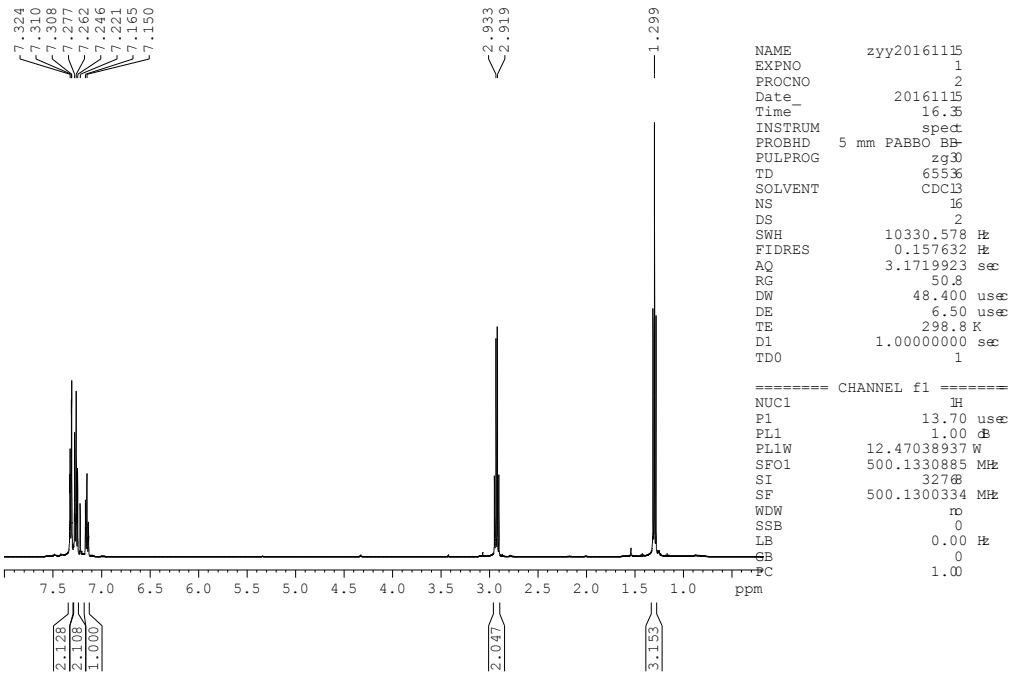


Fig. S6 ^{1}H NMR of ethyl phenyl sulfide

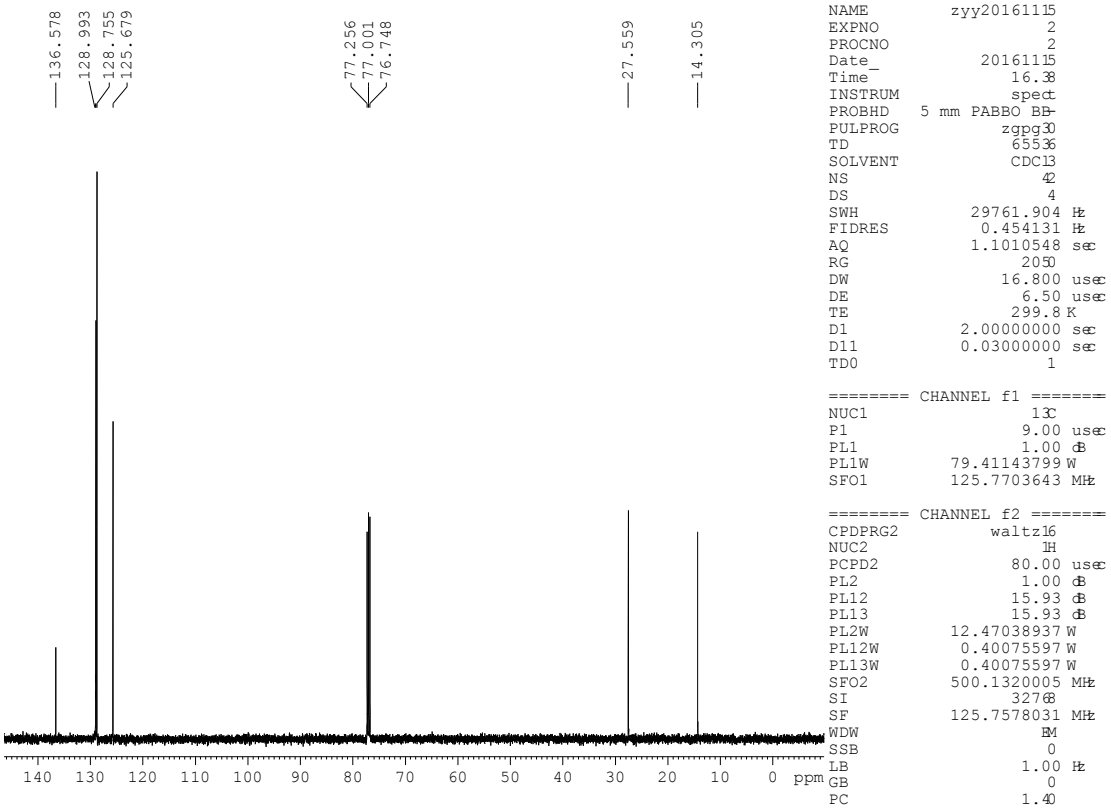


Fig. S7 ^{13}C NMR of ethyl phenyl sulfide

***n*-Butyl phenyl sulfide:** The product has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S8 and S9). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 0.91-1.21 (m, 3 H, Me), 1.42-1.45 (m, 2 H, -C*H*$_2$-), 1.62-1.65 (m, 2 H, -C*H*$_2$-), 2.91-2.94 (m, 2 H, -C*H*$_2$-), 7.16-7.17 (m, 1 H, Ar*H*), 7.25-7.26 (m, 2 H, Ar*H*), 7.26-7.27 (m, 2 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 13.57 (*C*H$_3$), 21.90 (*C*H$_2$), 31.19 (*C*H$_2$), 33.02 (*C*H$_2$), 125.56, 128.74, 128.79, 137.01 (Ar*C*).

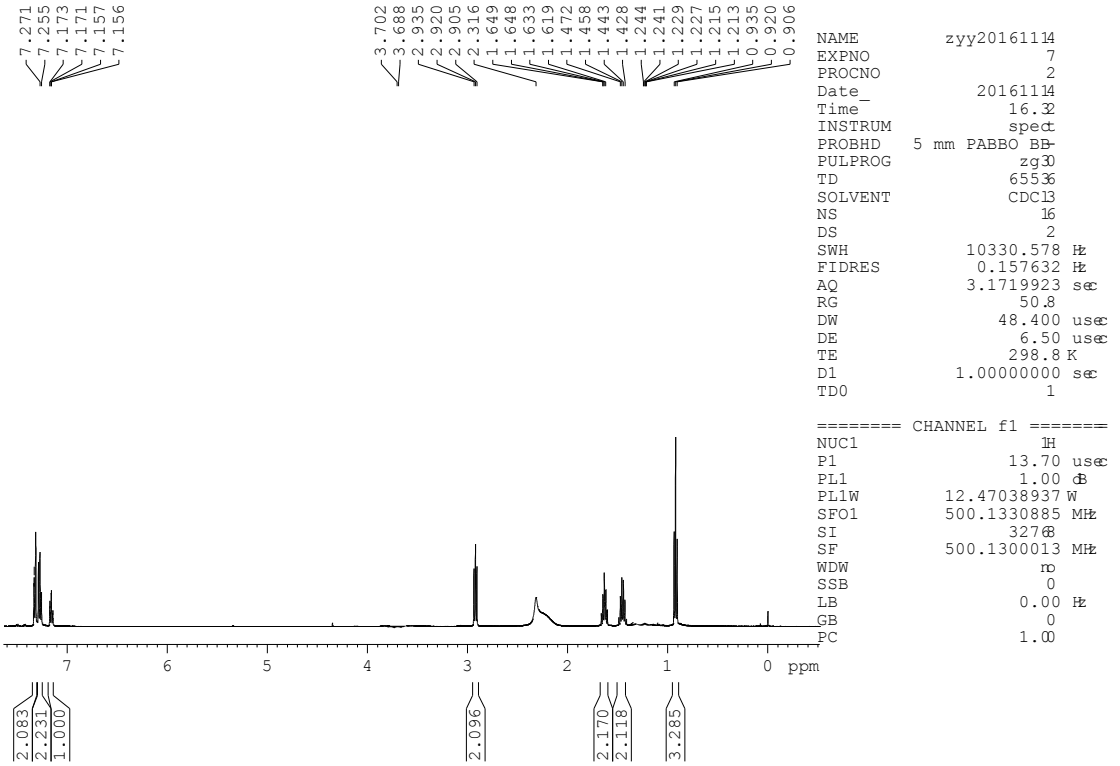


Fig. S8 ^{1}H NMR of *n*-butyl phenyl sulfide

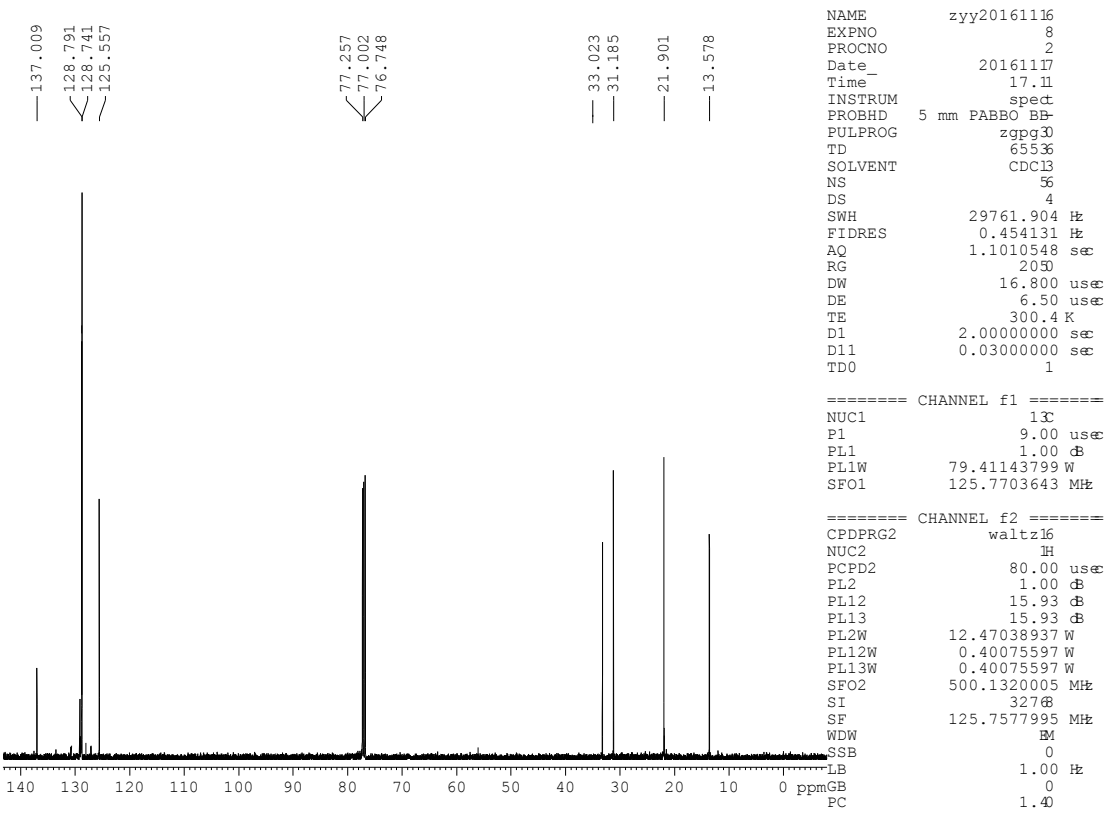


Fig. S9 ^{13}C NMR of *n*-butyl phenyl sulfide

***n*-Hexyl phenyl sulfide:** The product has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S10 and S11). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 0.85-0.89 (s, 3 H, Me), 1.26-1.35 (m, 2 H,-CH_2-), 1.39-1.46 (m, 2 H, -CH_2-), 1.51-1.56 (m, 2 H, -CH_2-), 1.64-1.69 (m, 2 H, -CH_2-), 2.86-2.89 (m, 2 H, -CH_2-), 7.17-7.18 (m, 1 H, Ar*H*), 7.27-7.29 (m, 2 H, Ar*H*), 7.31-7.34 (m, 2 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 13.98 (*C*H_3), 22.51 (*C*H_2), 28.50 (*C*H_2), 29.10 (*C*H_2), 31.34 (*C*H_2), 33.57 (*C*H_2), 125.58, 128.76, 128.81, 137.05 (Ar*C*).

