Supporting Information

Chiral salen Cr(III) complex encapsulated in thermo-responsive polymer nanoreactor for asymmetric epoxidation of alkenes in water

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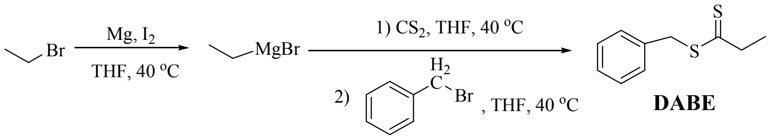
CONTENT:

1. Synthesis and characterization of dithiopropionic acid benzyl ester (**DABE**).

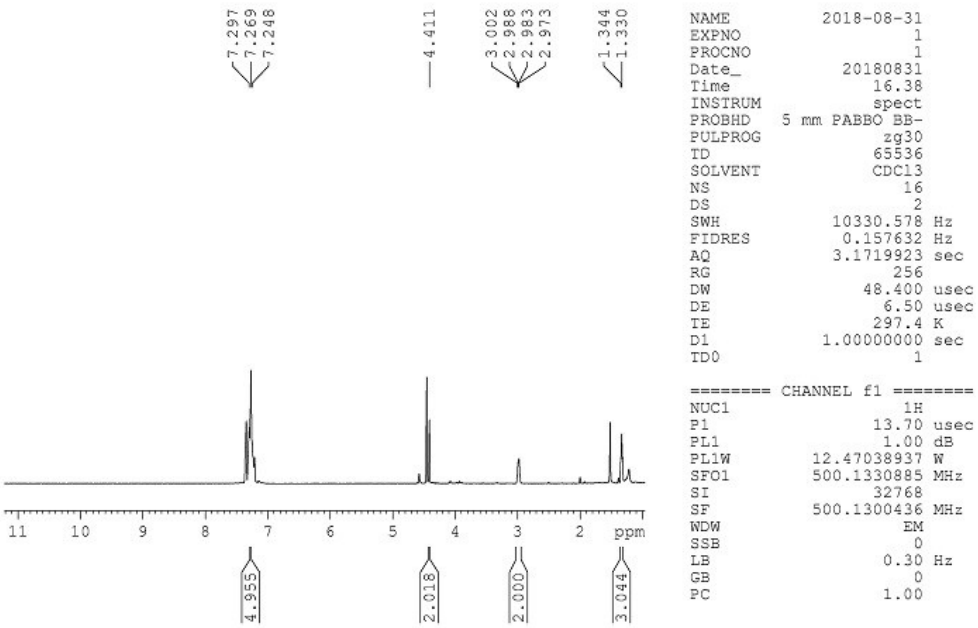
2. General procedure for asymmetric epoxidation of alkenes in water.

1. Synthesis and characterization of dithiopropionic acid benzyl ester (**DABE**).

The synthesis of **DABE** was outlined in Scheme S1. Magnesium strips (1.0 mmol, 0.024 g) and iodine (0.01 mmol, 0.0025 g) were dissolved in tetrahydrofuran (20 mL) at room temperature. A solution of ethyl bromide (1.0 mmol, 0.1 g) in tetrahydrofuran (50 mL) was added dropwise to the above mixture under an argon atmosphere. After being stirred at 40 °C for 1 h, carbon disulfide (1.0 mmol, 0.08 g) was slowly added. The mixture was stirred at 40 °C for 1 h. Benzyl bromide (1.0 mmol, 0.17 g) was then added dropwise to the reaction mixture, and followed by stirring at 40 °C for 5 h. The reaction solution was poured into ice water (150 mL), forming a large amount of white solid. Hydrochloric acid (2.0 mL, 12 M) was added into the solution until the white solid disappeared. The mixture was extracted with benzene (3 mL×15). After being dried with anhydrous magnesium sulfate, the combined extractant was concentrated in vacuum. Residue was purified with petroleum ether/ethyl acetate (v/v=100/1), giving **DABE** as pink oil (0.15 g, yield: 79%). Calc. for ($C_{10}H_{12}S_2$): C, 61.18; H, 6.16; S, 32.66%. Found: C, 61.14; H, 6.16; S, 32.70%. The structure of **DABE** was identified by ^{1}H NMR (see Fig. S1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.2 (m, 5 H, Ar*H*), 4.4 (m, 2 H, Ar-CH_2-S), 2.9 (m, 2 H, S=C-CH_2-CH_3), 1.3 ppm (m, 3 H, CH_2-CH_3).



Scheme S1. Synthesis of **DABE**.



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D1            1.00000000 sec
TD0                     1

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SI                  32768
SF            500.1300436 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
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PC                   1.00
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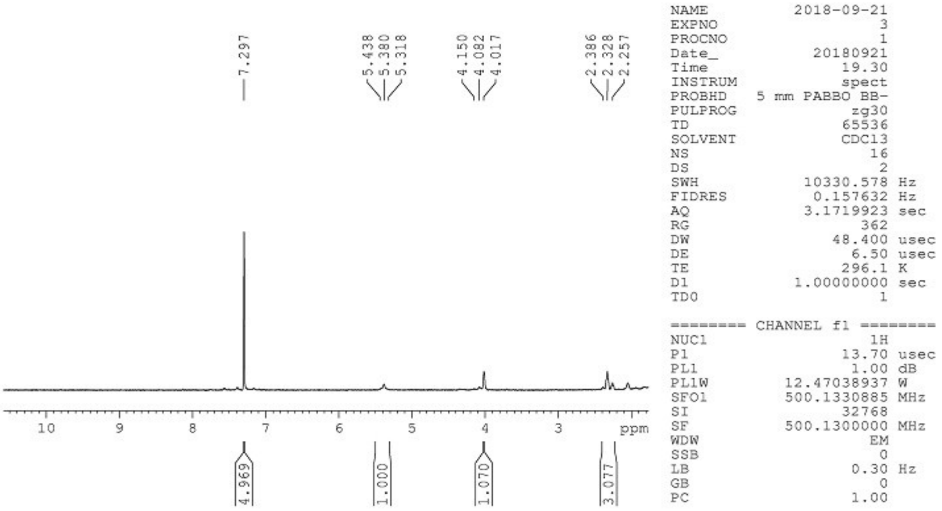
Fig. S1 ^{1}H NMR of **DABE**.

