Supporting Information

Visible light-controlled reaction-separation for asymmetric sulfoxidation in water with photo-responsive metallomicelles

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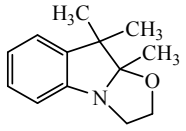
Number of pages: 24 (from S1 to S24)

Number of figures: 36

CONTENT:

1. Identification of the catalysts ($PS_{29}(IC)_2$, $PS_{10}(IC)_2$, $PS_6(IC)_2$, and $PS_{10}C_2$) and the intermediates.

*9,9,9a-Trimethyl-2,3,9,9a-tetrahydrooxazolo[3,2-a]indole (denoted as **1**).*



Compound 1

The structure of **compound 1** was identified by ^{1}H NMR spectrum (see Figure S1). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.18-6.79 (*m*, 4 H, Ar*H*), 3.89-3.86 (*m*, 2 H, N-CH_2-CH$_2$-O), 3.74-3.54 (*m*, 2 H, N-CH$_2$-CH_2-O), 1.47 (s, 3 H, N=C-CH_3), 1.41-1.22 (*m*, 6 H, -C(CH_3)$_2$). FT-IR (KBr): γ_{max}/cm^{-1} 3045, 3023, 2881, 1725, 1607, 1595, 1479, 1455, 1384, 1375, 1361, 1336, 1294, 1217, 1178, 1155, 1146, 1115, 1078, 1022,935, 884, 846, 802, 770, 747, 684, 650, 596, 571, 550, 541, 511, 462.

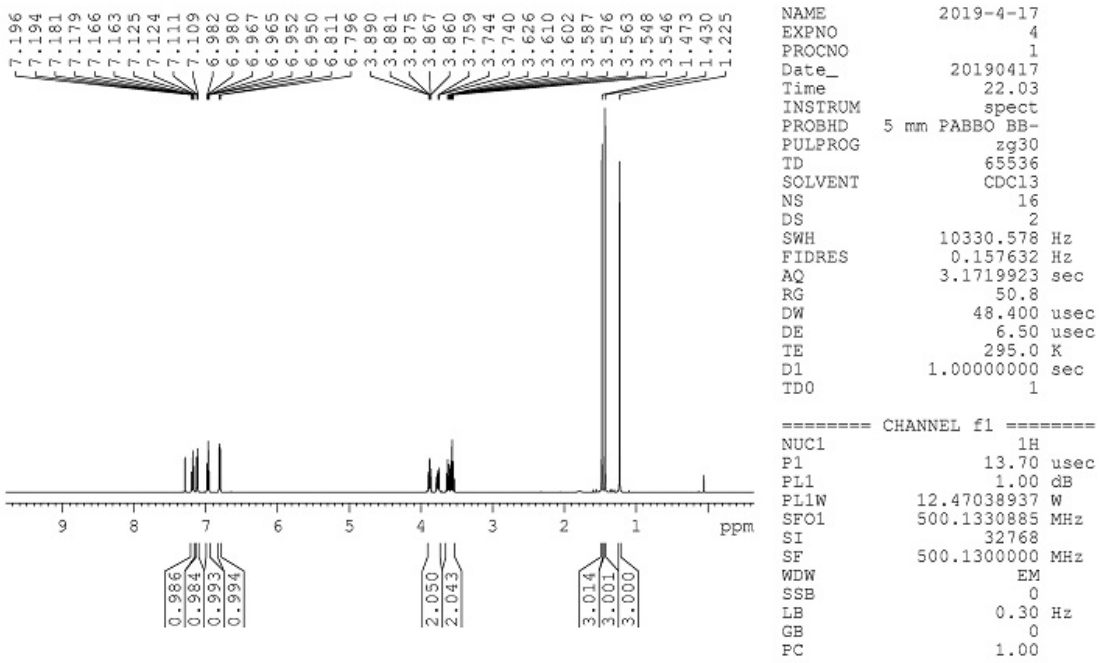
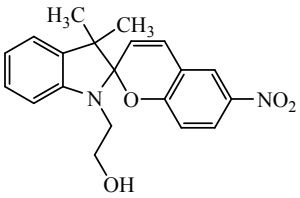


Figure S1. ^{1}H NMR of **compound 1**.

*2-(3,3'-dimethyl-6-nitro-3'H-spiro[chromene-2,2'-indol]-1'-yl)-ethanol (denoted as **2**).*



Compound 2

The structure of **compound 2** was identified by ^{1}H NMR spectrum (see Figure S2). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 8.06-7.20 (m, 3 H, Ar*H* in benzopyran), 7.14-7.12 (m, 1 H, -CH=C*H*-Ph), 6.95-6.77 (m, 4 H, Ar*H* in indoline), 6.70-6.68 (m, 1 H, -CH=C*H*-Ph), 5.92-5.90 (m, 1 H, -C*H*=CH-Ph), 3.77 (s, 1 H, -C_2H_4O*H*), 3.76-3.34 (*m*, 4 H, -C_2*H*$_4$OH), 1.31-1.22 (*m*, 6 H, -C(C*H*$_3$)$_2$). FT-IR (KBr): γ_{max}/cm^{-1} 3335, 3062, 2962, 2867, 1650, 1609, 1577, 1509, 1480, 1458, 1380, 1362, 1335, 1273, 1219, 1156, 1123, 1089, 1051, 1023, 952, 917, 836, 808, 787, 748, 719, 687, 553, 498, 476, 451.

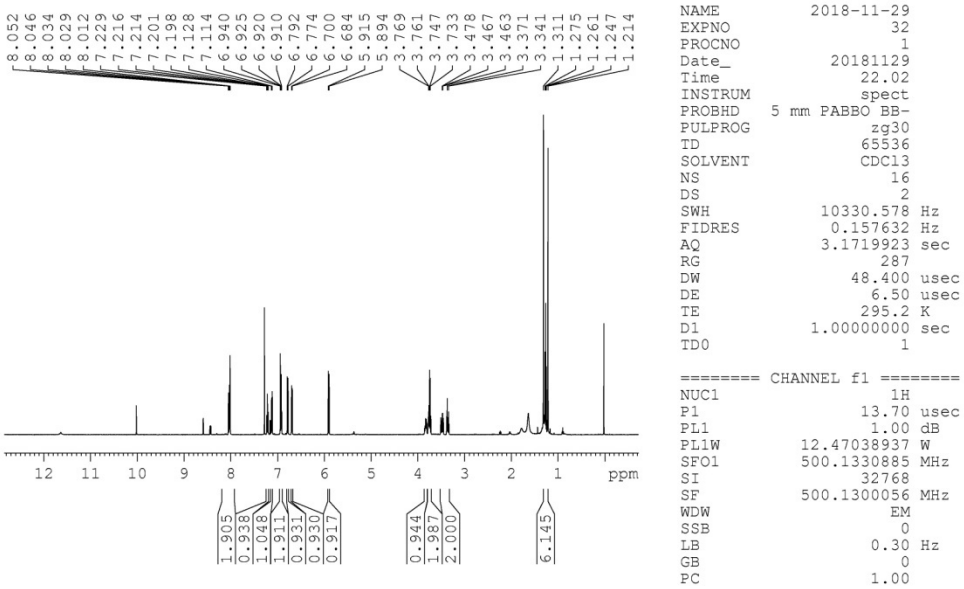
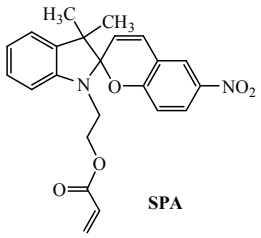


Figure S2. ^{1}H NMR of **compound 2**.

*1'-(2-methacryloxyethyl)-3',3'-dimethyl-6-nitro-spiro(2H-1-benzopyran-2,2'-indoline) (denoted as **SPA**)*



SPA

The structure of **SPA** was identified by ^{1}H NMR (see Figure S3) and ^{13}C NMR spectra (see Figure S4). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm): 8.49-8.07 (m, 3 H, Ar*H* in benzopyran), 8.00-7.49 (m, 4 H, Ar*H* in indoline), 7.32-7.10 (m, 1 H, -CH=C*H*-Ph), 7.02-6.79 (m, 1 H, -C*H*=CH-Ph), 6.77-6.53 (m, 1 H, CH_2=C*H*-C=O), 5.70-5.48 (m, 2 H, CH_2=CH-C=O), 4.93-4.76 (m, 2 H, N-CH_2-CH_2-O-C=O), 4.00-3.91 (m, 2 H, N-CH_2-CH_2-O-C=O), 1.82 (s, 6 H, -C(CH_3)$_2$). ^{13}C NMR (500 MHz, DMSO-d_6): δ (ppm): 183.63 (s), 144.15 (s), 141.35 (s), 140.09 (s), 129.97 (s), 129.49 (s), 129.42 (s), 126.91 (s), 123.44 (s), 121.82 (s), 118.06 (s), 116.37 (s), 115.71 (s), 106.84 (s), 58.87 (s), 52.80 (s), 52.71 (s), 50.30 (s), 39.90 (s), 39.97 (s), 39.92 (s), 31.26 (s), 26.62 (s). FT-IR (KBr): γ_{max}/cm^{-1} 3364, 3226, 2975, 2937, 2738, 2676, 2601, 2528, 2491, 1726, 1609, 1586, 1540, 1515, 1474, 1434, 1397, 1383,1366, 1339, 1320, 1294, 1263, 1169, 1131, 1078, 1036, 981, 967, 955, 860, 839, 805, 763, 751, 703, 668, 653, 571, 455.