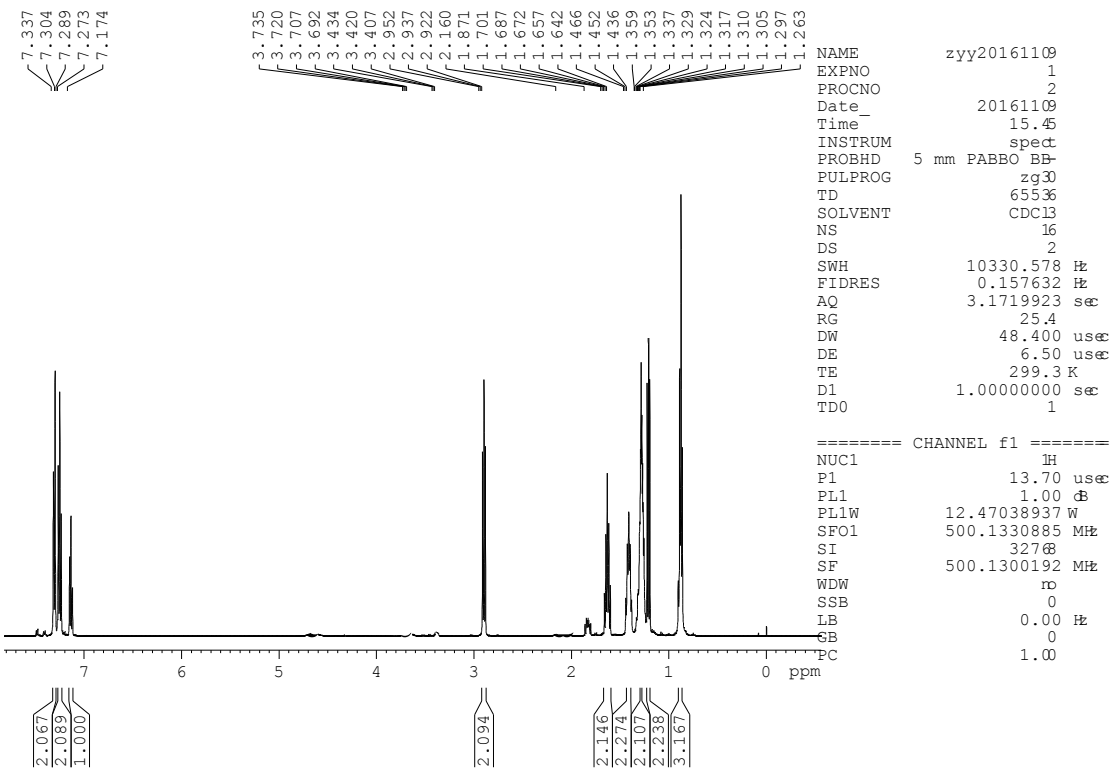


Fig. S10 ^{1}H NMR of *n*-hexyl phenyl sulfide

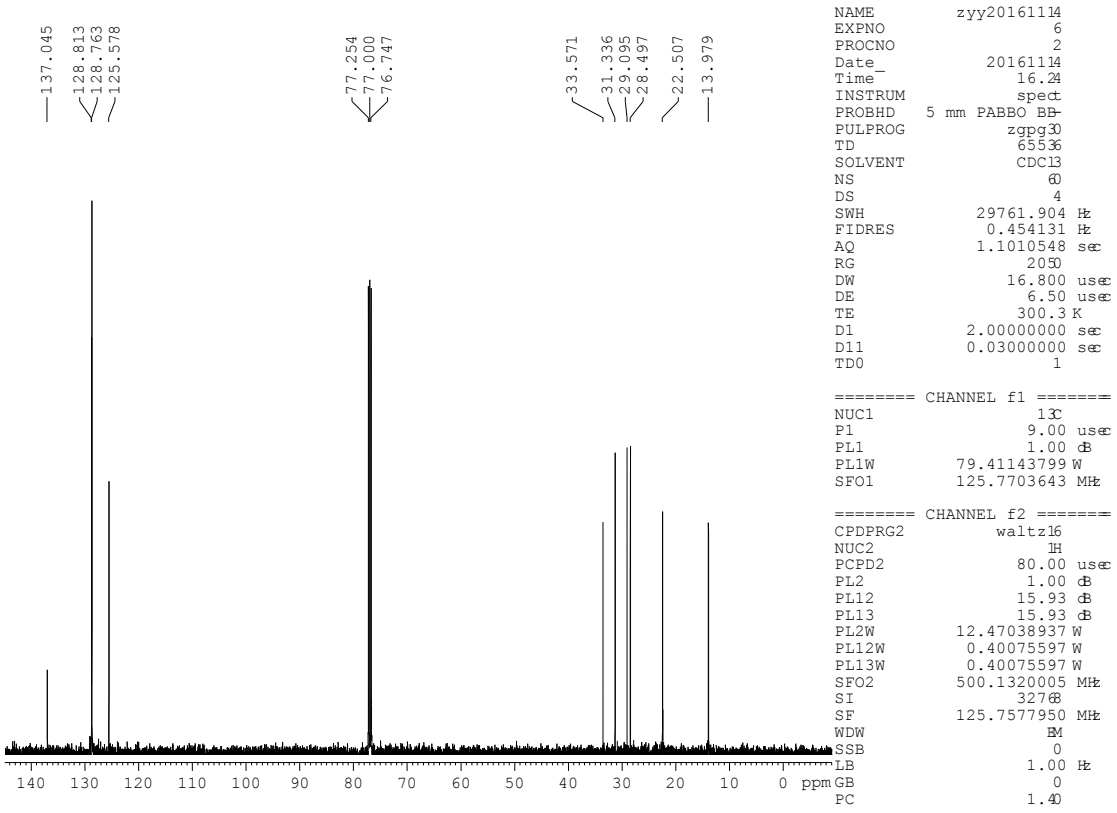


Fig. S11 ^{13}C NMR of *n*-hexyl phenyl sulfide

3. Identification of the obtained chiral sulfoxides (methyl phenyl sulfoxide, methyl *p*-bromophenyl sulfoxide, methyl *p*-methoxyphenyl sulfoxide, methyl *p*-nitrophenyl sulfoxide, methyl *o*-methoxyphenyl sulfoxide, ethyl phenyl sulfoxide, *n*-butyl phenyl sulfoxide, and *n*-hexyl phenyl sulfoxide).

Methyl phenyl sulfoxide: The product has been identified by ^{1}H and ^{13}C NMR spectra (see Fig. S12 and S13). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 2.55-2.57 (s, 3H, Me), 7.27-7.38 (m, 3H, Ar*H*), 7.39-7.51 (m, 2H, Ar*H*).^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 43.9 (S*C*H_3), 123.5, 129.3, 130.9, 145.6(Ar*C*). 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 programmed from 80 to 180 °C with 6 °C· min^{-1}, $t_{methyl\ phenyl\ sulfoxide}$ = 6.9 min; ee value was determined by HPLC (*i*-PrOH/*n*-hexane = 1: 9 (v/v)); flow rate = 1.0 mL.min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 18.7 min, minor enantiomer t_S = 21.2 min (Fig. S14, S15, and S16).

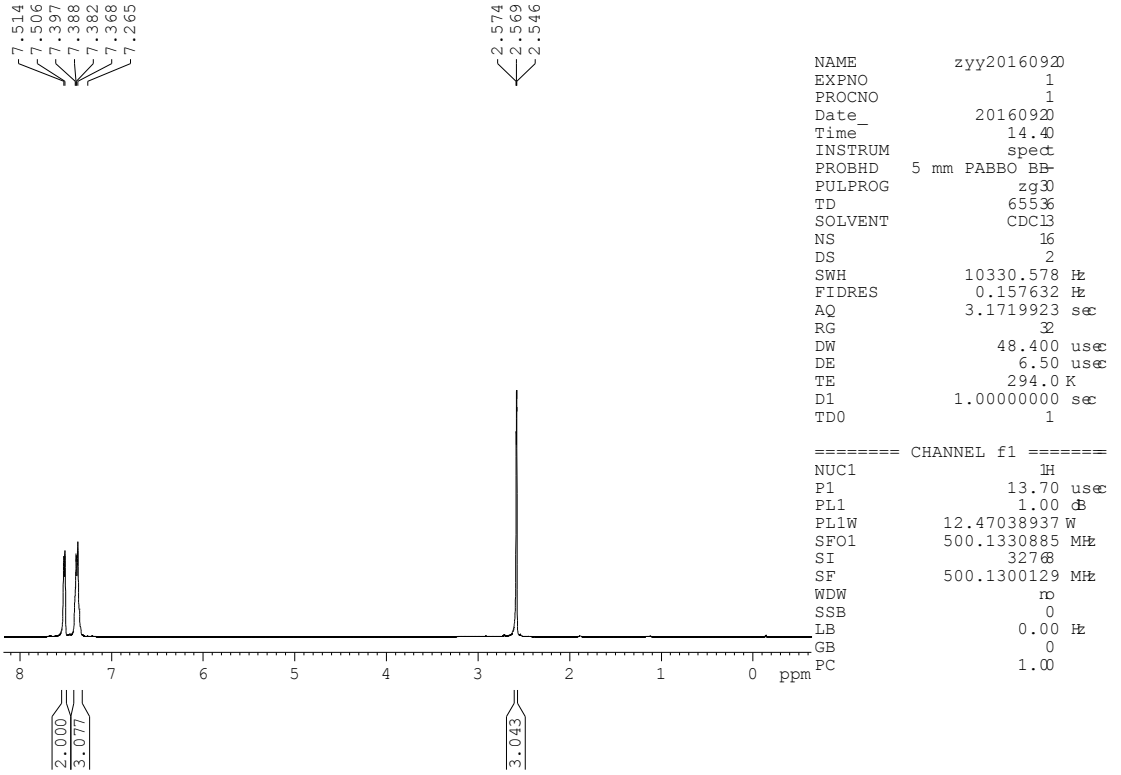


Fig. S12 ^{1}H NMR of methyl phenyl sulfoxide.

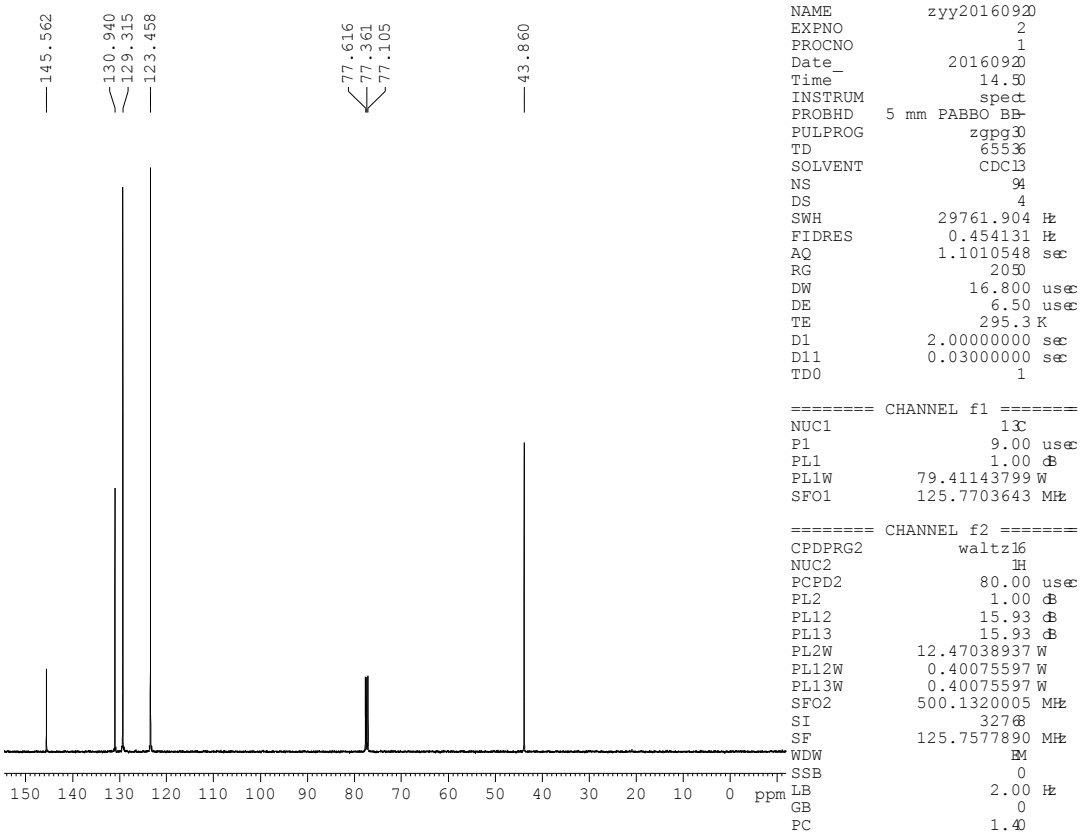


Fig. S13 ^{13}C NMR of methyl phenyl sulfoxide.