2. General procedure for asymmetric epoxidation of alkenes in water.

The selected catalyst (0.5 mol% of substrate based on chromium content) and PhI(OAc)$_2$ (0.625 mmol, 0.20 g) were stirred in water (1.0 mL) for 30 min at 25 °C. The solution was initially dark green, and then became orange-yellow. Then unfunctionalized alkene (0.25 mmol) was added. The resulting mixture was stirred at room temperature until the reaction was judged to be complete based on TLC analysis. Catalyst was then separated as precipitation by heating the reaction mixture to above 54 °C, and washed with *n*-hexane (3×5.0 mL). Reaction solution was extracted with dichloromethane (3×0.5 mL). Notably, this extraction process was expected in large-scale industrial processes, in which the oily product phase could be directly separated from water. Combined organic phase was dried with anhydrous Na$_2$SO$_4$. After the evaporation of solvent, the residue was further purified by column chromatography on silica gel (Acros, 40–60 µm, 60 Å, eluent: petroleum ether/ethyl acetate = 5/1 (v/v)) to afford the pure chiral epoxides. All products were identified by ^{1}H NMR spectra. Ee values of corresponding chiral epoxides were determined by a 6890N gas chromatograph (Agilent Co.) equipped with a capillary column (HP19091G-B213, 30 m × 0.32 mm × 0.25 μm) and a FID detector.

β-Methylstyrene epoxide: The product has been identified by ^{1}H NMR spectrum (see Fig. S2). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.2$ (s, 5 H, Ar*H*), 5.3 (m, 1 H, Ar-C*H*), 4.1 (m, 1 H, CH-C*H*-CH_3), 2.3 ppm (m, 3 H, CH-CH_3). Ee value of β-methylstyrene epoxide was determined by GC using nitrogen as the carrier gas at a gas flow rate of 30 mL/min, an injector temperature and a detector temperature of 250 °C, and a column temperature of 100 °C. Major enantisomer: $t_{R,\ R} = 13.4$ min, minor enantisomer $t_{S,\ S} = 12.8$ min (see Fig. S3-S6).



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RG                   362
DW                48.400 usec
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D1            1.00000000 sec
TD0                    1

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Fig. S2 ^{1}H NMR of β-methylstyrene epoxide.

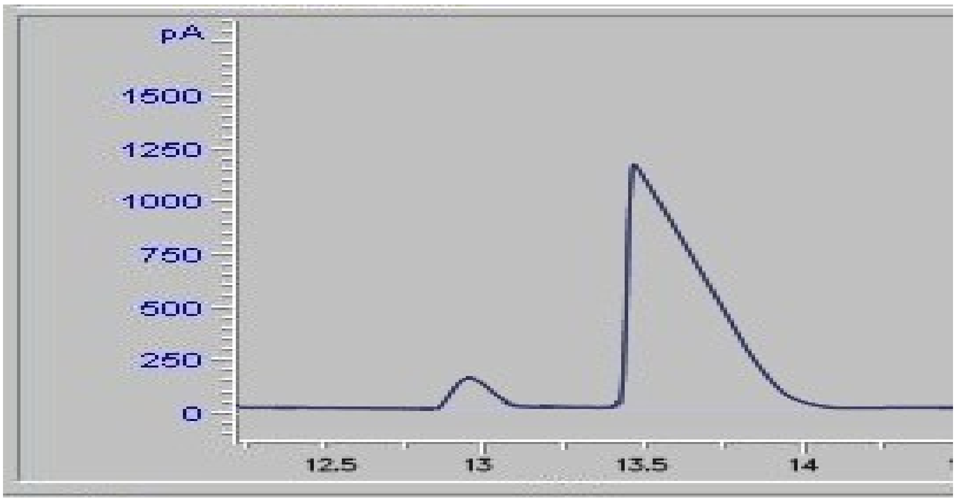


Fig. S3 GC of β-methylstyrene epoxide obtained over **PN$_{84}$(*IL*-C)$_{3}$** (ee value = 94%).

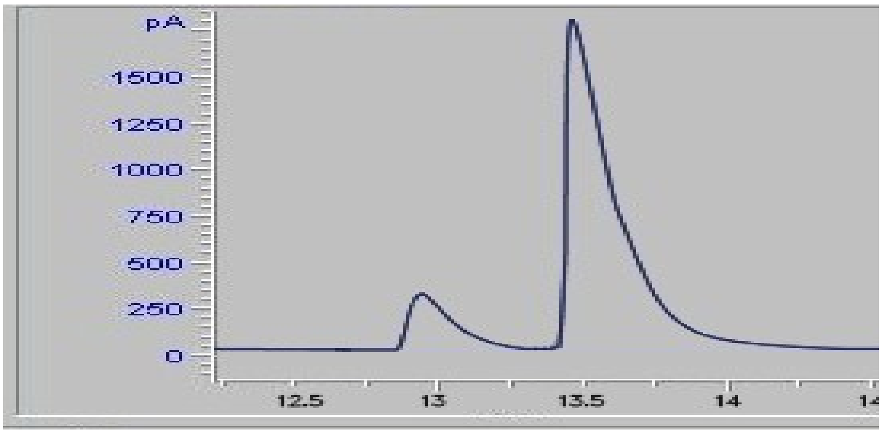


Fig. S4 GC of β-methylstyrene epoxide obtained over **PN$_{84}$C$_{3}$** (ee value = 93%).

