Supporting Information

Imidazolium-based ionic liquids functionalized chiral metal-organic framework as efficient catalyst for the asymmetric catalytic sulfoxidation

Shiye Li[a, b], Yudan Chai[b] and Jian Zhang*[b]

[a] School of Chemical Engineering, Shanxi Institute of Science and Technology,No.666, Lingqin Line, Jincheng, 048000, China.

[b] School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan, 030006 China.

*Corresponding authors: zhangjian@sxu.edu.cn

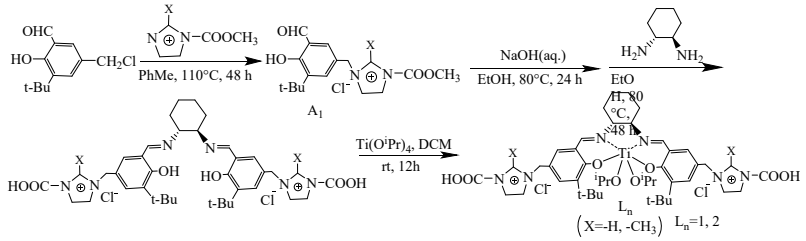
Contents

1. Preparation of ionic liquid-functionalized *IL*-Ti(salen)-derived dicarboxylic linkers (Ln=1, 2)

Ionic liquid-functionalized salen-derived dicarboxylic linkers of *IL*-Ti(salen)-n (Ln=1, 2) were synthesized by Schiff base condensation reactions between (R, R)-cyclohexanediamine and corresponding 3-(tert-tutyl)-2-hydroxybenzaldehyde derivatives with pendant ionic liquid functionalised carboxylic acid groups (Ln=1, 2), followed by metalation with $Ti(O^iPr)_4$ to afford *IL*-Ti(salen)-n (Ln=1, 2) (Scheme S1). The 3-(tert-tutyl)-2-hydroxybenzaldehyde derivatives were synthesized by carbon-nitrogen coupling reaction between the 3-(tert-butyl)-5-(chloromethyl)-2-hydroxybenzaldehyde and imidazole esters, followed by hydrolysis of the esters.[1] The specific experimental steps are as follows: firstly, the 1H-imidazole-1-carboxylate (5.0 mmol) in toluene (25 mL) was mixed with 3-tert-butyl-5-chloromethyl-2-hydroxy-benzaldehyde (5.5 mmol, 1.13 g) in toluene (25 mL) under Ar atmosphere. The mixture was refluxed for 48 h and then concentrated in vacuum. The crude product was washed with ethyl acetate (15 × 3 mL) to remove the unreacted 1H-imidazole-1-carboxylate and 3-tert-butyl-5-chloromethyl-2-hydroxy-benzaldehyde. After being dried in vacuo, the compound (A_1) was obtained as a yellow oily liquid. A_1 (n=1) Calc. for ($C_{17}H_{21}ClN_2O_4$): C: 57.87, H: 6.00, Cl: 10.05, N: 7.94, O: 18.14%. Found: C: 57.80, H: 6.12, Cl: 10.01, N: 7.96, O: 18.10%.

Next, a mixture of A_1 (12.8 mmol), 6 M NaOH solution (80 mL) and EtOH (150 mL) were added sequentially to a 250 mL round-bottomed flask and the mixture was refluxed at 80 °C for 24 h. After removing EtOH in vacuo, the residue was diluted with H_2O and washed with CH_2Cl_2 for 3 times. pH value of the solution was adjusted to 3 by the addition of concentrated HCl. The obtained suspension was filtered. Filter cake was washed with water (10 mL × 3) and then dried in vacuo at 80 °C overnight, yielding intermediates as the brown solid. The brown intermediates, (1R, 2R)-cyclohexane-1,2-diamine (0.39 g, 3.4 mmol) and EtOH (90 mL) were mixed sequentially and added to the reaction flask under Ar atmosphere. The reaction mixture was stirred at 80 °C for 24 h and cooled to room temperature. The resulting solid was collected by filtration, washed with small amount of EtOH and dried in air. Finally, the above obtained solids, $Ti(O^iPr)_4$ (0.06 g, 0.22 mmol) and CH_2Cl_2 (30 mL) were added to a 3-necked round-bottom flask under Ar atmosphere, and stirred at room temperature for 12 h. The resulting yellow solid was dissolved in dichloromethane (10 mL),

and treated with water (2 mL) to remove any traces of TiO_2 by filtration. The product was dried in vacuum at 40 °C overnight, giving yellow powders of *IL*-Ti(salen)-derived dicarboxylic linkers (L_1). The typical *IL*-Ti(salen) linker (L_1) Anal (%). Calc. for ($C_{44}H_{60}C_{l2}N_6O_8Ti$): C: 57.46, H: 6.58, Cl: 7.71, N: 9.14, O: 13.92, Ti: 5.20. Found: C: 57.43, H: 6.61, Cl: 7.68, N: 9.19, O: 13.85, Ti: 5.28. FT-IR (KBr): γmax/cm^{-1} 3431, 2964, 2858, 1739, 1650, 1443, 1363, 1227, 1078, 1019, 889, 815, 754, 692, 646, 551. The synthesis of L_2 is similar to that of L_1.



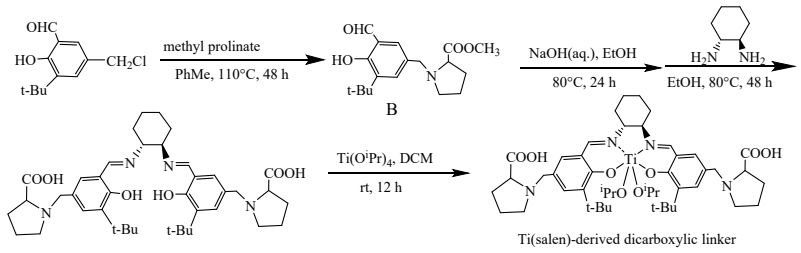
Scheme S1 The synthesis of *IL*-Ti(salen)-derived dicarboxylic linkers (L_n=1, 2)

2. Preparation of Ti(salen)-derived dicarboxylic linker without ionic liquid modification

Ti(salen)-derived dicarboxylic linker was synthesized by Schiff base condensation reactions between (R, R)-cyclohexanediamine and corresponding 3-(tert-tutyl)-2-hydroxybenzaldehyde derivatives with pendant proline methyl ester, followed by metalation with $Ti(O^iPr)_4$ to afford Ti(salen)-derived dicarboxylic linker (Scheme S2). The 3-(tert-tutyl)-2-hydroxybenzaldehyde derivatives were synthesized by carbon-nitrogen coupling reaction between the 3-(tert-butyl)-5-(chloromethyl)-2-hydroxybenzaldehyde and proline methyl ester, followed by hydrolysis of the esters.[2] Firstly, proline methyl ester (0.65g, 5.0 mmol) in toluene (25 mL) was mixed with 3-tert-butyl-5-chloromethyl-2-hydroxy-benzaldehyde (1.13 g, 5.5 mmol) in toluene (25 mL) under Ar atmosphere. The mixture was refluxed for 48 h and then concentrated in vacuum. The crude product was washed with ethyl acetate (15 × 3 mL) to remove the unreacted proline methyl ester and 3-tert-butyl-5-chloromethyl-2-hydroxy-benzaldehyde. After being dried in vacuo, the compound (B) was obtained as a yellow oily liquid (1.60 g, yield: 90%). B Calc. for ($C_{18}H_{25}NO_4$): C: 67.69, H: 7.89, N: 4.39, O: 20.04%. Found: C: 67.67, H: 7.86, N: 4.35, O: 20.01%.

Next, a mixture of B (4.088 g, 12.8 mmol), 6 M NaOH solution (80 mL) and EtOH (200 mL) was refluxed for 24 h. After removing EtOH in vacuo, the residue was diluted with H_2O and washed with CH_2Cl_2 for 3 times. pH value of the solution was adjusted to 3 by the addition of concentrated HCl. The obtained suspension was filtered, and filter cake was washed with water (10 mL × 3) and then dried in vacuo at 80 °C overnight, yielding intermediate as the brown solid (3.88 g, yield: 95%). (1R, 2R)-cyclohexane-1,2-diamine (0.39 g, 3.4 mmol) in EtOH (40 mL) was mixed with brown intermediate (2.077 g, 6.8 mmol) in EtOH (45 mL) under Ar atmosphere. The reaction mixture was

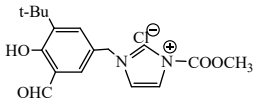
stirred at 80 °C for 24 h and cooled to room temperature. The resulting solid was collected by filtration, washed with small amount of EtOH and dried in air. Finally, the above obtained solid, $Ti(O^iPr)_4$ (0.06 g, 0.22 mmol) and CH_2Cl_2 (30 mL) were added to a three-necked round-bottom flask under Ar atmosphere. The mixture was stirred at room temperature for 12 h. The resulting yellow solid was dissolved in dichloromethane (10 mL), and treated with water (2 mL) to remove any traces of TiO_2 by filtration. The product was dried in vacuum at 40 °C overnight, giving yellow powders of Ti(salen)-derived dicarboxylic linker. FT-IR spectrum for Ti(salen) linker: γmax/cm^{-1} 3431, 2964, 2858, 1739, 1650, 1443, 1376, 1294, 1214, 1078, 903, 876, 782, 646,551.



Scheme S2 The synthesis of Ti(salen)-derived dicarboxylic linker

3. Identification of the intermediates and asymmetric oxidation product.

3.1 Characterization of A_1



The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 1: 1). Depurated product A_1 was identified by ^1H NMR and ^{13}C NMR spectrum (see Fig. S1 and 2). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 11.86 (s, 1 H, Ar-O*H*), 9.84 (s, 1 H, Ar-C*H*O), 7.63-7.37 (s, 2 H, Ar*H*), 7.17-7.14 (m, 3 H, N-C*H*=CH-N), 6.94 (s, 1 H, N-C*H*=N), 5.13 (s, 2 H, Ar-CH_2), 1.42 (s, 12 H, Ar-C(CH_3)$_3$ and OCH_3). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 196.79, 161.13, 139.51, 137.22, 133.05, 130.29, 129.72, 126.80, 120.47, 119.13, 77.35, 77.10, 76.84, 50.21, 35.00, 34.94, 29.07.