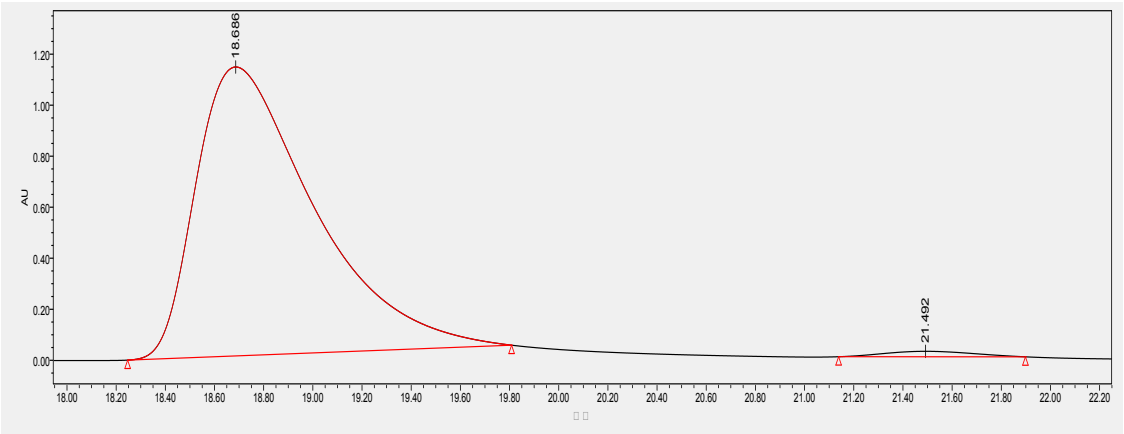


Fig. S14 HLPC of methyl phenyl sulfoxide obtained over $\mathbf{PN_{68}(IS)_4}$ (ee value = 98%).

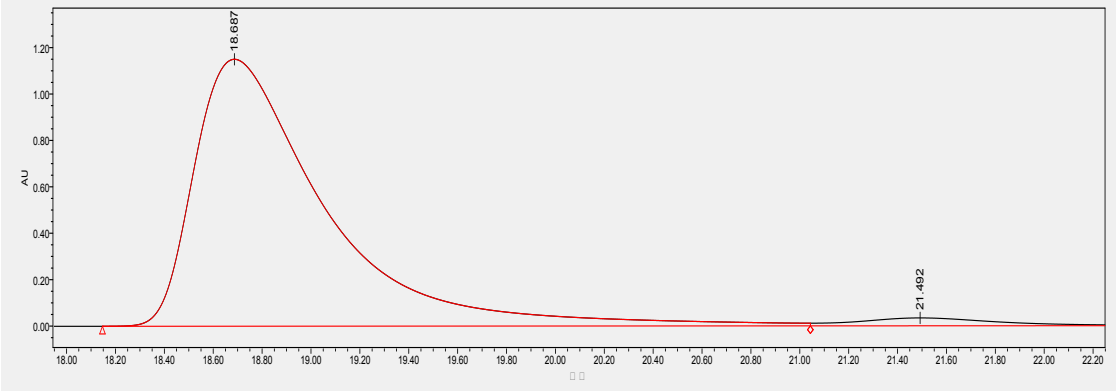


Fig. S15 HLPC of methyl phenyl sulfoxide obtained over **$PN_{68}S_4$** (ee value = 95%).

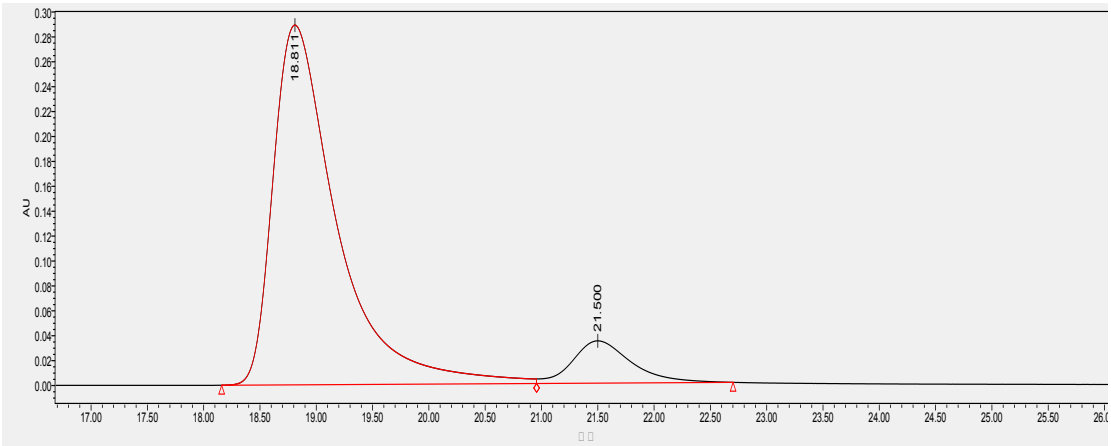


Fig. S16 HLPC of methyl phenyl sulfoxide obtained over neat complex (ee value = 76%).

Methyl *p*-bromophenyl sulfoxide: The product has been identified by ^{1}H and ^{13}C NMR spectra (see Fig. S17 and S18). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 3.15 (s, 3H, SC*H*$_3$), 7.74-7.76 (d, 2H, Ar*H*), 7.83-7.84 (d, 2H, Ar*H*).^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 44.5 (S*C*H$_3$), 125.3, 129.1, 132.8, 139.6(Ar*C*). 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 ^{o}C, the column temperature was 180 ^{o}C, $t_{methyl\ p\text{-}bromophenyl\ sulfoxide}$ = 11.2 min; ee value was determined by HPLC (*i*-PrOH/*n*-hexane = 5:5 (v/v)); flow rate = 1.0 mL min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 8.2 min and minor enantiomer t_S =10.0 min (see Fig. S19, S20 and S21).

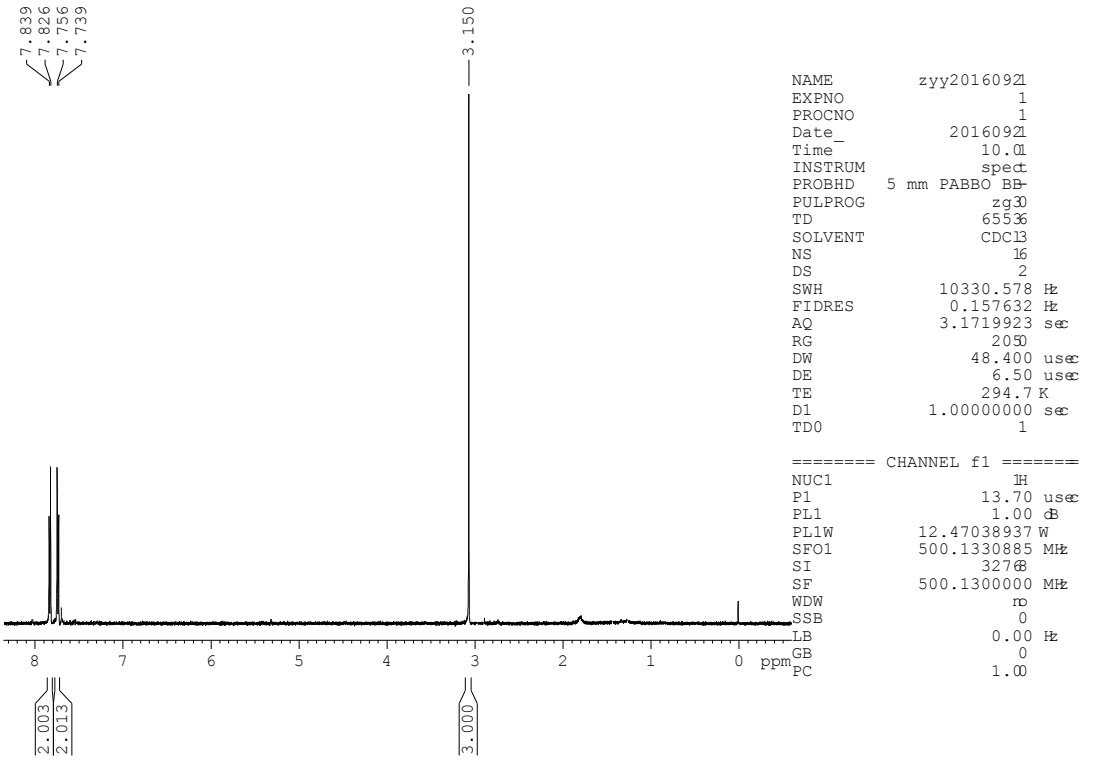


Fig. S17 [1]H NMR of methyl *p*-bromophenyl sulfoxide.

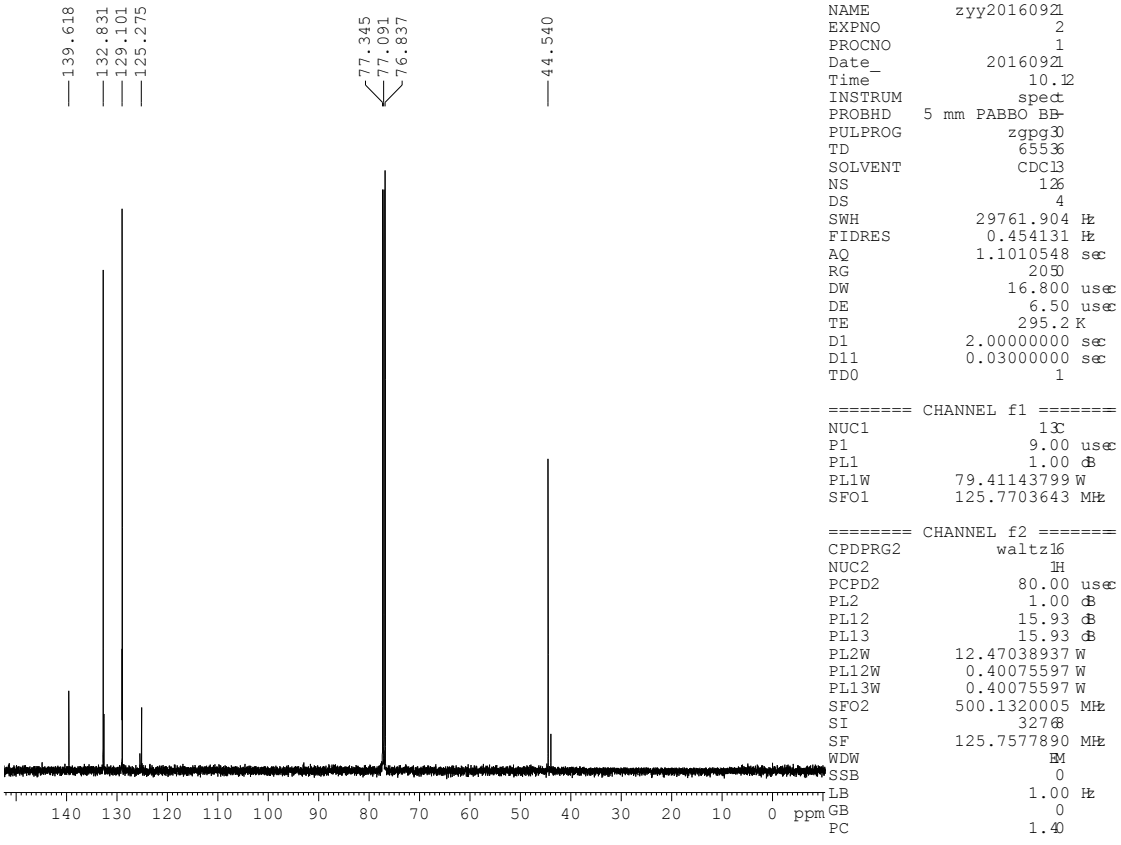


Fig. S18 [13]C NMR of methyl *p*-bromophenyl sulfoxide.