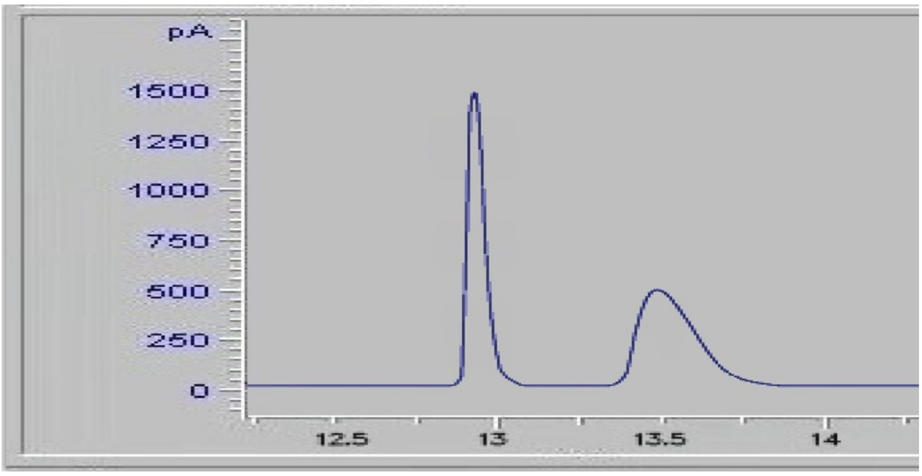


Fig. S5 GC of β-methylstyrene epoxide obtained over neat-C (ee value = 29%).

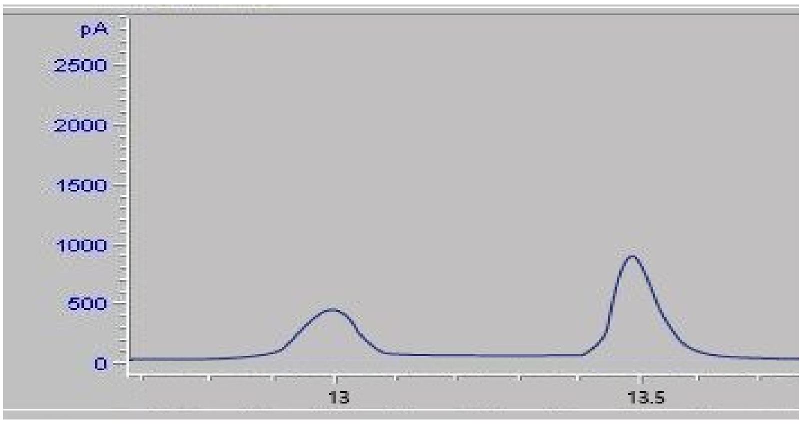
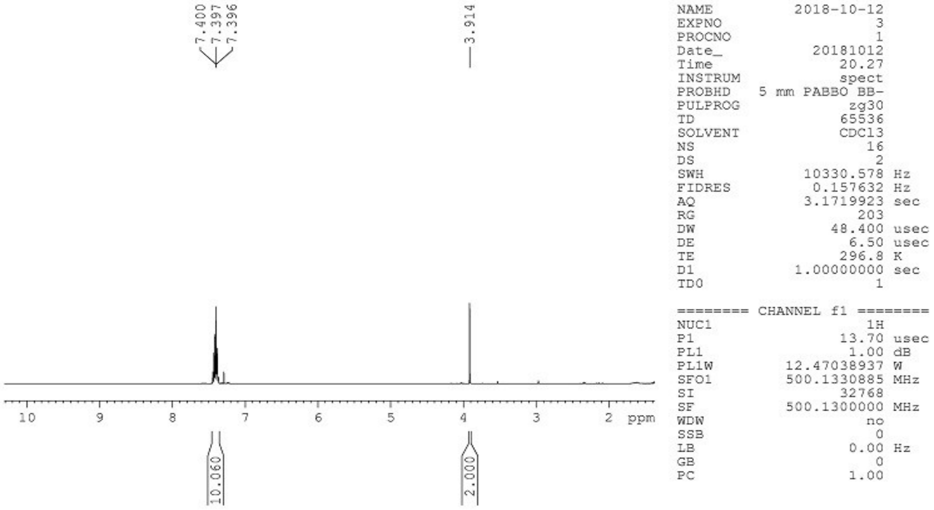


Fig. S6 GC of β-methylstyrene epoxide obtained over *IL*/Cr(salen) (ee value = 46%).

*Trans-stilbene epoxid*e: The product has been identified by ^{1}H NMR spectrum (see Fig. S7). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.3 (m, 10 H, Ar*H*), 3.9 ppm (s, 2 H, Ar-C*H*-C*H*-Ar). Ee value of *trans*-stilbene epoxide was determined by GC using nitrogen as the carrier gas at a gas flow rate of 30 mL/min, an injector temperature and a detector temperature of 250 °C, and a column temperature of 100 °C. Major enantisomer: $t_{R,\ R}$ = 26.1 min, minor enantisomer $t_{S,\ S}$ = 25.0 min (see Fig. S8-S11).



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FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                   203
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DE                  6.50 usec
TE                 296.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
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SFO1         500.1330885 MHz
SI                 32768
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Fig. S7 ^{1}H NMR of *trans*-stilbene epoxide.

