Supporting Information

Ultraviolet-responsive self-assembled metallomicelles for photocontrollable catalysis of asymmetric sulfoxidation in water

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CONTENT:

1. Preparation and identity of the copolymers ($PN_{422}A_{25}$-C, $PN_{427}A_{10}$-C, and $PN_{429}A_5$-C)

1.1 Preparation of the copolymers of ***$PN_{422}A_{25}$-C*** *and* ***$PN_{429}A_5$-C****.*

To regulate the LCST of copolymers close to room temperature (25 °C), various rations of NIPAAm to azobenzene blocks have been modulated in the chiral salen Ti^{IV}-containing amphiphiles. The synthetic procedure was similar to that of **$PN_{427}A_{10}$-C** excepted for the varied molar feeds of NIPAAm and N-azo-acrylamide.

During the procedure, monomers of NIPAAm and *N*-azo-acrylamide with different molar feed (9.8 mmol of NIPAAm and 0.49 mmol of *N*-azo-acrylamide for **$PN_{422}A_{25}$-C**, 39.2 mmol of NIPAAm and 0.49 mmol of *N*-azo-acrylamide for **$PN_{429}A_5$-C**), were dissolved in THF in a Schlenk tube. AIBN (0.051 mmol for **$PN_{422}A_{25}$-C**, and 0.199 mmol for **$PN_{429}A_5$-C**) and 2-aminoethanethiol hydrochloride (0.10 mmol for **$PN_{422}A_{25}$-C**, and 0.40 mmol for **$PN_{429}A_5$-C**), which acted as a radical initiator and chain transfer reagent, were then added into the solutions. The reaction mixtures were degassed by bubbling with nitrogen gas at room temperature for 30 min. Polymerizations were carried out at 60 °C for 24 h with nitrogen protection. The mixtures were then cooled to room temperature, and followed by treating with solid KOH to liberate the terminal amino group. The obtained solutions were concentrated under vacuum. The crude products were purified by repeated precipitating from diethyl ether and followed from THF to remove unreacted monomers. After drying under vacuum for 6 h at 40 °C, the copolymers of poly(NIPAAm-*co*-Azo) was obtained as yellow powders.

The obtained copolymers of poly(NIPAAm-*co*-Azo) (0.18 mmol), (*R*,*R*)-*N*- (3,5-di-*tert*-butylsalicylidene)-*N*′-(3-*tert*-butyl-5-chloromethyl-salicylidene)-1,2-cyclohexanediamine (0.25 mmol, 0.137 g) and triethylamine (0.2 mmol, 0.02 g) were mixed in dry toluene (30 mL) under

room temperature. The mixtures were refluxed for 48 h under nitrogen protection. After removal of solvent, the residues were dissolved in tetrahydrofuran to remove the formed triethylamine hydrochloride through filtration. Filtrates were concentrated in vacuo, and were treated with $Ti(O^iPr)_4$ (0.25 mmol, 0.07 g) in dichloromethane (30 mL) for 12 h at room temperature. The mixtures were concentrated under vacuum. Crude products were purified by repeatedly precipitating from tetrahydrofuran using diethyl ether as precipitant. The resulting orange solids were dissolved in chloroform (20 mL), and treated with water (2 mL) to remove any traces of TiO_2 by filtration. Filtrates were concentrated in vacuum and further dried in vacum at 40 ^oC overnight, giving orange powder of poly(NIPAAm-*co*-Azo)-modified chiral salen Ti^{IV} catalyst, denoted as **PN_xA_y-C** (where x represented the repeated units number of NIPAAM, and y represented the repeated units number of N-azo-acrylamide in copolymers. The numbers were determined by ^1H NMR spectra).

1.2 Identity of the **PN_xA_y-C** by ^1H NMR spectra

Given mass of **PN_xA_y-C** (**$PN_{422}A_{25}$-C**, **$PN_{427}A_{10}$-C**, and **$PN_{429}A_5$-C**) were placed in NMR tubes, and the tubes were backfilled with N_2. In dark room, D-substituted solvent was added *via* syringe, and the sample was carefully shaken until full dissolution was obtained. The solutions were irradiated by visible light (λ= 410 nm) for 30 min, and then being kept in the dark for 72 h to give dark-adapted samples for NMR determination.

$PN_{422}A_{25}$-C in DMSO-d_6: The structure and chemical composition of **$PN_{422}A_{25}$-C** were identified by ^1H NMR spectrum carried out in DMSO-d_6 (see Fig. S1). ^1H NMR (500 MHz, DMSO-d_6) δ (ppm): δ 7.91 (s, 2 H, Ph-*H* in Ti(salen)), 7.84 (m, 102 H, -N=N-Ph-*H* and Ph-*H* in Ti(salen)), 7.55 (m, 50 H, -NH-Ph-*H*), 7.52 (m, 75 H, N=N-Ph-*H*), 7.19 (m, 447 H, O=C-N*H*-CH