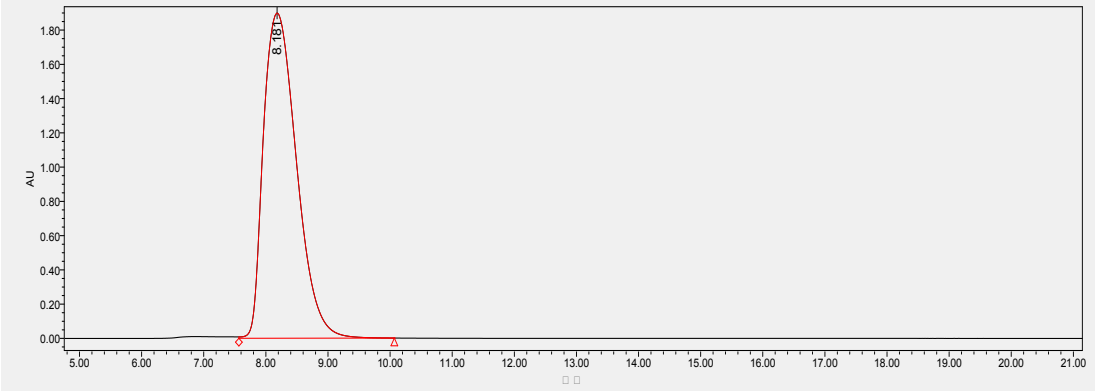


Fig. S19 HLPC of methyl *p*-bromophenyl sulfoxide obtained over $\mathbf{PN_{68}(IS)_4}$ (ee value >99%).

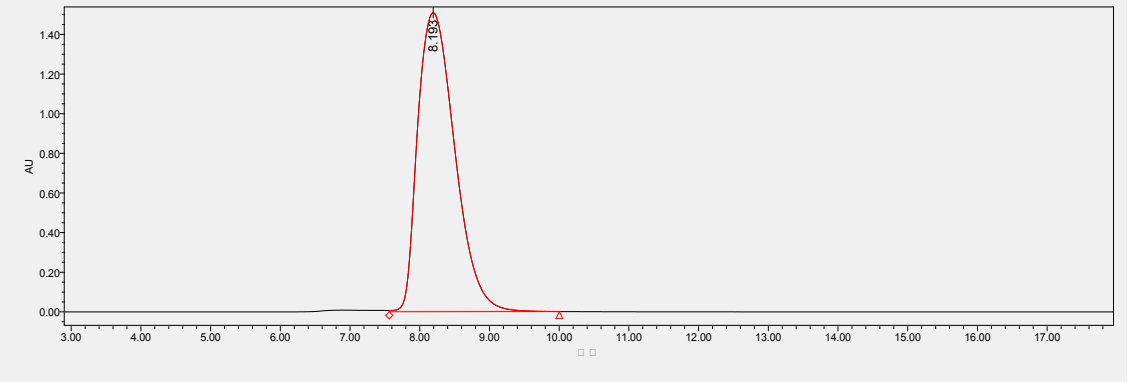


Fig. S20 HLPC of methyl *p*-bromophenyl sulfoxide obtained over $\mathbf{PN_{68}S_4}$ (ee value >99%).

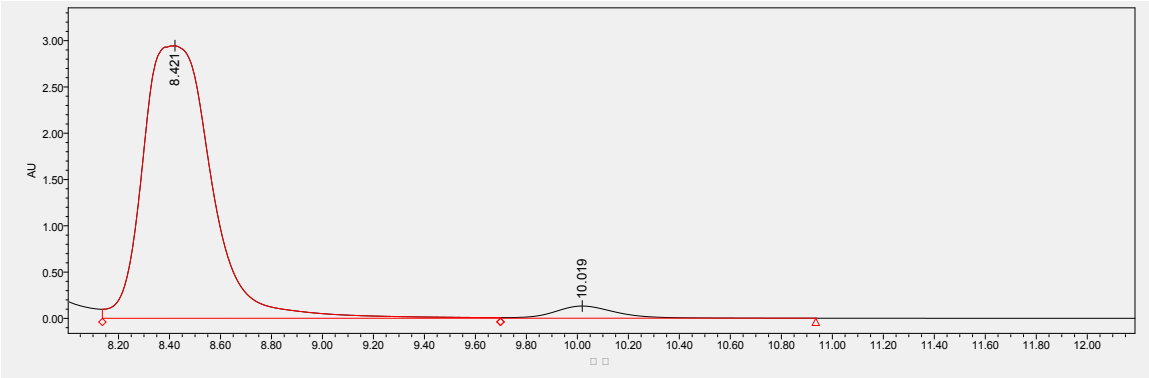


Fig. S21 HLPC of methyl *p*-bromophenyl sulfoxide obtained over neat complex (ee value = 81%).

Methyl *p*-methoxyphenyl sulfoxide: The product has been identified by ^{1}H and ^{13}C NMR spectra (see Fig. S22 and S23). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 3.07 (s, 3 H, SCH_3), 3.95 (s, 3 H, OCH_3), 7.06-7.10 (d, 2 H, Ar*H*), 7.84-7.91 (d, 2 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm):

44.8 (S*C*H$_3$), 55.8 (O*C*H$_3$), 114.6, 129.6, 132.3, 163.7 (Ar*C*). 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, the column temperature was programmed from 80 to 180 °C with 6 °C·min^{-1}, $t_{methyl\ p\text{-}methoxyphenyl\ sulfoxide}$ = 11.7 min; ee value was determined by HPLC (*i*-PrOH/*n*-hexane = 2:8 (v/v)); flow rate = 1.0 mL.min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 8.9 min and minor enantiomer t_S = 10.2 min (see Fig. S24, S25 and S26).

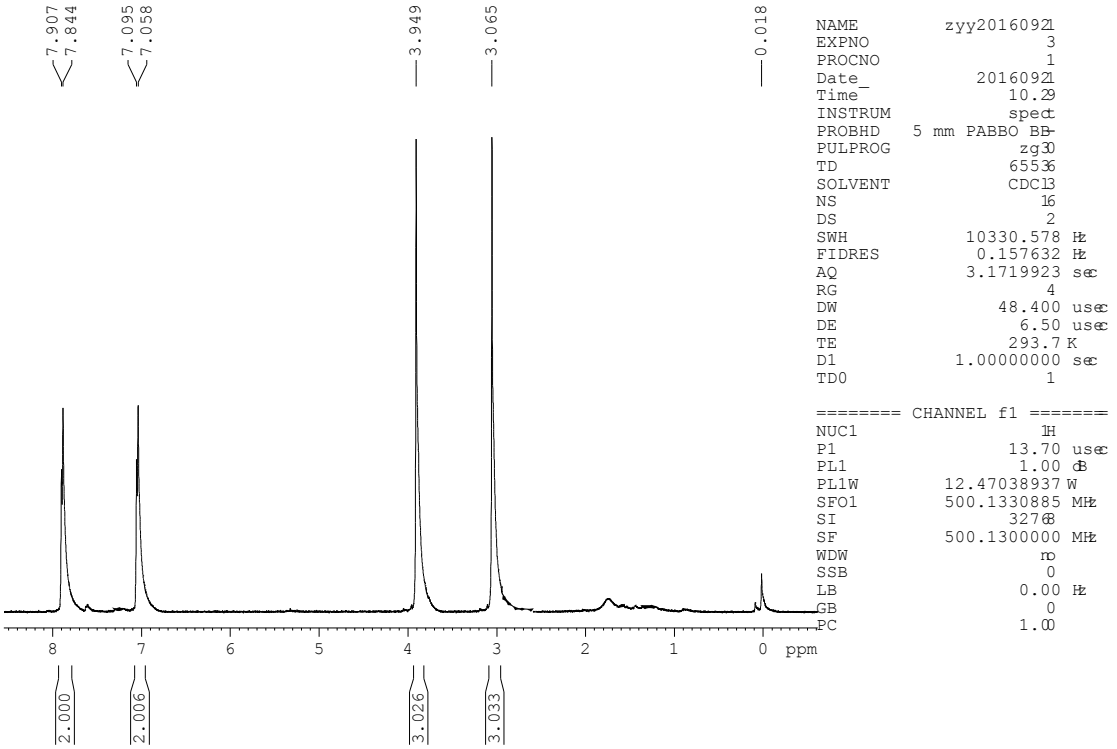


Fig. S22 ^{1}H NMR of methyl *p*-methoxyphenyl sulfoxide.

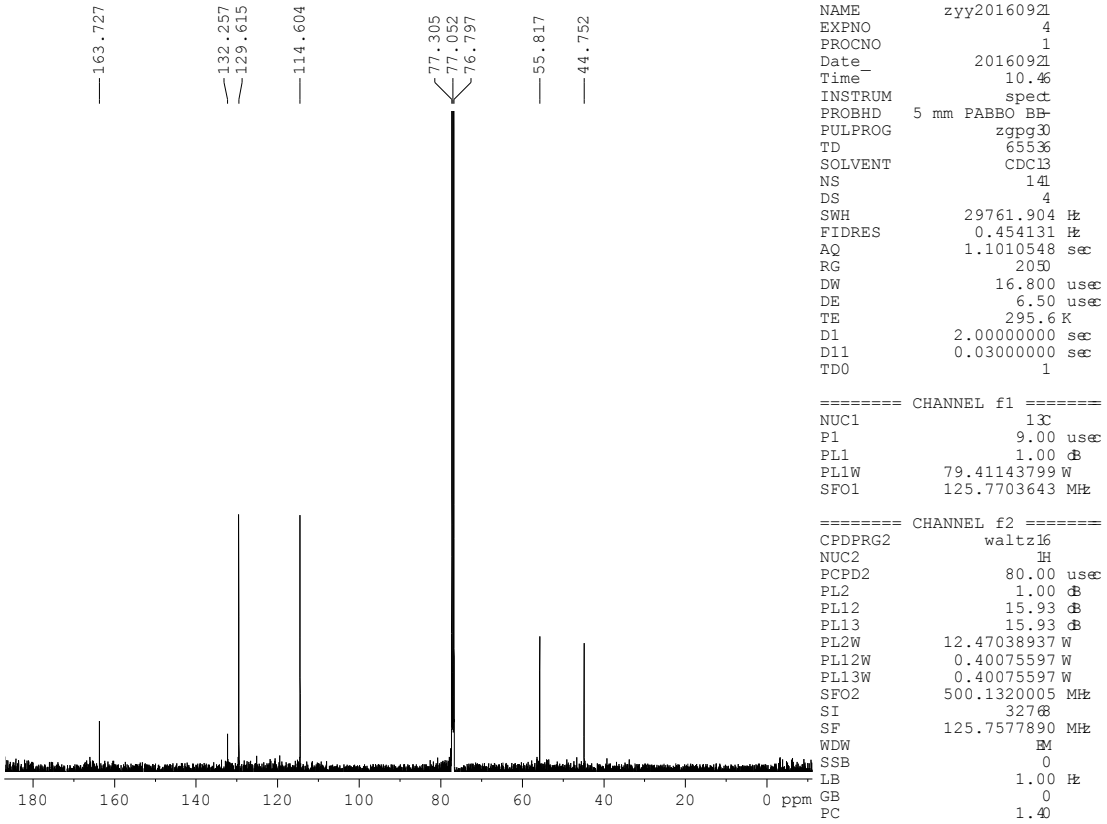


Fig. S23 ^{13}C NMR of methyl *p*-methoxyphenyl sulfoxide.

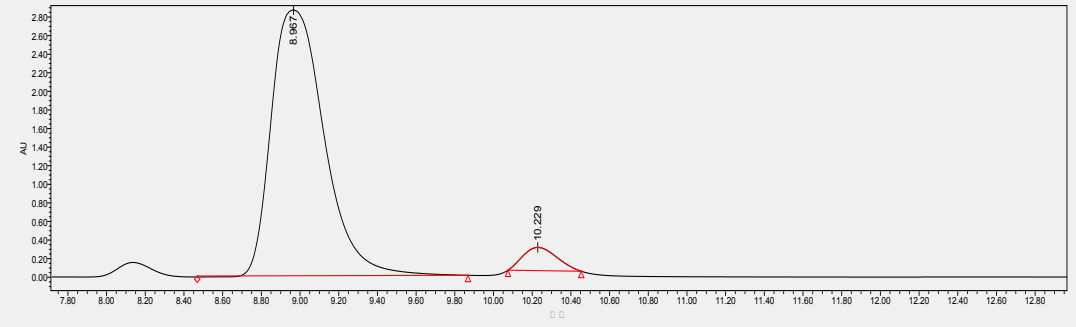


Fig. S24 HLPC of methyl *p*-methoxyphenyl sulfoxide obtained over **$PN_{68}(IS)_4$** (ee value = 94%).