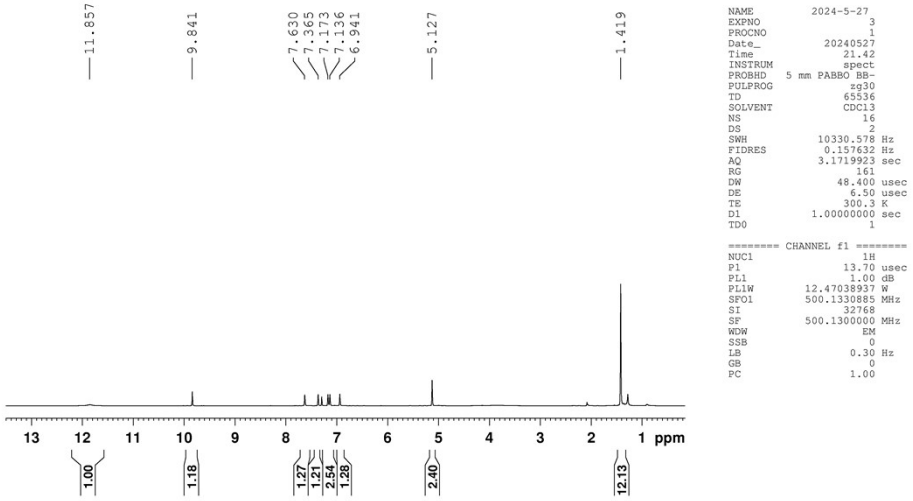


Fig. S1 ^{1}H NMR of A_1

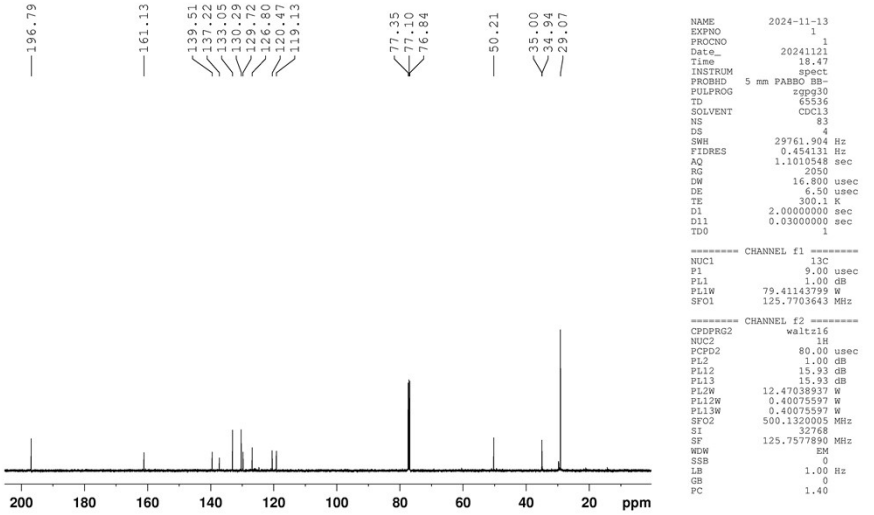
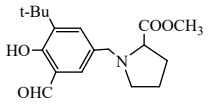


Fig. S2 ^{13}C NMR of A_1

3.2 Characterization of B



The crude product B was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5: 1). Depurated product B was identified by ^{1}H NMR and ^{13}C NMR (see Fig. S3 and 4). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 11.81 (s, 1 H, Ar-O*H*), 9.91 (s, 1 H, Ar-C*H*O), 7.56-7.45 (s, 2 H, Ar*H*), 5.39-5.36 (s, 2 H, Ar-CH_2), 4.70 (s, 1 H, NC*H*COOCH_3), 2.39-2.36 (m, 2 H, NCH_2CH_2), 2.27-2.24 (m, 2 H, CHCH_2CH_2), 2.04-2.03 (m, 2 H, CH_2CH_2CH_2), 1.65 (s, 3 H, COOCH_3), 1.45-1.28 (s, 9 H, Ar-(CH_3)$_3$). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 196.79, 161.13, 139.51, 137.22, 133.05, 130.29, 129.71, 126.80, 120.47, 119.13, 77.35, 77.10, 76.84, 50.21, 34.94, 31.90, 29.67, 29.06.

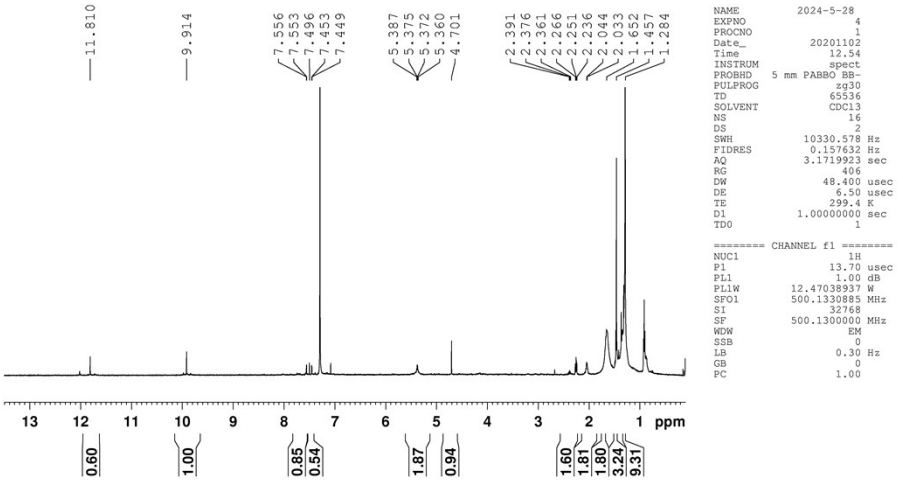


Fig. S3 ^{1}H NMR of B

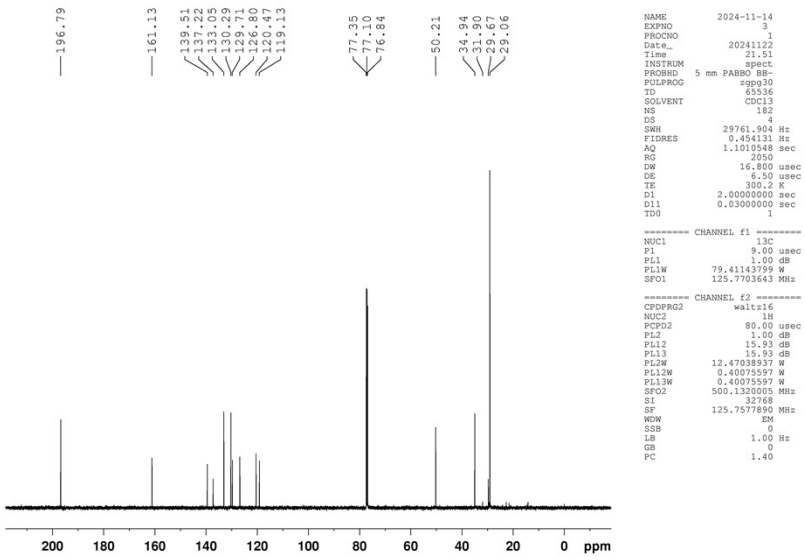


Fig. S4 ^{13}C NMR of B

3.3 Characterization of asymmetric oxidation products

Methyl phenyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 8: 1).The product has been identified by ^{1}H NMR and ^{13}C NMRspectrum (see Fig. S5 and 6). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.98-7.59 (m, 5 H, Ar*H*), 3.08 (s, 3 H, -SCH_3). ^{13}C NMR ($CDCl_3$, 500 MHz) δ (ppm): 145.73, 131.05, 129.37, 123.51, 43.98. ee 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 = 6.06 min and minor enantiomer t_S = 7.37 min (see Fig. S7- S10).

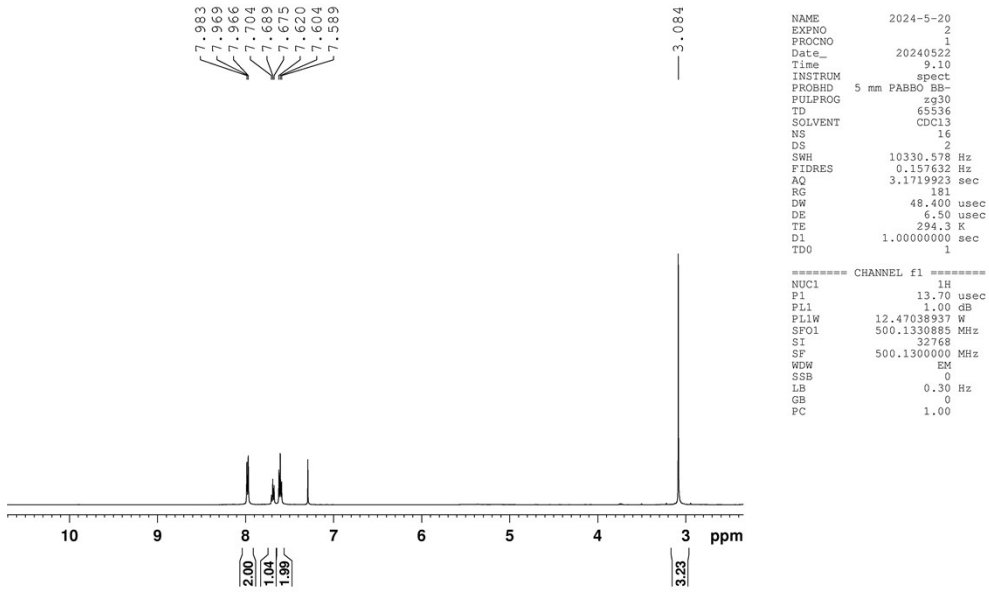


Fig. S5 ^{1}H NMR of methyl phenyl sulfoxide

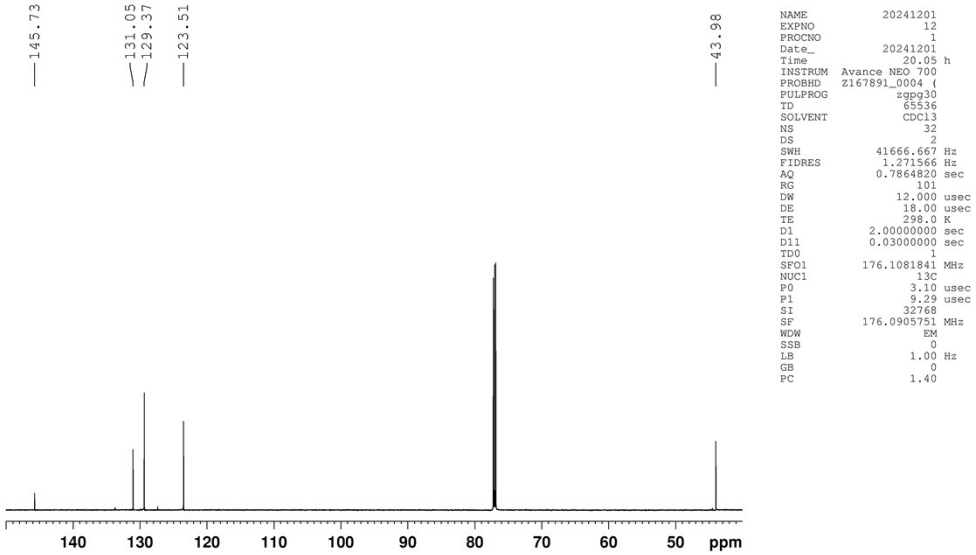


Fig. S6 ^{13}C NMR of methyl phenyl sulfoxide

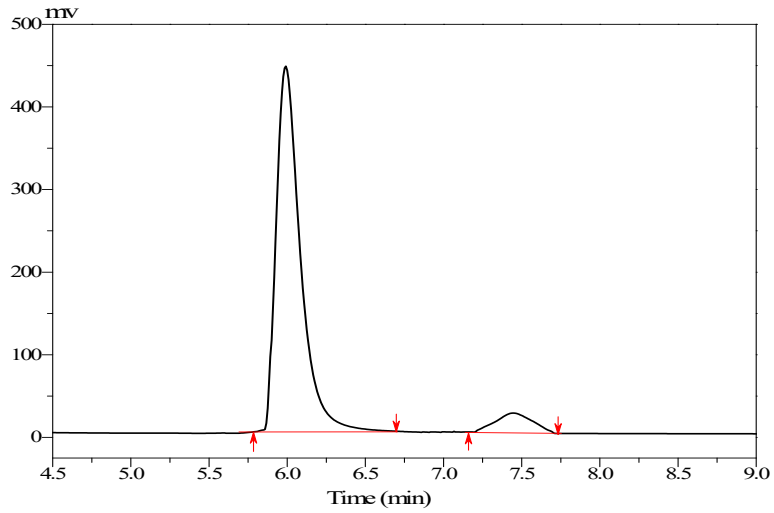


Fig. S7 HLPC of methyl phenyl sulfoxide obtained over Ti(salen) complex (ee value 86%)