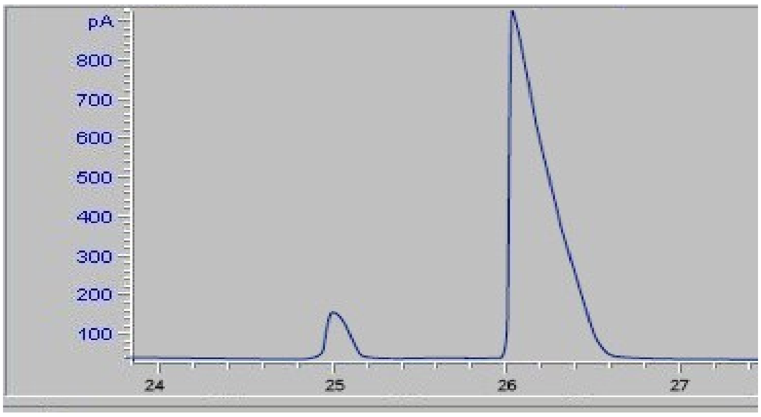

Fig. S8 GC of *trans*-stilbene epoxide obtained over **PN_{84}(*IL*-C)$_3$** (ee value = 92%).

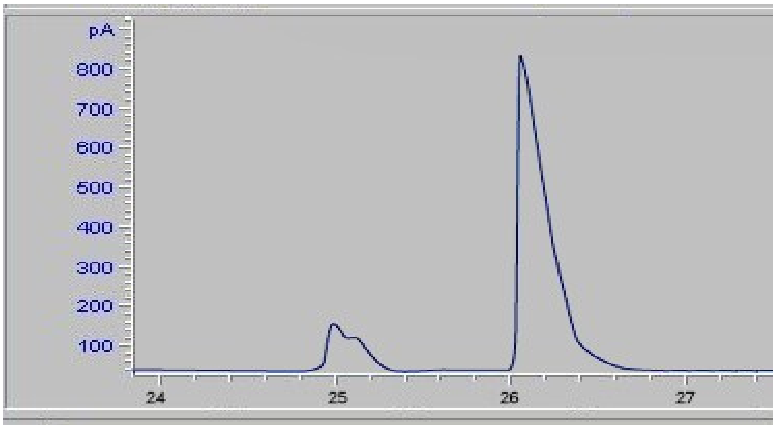

Fig. S9 GC of *trans*-stilbene epoxide obtained over **$PN_{84}C_3$** (ee value = 91%).

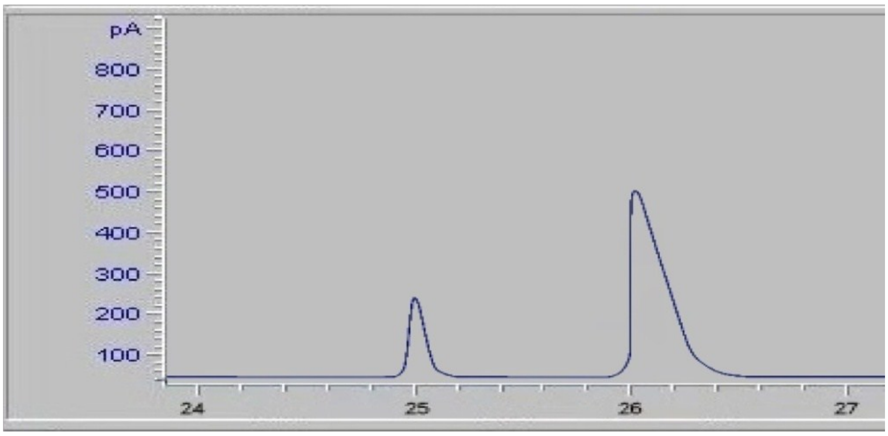

Fig. S10 GC of trans-stilbene epoxide obtained over neat-C (ee value = 31%).

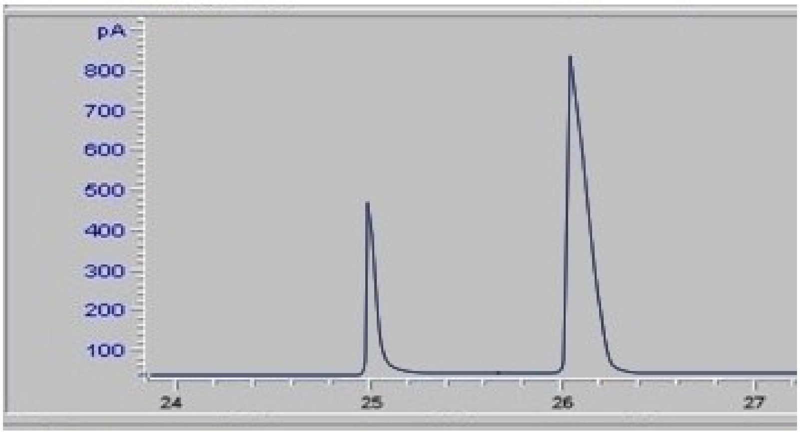

Fig. S11 GC of *trans*-stilbene epoxide obtained over *IL*/Cr(salen) (ee value = 42%).

Styrene epoxide: The product has been identified by ^{1}H NMR spectrum (see Fig. S12). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.3$ (m，5 H, Ar*H*), 3.9 (m, 1 H, Ar-C*H*), 3.1 (m, 1 H, CH-CH_2), 2.8 ppm (m, 1 H, CH-CH_2). Ee value of styrene epoxide determined by GC using nitrogen as the carrier gas at a gas flow rate of 30 mL/min, an injector temperature and a detector temperature of 250 °C, and a column temperature of 100 °C. Major enantisomer: $t_{R,\ R}$ =8.2 min, minor enantisomer: $t_{S,\ S}$ = 7.9 min (see Fig. S13-S16).