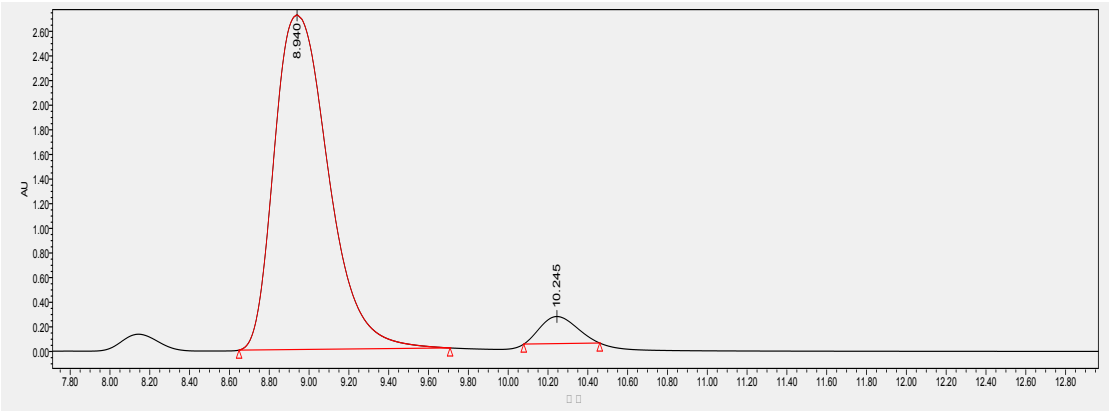


Fig. S25 HLPC of methyl *p*-methoxyphenyl sulfoxide obtained over $\mathbf{PN_{68}S_4}$ (ee value = 90%).

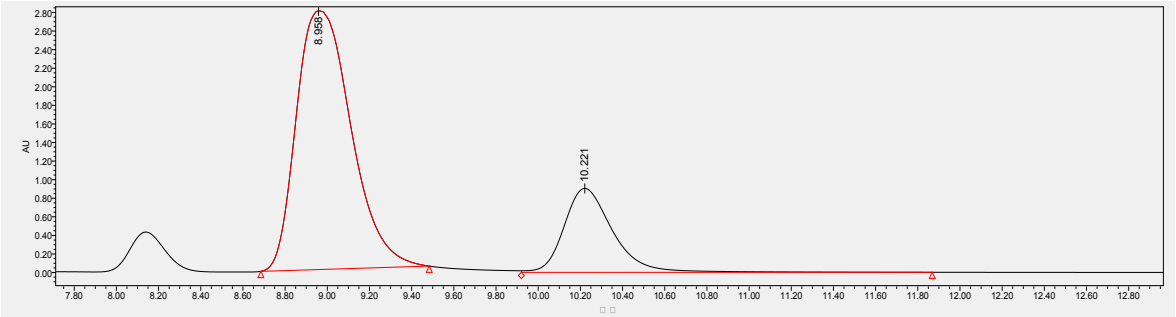


Fig. S26 HLPC of methyl *p*-methoxyphenyl sulfoxide obtained over neat complex (ee value = 45%).

Methyl *p*-nitrophenyl sulfoxide: The product has been identified by ^{1}H and ^{13}C NMR spectra (see Fig. S27 and S28). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 2.59 (s, 3 H, SC*H*$_3$), 7.27-7.42 (d, 2 H, Ar*H*), 8.09-8.20 (d, 2 H, Ar*H*).^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 43.8 (S*C*H$_3$), 123.9, 124.9, 144.7, 148.8 (Ar*C*). 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 ^{o}C, the column temperature was 180 ^{o}C, $t_{methyl\ p\text{-}nitrophenyl\ sulfoxide}$ = 8.6 min; ee value was determined by HPLC (*i*-PrOH/*n*-hexane = 3:7 (v/v)); flow rate = 1.0 mL.min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 11.5 min and minor enantiomer t_S =21.5 min (see Fig. S29, S30 and S31).

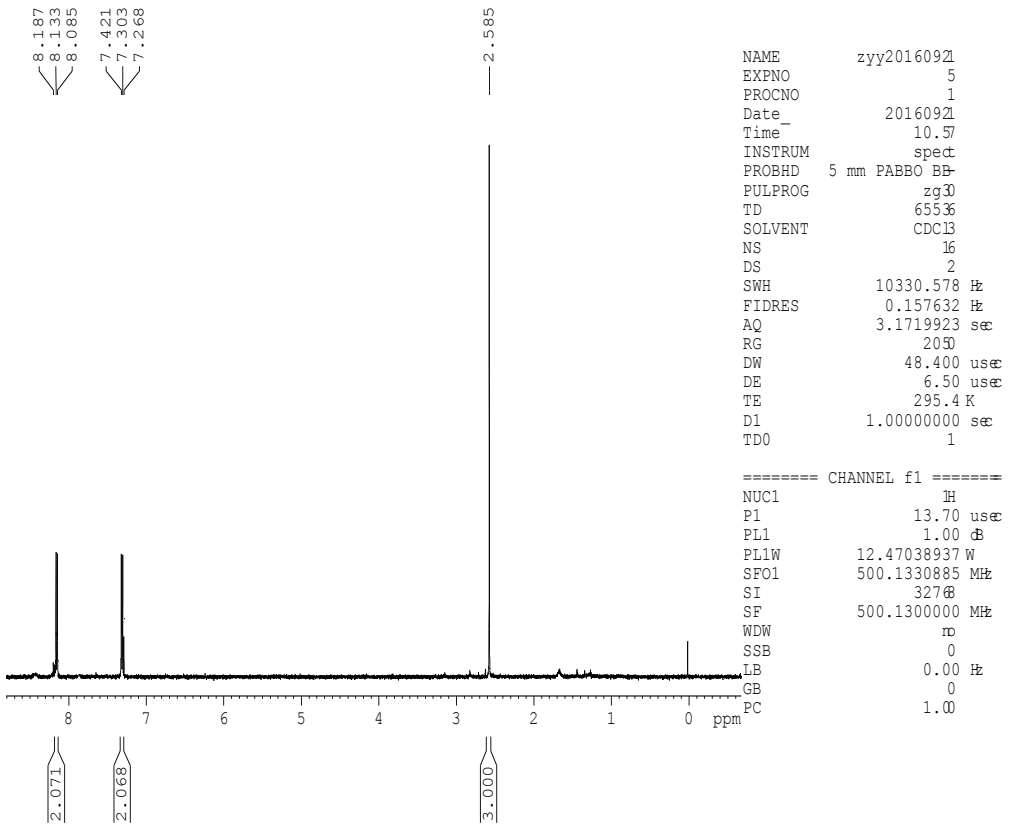


Fig. S27 [1]H NMR of methyl *p*-nitrophenyl sulfoxide.

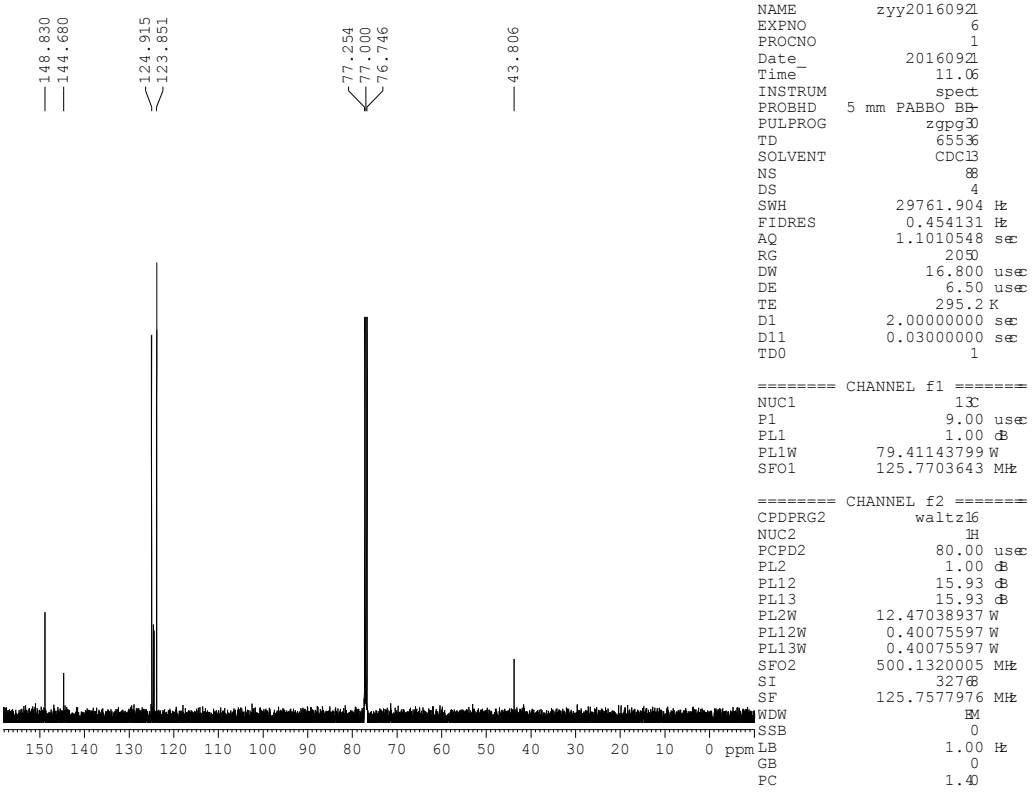


Fig. S28 [13]C NMR of methyl *p*-nitrophenyl sulfoxide.

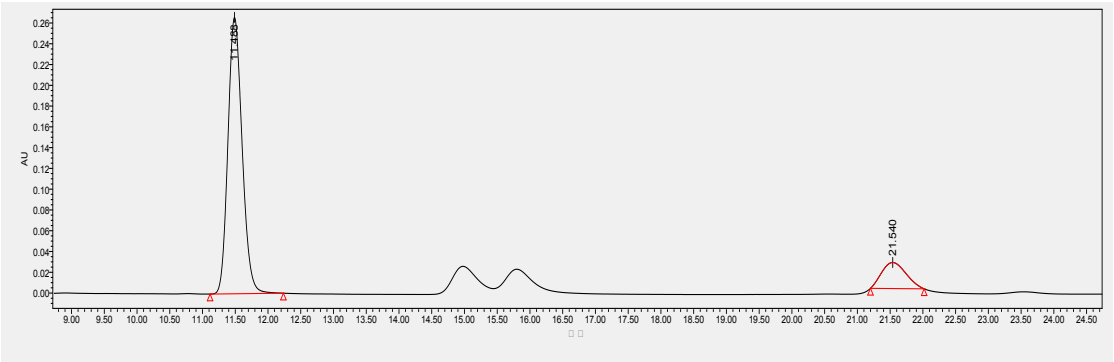


Fig. S29 HLPC of methyl *p*-nitrophenyl sulfoxide obtained over **$PN_{68}(IS)_4$** (ee value = 88%).

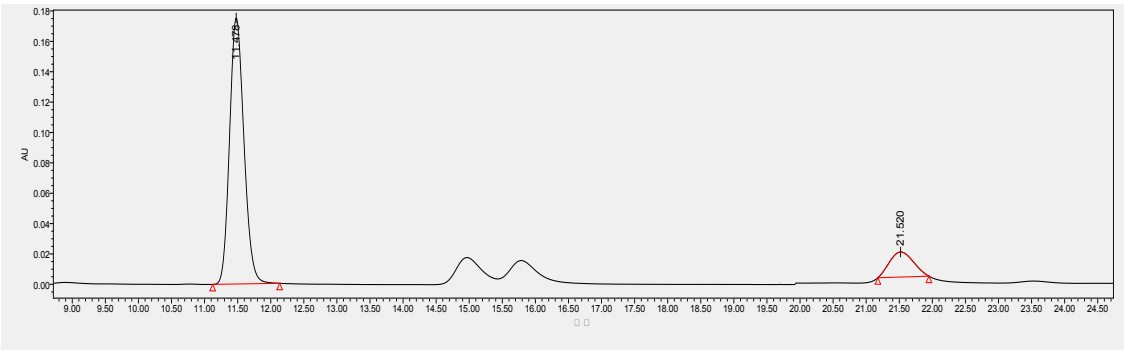


Fig. S30 HLPC of methyl *p*-nitrophenyl sulfoxide obtained over **$PN_{68}S_4$** (ee value = 84%).

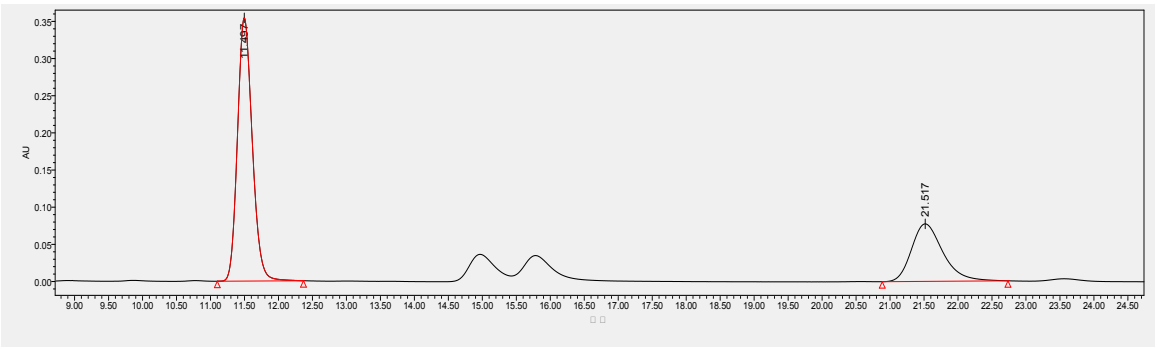


Fig. S31 HLPC of methyl *p*-nitrophenyl sulfoxide obtained over neat complex (ee value = 56%).