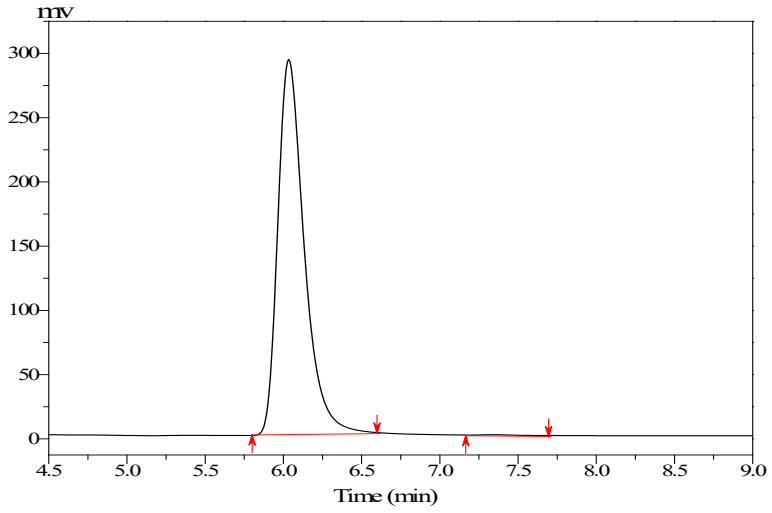


Fig. S8 HLPC of methyl phenyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value >99%)

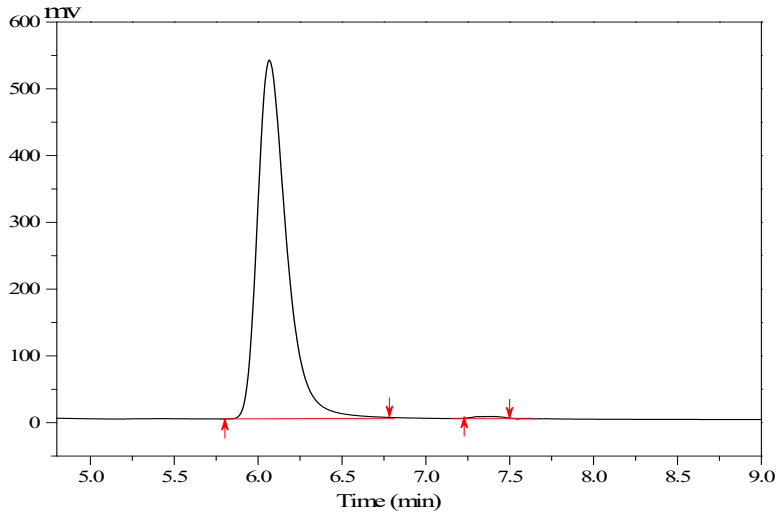


Fig. S9 HLPC of methyl phenyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-2** (ee value 99%)

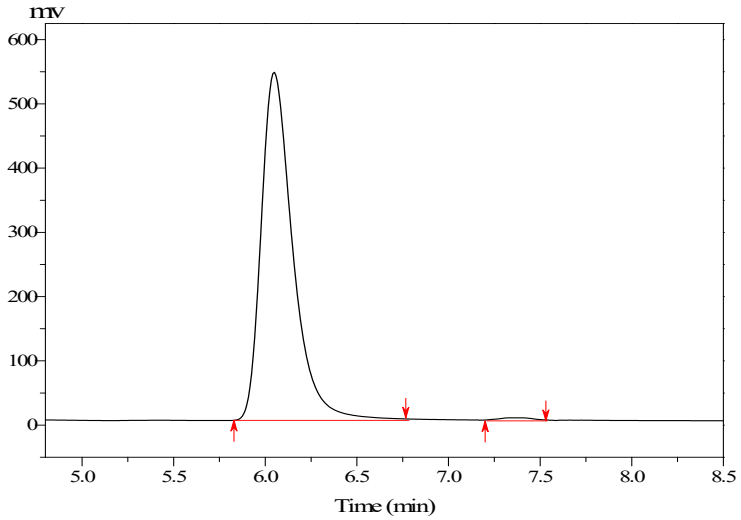


Fig. S10 HLPC of methyl phenyl sulfoxide obtained over **Ti(salen) CMOF** (ee value 98%)

Ethyl phenyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 8: 1). The product has been identified by ^{1}H NMR and ^{13}C NMRspectrum (see Fig. S11 and 12). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.61-7.49 (m, 5 H, Ar*H*), 2.92-2.74 (m, 2 H, -C*H*$_2$-CH$_3$), 1.20-1.17 (t, 3 H, -CH$_2$-C*H*$_3$). ^{13}C NMR ($CDCl_3$, 500 MHz) δ (ppm): 143.35, 130.94, 129.16, 124.20, 50.32, 5.98. ee 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 = 5.72 min and minor enantiomer t_S = 7.28 min (see Fig. S13).

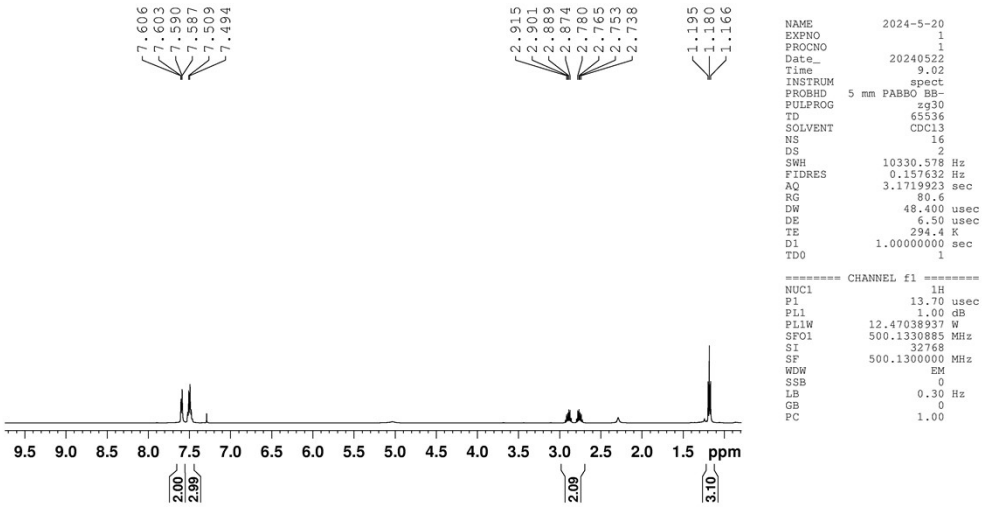


Fig. S11 ^{1}H NMR of ethyl phenyl sulfoxide

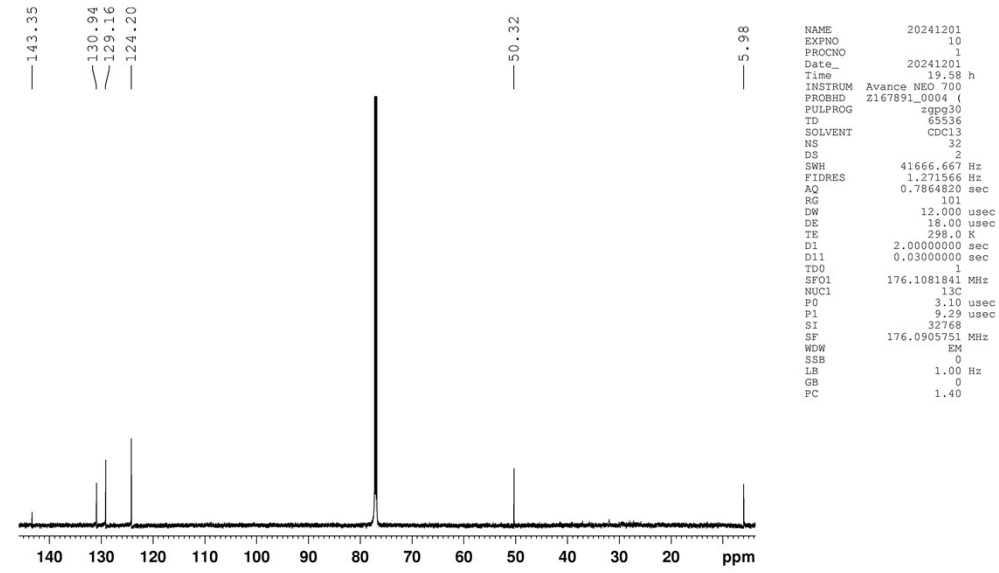


Fig. S12 ^{13}C NMR of ethyl phenyl sulfoxide

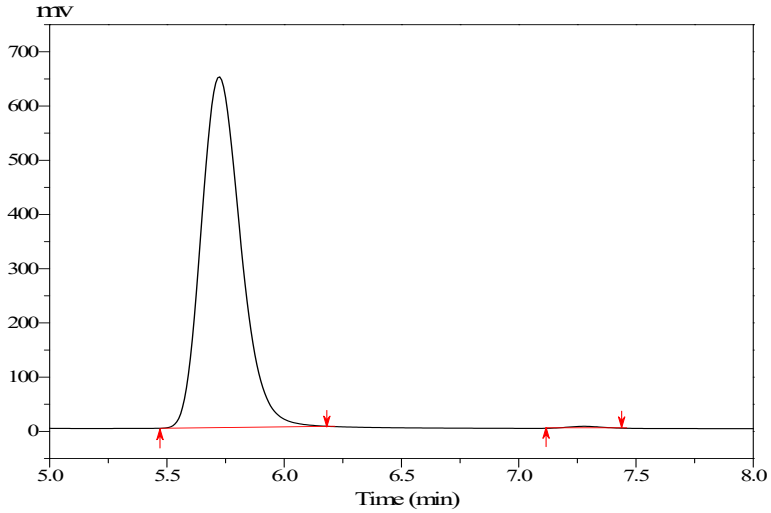


Fig. S13 HLPC of ethyl phenyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value 99%)

n-Butyl phenyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10: 1). The product has been identified by ^{1}H NMR and ^{13}C NMR spectrum (see Fig. S14 and 15). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.62-7.48 (m, 5 H, Ar*H*), 2.79-2.76 (m, 2 H, -C*H*$_2$-CH$_2$-CH$_2$-CH$_3$), 1.74-1.24 (m, 4 H, -CH$_2$-C*H*$_2$-C*H*$_2$-CH$_3$), 0.91-0.88 (t, 3 H, -CH$_2$-CH$_2$-CH$_2$-C*H*$_3$). ^{13}C NMR ($CDCl_3$, 500 MHz) δ (ppm): 143.35, 130.94, 129.16, 124.20, 50.12, 26.28, 18.07, 9.73. ee 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 = 5.46 min and minor enantiomer t_S = 6.34 min (see Fig. S16).