and O=C-N*H*-Ph), 3.83 (m, 422 H, CH_3-C*H*-CH_3), 3.5 (m, 2 H, CH=N-C*H*), 2.96 (m, 2 H, NH-CH_2-Ph), 2.63 (m, 2 H, S-CH_2-CH_2-), 2.36 (m, 2 H, S-CH_2-CH_2-), 2.17 (m, 2 H, CH_3-C*H*-CH_3 of ^{i}PrO- in Ti(salen)), 1.96 (m, 447 H, CH_2-C*H*- in NIPAAm and *N*-azo-acrylamide), 1.45 (s, 894 H, -CH_2-CH- in NIPAAm and *N*-azo-acrylamide), 1.22 (m, 8 H, cyclohexyl-*H*), 1.18 (m, 39 H, -CH_3 of *t*-Bu and ^{i}PrO- in Ti(salen)), 1.03 (s, 2532 H, CH_3-CH-CH_3).

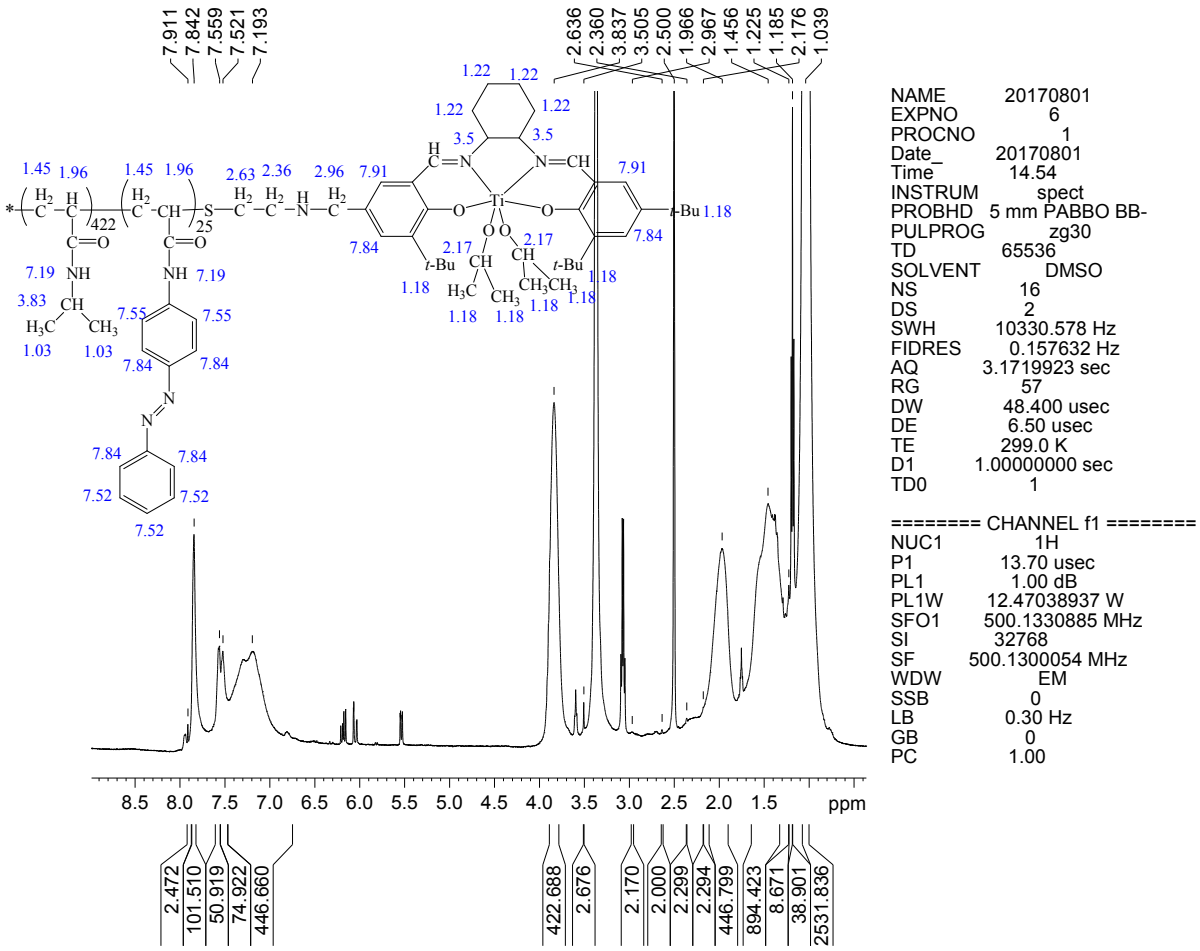

Fig. S1 ^{1}H NMR spectrum of dark-adapted **$PN_{422}A_{25}$-C** in DMSO-d_6.