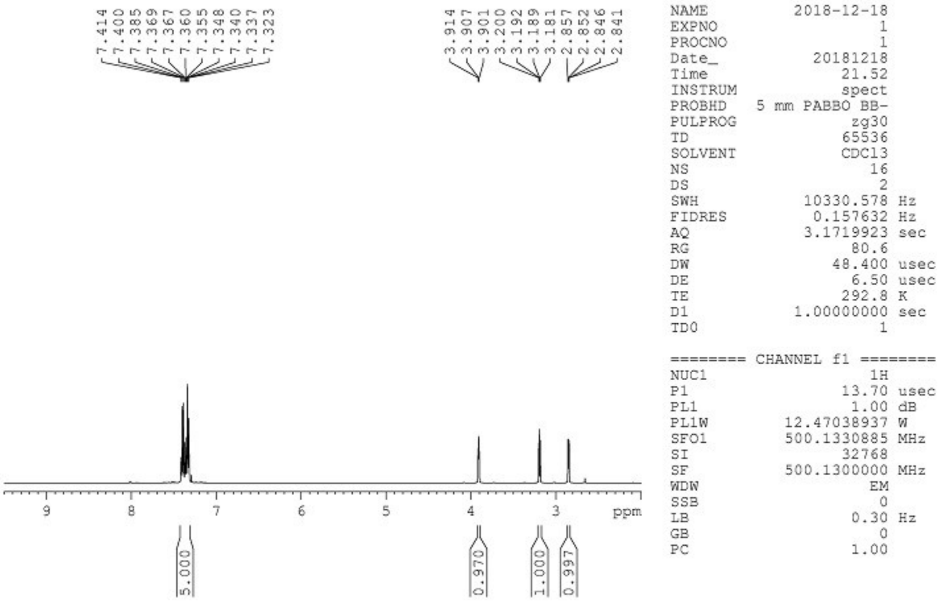

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Fig. S12 ^{1}H NMR of styrene epoxide.

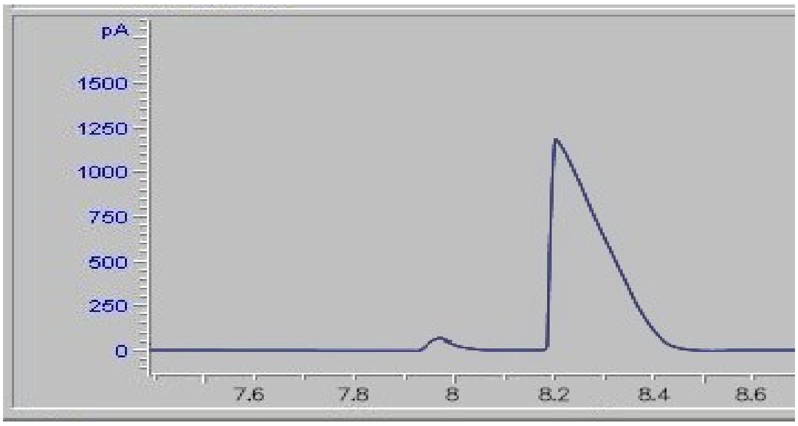

Fig. S13 GC of styrene epoxide obtained over **PN$_{84}$(*IL*-C)$_3$** (ee value = 99%).

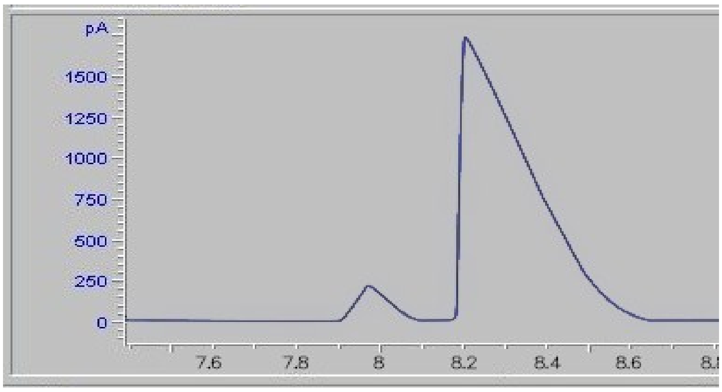

Fig. S14 GC of styrene epoxide obtained over **PN$_{84}$C$_3$** (ee value = 93%).

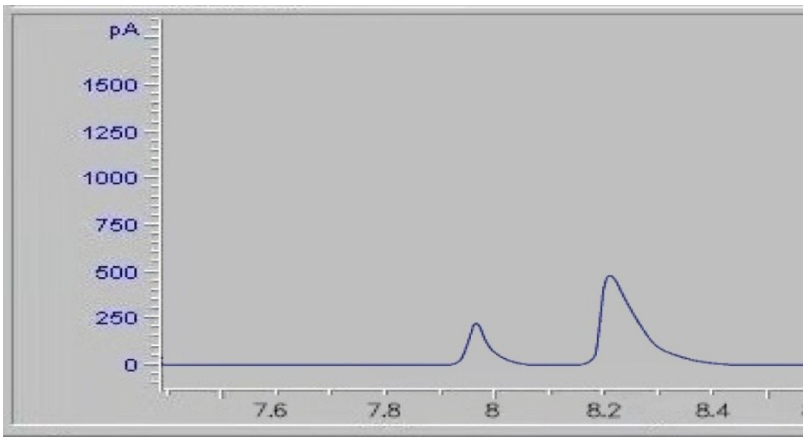

Fig. S15 GC of styrene epoxide obtained over neat-C (ee value = 38%).