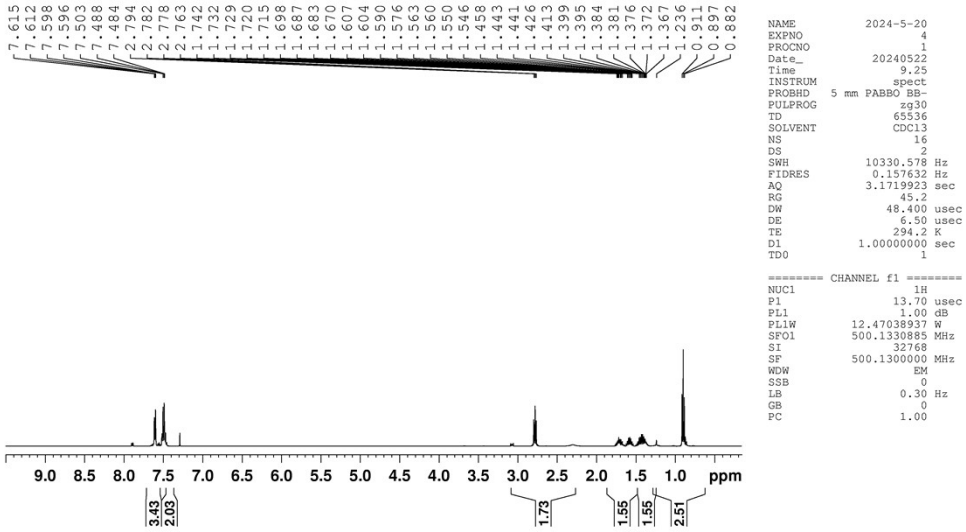


Fig. S14 ^{1}H NMR of n-butyl phenyl sulfoxide

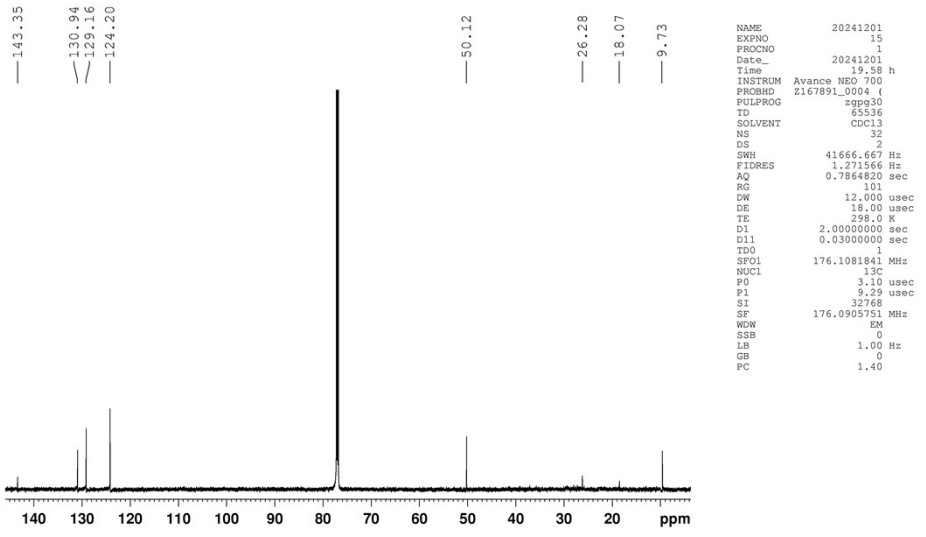


Fig. S15 ^{13}C NMR of n-butyl phenyl sulfoxide

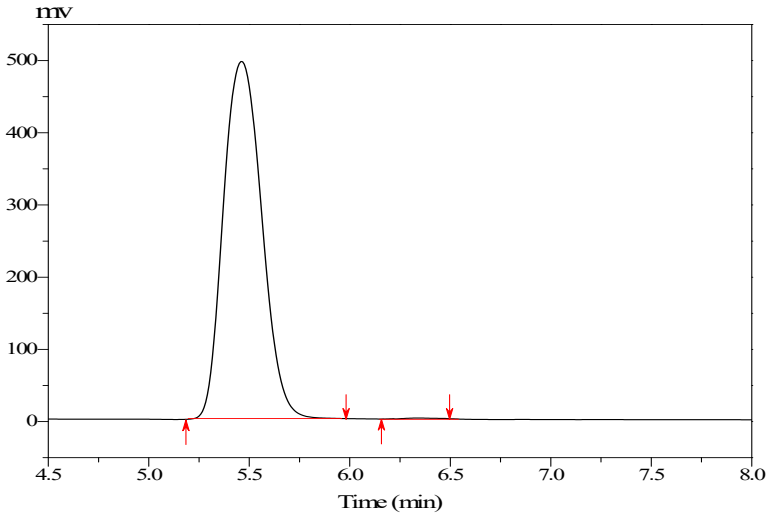


Fig. S16 HLPC of n-butyl phenyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value >99%)

4-Methylphenyl methyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10: 1). The product has been identified by ^{1}H NMR and ^{13}C NMR spectrum (see Fig. S17 and 18). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.57-7.35 (m, 4 H, Ar*H*), 2.73 (s, 3 H, S-CH_3), 2.44 (s, 3 H, Ar-CH_3). ^{13}C NMR ($CDCl_3$, 500 MHz) δ (ppm): 142.53, 141.54, 130.05, 123.57, 44.01, 29.71. ee 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 = 9.05 min and minor enantiomer t_S = 16.80 min (see Fig. S19).

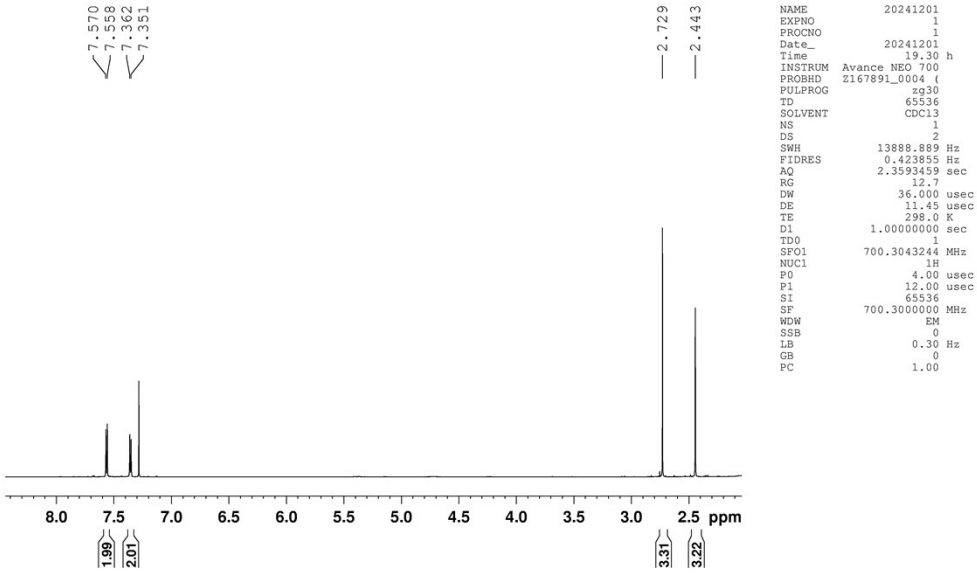


Fig. S17 ^{1}H NMR of 4-methylphenyl methyl sulfoxide

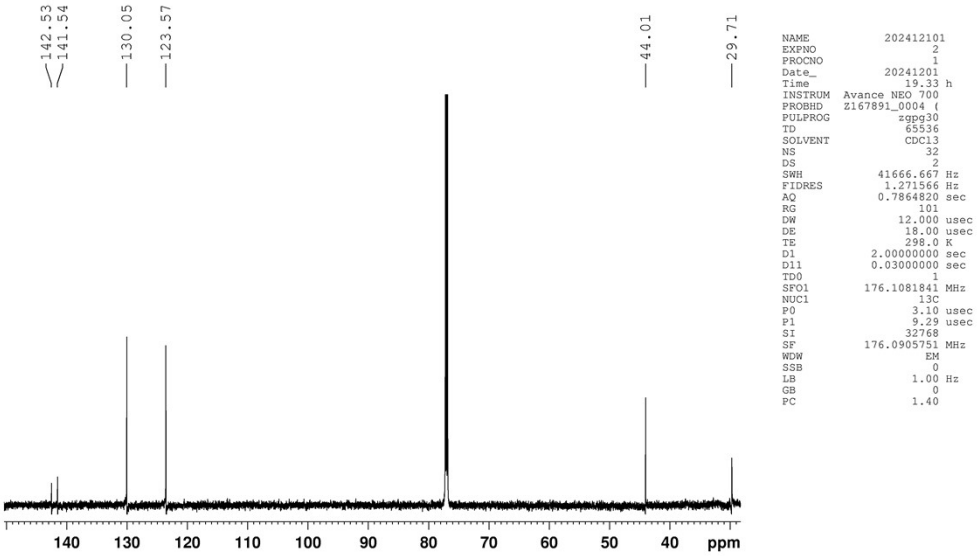


Fig. S18 ^{13}C NMR of 4-methylphenyl methyl sulfoxide

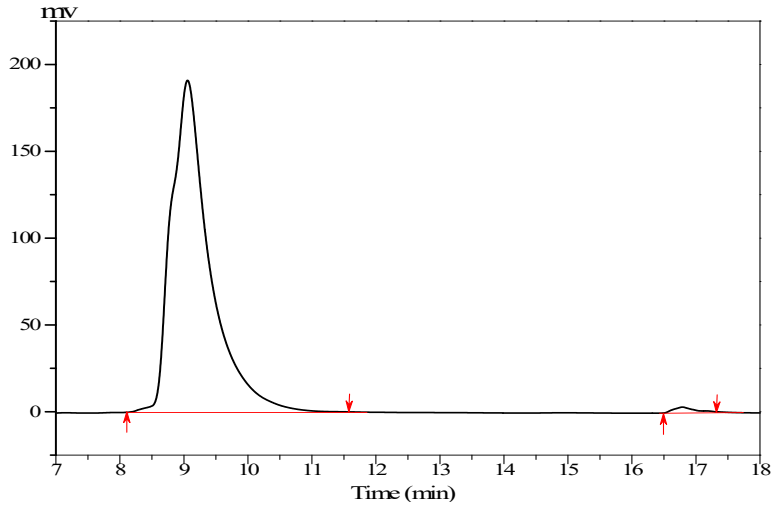
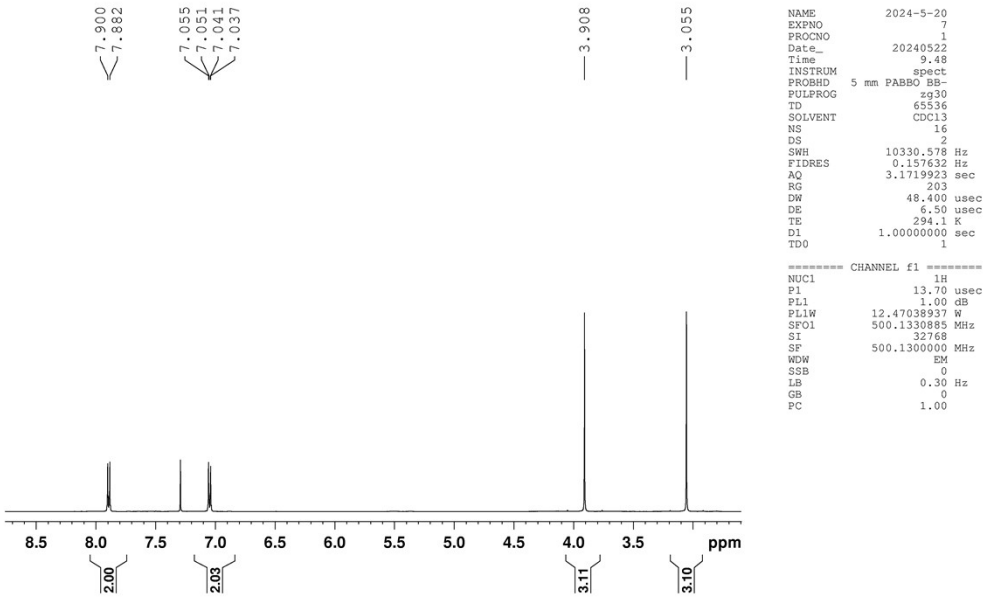


Fig. S19 HLPC of 4-methylphenyl methyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value 96%)