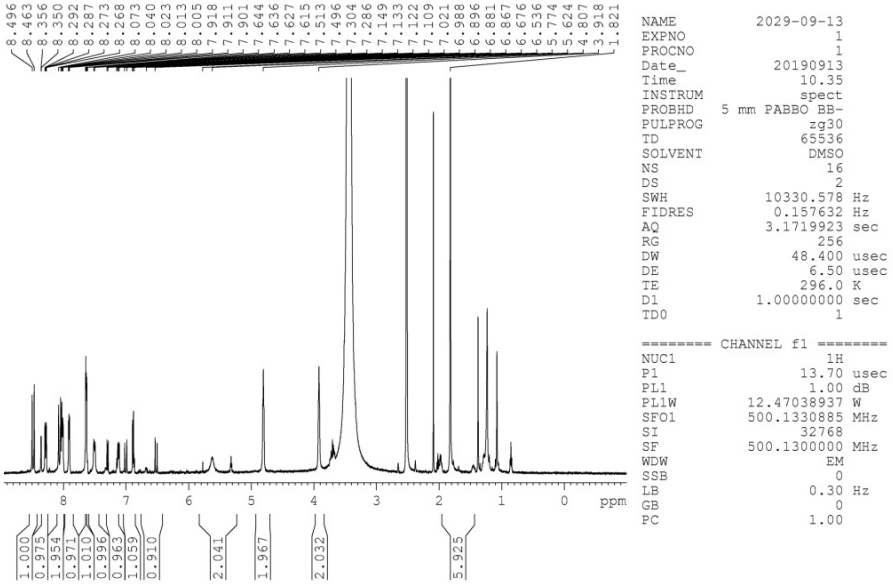


Figure S3. ^{1}H NMR of **SPA**.

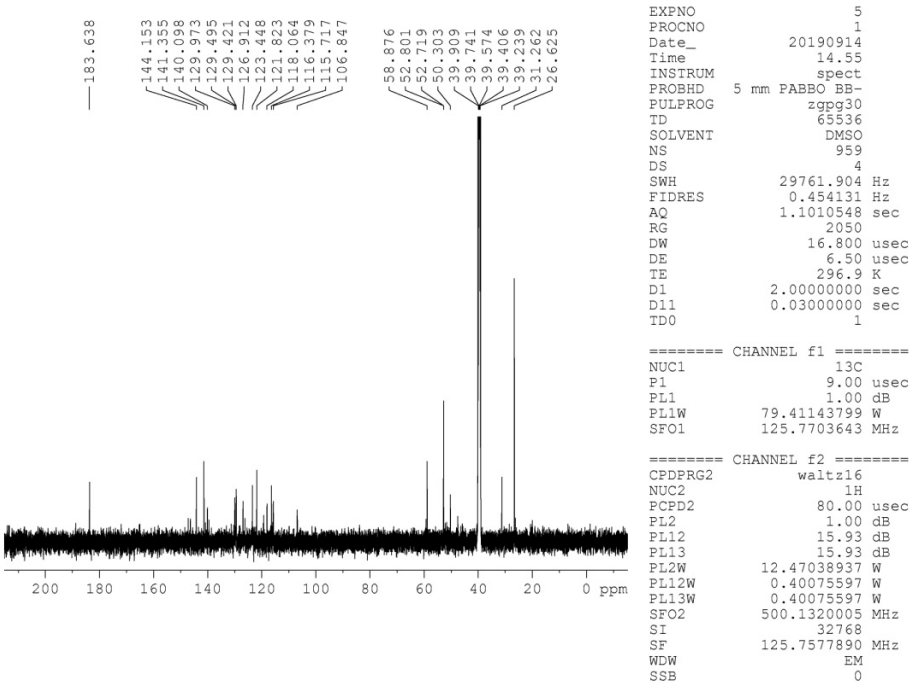
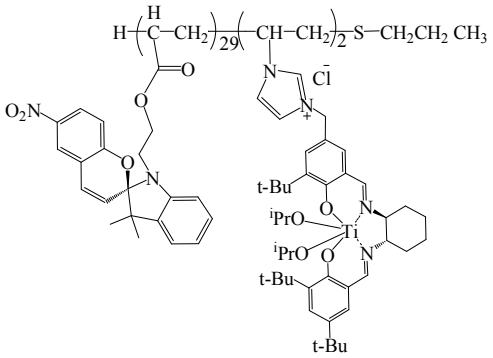


Figure S4. ^{13}C NMR of **SPA**.

$PS_{29}(IC)_2$



The structure and chemical composition of **$PS_{29}(IC)_2$** were identified by ^{1}H NMR spectrum (see Figure S5). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 8.28 (m, 29 H, Ar*H* in SPA), 7.98 (m, 29 H, Ar*H* in SPA), 7.59-7.58 (m, 58 H, Ar*H* in SPA), 7.45-7.48 (m, 29 H, Ar*H* in SPA), 7.37 (m, 8 H, Ar*H* in Ti(salen)), 7.33 (m, 29 H, Ar*H* in SPA), 7.04-7.13 (m, 29 H, Ar*H* in SPA), 6.86-6.90 (m, 29 H, -CH=C*H*-Ph in SPA), 6.01 (m, 2 H, N-C*H*-CH_2- of N-vinyl in IL), 5.81-5.91 (m, 29 H, -C*H*=CH-Ph in SPA), 4.29-3.81 (m, 58 H, N-CH_2-CH_2-O in SPA), 3.58-3.53 (m, 58 H,

N-CH_2-CH_2-O in SPA), 3.25-3.22 (m, 8 H, -CH-CH_2- of N-vinyl and –N-CH_2-N- in IL), 3.07 (m, 12 H, -N-CH_2-CH_2-N- and –N-CH_2-Ph in *IL*/Ti(salen)), 2.95 (m, 2 H, S-CH_2-CH_2-CH_3), 2.93 (m, 2 H, S-CH_2-CH_2-CH_3), 2.78 (m, 4 H, CH_3-C*H*-CH_3 of ^{i}PrO- in Ti(salen)), 1.61-1.58 (m, 58 H, -CH_2-CH- in SPA), 1.53 (s, 3 H, S-CH_2-CH_2-CH_3), 1.36-1.34 (54 H, -C(CH_3)$_3$ in Ti(salen)), 1.31-1.28 (m, 24 H, cyclohexyl-*H*), 1.27-1.26 (m, 24 H, -CH(CH_3)$_2$ in Ti(salen)), 0.86-0.83 (m, 174 H, -C(CH_3)$_2$ in SPA). The degrees of polymerization of the individual SPA and *IL*/Ti(salen) were determined in the ^{1}H NMR spectrum (see Figure S4) by comparing the signals attributable to individual blocks (SPA at 0.86-0.83ppm assigned to -C(CH_3)$_2$ and *IL*/Ti(salen) at *ca.* 6.01 ppm assigned to N-C*H*-CH_2- of N-vinyl in IL) with that of end methyl group (-SH-CH_2-CH_2-CH_3) (at *ca*. 1.53 ppm). FT-IR (KBr): γ_{max}/cm^{-1} 3425, 2973, 2965, 2884, 1724, 1607, 1656, 1583, 1537, 1523, 1480, 1461, 1399, 1370, 1340, 1316, 1294, 1269, 1232, 1170, 1130, 1088, 1049, 955, 881, 840, 808, 766, 749, 701, 634, 570, 545, 493, 446, 421. GPC (THF): M_n= 15412, M_w= 23426, PDI= 1.52. α_{25}^{D} = -23.1 (C = 0.005 g.mL^{-1}, CH_2Cl_2), titanium content: 0.075 mmol.g^{-1}.

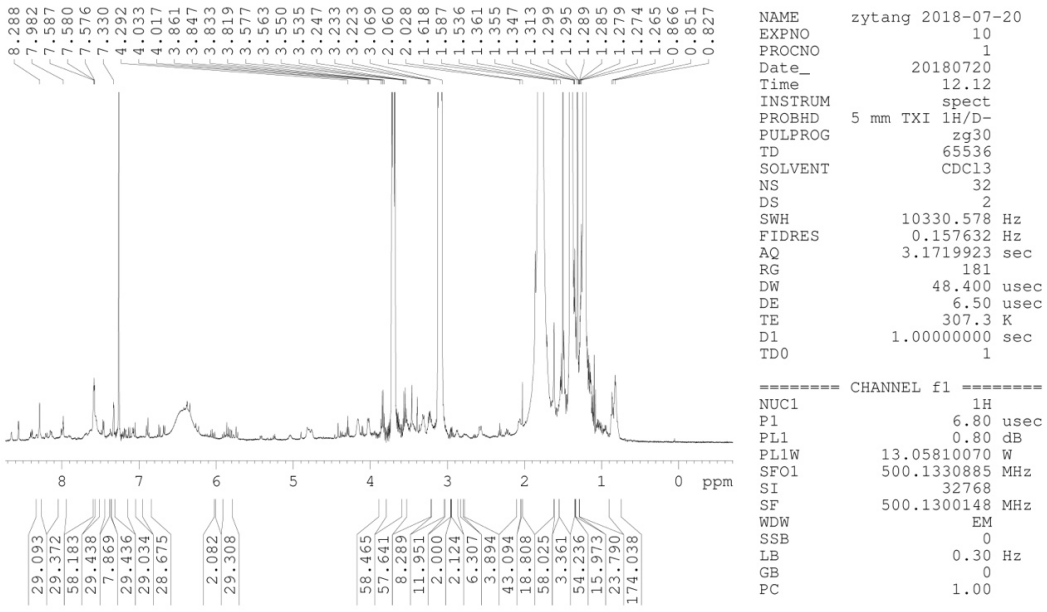
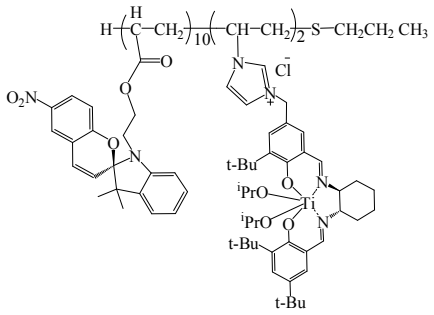


Figure S5. ^{1}H NMR of the **$PS_{29}(IC)_2$**.