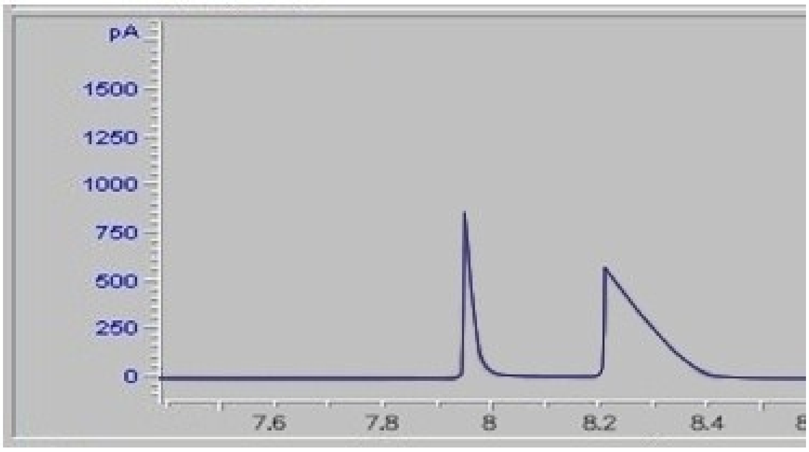

Fig. S16 GC of styrene epoxide obtained over *IL*/Cr(salen) (ee value = 53%).

Indene epoxide: The product has been identified by ^{1}H NMR spectrum (see Fig. S17). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.2 (m, 4 H, Ar*H*), 4.0 (m, 2 H, Ar-C*H*-C*H*-CH_2), 2.3 ppm (m, 2 H, Ar-CH_2). Ee value of indene epoxide was determined by GC using nitrogen as the carrier gas at a gas flow rate of 30 mL/min, an injector temperature and a detector temperature of 250 °C. The column temperature was programmed from 80 to 180 °C with 5 °C.min^{-1}. Major enantisomer: $t_{R,\ R}$ = 12.9 min, minor enantisomer: $t_{S,\ S}$ = 12.2 min (see Fig. S18-S21).

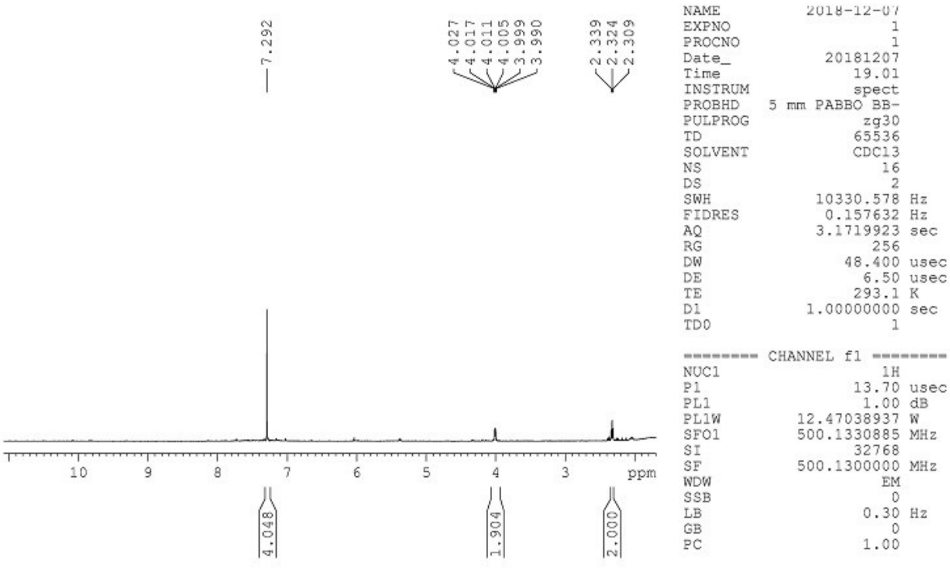

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Fig. S17 ^{1}H NMR of indene epoxide.

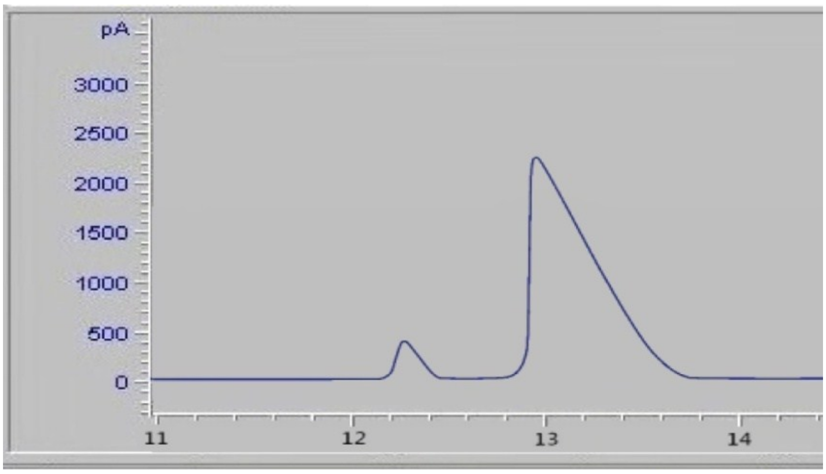


Fig. S18 GC of indene epoxide obtained over **$PN_{84}(\textit{IL}\text{-}C)_3$** (ee value = 94%).