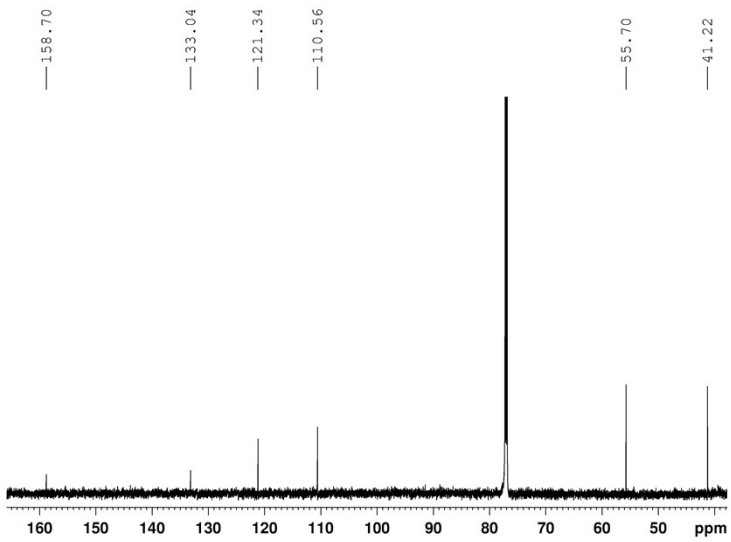
4-Methoxyphenyl methyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10: 1). The product has been identified by ^{1}H and ^{13}C NMR spectrum (see Fig. S20 and 21). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.90-7.04 (m, 4 H, Ar*H*), 3.91 (s, 3 H, -OCH_3), 3.06 (s, 3 H, -SCH_3). ^{13}C NMR ($CDCl_3$, 500 MHz) δ (ppm): 158.70, 133.04, 121.34, 110.56, 55.70, 41.22. ee was determined by HPLC (*i*-PrOH/n-hexane = 1:9 (v/v)); flow rate = 0.7 mL·min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 18.19 min and minor enantiomer t_S = 20.93 min (see Fig. S22).




```
NAME            2024-5-20
EXPNO                   7
PROCNO                  1
Date_            20240522
Time                 9.48
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719923 sec
RG                    203
DW                48.400 usec
DE                 6.50 usec
TE                294.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.70 usec
PL1                 1.00 dB
PL1W         12.47038937 W
SFO1         500.1330885 MHz
SI                  32768
SF           500.1300000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

Fig. S20 ^{1}H NMR of 4-methoxyphenyl methyl sulfoxide