Methyl *o*-methoxyphenyl sulfoxide: The product has been identified by ^{1}H and ^{13}C NMR spectra (see Fig. S32 and S33). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 2.68 (s, 3 H, SCH_3), 3.78 (s, 3 H, OCH_3), 6.79-7.90 (m, 4 H, Ar*H*).^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 41.1 (SCH_3), 55.7 (OCH_3), 110.5, 121.5, 124.4, 132.0, 132.8, 154.7 (Ar*C*).

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 ^{o}C, the column temperature was 180 ^{o}C, $t_{methyl\ o\text{-}methoxyphenyl\ sulfoxide}$ = 9.8 min; ee value was determined by HPLC (*i*-PrOH/*n*-hexane = 2: 8 (v/v)); flow rate = 1.0 mL.min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 9.0 min and minor enantiomer t_S =10.3 min (see Fig. S34, S35 and S36).

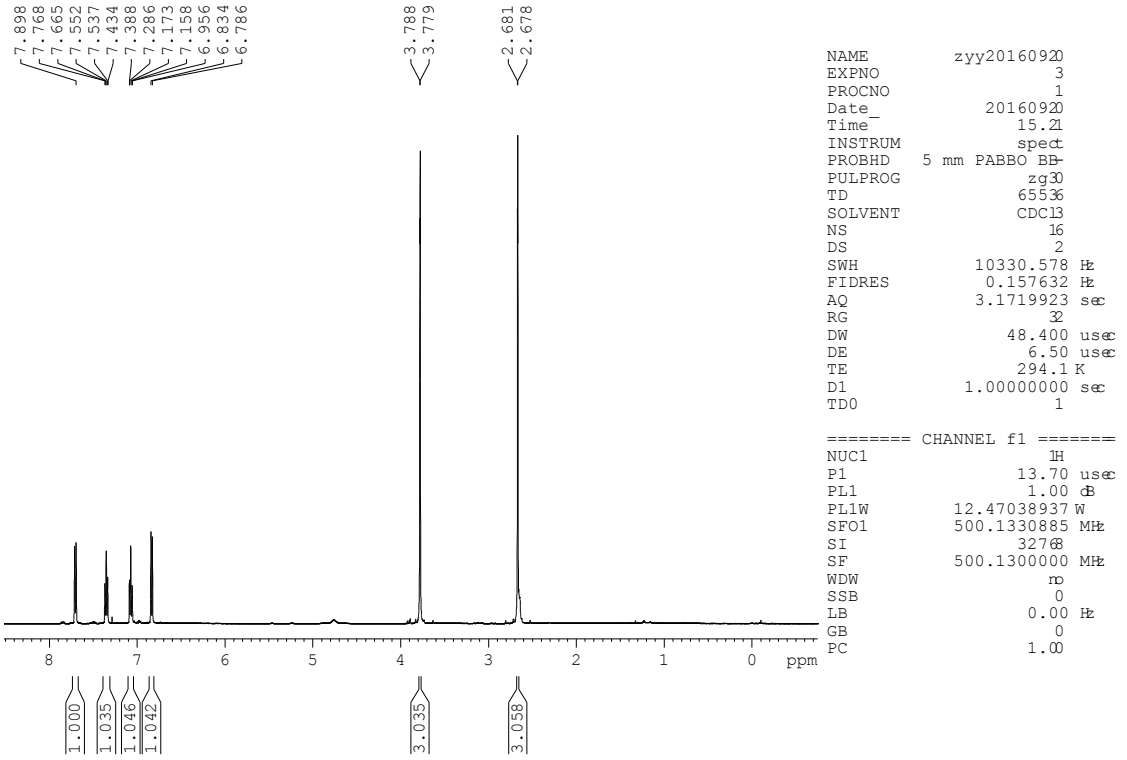


Fig. S32 ^{1}H NMR of methyl *o*-methoxyphenyl sulfoxide.

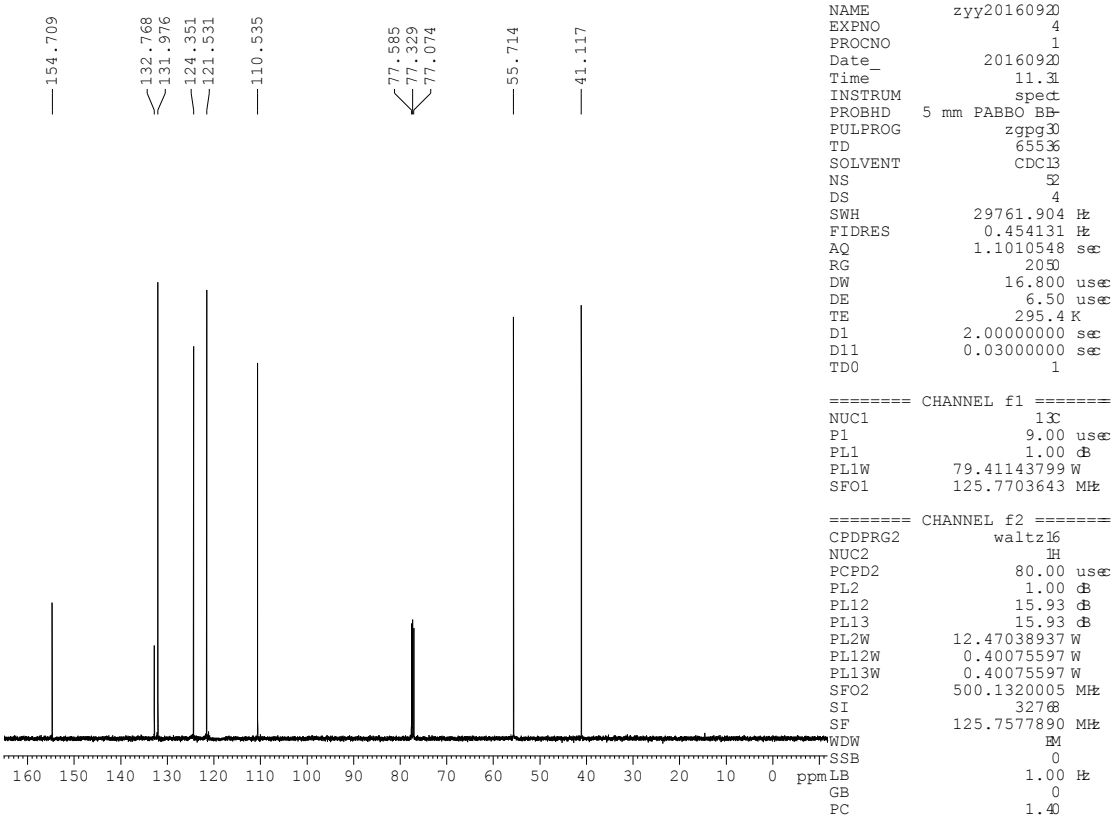


Fig. S33 ^{13}C NMR of methyl *o*-methoxyphenyl sulfoxide.

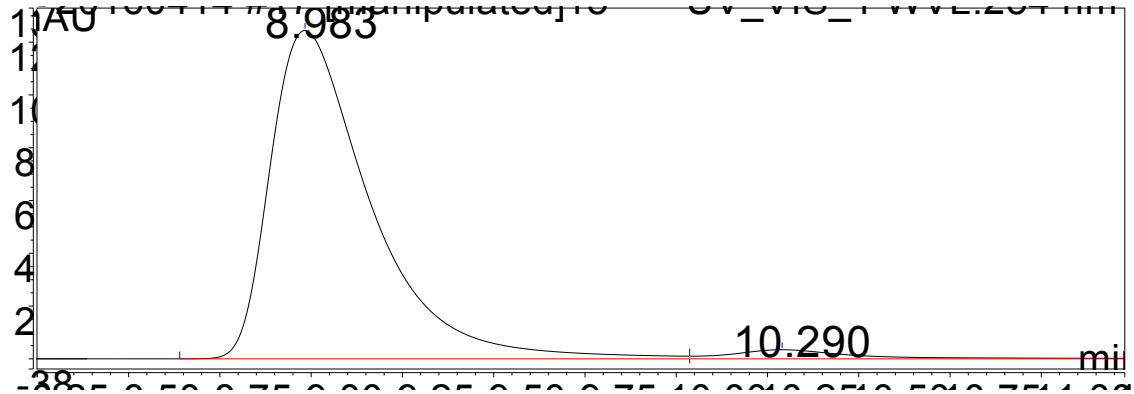


Fig. S34 HLPC of methyl *o*-methoxyphenyl sulfoxide obtained over $\mathbf{PN_{68}(IS)_4}$ (ee value = 99%).

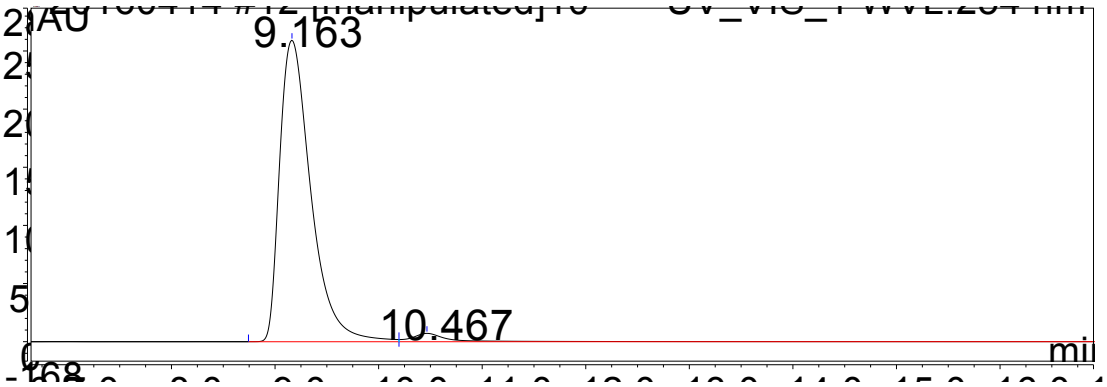


Fig.35 HLPC of methyl *o*-methoxyphenyl sulfoxide obtained over $\mathbf{PN_{68}S_4}$ (ee value = 98%).

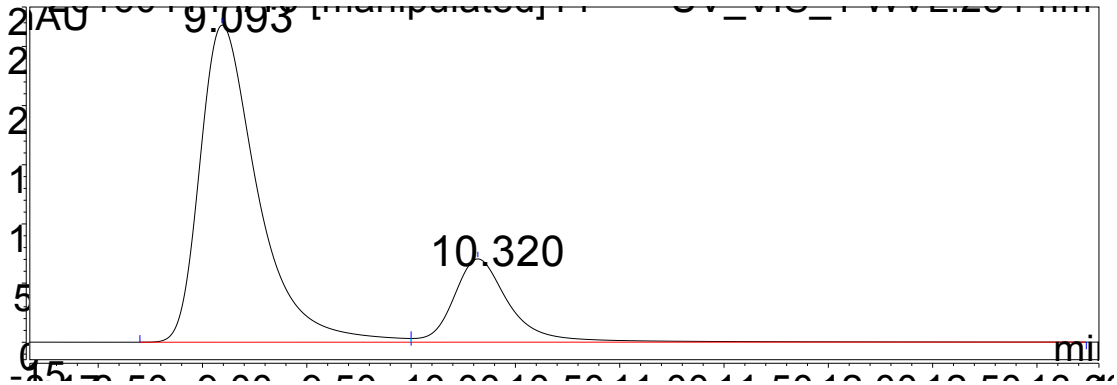


Fig. S36 HLPC of methyl *o*-methoxyphenyl sulfoxide obtained over neat complex (ee value = 67%).