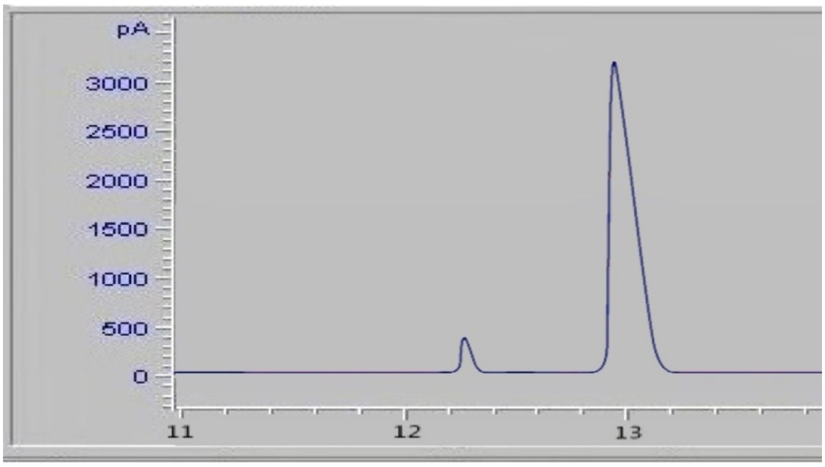


Fig. S19 GC of indene epoxide obtained over **$PN_{84}C_3$** (ee value = 92%).

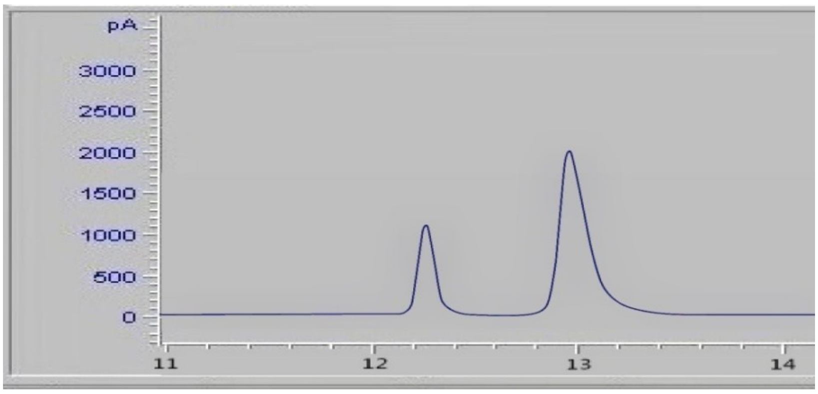


Fig. S20 GC of indene epoxide obtained over neat-C (ee value = 37%).

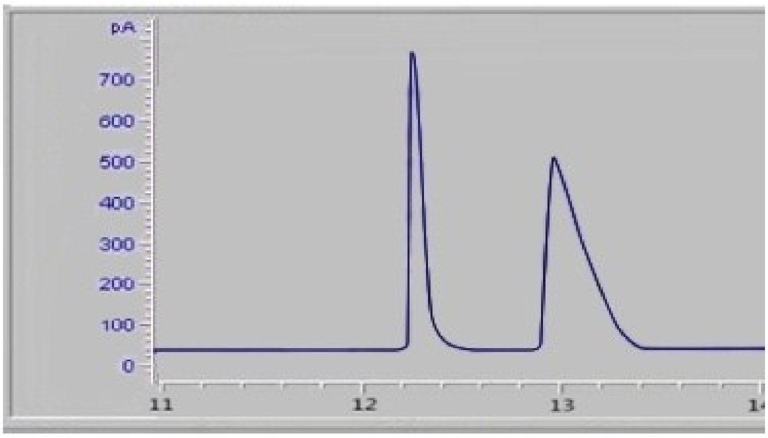
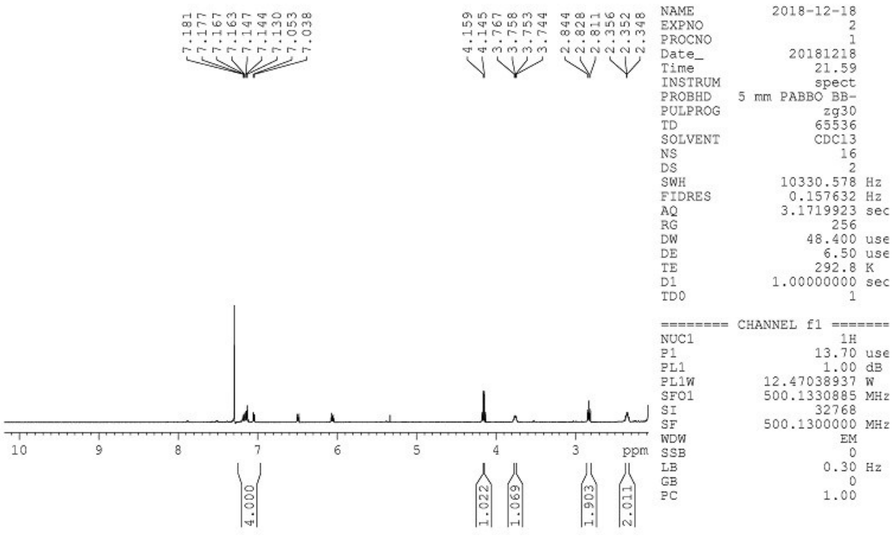


Fig. S21 GC of indene epoxide obtained over *IL*/Cr(salen) (ee value = 56%).