```
NAME            20241130
EXPNO                  2
PROCNO                 1
Date_           20241130
Time               11.54 h
INSTRUM  Avance NEO 700
PROBHD   Z167891_0004 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           41666.667 Hz
FIDRES         1.271566 Hz
AQ             0.7864820 sec
RG                  101
DW                12.000 usec
DE                18.00 usec
TE                298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          176.1081841 MHz
NUC1                  13C
P0                 3.33 usec
P1                10.00 usec
SI                32768
SF          176.0905751 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  1.40
```

Fig. S21 ^{13}C NMR of 4-methoxyphenyl methyl sulfoxide

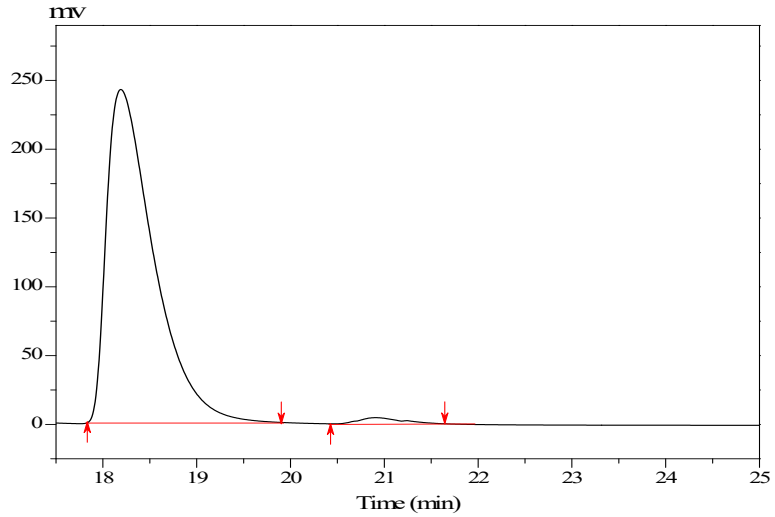


Fig. S22 HLPC of 4-methoxyphenyl methyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value 94%)

2-Methoxyphenyl methyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10: 1). The product has been identified by ^{1}H and ^{13}C NMR spectrum (see Fig. S23 and 24). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.78-6.90 (m, 4 H, Ar*H*), 3.86 (s, 3 H, -OCH_3), 2.75 (s, 3 H, -SCH_3). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 154.82, 133.14, 131.94, 124.69, 121.74, 110.56, 55.70, 41.22. ee was determined by HPLC (*i*-PrOH/n-hexane = 1:9 (v/v)); flow rate = 0.8 mL·min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 19.37 min and minor enantiomer t_S = 22.47 min (see Fig. S25).

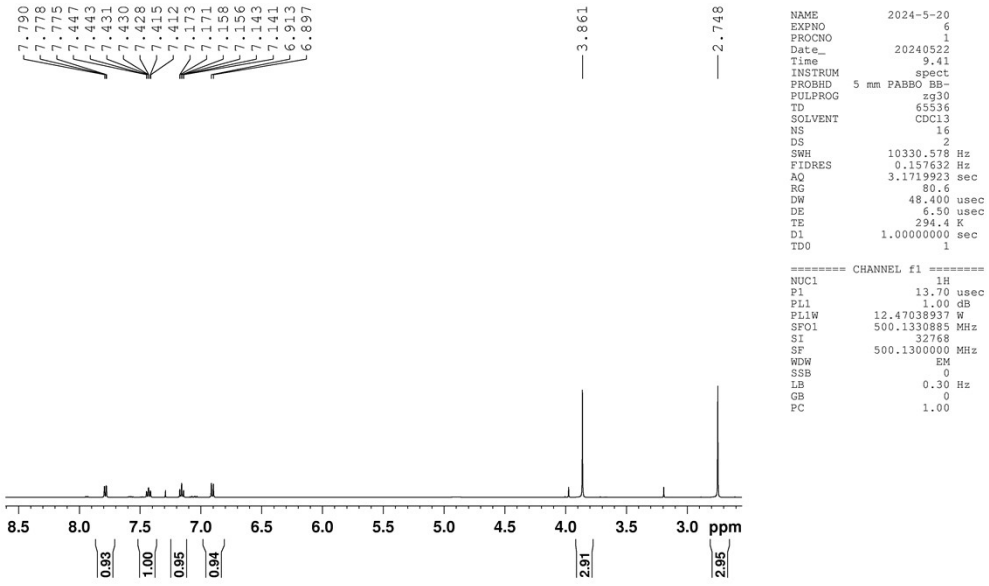


Fig. S23 ^{1}H NMR of 2-methoxyphenyl methyl sulfoxide

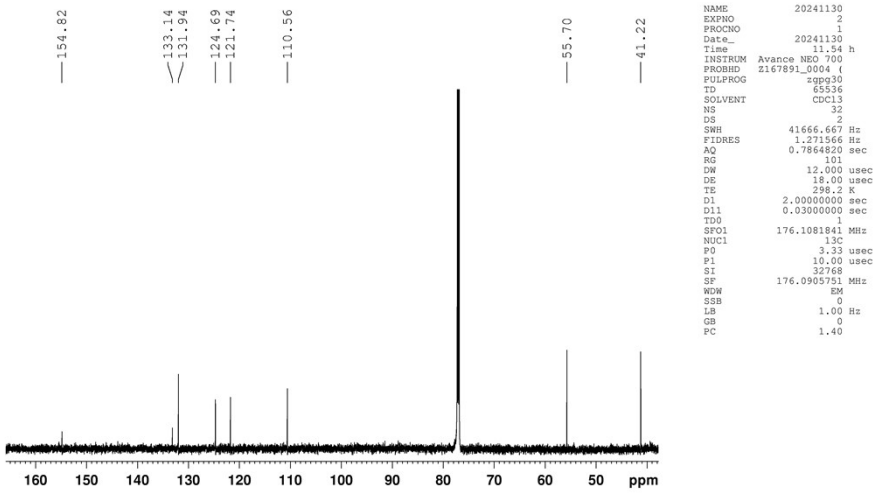


Fig. S24 ^{13}C NMR of 2-methoxyphenyl methyl sulfoxide

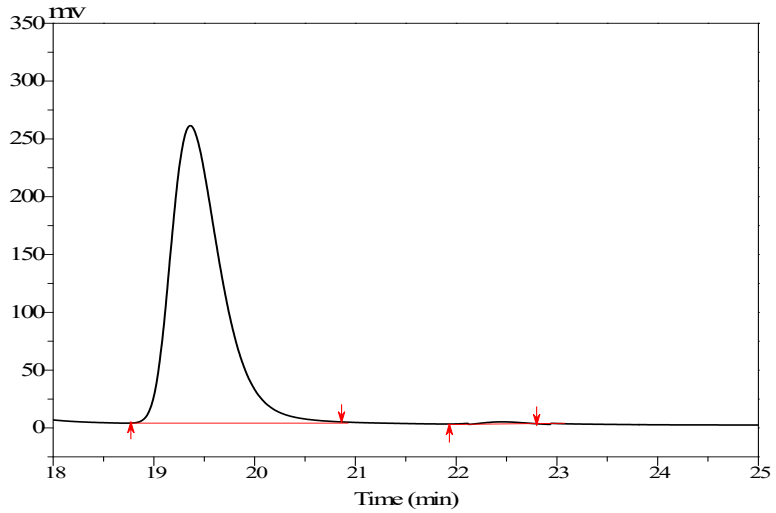


Fig. S25 HLPC of 2-methoxyphenyl methyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value 99%)

2-Chlorophenyl methyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 8: 1). The product has been identified by ^{1}H and ^{13}C NMR spectrum (see Fig. S26 and 27). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.98-7.42 (m, 4 H, Ar*H*), 2.85 (s, 3 H, -SCH_3). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 143.63, 131.99, 129.78, 128.18, 125.36, 44.66. ee 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 = 10.70 min and minor enantiomer t_S = 13.87 min (see Fig. S28).

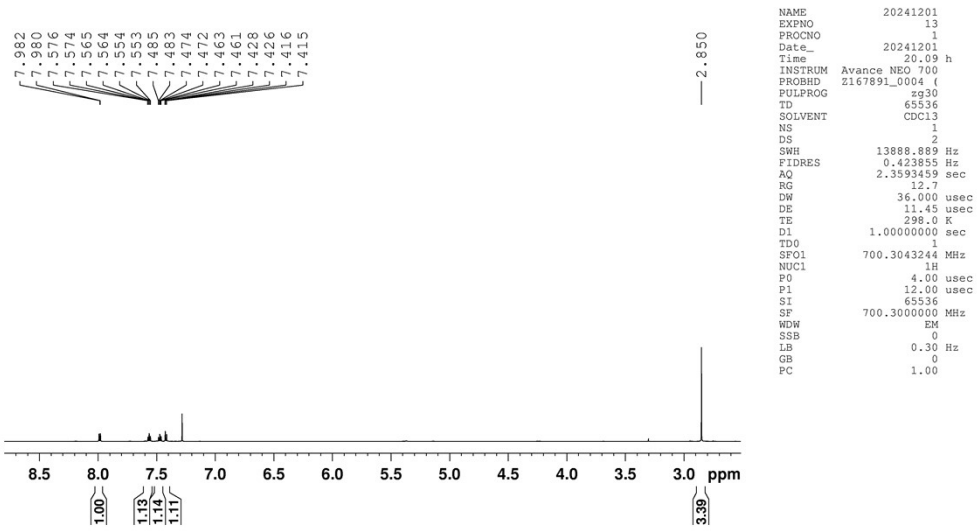


Fig. S26 ^{1}H NMR of 2-chlorophenyl methyl sulfoxide

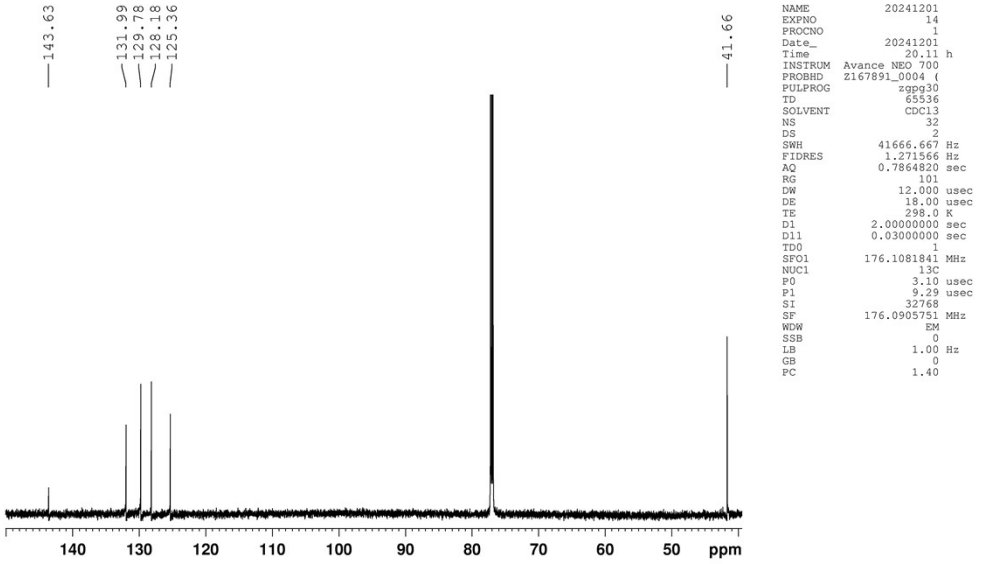


Fig. S27 ^{13}C NMR of 2-chlorophenyl methyl sulfoxide

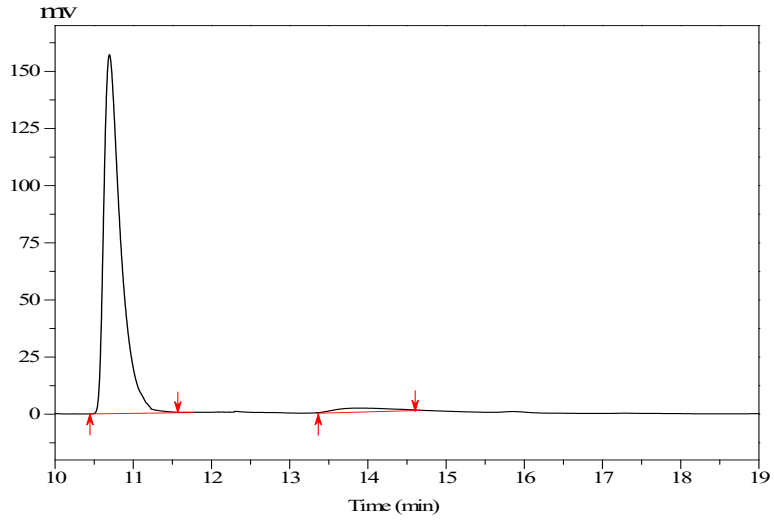


Fig. S28 HLPC of 2-chlorophenyl methyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value 97%)