$PS_{10}(IC)_2$



The structure and chemical composition of **$PS_{10}(IC)_2$** were identified by ^{1}H NMR spectrum (see Figure S6). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 8.15-8.13(m, 10 H, Ar*H* in SPA), 8.09-8.06 (m, 10 H, Ar*H* in SPA), 7.89-7.87 (m, 10 H, Ar*H* in SPA), 7.74 (m, 10 H, Ar*H* in SPA), 7.49-7.45 (m, 8 H, Ar*H* in Ti(salen)), 7.07 (m, 10 H, Ar*H* in SPA), 6.90-6.89 (m, 10 H, Ar*H* in SPA), 6.74-6.73 (m, 10 H, Ar*H* in SPA), 6.25-6.21 (m, 10H, -CH=C*H*-Ph in SPA), 5.89 (m, 2 H, N-C*H*-CH_2- of N-vinyl in IL), 5.87-5.80 (m, 10 H, -C*H*=CH-Ph in SPA), 3.70 (m, 20 H, N-CH_2-CH_2-O in SPA), 3.58-3.55 (m, 20 H, N-CH_2-CH_2-O in SPA), 3.39 (m, 8 H, -CH-CH_2- of N-vinyl and –N-CH_2-N- in IL), 3.08 (m, 12 H, -N-CH_2-CH_2-N- and –N-CH_2-Ph- in *IL*/Ti(salen)), 2.95 (m, 2 H, S-CH_2-CH_2-CH_3), 2.80-2.78 (m, 4 H, CH_3-C*H*-CH_3 of ^{i}PrO- in Ti(salen)), 2.56 (m, 2 H, S-CH_2-CH_2-CH_3), 1.71 (m, 3 H, S-CH_2-CH_2-CH_3), 1.50-1.48 (m, 20 H, -CH_2-CH- in SPA), 1.36-1.31 (m, 54 H, -C(CH_3)$_3$ in Ti(salen)), 1.26 (m, 16 H, cyclohexyl-*H*), 1.23 (m, 24 H, -CH(CH_3)$_2$ in Ti(salen)), 0.88-0.83 (m, 60 H, -C(CH_3)$_2$ in SPA). The degrees of polymerization of the individual SPA and *IL*/Ti(salen) were determined in the ^{1}H NMR spectrum (see Figure S5) by comparing the signals attributable to individual blocks (SPA at 0.88-0.83 ppm assigned to -C(CH_3)$_2$ and *IL*/Ti(salen) at *ca.* 5.89 ppm assigned to N-C*H*-CH_2- of N-vinyl in IL) with that of end methyl group (-SH-CH_2-CH_2-CH_3) (at *ca*. 1.71 ppm). FT-IR (KBr): γ_{max}/cm^{-1} 3434, 2970, 2958, 2879, 1708, 1598, 1654, 1581, 1531, 1521, 1478, 1460, 1397, 1368, 1328, 1308, 1290, 1270,

1235, 1167, 1127, 1085, 1048, 951, 880, 839, 806, 766, 749, 699, 635, 565, 540, 486, 441, 418. GPC (THF): M_n = 6790, M_w = 9590, PDI= 1.62. α_{25}^{D} = -17.5 (C = 0.005 g.mL^{-1}, CH_2Cl_2), Titanium content: 0.176 mmol.g^{-1}.

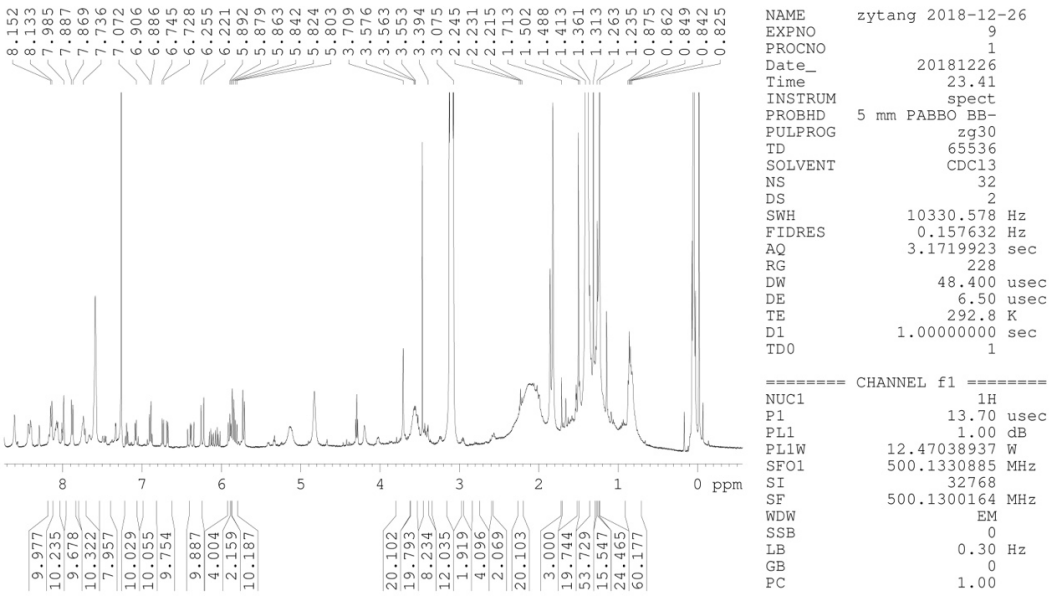
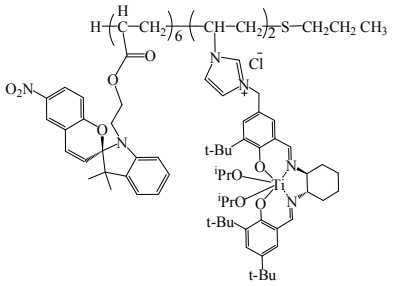


Figure S6. ^{1}H NMR of the **$PS_{10}(IC)_2$**.

$PS_6(IC)_2$



The structure and chemical composition of **$PS_6(IC)_2$** were identified by ^{1}H NMR spectrum (see Figure S7). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 8.50 (m, 6 H, Ar*H* in SPA), 8.34-8.31 (m, 6 H, Ar*H* in SPA), 8.23-8.22 (m, 6 H, Ar*H* in SPA), 8.06 (m, 6 H, Ar*H* in SPA), 8.03-8.00 (m, 6 H, Ar*H* in SPA), 7.99-7.97 (m, 6 H, Ar*H* in SPA), 7.92-7.91 (m, 6 H, Ar*H* in SPA), 7.23-7.20 (m, 8 H, Ar*H* in Ti(salen)), 6.88-6.86 (m, 6 H, -CH=C*H*-Ph in SPA), 5.98-5.96 (m, 6 H, -C*H*=CH-Ph in SPA), 4.20-4.19 (m, 2 H, N-C*H*-CH_2- of N-vinyl in IL), 3.94-3.92 (m, 12 H, N-CH_2-CH_2-O in

SPA), 3.28-3.23 (m, 12 H, -N-C*H*$_2$-C*H*$_2$-N- and –N-C*H*$_2$-Ph- in *IL*/Ti(salen)), 3.17 (m, 8 H, -CH-C*H*$_2$- of N-vinyl and –N-C*H*$_2$-N- in IL), 2.77-2.74 (m, 12 H, N-CH$_2$-C*H*$_2$-O in SPA), 2.65 (m, 2 H, SH-C*H*$_2$-CH$_2$-CH$_3$), 2.55 (m, 2 H, SH-CH$_2$-C*H*$_2$-CH$_3$), 1.55 (m, 3 H, SH-CH$_2$-CH$_2$-C*H*$_3$), 1.24-1.21 (m, 54 H, -C(C*H*$_3$)$_3$ in Ti(salen)), 1.20-1.18 (16 H, cyclohexyl-*H*), 1.17-1.60 (m, 24 H, -CH(C*H*$_3$)$_2$ in Ti(salen)), 1.01-1.07 (m, 36 H, -C(C*H*$_3$)$_2$ in SPA). The degrees of polymerization of the individual SPA and *IL*/Ti(salen) were determined in the ^{1}H NMR spectrum (see Figure S6) by comparing the signals attributable to individual blocks (SPA at 1.01-1.07 ppm assigned to -C(C*H*$_3$)$_2$ and *IL*/Ti(salen) at 4.20-4.19 ppm assigned to N-C*H*-CH$_2$- of N-vinyl in IL) with that of end methyl group (-SH-CH$_2$-CH$_2$-C*H*$_3$) (at *ca*. 1.55 ppm). FT-IR (KBr): γ_{max}/cm^{-1} 3431, 3431, 2981, 2978, 2990 1726, 1610, 1661, 1590, 1542, 1525, 1481, 1470, 1343, 1371, 1341, 1319, 1301, 1261, 1225, 1165, 1133, 1088, 1054, 959, 884, 841, 811, 764, 751, 703, 635, 573, 541, 491, 451, 421. GPC (THF): M_n= 5276, M_w= 7334, PDI= 1.39. α_{25}^D = -18.3 (C = 0.005 g.mL^{-1}, CH_2Cl_2), Titanium content: 0.247 mmol.g^{-1}.

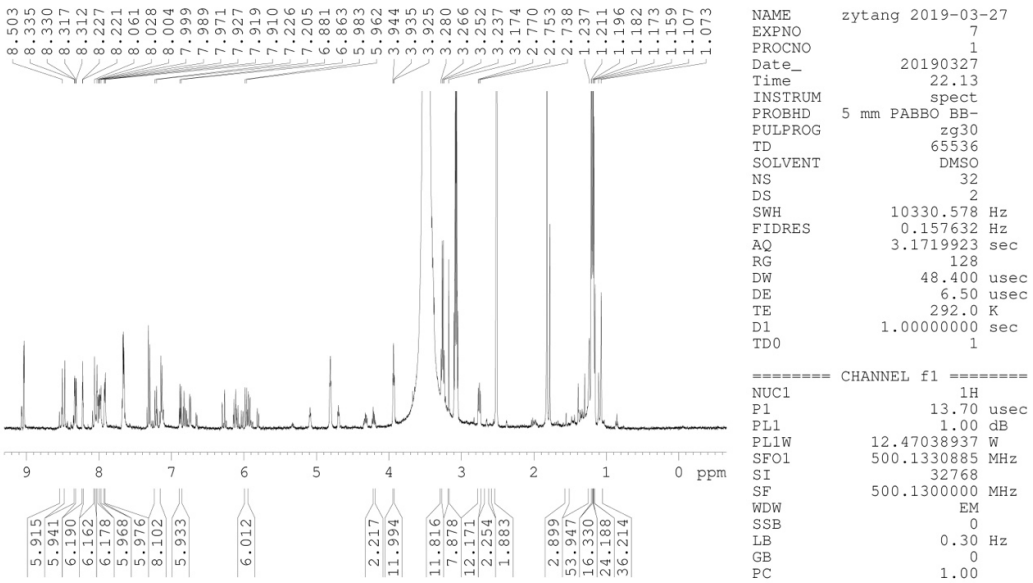
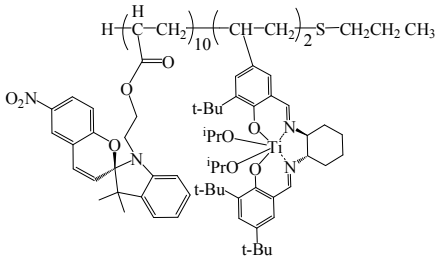