1,2-Dihydronaphthalene epoxide: The product has been identified by ^{1}H NMR spectrum (see Fig. S22). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 7.1$ (m, 4 H, Ar*H*), 4.1 (m, 1 H, Ar-C*H*-CH), 3.7 (m, 1 H, CH-C*H*-CH$_2$), 2.8 (m, 2 H, Ar-C*H*$_2$), 2.3 ppm (m, 2 H, CH$_2$-C*H*$_2$-CH). Ee value of 1,2-dihydronaphthalene epoxide was determined by GC using nitrogen as the carrier gas at a gas flow rate of 30 mL/min, an injector temperature and a detector temperature of 250 °C. The column temperature was programmed from 80 to 180 °C with 5 °C.min^{-1}. Major enantisomer: $t_{R,\,R} = 24.3$ min, minor enantisomer: $t_{S,\,S} = 23.4$ min (see Fig. S23-S26).



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TE                  292.8 K
D1             1.00000000 sec
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Fig. S22 ^{1}H NMR of 1, 2-dihydronaphthalene epoxide.

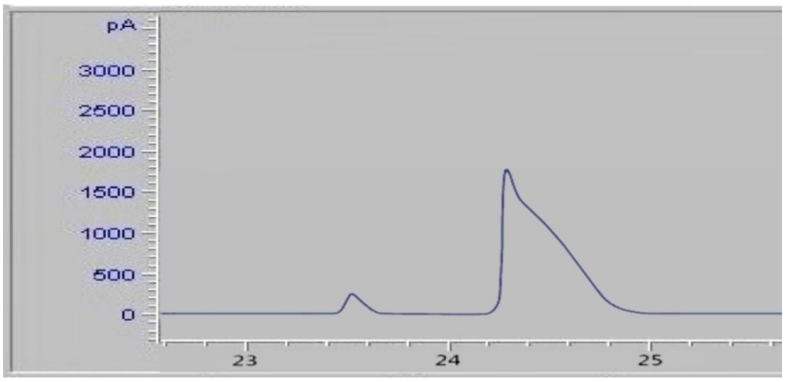

Fig. S23 GC of 1, 2-dihydronaphthalene epoxide obtained over **PN$_{84}$(*IL*-C)$_3$** (ee value = 93%).

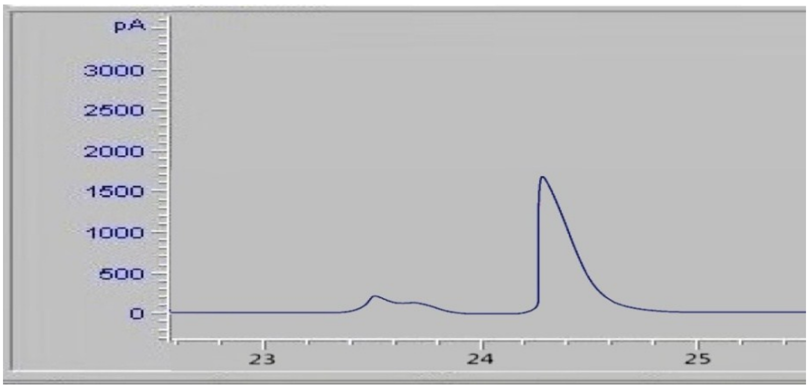

Fig. S24 GC of 1, 2-dihydronaphthalene epoxide obtained over **PN$_{84}$C$_3$** (ee value = 93%).

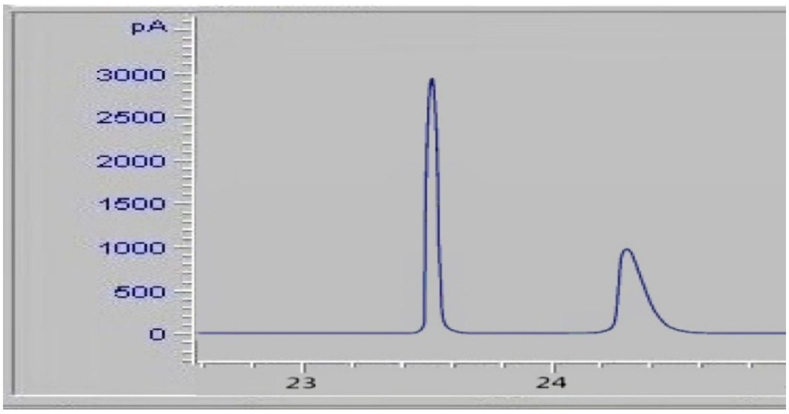

Fig. S25 GC of 1, 2-dihydronaphthalene epoxide obtained over neat-C (ee value = 44%).

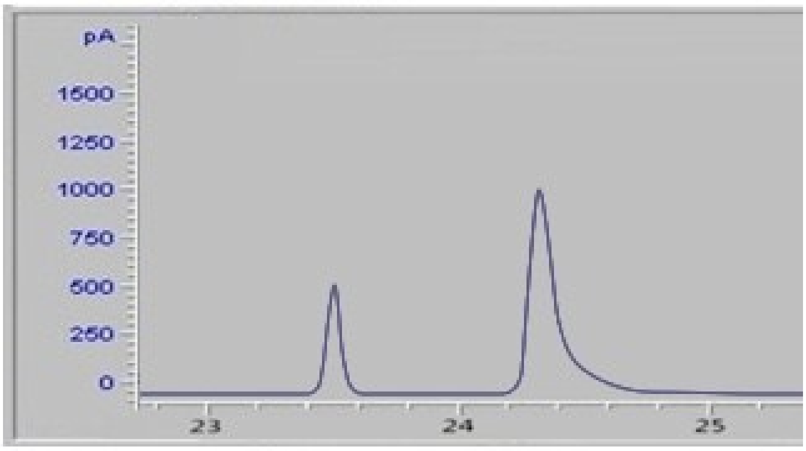

Fig. S26 GC of 1, 2-dihydronaphthalene epoxide obtained over *IL*/Cr(salen) (ee value = 49%).