3-Chlorophenyl methyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 8: 1). The product has been identified by ^{1}H and ^{13}C NMR spectrum (see Fig. S29 and 30). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.52-7.49 (m, 4 H, Ar*H*), 2.77 (s, 3 H, -SCH_3). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 135.76, 131.23, 130.61, 123.68, 121.62, 44.05. ee was determined by HPLC (*i*-PrOH/n-hexane = 1:9 (v/v)); flow rate = 1.1 mL·min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 8.06 min and minor enantiomer t_S = 10.49 min (see Fig. S31).

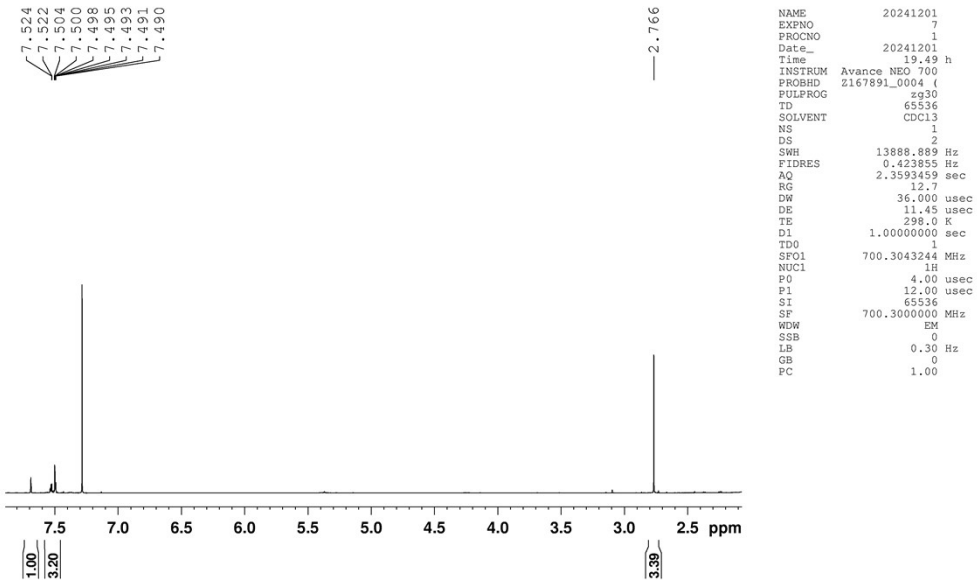


Fig. S29 ^{1}H NMR of 3-chlorophenyl methyl sulfoxide

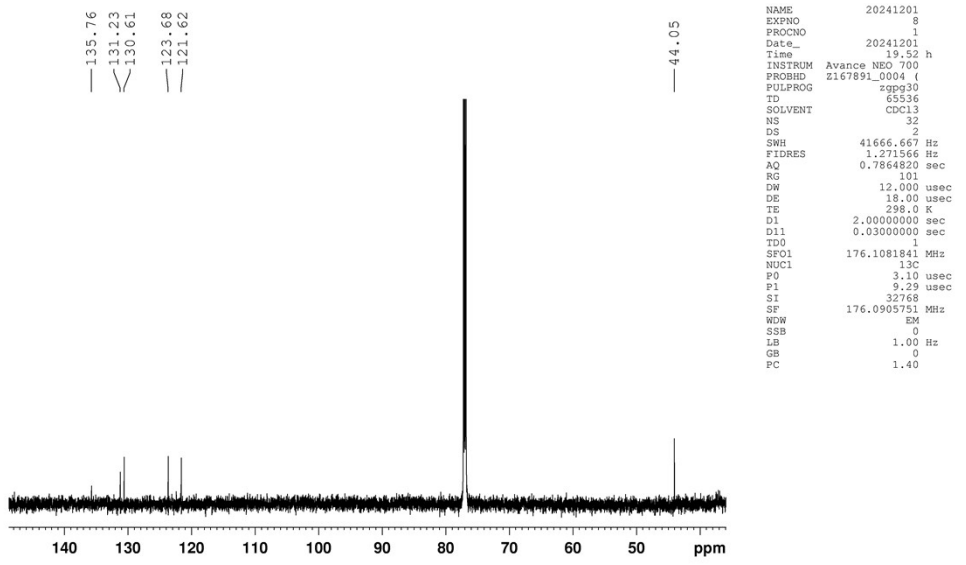


Fig. S30 ^{13}C NMR of 3-chlorophenyl methyl sulfoxide

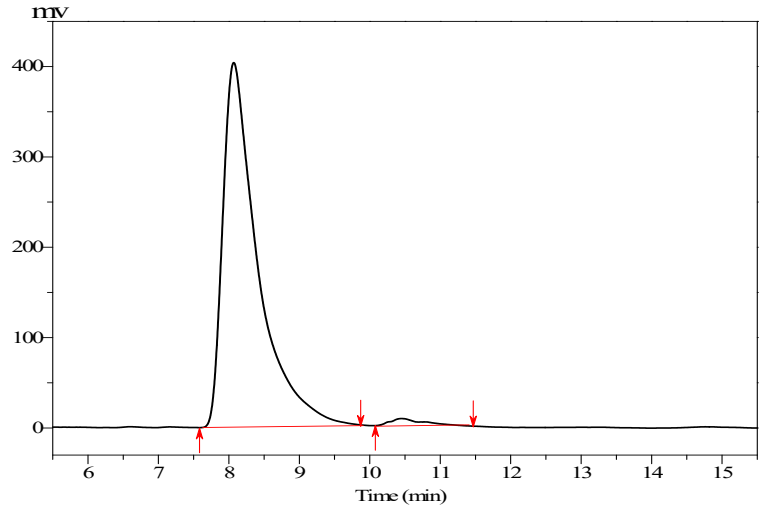


Fig. S31 HLPC of 3-chlorophenyl methyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value 95%)

3-Bromophenyl methyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 8: 1). The product has been identified by ^{1}H and ^{13}C NMR spectrum (see Fig. S32 and 33). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.82-7.40 (m, 4 H, Ar*H*), 2.75 (s, 3 H, -SCH_3). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 148.03, 134.12, 130.84, 126.49, 123.61, 122.08, 44.06. ee was determined by HPLC (*i*-PrOH/n-hexane = 2:8 (v/v)); flow rate = 1.1 mL·min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 8.43 min and minor enantiomer t_S = 10.22 min (see Fig. S34).

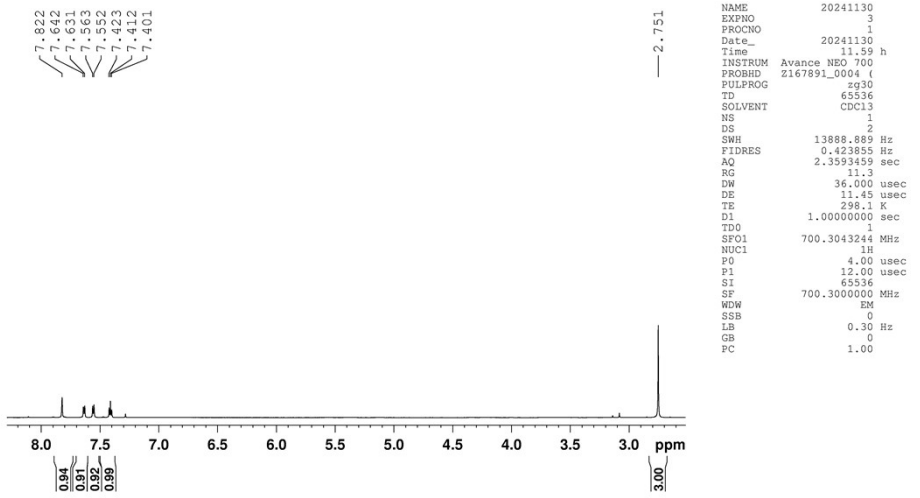


Fig. S32 ^{1}H NMR of 3-bromophenyl methyl sulfoxide

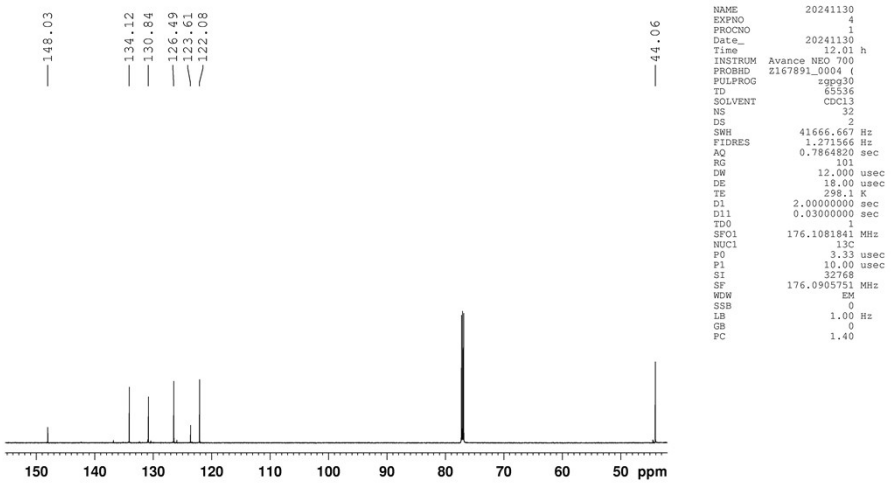


Fig. S33 ^{13}C NMR of 3-bromophenyl methyl sulfoxide

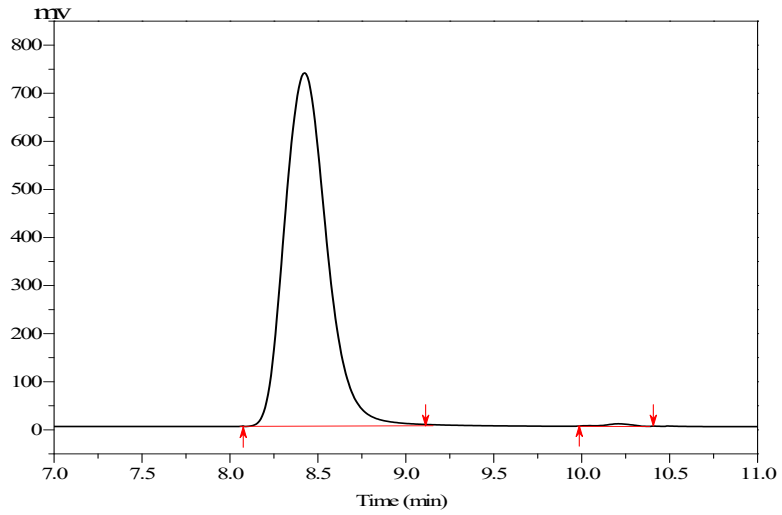


Fig. S34 HLPC of 3-bromophenyl methyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value 97%)

4-Bromophenyl methyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 8: 1). The product has been identified by ^{1}H and ^{13}C NMR spectrum (see Fig. S35 and 36). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.71-7.54 (m, 4 H, Ar*H*), 2.75 (s, 3 H, -SCH_3). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 140.07, 130.84, 123.61, 122.08, 44.06. ee was determined by HPLC (*i*-PrOH/n-hexane = 2:8 (v/v)); flow rate = 1.2 mL·min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 8.32 min and minor enantiomer t_S = 10.17 min (see Fig. S37).

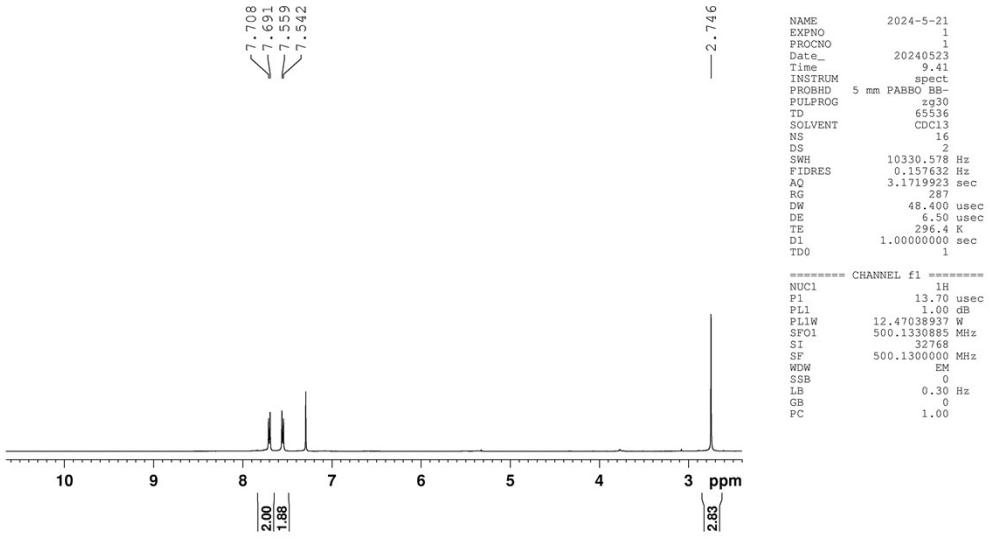


Fig. S35 ^{1}H NMR of 4-bromophenyl methyl sulfoxide

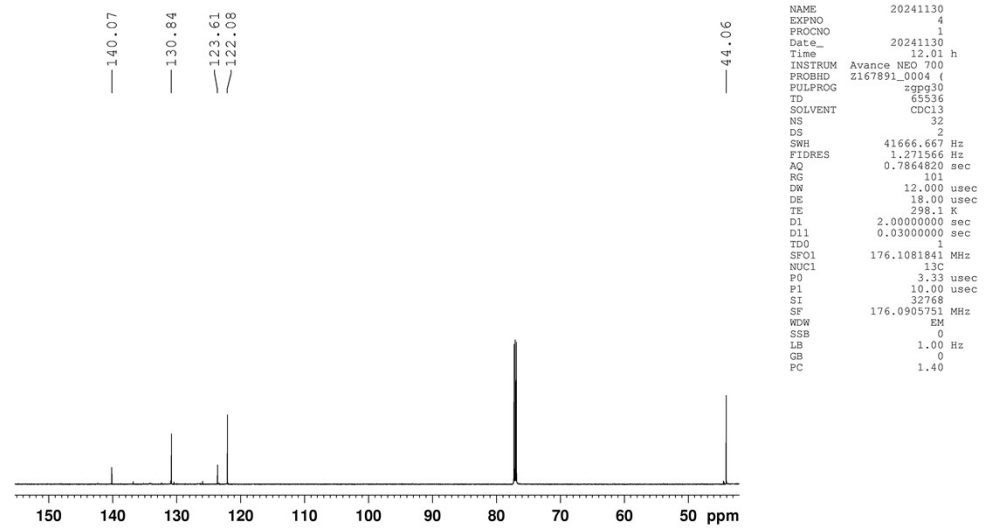


Fig. S36 ^{13}C NMR of 4-bromophenyl methyl sulfoxide

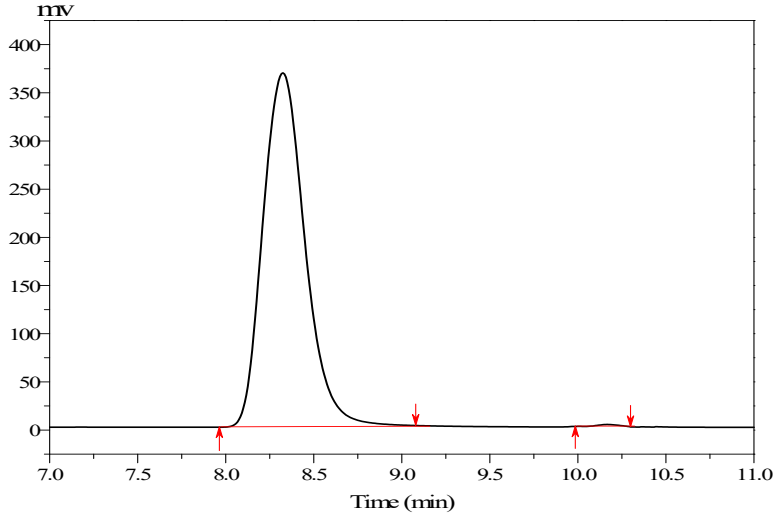


Fig. S37 HLPC of 4-bromophenyl methyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value 99%)