Figure S7. ^{1}H NMR of the **PN$_6$(IS)$_2$**

$PS_{10}C_2$



The structure and chemical composition of **$PS_{10}C_2$** were identified by ^{1}H NMR spectrum (see Figure S8). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm): 8.35-8.31 (m, 10 H, Ar*H* in SPA), 8.09-8.00 (m, 10 H, Ar*H* in SPA), 7.94-7.92 (m, 10 H, Ar*H* in SPA), 7.67-7.65 (m, 10 H, Ar*H* in SPA), 7.45-7.40 (m, 10 H, Ar*H* in SPA), 5.96 (m, 10 H, -C*H*=CH-Ph in SPA), 5.11-5.10 (m, 10 H, -CH=C*H*-Ph in SPA), 3.95-3.93 (m, 20 H, N-CH_2-CH_2-O in SPA), 3.30-3.25 (m, 20 H, N-CH_2-CH_2-O in SPA), 2.77 (m, 4 H, CH_3-C*H*-CH_3 of ^{i}PrO- in Ti(salen)), 1.48-1.44 (m, 3H, S-CH_2-CH_2-CH_3), 1.24 (m, 16 H, cyclohexyl-*H*), 1.23-1.21 (m, 24 H, CH_3-CH-CH_3 of ^{i}PrO- in Ti(salen)), 1.20 (m, 54 H, -C(CH_3)$_3$ in Ti(salen)), 1.18-1.17 (m, 60 H, -C(CH_3)$_2$ in SPA). The degress of polymerization of the individual SPA and Ti(salen) were determined using the ^{1}H NMR spectrum (see Figure S7) by comparing the signals attributable to individual blocks (SPA at 1.16-1.17 ppm assigned to -C(CH_3)$_2$, and Ti(salen) at 2.75-2.78 ppm assigned to CH_3-C*H*-CH_3 of ^{i}PrO- groups) with that of an end methyl group (–SH–CH_2–CH_2–CH_3, at 1.44-1.48 ppm). FT-IR (KBr): γ_{max}/cm^{-1} 3428, 2973, 2954, 2871, 1701, 1590, 1655, 1581, 1531, 1521, 1478, 1460, 1397, 1368, 1328, 1308, 1290, 1270, 1235, 1167, 1127, 1085, 1048, 951, 880, 839, 801, 766, 749, 697, 565, 540. GPC (THF): M_n= 6982, M_w= 8624, PDI= 1.24. α_{25}^D = -20.9 (C = 0.005 g.mL^{-1}, CH_2Cl_2), Titanium content: 0.175 mmol.g^{-1}.

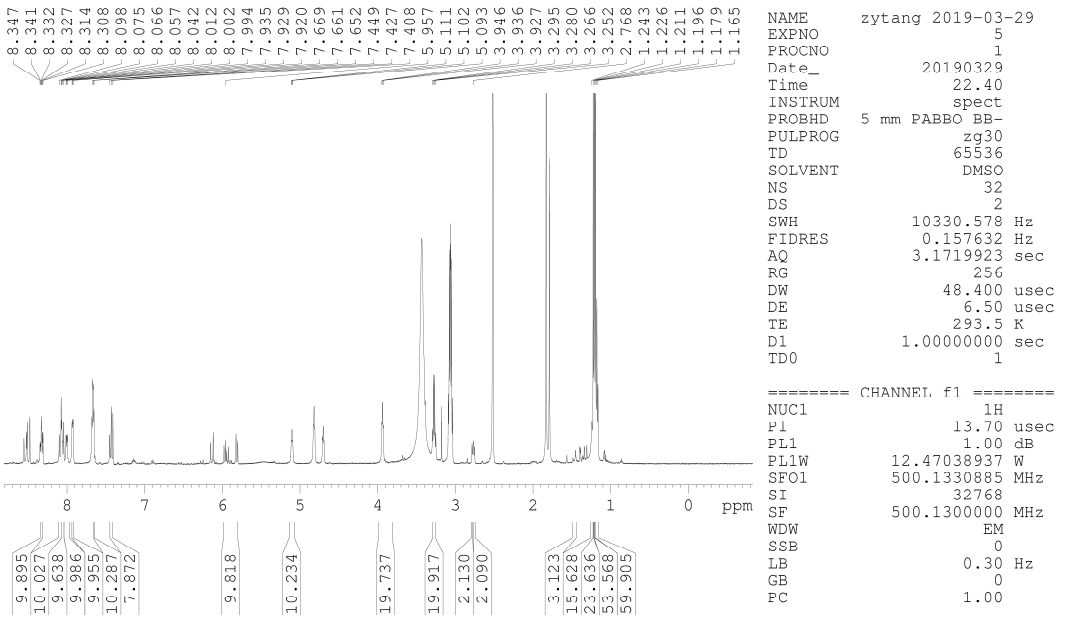


Figure S8. ^{1}H NMR of the **$PS_{10}C_2$**.

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

***Phenyl methyl sulfoxide*:** The product has been identified by ^{1}H NMR spectrum (see Figure S9). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.69-7.53 (m, 5 H, Ar*H*), 2.76 (s, 3 H, -SCH_3). 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, column temperature was programmed from 80 to 180 ^{o}C with 6 ^{o}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 = 6.66 min, minor enantiomer t_S = 8.11 min (see Figure S10-S12).

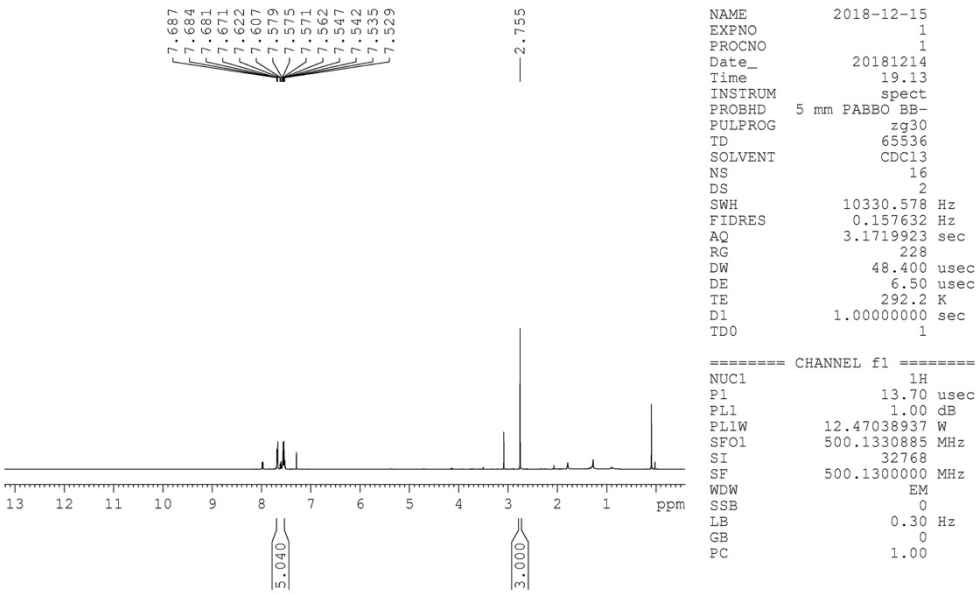


Figure S9. ^{1}H NMR of phenyl methyl sulfoxide.

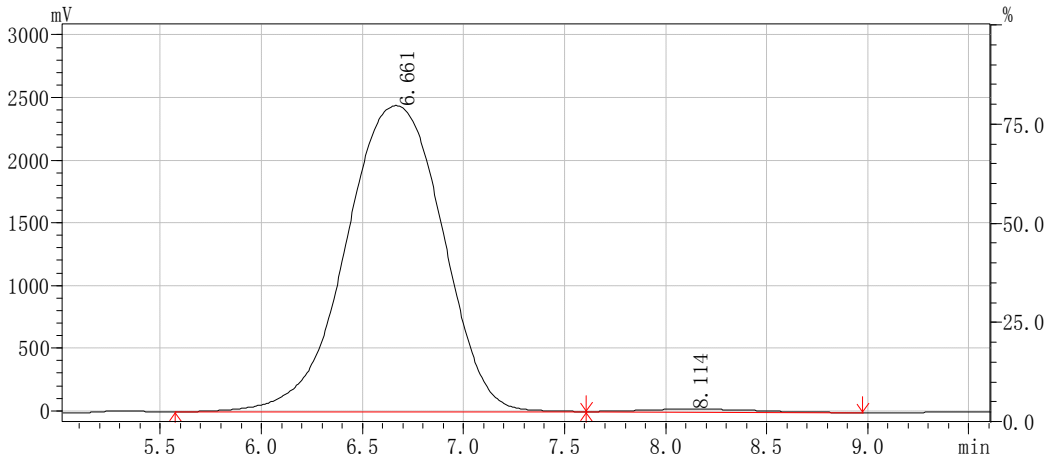


Figure S10. HLPC of phenyl methyl sulfoxide obtained over **$PS_{10}(IS)_2$** (ee value = 99%).