Ethyl phenyl sulfoxide: The product has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S37 and S38). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 1.18 (m, 3 H, Me), 2.90-2.98 (m, 2 H, -C*H*$_2$-), 7.28-7.29 (m, 1 H, Ar*H*), 7.33-7.49 (m, 2 H, Ar*H*), 7.50-7.62 (m, 2 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 5.90 (*C*H$_3$), 50.23 (S*C*H$_2$), 124.12, 128.76, 129.08, 145.87 (Ar*C*). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL. min^{-1}, the injector temperature and the detector temperature were 250 ^{o}C, the column temperature was 180 ^{o}C, $t_{ethyl\ phenyl\ sulfoxide}$ = 2.5 min; ee value was determined by HPLC (*i*-PrOH/ *n*-hexane = 1: 9 (v/ v)); flow rate = 1.0 mL. min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 8.2 min (see Fig. S39).

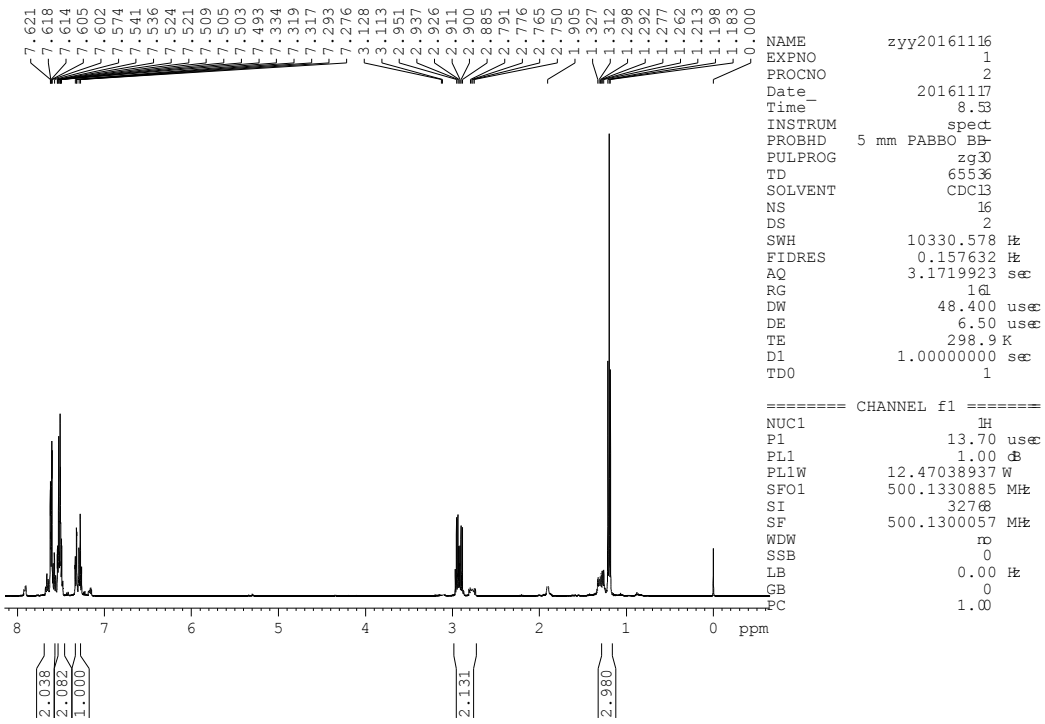


Fig. S37 ^{1}H NMR of ethyl phenyl sulfoxide

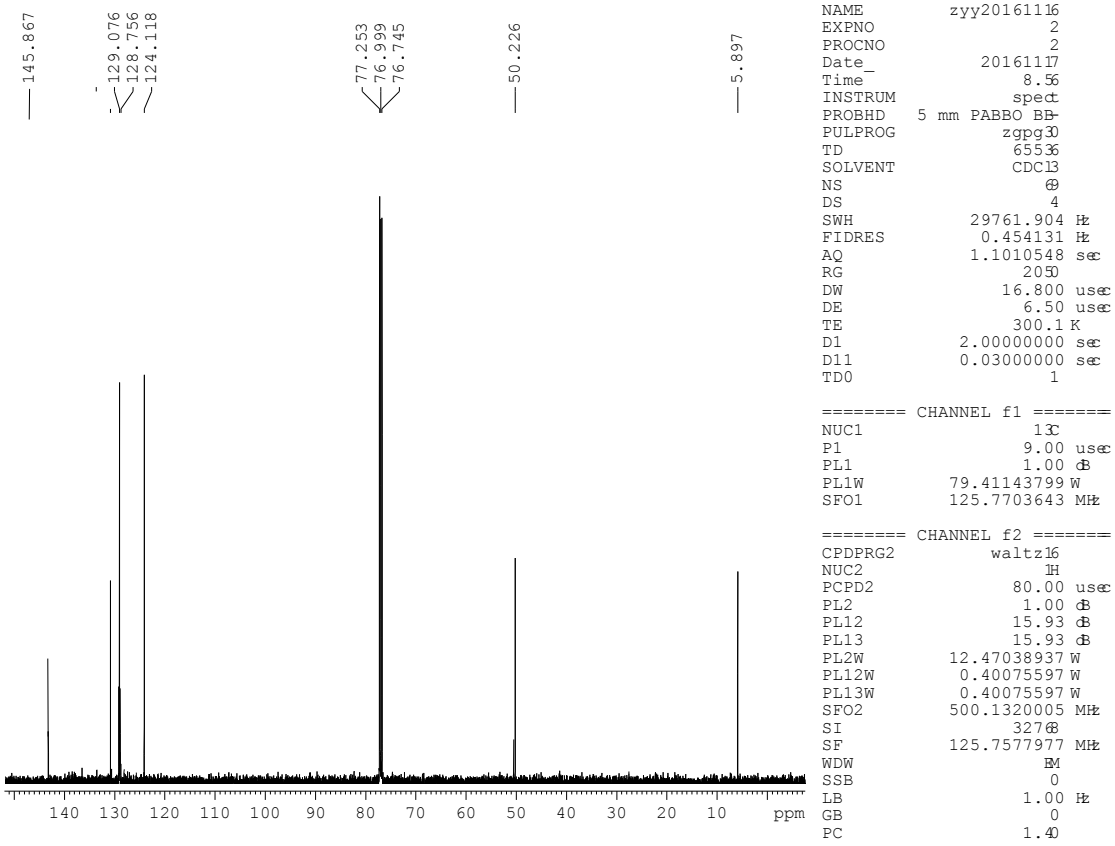


Fig. S38 ^{13}C NMR of ethyl phenyl sulfoxide

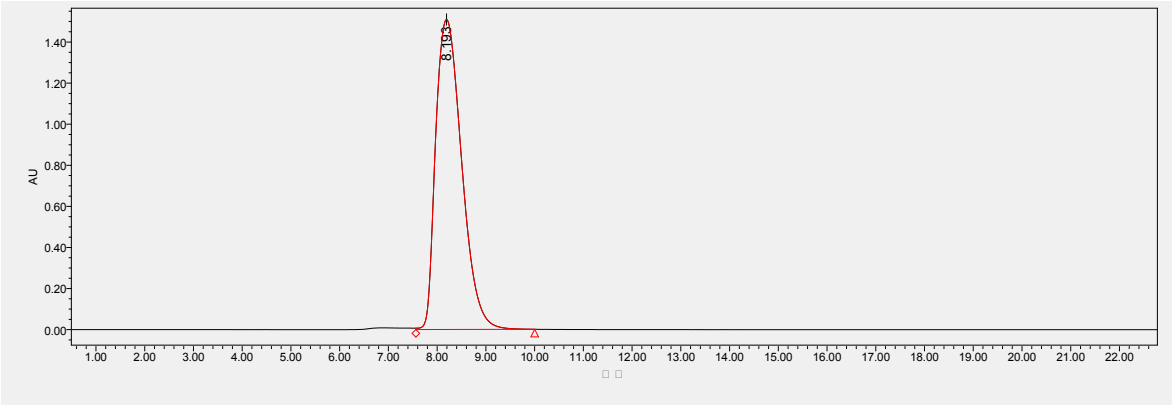


Fig. S39 HLPC of ethyl phenyl sulfoxide obtained over **$PN_{68}(IS)_4$** (ee value > 99%).

***n*-Butyl phenyl sulfoxide:** The product has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S40 and S41). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 0.90-0.93 (m, 3 H, Me), 1.41-1.48 (m, 2 H,-C*H*$_2$-), 1.60-1.67 (m, 2 H,-C*H*$_2$-), 2.90-2.93 (m, 2 H,-C*H*$_2$-), 7.15-7.16 (m, 1 H, Ar*H*), 7.24-7.26 (m, 2 H, Ar*H*), 7.28-7.31 (m, 2 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 13.52 (*C*H_3), 21.86 (*C*H_2), 31.13 (*C*H_2), 58.12 (*C*H_2), 125.56, 128.72, 128.77, 136.91 (Ar*C*). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL. min^{-1}, the injector temperature and the detector temperature were 250 ^{o}C, the column temperature was 180 ^{o}C, $t_{n\text{-}butyl\ phenyl\ sulfoxide}$ = 2.9 min; ee value was determined by HPLC (i-PrOH/ *n*-hexane = 1: 9 (v/v)); flow rate = 1.0 mL. min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 9.2 min (see Fig. S42).