4-Nitrophenyl methyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5: 1). The product has been identified by ^{1}H and ^{13}C NMR spectrum (see Fig. S38 and 39). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 8.44-7.86 (m, 4 H, Ar*H*), 2.83 (s, 3 H, -SCH_3). ^{13}C NMR ($CDCl_3$, 500 MHz) δ (ppm): 148.80, 147.30, 122.80, 44.06. ee 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 = 5.48 min and minor enantiomer t_S = 10.05 min (see Fig. S40).

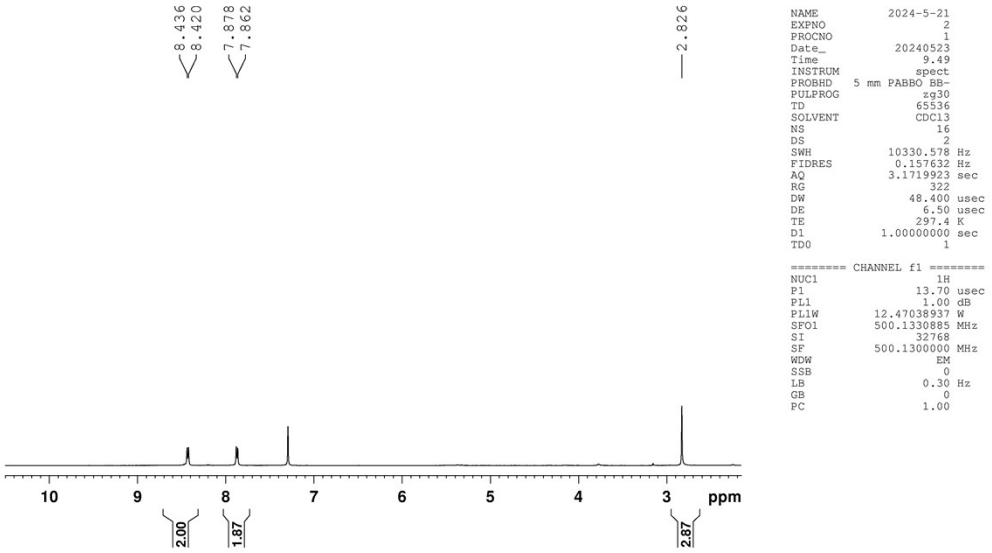


Fig. S38 ^{1}H NMR of 4-nitrophenyl methyl sulfoxide

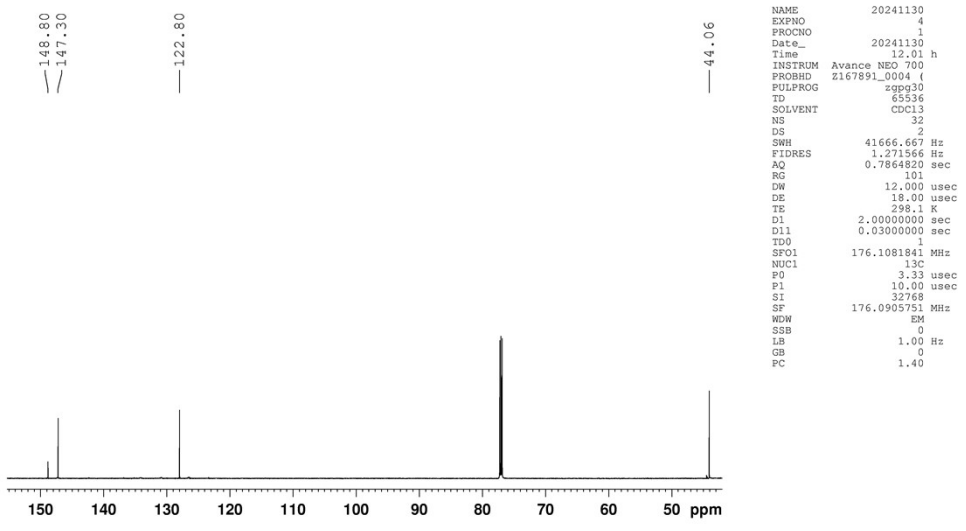


Fig. S39 ^{13}C NMR of 4-nitrophenyl methyl sulfoxide

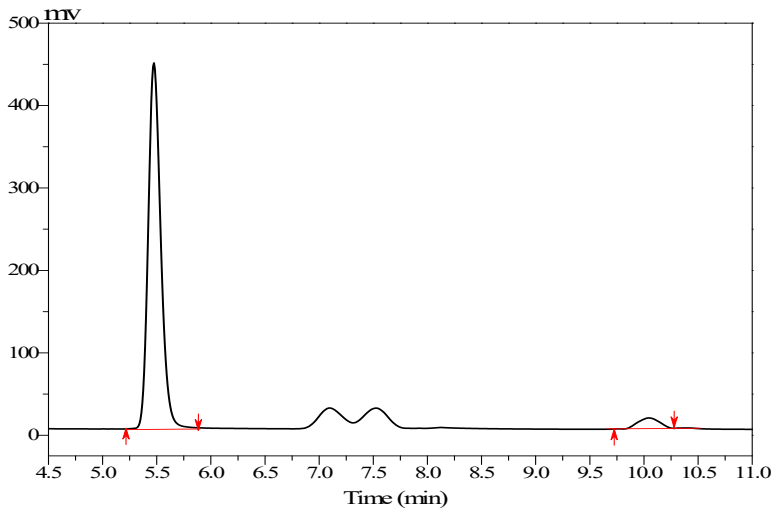


Fig. S40 HLPC of 4-nitrophenyl methyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value 90%)

Benzyl methyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 9: 1). The product has been identified by ^{1}H and ^{13}C NMR spectrum (see Fig. S41 and 42). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.44 (m, 5 H, Ar*H*), 4.28 (s, 2 H, Ar-CH_2), 2.78 (s, 3 H, SCH_3). ^{13}C NMR ($CDCl_3$, 500 MHz) δ (ppm): 130.52, 129.18, 128.32, 61.37, 39.01. ee was determined by HPLC (*i*-PrOH/n-hexane = 1:9 (v/v)); flow rate = 1.3 mL·min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 13.44 min and minor enantiomer t_S = 24.09 min (see Fig. S43).

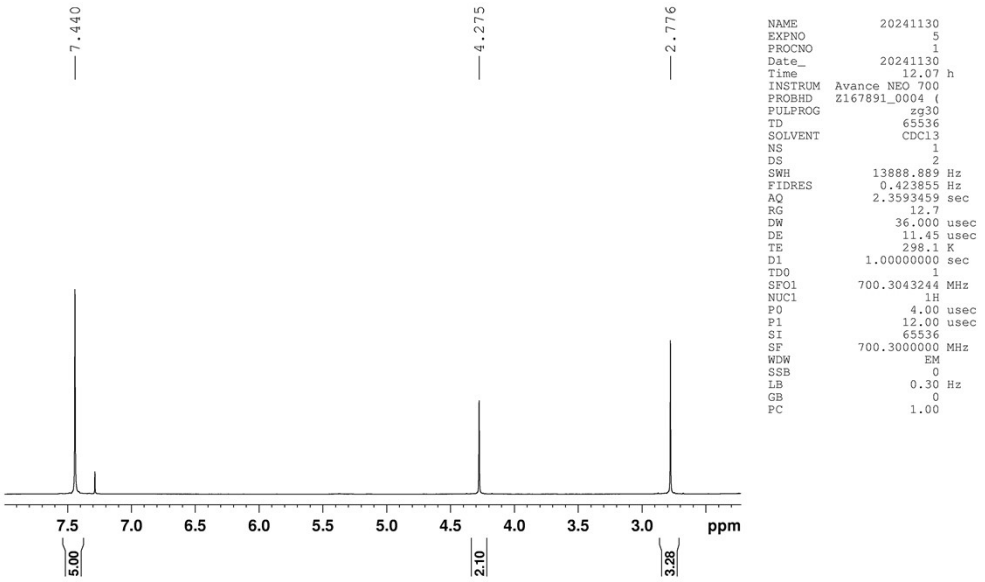


Fig. S41 ^{1}H NMR of benzyl methyl sulfoxide

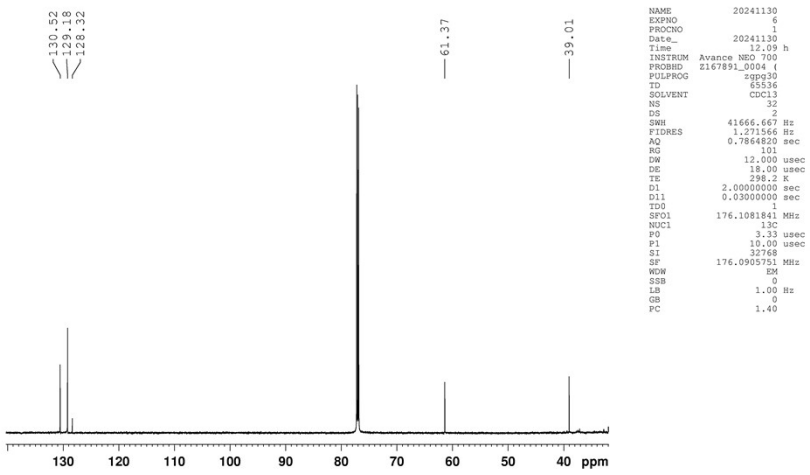


Fig. S42 ^{13}C NMR of benzyl methyl sulfoxide

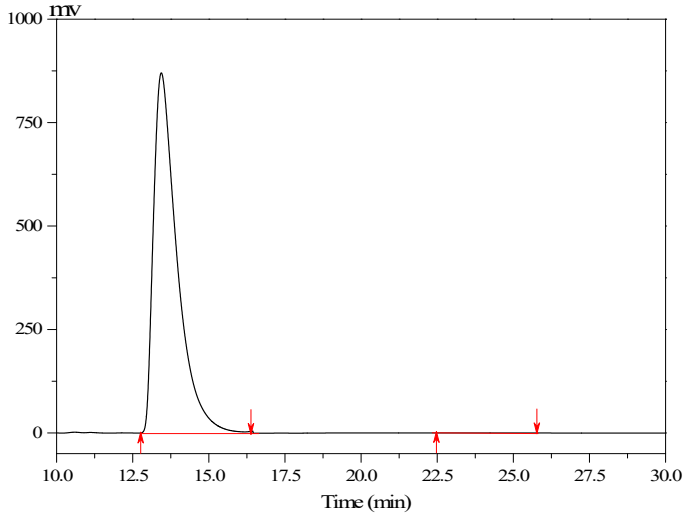


Fig. S43 HLPC of benzyl methyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value >99%)

Phenyl vinyl sulfoxide: The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5: 1). The product has been identified by ^{1}H and ^{13}C NMR spectrum (see Fig. S44 and 45). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.57-7.52 (m, 5 H, Ar*H*), 6.71-6.61 (m, 1 H, -SC*H*=CH_2), 6.25-6.22 and 5.93-5.92 (m, 2 H, -SCH=CH_2). ^{13}C NMR ($CDCl_3$, 500 MHz) δ (ppm): 143.01, 129.49, 129.37, 127.95, 124.69, 120.74. ee 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 = 18.65 min and minor enantiomer t_S = 21.93 min (see Fig. S46).

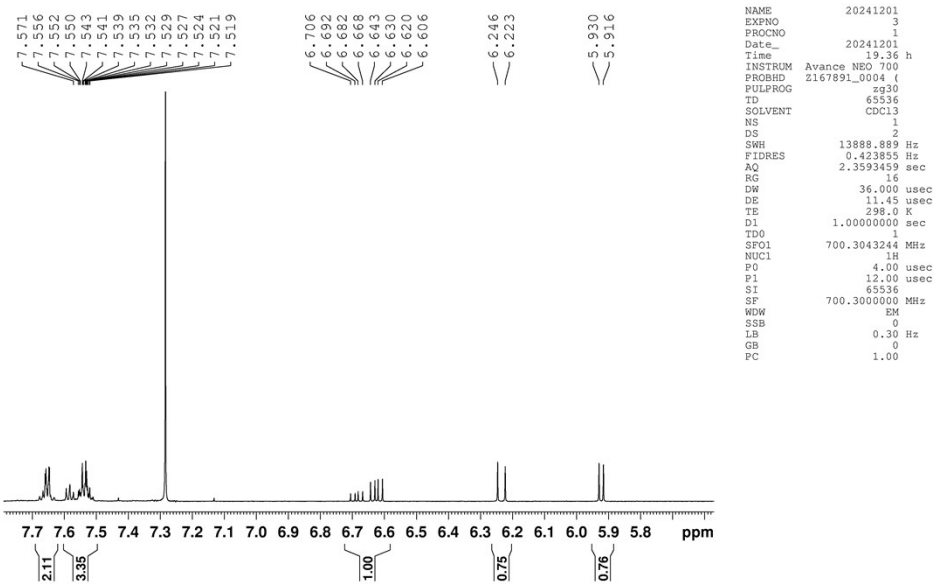


Fig. S44 ^{1}H NMR of phenyl vinyl sulfoxide

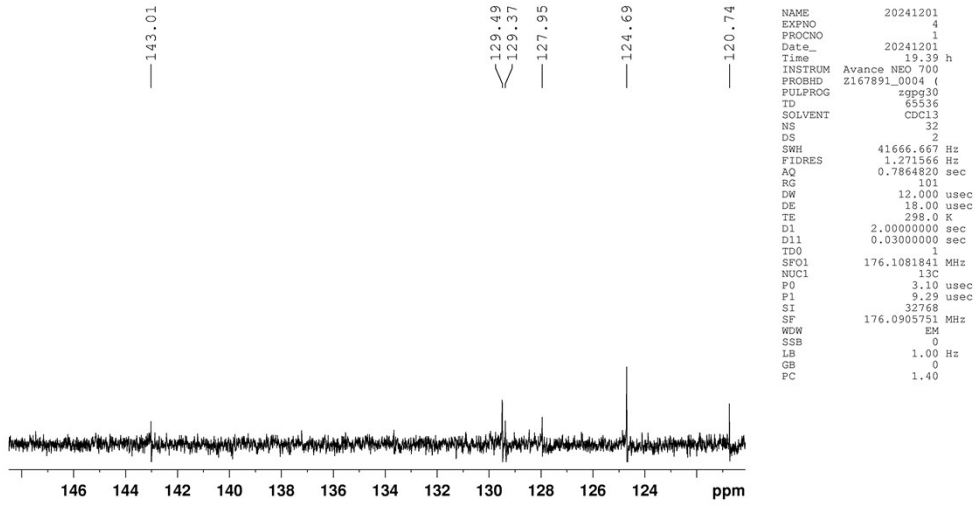


Fig. S45 ^{13}C NMR of phenyl vinyl sulfoxide

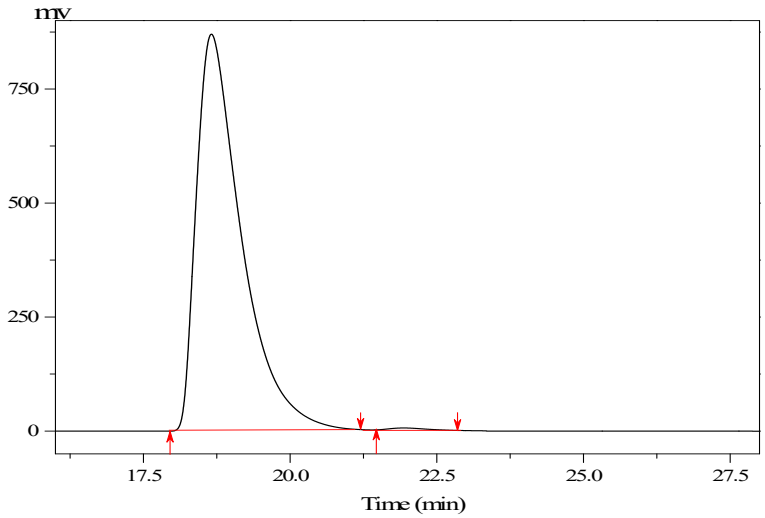


Fig. S46 HLPC of phenyl vinyl sulfoxide obtained over ***IL*-Ti(salen) CMOF-1** (ee value 99%)

References

1 Y. Zhang, R. Tan, M. Gao, P. Hao, D. Yin, *Green Chem.,* 2017, **19**, 1182-1193.

2 S. Lirio, Y. Shih, P. B. So, L. Liu, Y. Yen, S. Furukawa, W. Liu, H. Huang, C.Lin, *Dalton Trans*. 2021, **50**, 1866-1873.