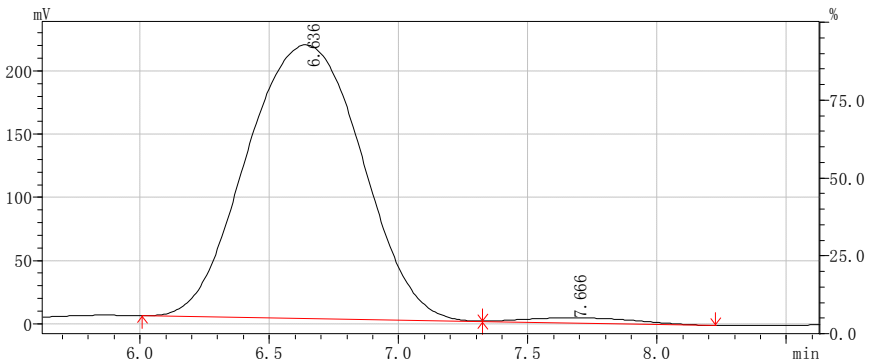


Figure S11. HLPC of phenyl methyl sulfoxide obtained over $\mathbf{PS_{10}C_2}$ (ee value = 92%).

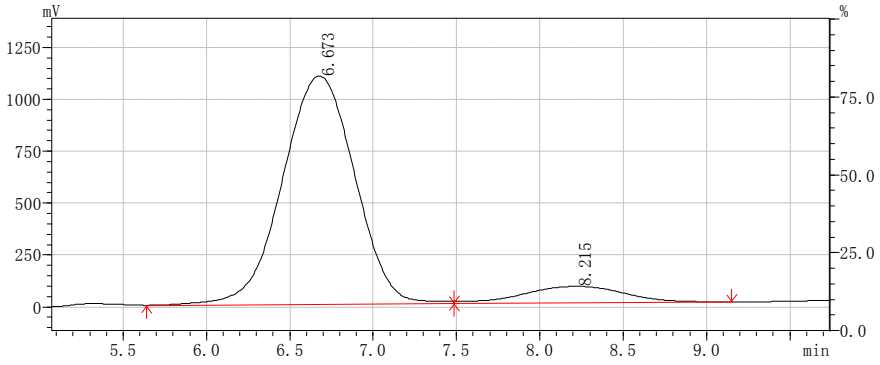


Figure S12. HLPC of phenyl methyl sulfoxide obtained over *IL*/Ti(salen) (ee value = 80%).

***p-Methoxyphenyl methyl sulfoxide*:** The product has been identified by ^{1}H NMR spectrum (see Figure S13). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.64-7.00 (m, 4 H, Ar*H*), 3.89 (s, 3 H, -OCH_3), 2.73 (s, 3 H, -SCH_3). 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, column temperature was programmed from 80 to 180 ^{o}C with 6 ^{o}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 = 1.2 mL.min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 6.65 min and minor enantiomer t_S = 7.79 min (see Figure S14-S16).

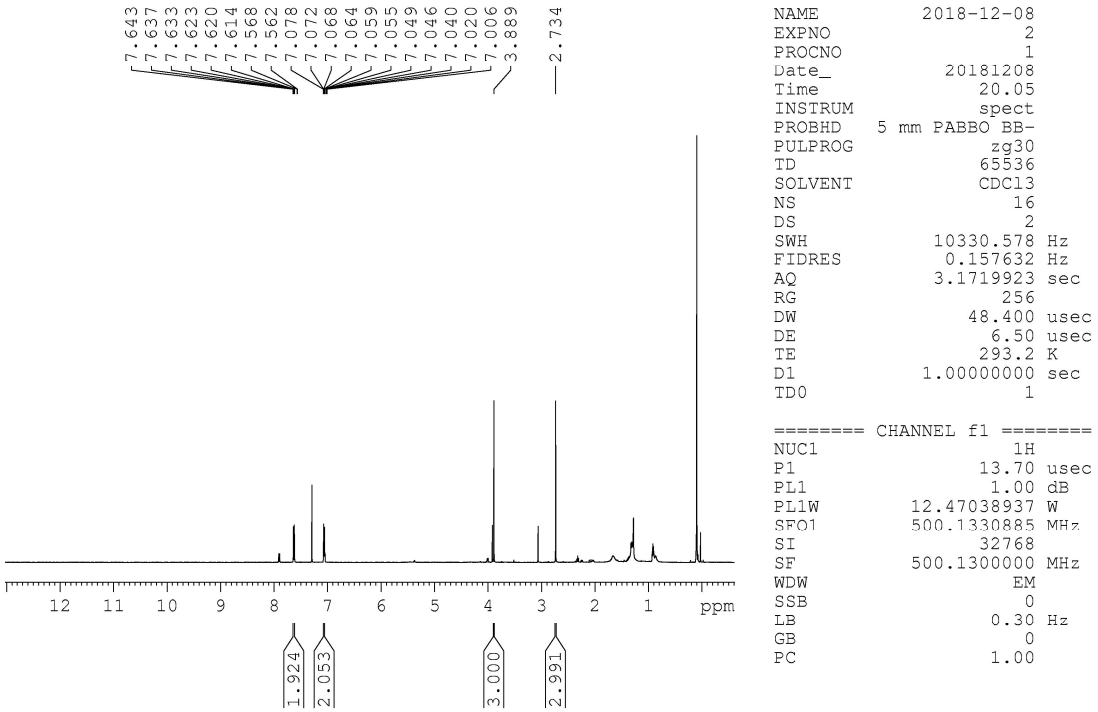


Figure S13. ^{1}H NMR of *p*-methoxyphenyl methyl sulfoxide.

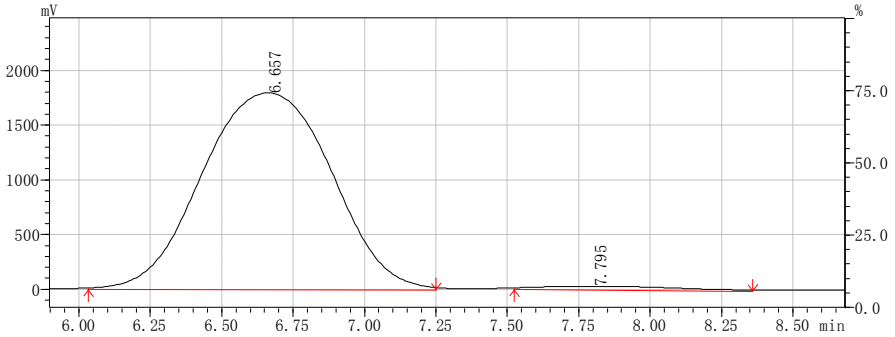


Figure S14. HLPC of *p*-methoxyphenyl methyl sulfoxide obtained over **$PS_{10}(IC)_2$** (ee value = 96%).

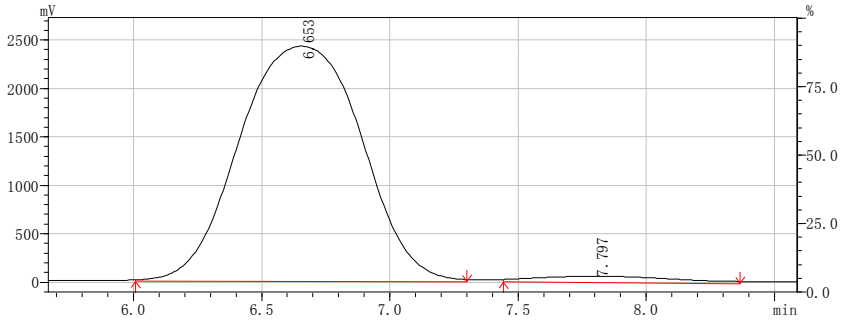


Figure S15. HLPC of methyl *p*-methoxyphenyl sulfoxide obtained over **$PS_{10}C_2$** (ee value = 94%).

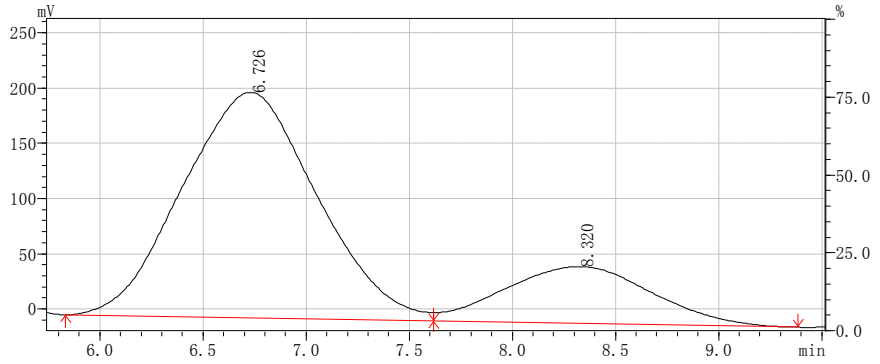


Figure S16. HLPC of *p*-methoxyphenyl methyl sulfoxide obtained over *IL*/Ti(salen) (ee value = 58%).

***o-Methoxyphenyl methyl sulfoxide*:** The product has been identified by ^{1}H NMR spectrum (see Figure S17). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.85-6.94 (m, 4 H, Ar*H*), 3.91 (s, 3 H, -OCH_3), 2.80 (s, 3 H, -SCH_3). 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, 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 = 1.2 mL.min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 6.66 min and minor enantiomer t_S =7.79 min (see Figure S18- S20).

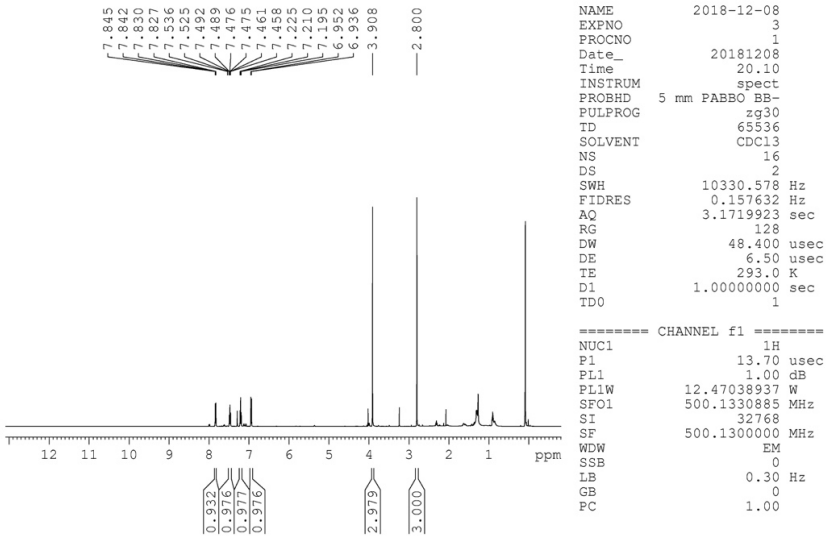


Figure S17. ^{1}H NMR of *o*-methoxyphenyl methyl sulfoxide.