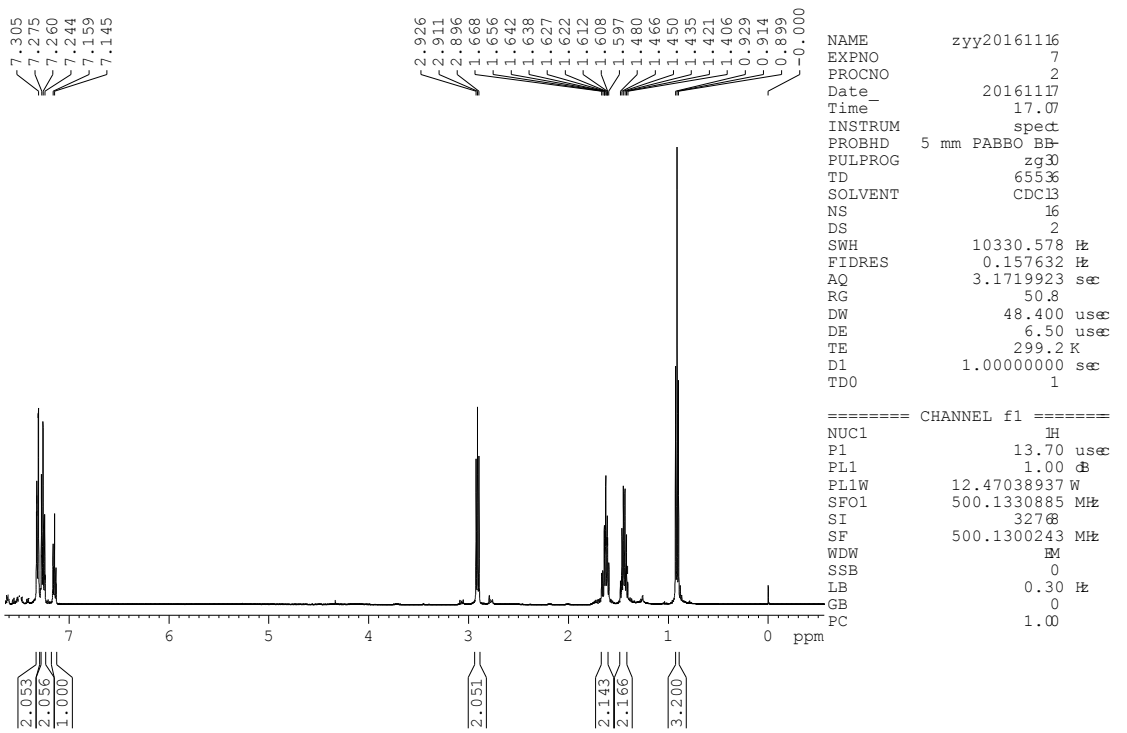


Fig. S40 ^{1}H NMR of *n*-butyl phenyl sulfoxide

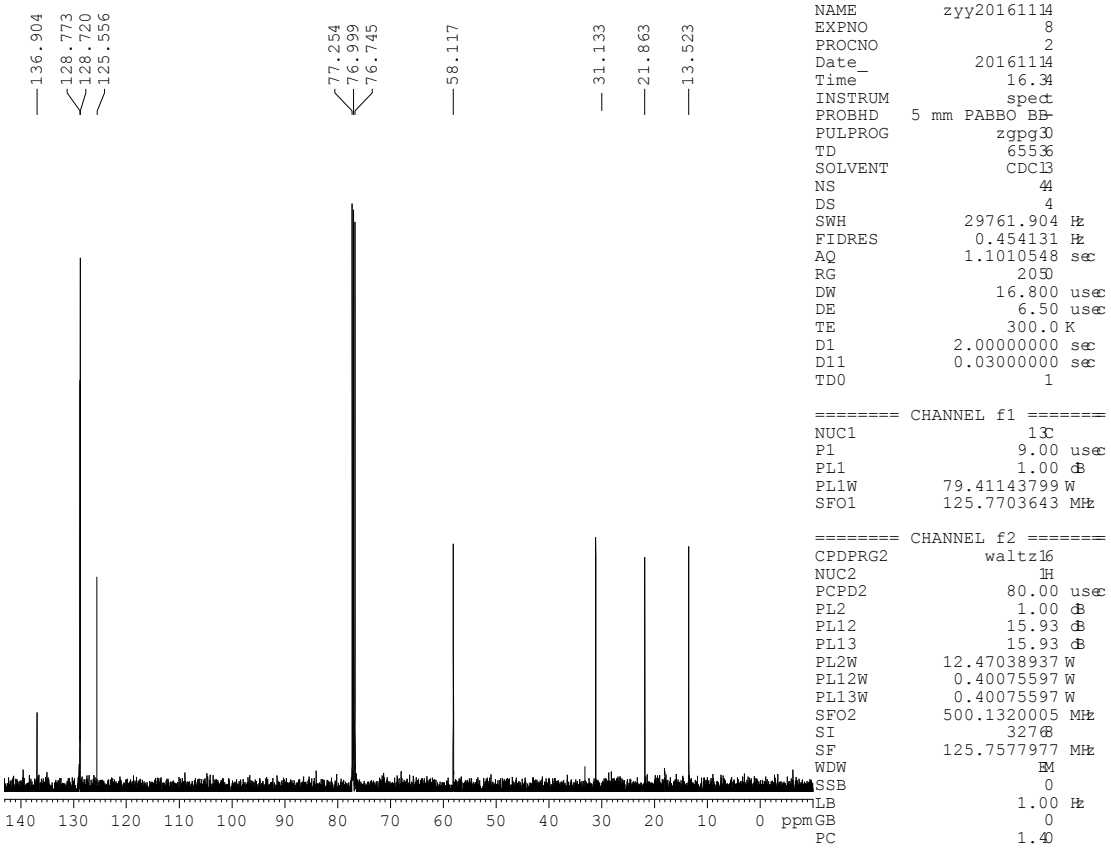


Fig. S41 ^{13}C NMR of *n*-butyl phenyl sulfoxide

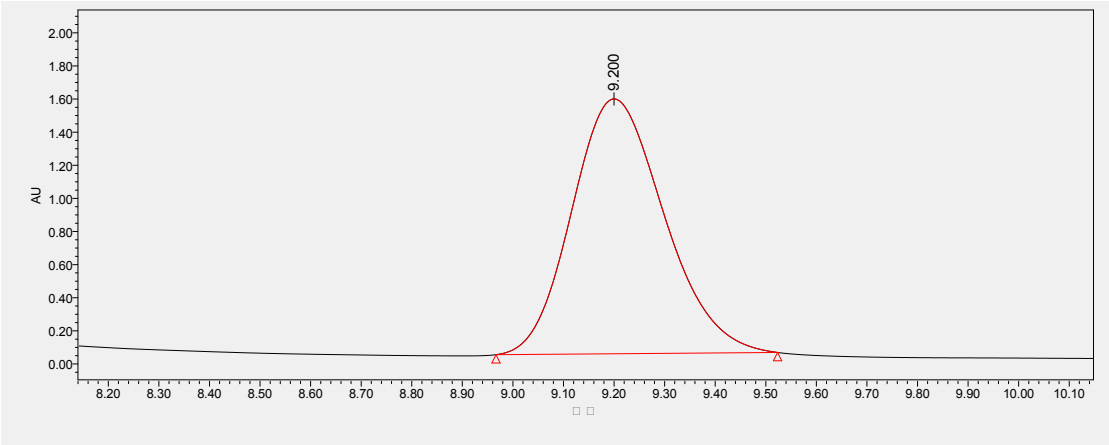


Fig. S42 HLPC of *n*-butyl phenyl sulfoxide obtained over **$PN_{68}(IS)_4$** (ee value > 99%).

***n*-Hexyl phenyl sulfide**: The product has been identified by ^{1}H NMR and ^{13}C NMR spectra (see Fig. S43 and S44). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 0.87-0.90 (s, 3 H, Me), 1.26-1.68 (m, 4 H,-CH_2- CH_2-), 1.66-1.69 (m, 2 H, -CH_2-), 2.89-2.93 (m, 2 H, -CH_2-), 7.15-7.16 (m, 1 H, Ar*H*), 7.25-7.28 (m, 2 H, Ar*H*), 7.31-7.32 (m, 2 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 14.04 (*C*H_3), 22.55 (*C*H_2), 28.54 (*C*H_2), 31.38 (*C*H_2), 33.60 (*C*H_2), 58.21 (*C*H_2), 125.62, 128.80, 128.85, 137.08 (Ar*C*). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL.min^{-1}, the injector temperature and the detector temperature were 250 ^{o}C, the column temperature was 180 ^{o}C, $t_{n\text{-}hexyl\ phenyl\ sulfoxide}$ = 4.3 min; ee value was determined by HPLC (i-PrOH/ *n*-hexane = 1: 9 (v/v)); flow rate = 1.0 mL. min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 17.5 min (see Fig. S45)

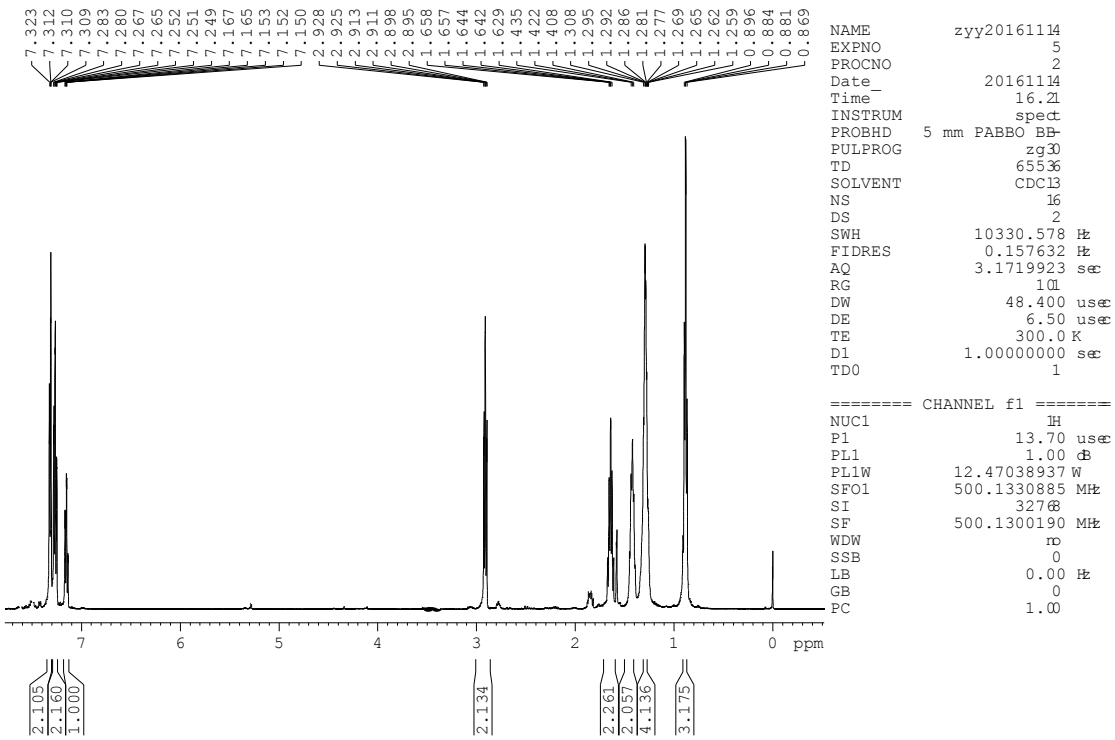


Fig. S43 ^{1}H NMR of *n*-hexyl phenyl sulfide

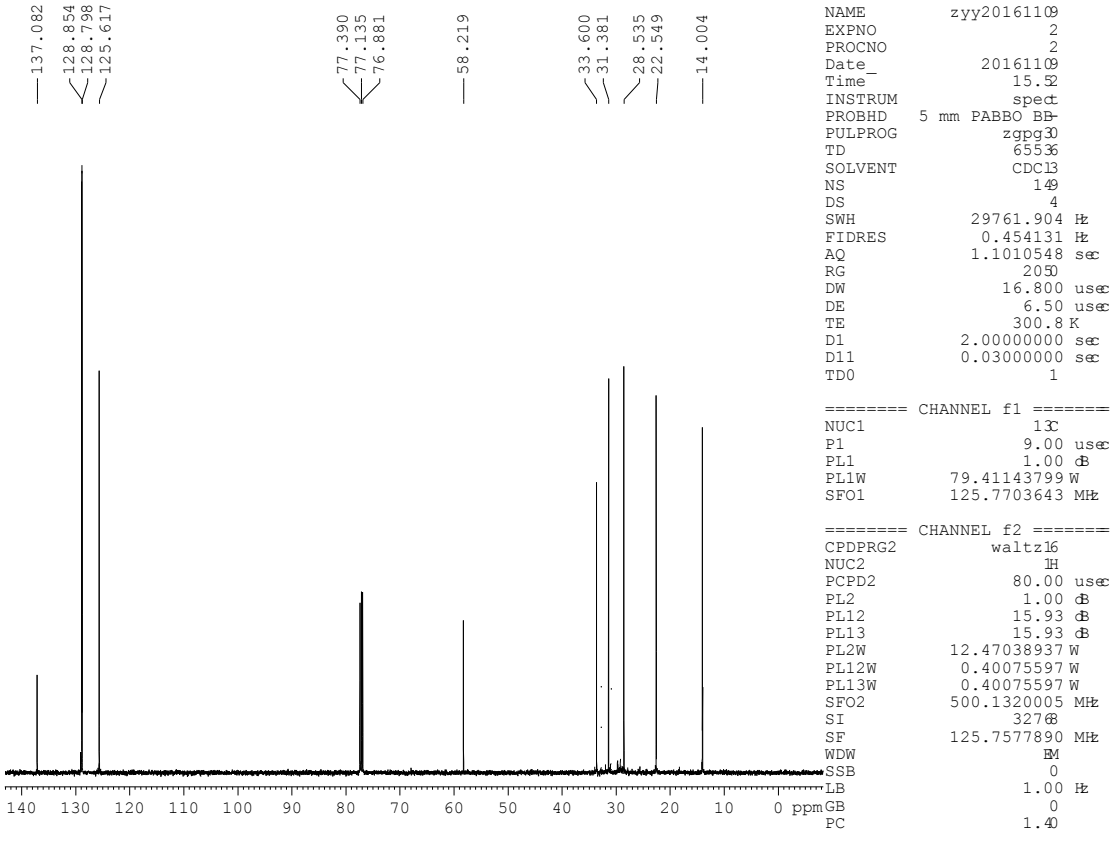


Fig. S44 ^{13}C NMR of *n*-hexyl phenyl sulfide

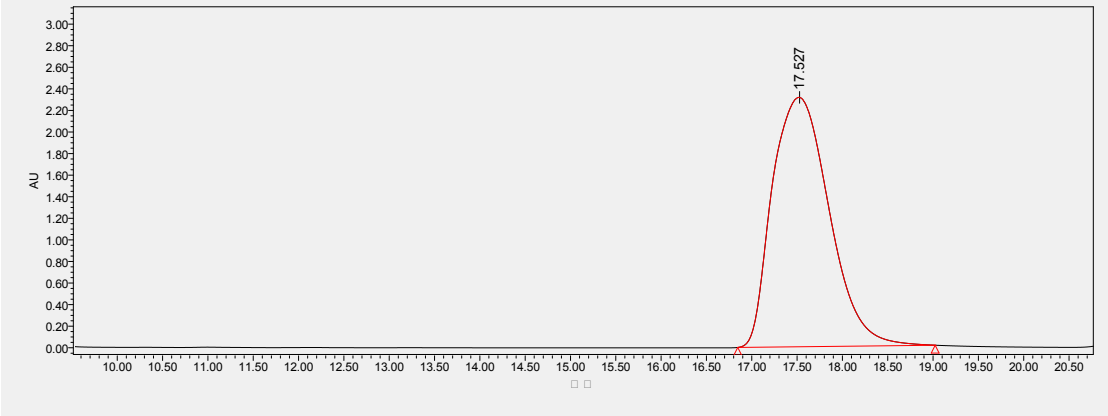


Fig. S45 HLPC of *n*-hexyl phenyl sulfide obtained over **$PN_{68}(IS)_4$** (ee value > 99%)