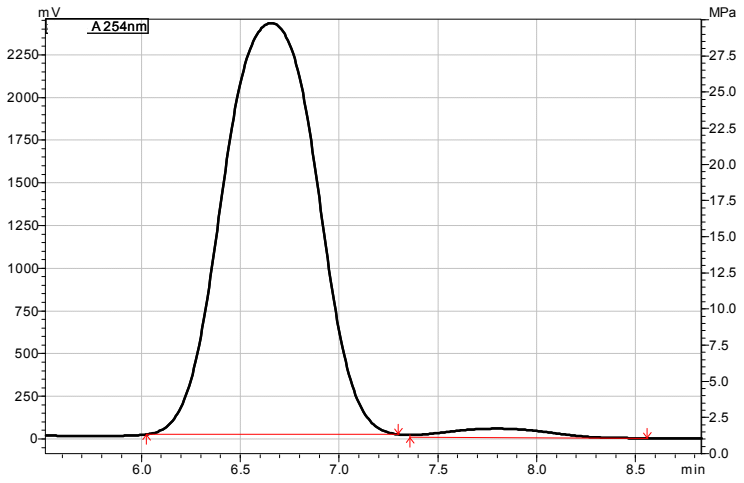


Figure S18. HLPC of *o*-methoxyphenyl methyl sulfoxide obtained over **$PS_{10}(IC)_2$** (ee value = 96%).

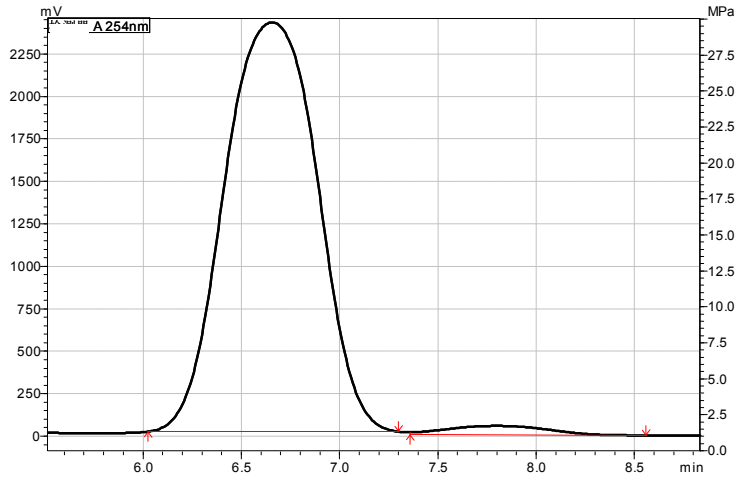


Figure19. HLPC of *o*-methoxyphenyl methyl sulfoxide obtained over **$PS_{10}C_2$** (ee value = 95%).

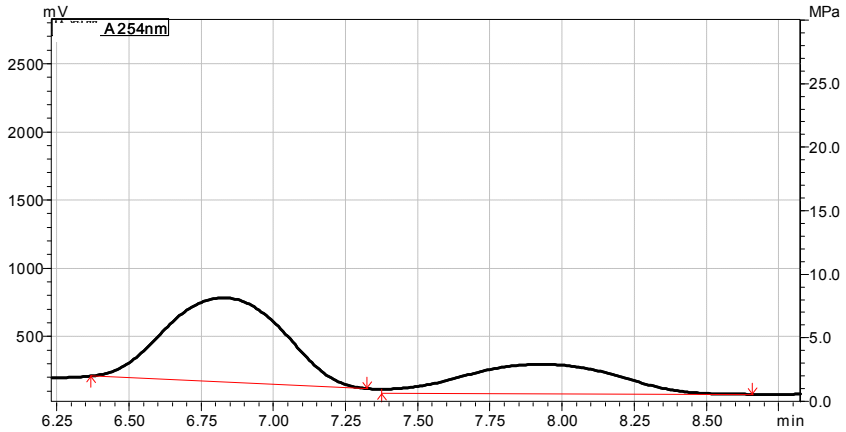


Figure S20. HLPC of *o*-methoxyphenyl methyl sulfoxide obtained over *IL*/Ti(salen) (ee value = 37%).

Phenyl ethyl sulfoxide: The product has been identified by ^{1}H NMR spectrum (see Figure S21). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.69-7.61 (m, 5 H, Ar*H*), 2.97-2.77 (m, 2 H, -C*H*$_2$-CH_3), 1.24 (m, 3 H, -CH_2-C*H*$_3$). 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, 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 = 1.2 mL.min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 5.75 min and minor enantiomer t_S = 6.87 min (see Figure S22- S24).

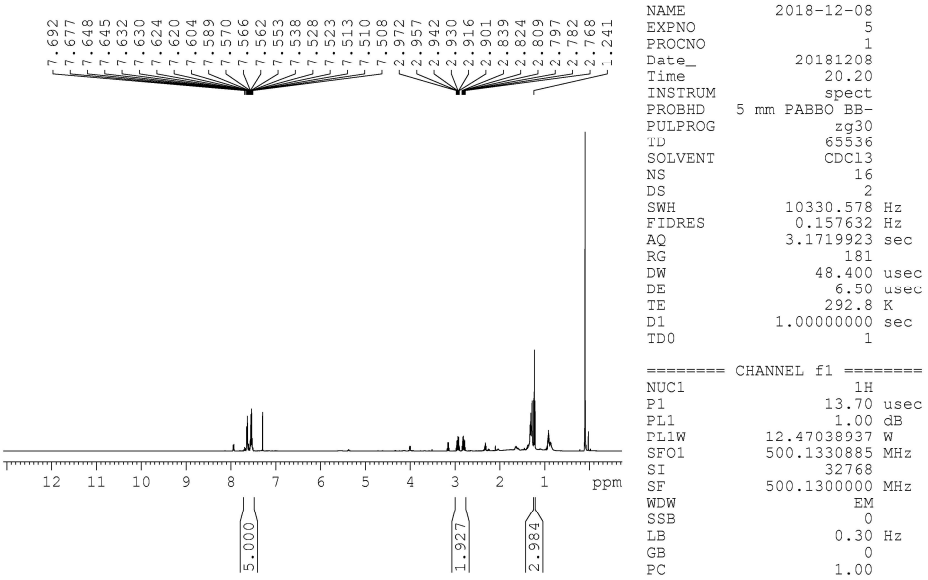


Figure S21. ^{1}H NMR of phenyl ethyl sulfoxide.

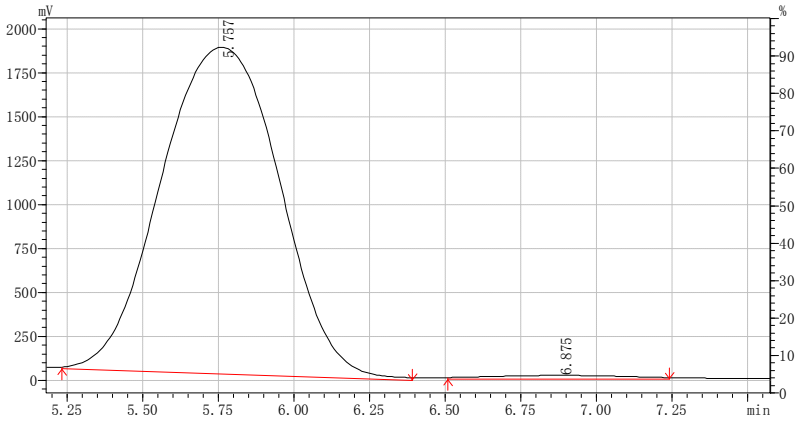


Figure S22. HLPC of phenyl ethyl sulfoxide obtained over **$PS_{10}(IC)_2$** (ee value = 97%).

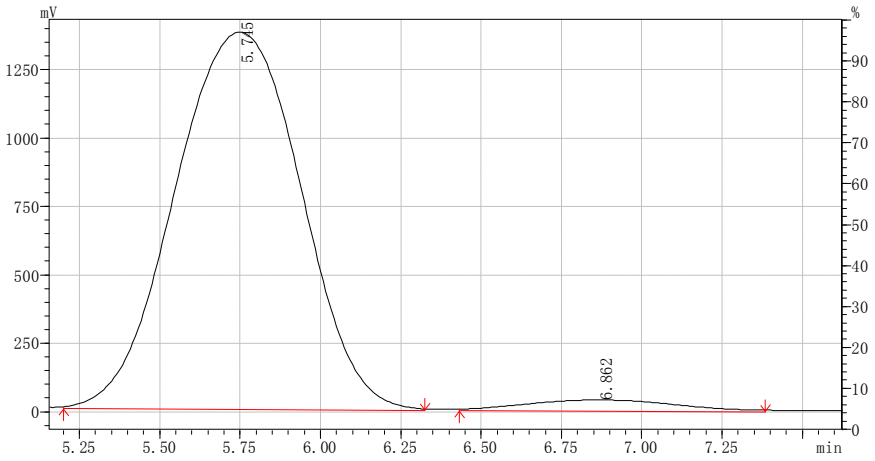


Figure S23. HLPC of phenyl ethyl sulfoxide obtained over **$PS_{10}C_2$** (ee value = 93%).

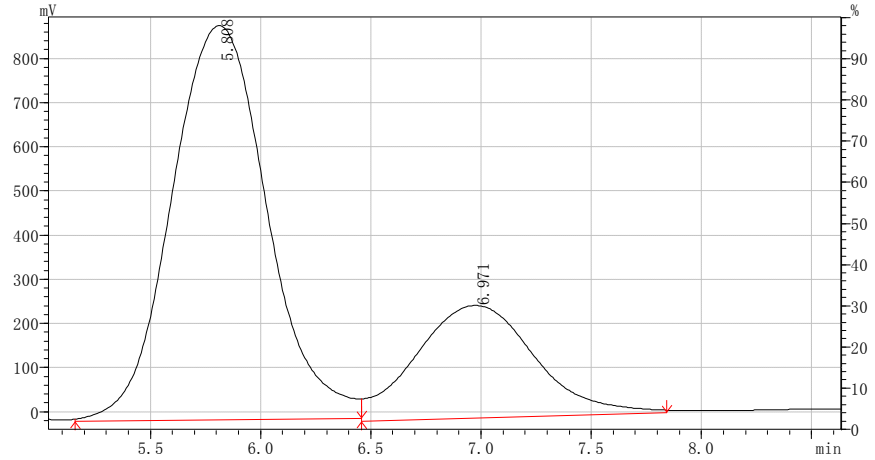


Figure S24. HLPC of phenyl ethyl sulfoxide obtained over *IL*/Ti(salen) (ee value = 57%).

***Phenyl n-butyl sulfoxide*:** The product has been identified by ^{1}H NMR spectrum (see Figure S25). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.36-7.18 (m, 5 H, Ar*H*), 2.97-2.94 (m, 2 H,-C*H*$_2$-CH_2-CH_2-CH_3), 1.70-1.62 (m, 2 H,-CH_2-C*H*$_2$-CH_2-CH_3), 1.51-1.48 (m, 2 H,-CH_2-CH_2-C*H*$_2$-CH_3), 0.93-0.90 (m, 3 H,-CH_2-CH_2-CH_2-C*H*$_3$). 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 180 °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 = 1.2 mL. min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 4.01 min and minor enantiomer t_S = 4.88 min (see Figure S26-S28).

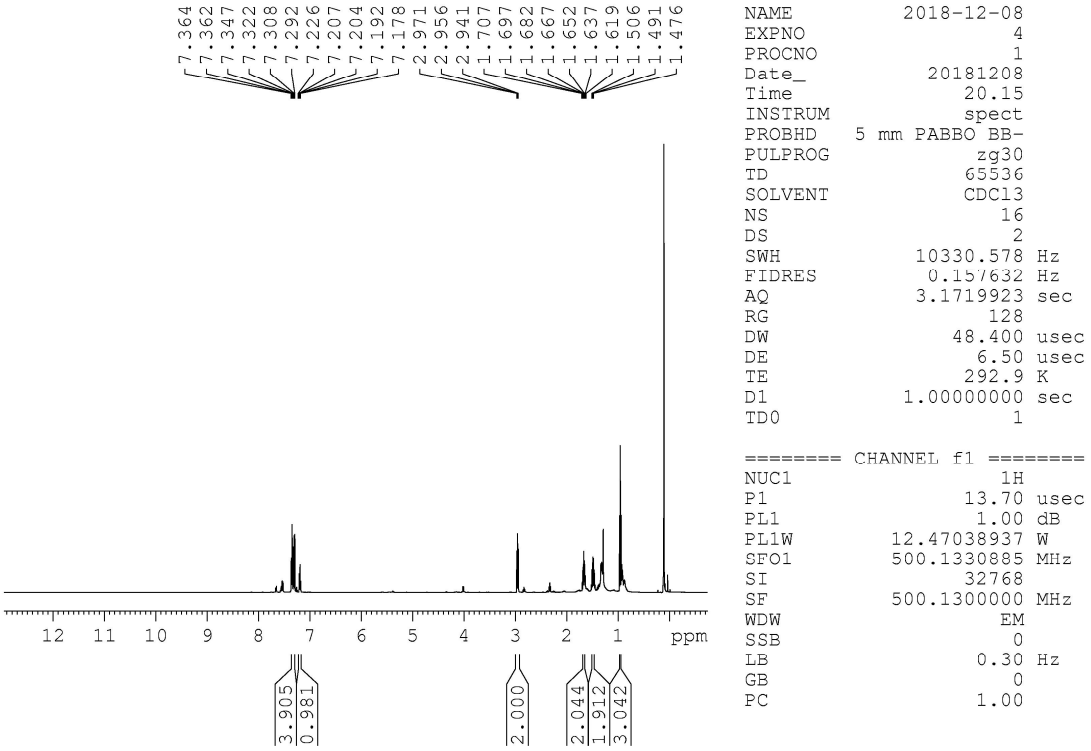


Figure S25. ^{1}H NMR of phenyl *n*-butyl sulfoxide.

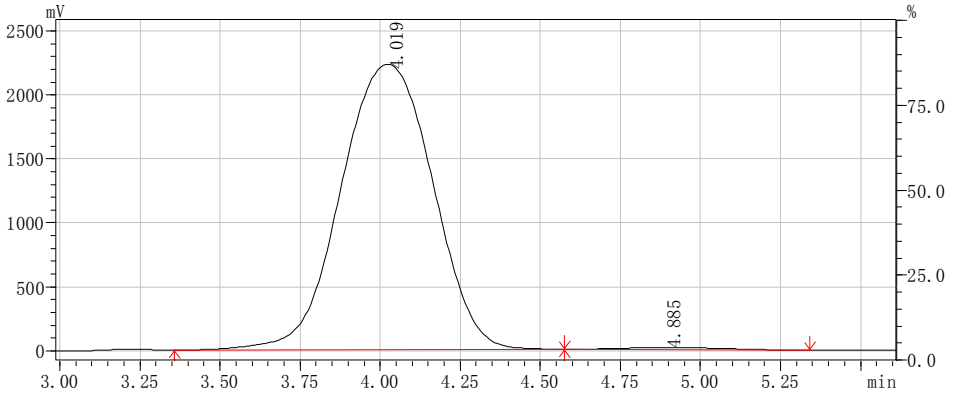


Figure S26. HLPC of phenyl *n*-butyl sulfoxide obtained over **$PS_{10}(IC)_2$** (ee value = 99%).

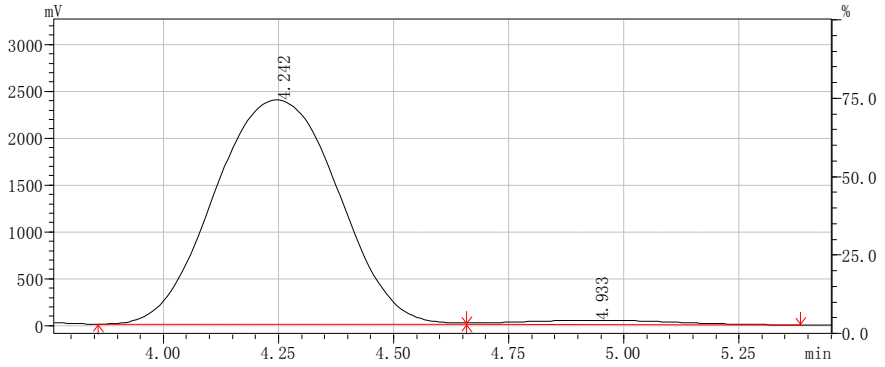


Figure S27. HLPC of phenyl *n*-butyl sulfoxide obtained over **$PS_{10}C_2$** (ee value = 94%).

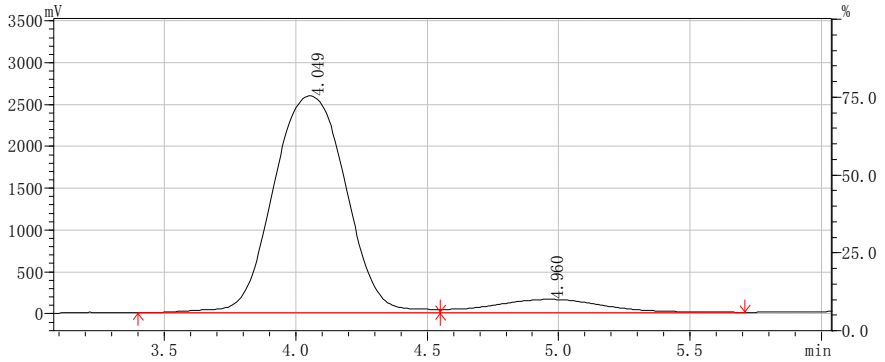


Figure S28. HLPC of phenyl *n*-butyl sulfoxide obtained over *IL*/Ti(salen) (ee value = 86%).

Phenyl n-hexyl sulfoxide: The product has been identified by ^{1}H NMR spectrum (see Figure S29). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.36-7.18 (m, 5 H, Ar*H*), 2.97-2.94 (m, 2 H, -C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 1.71-1.65 (m, 2 H, -CH$_2$-C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 1.49-1.43 (m, 2 H, -CH$_2$-CH$_2$-C*H*$_2$-CH$_2$-CH$_2$-CH$_3$), 1.33-1.32 (m, 4 H, -CH$_2$-CH$_2$-CH$_2$-C*H*$_2$-C*H*$_2$-CH$_3$), 0.91-0.87 (s, 3 H, -C*H*$_3$). 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, 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 = 1.2 mL.min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 4.23 min and minor enantiomer t_S = 4.81 min (see Figure S30- S32).

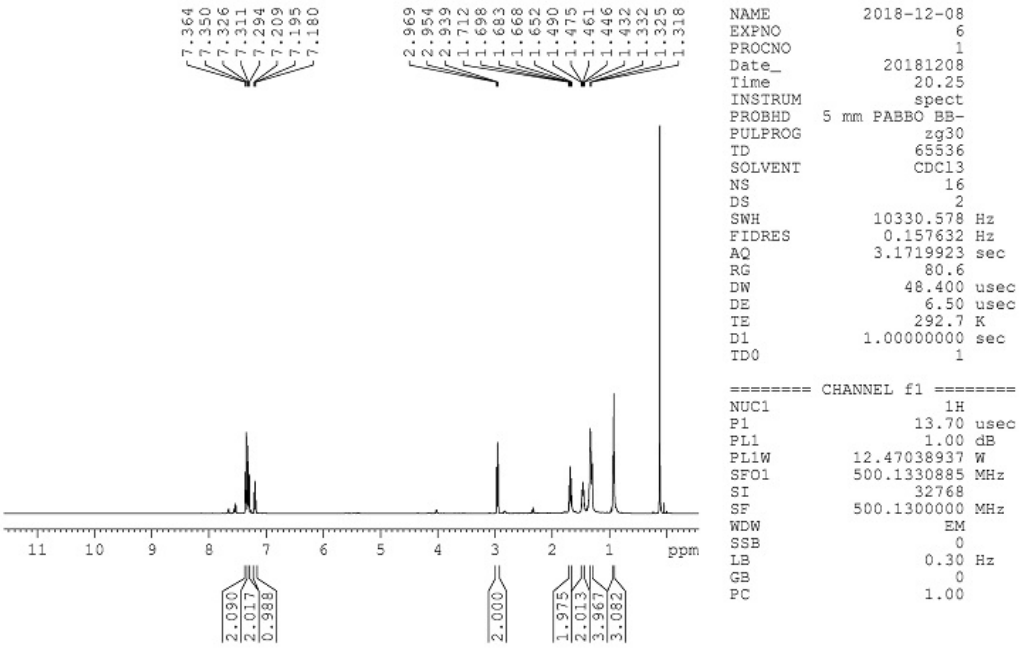


Figure S29. ^{1}H NMR of phenyl *n*-hexyl sulfoxide.

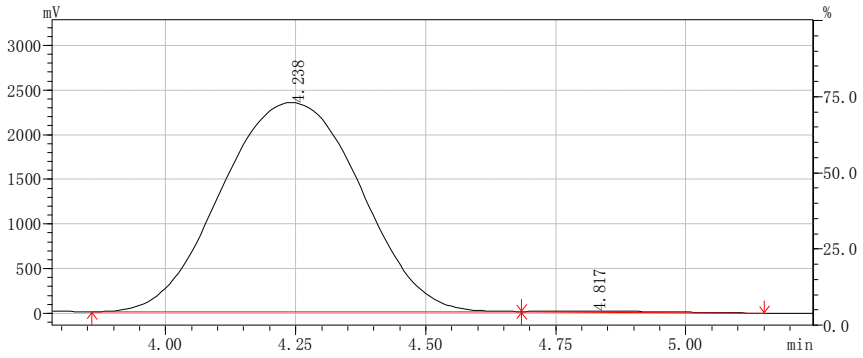


Figure S30. HLPC of phenyl *n*-hexyl sulfoxide obtained over **$PS_{10}(IC)_2$** (ee value = 99%).

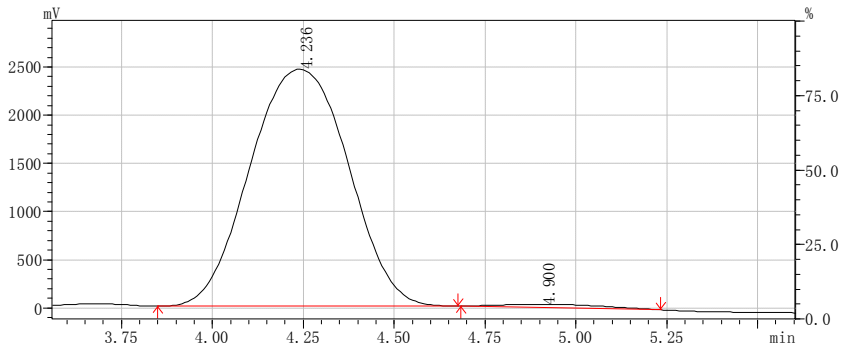


Figure S31. HLPC of phenyl *n*-hexyl sulfoxide obtained over **$PS_{10}C_2$** (ee value = 97%).

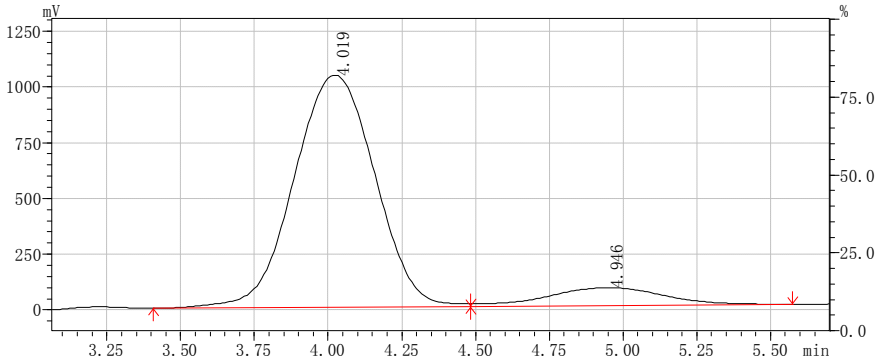


Figure S32. HLPC of phenyl *n*-hexyl sulfoxide obtained over *IL*/Ti(salen) (ee value = 79%).

p-Bromophenyl methyl sulfoxide: The product has been identified by ^{1}H NMR spectrum (see Figure S33). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.47-7.14 (m, 4 H, Ar*H*), 2.94 (s, 3 H, -SCH_3). 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, 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 = 1.2 mL.min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 6.10 min and minor enantiomer t_S = 7.33 min (see Figure S34-S36).

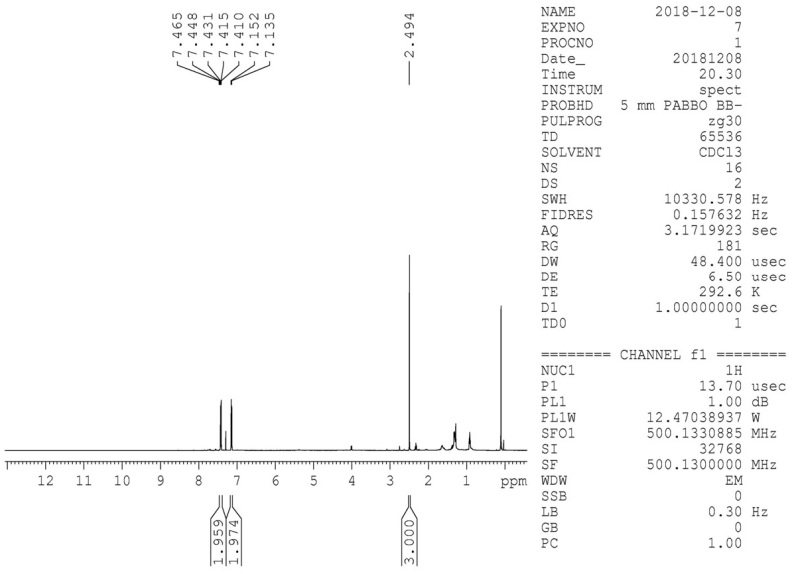


Figure S33. ^{1}H NMR of *p*-bromophenyl methyl sulfoxide.

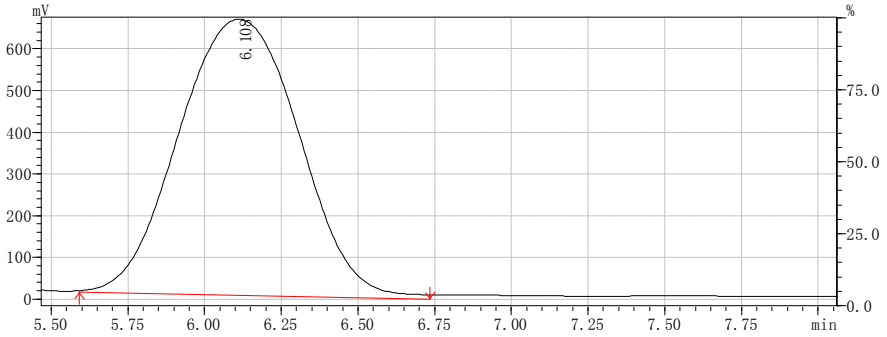


Figure S34. HLPC of *p*-bromophenyl methyl sulfoxide obtained over **$PS_{10}(IS)_2$** (ee value >99%).

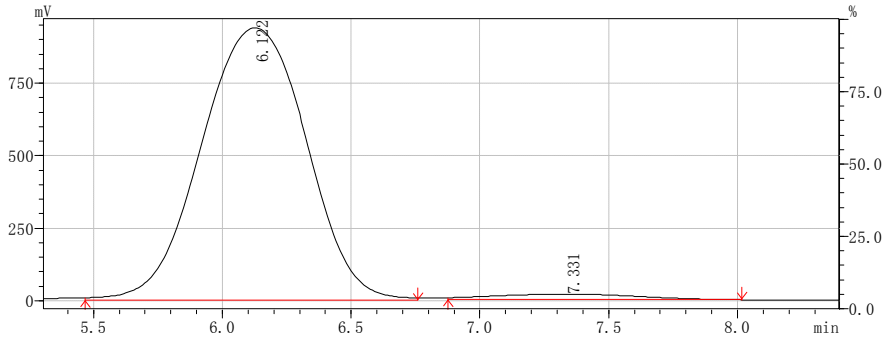


Figure S35. HLPC of *p*-bromophenyl methyl sulfoxide obtained over **$PS_{10}C_2$** (ee value =93%).

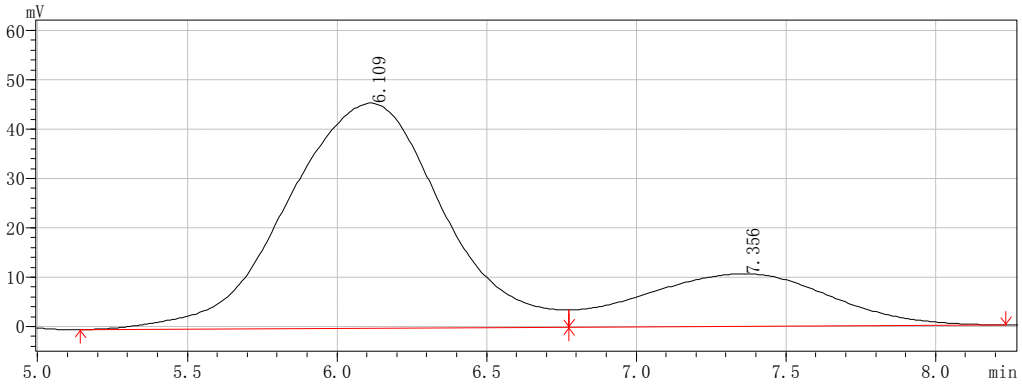


Figure S36. HLPC of *p*-bromophenyl methyl sulfoxide obtained over *IL*/Ti(salen) (ee value = 54%).