$PN_{427}A_{10}$-C in DMSO-d_6: The structure and chemical composition of **$PN_{427}A_{10}$-C** were identified by ^{1}H NMR spectrum carried out in DMSO-d_6 (see Fig. S2). ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): δ 9.97 (s, 2H, Ph-*H*C=N-), 7.90 (s, 2H, Ph-*H* in Ti(salen)), 7.84 (m, 42 H, -N=N-Ph-*H*), 7.60-7.56 (m, 20 H, O=C-NH-Ph-*H*), 7.52 (m, 30 H, N=N-Ph-*H*), 7.29-7.20 (m, 437

H, O=C-N*H*-CH and O=C-N*H*-Ph), 3.83 (m, 427 H, CH_3-C*H*-CH_3 in NIPAAm), 3.17-3.16 (m, 2 H, cyclohexyl-*H*), 2.92-2.90 (m, 2 H, NH-CH_2-Ti(salen)), 2.63 (m, 2 H, S-CH_2-CH_2-NH), 2.36 (m, 2 H, S-CH_2-CH_2-NH), 2.17 (m, 2 H, CH_3-C*H*-CH_3 of ^{i}PrO- in Ti(salen)), 1.95 (m, 437 H, CH_2-C*H*- in NIPAAm and *N*-azo-acrylamide), 1.44 (s, 874 H, -CH_2-CH- in NIPAAm and *N*-azo-acrylamide), 1.22 (m, 8 H, cyclohexyl-*H*), 1.17 (m, 39 H, -CH_3 of *t*-Bu and ^{i}PrO- in Ti(salen)), 1.03 (s, 2562 H, CH_3-CH-CH_3).

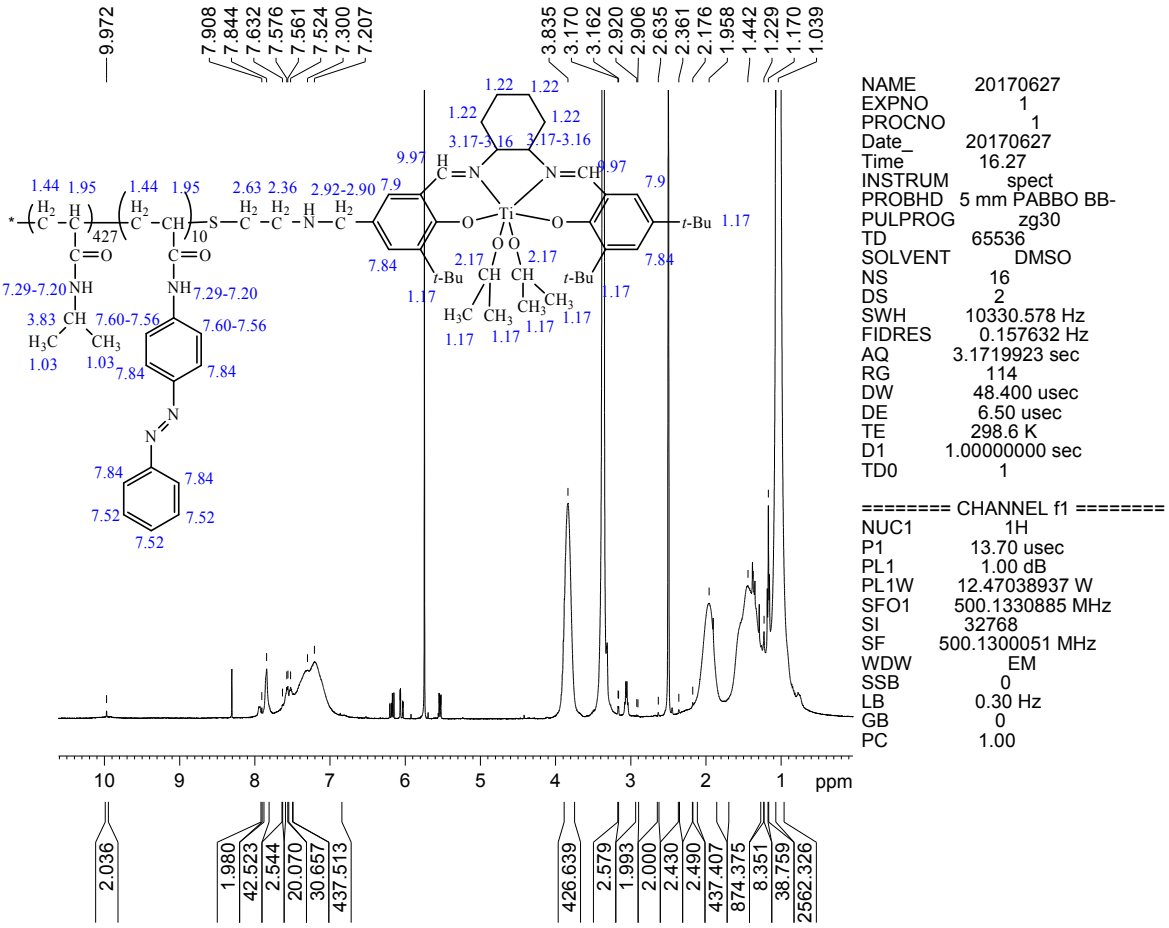

Fig. S2 ^{1}H NMR spectrum of dark-adapted **$PN_{427}A_{10}$-C** in DMSO-d_6.

$PN_{427}A_{10}$-C in D_2O: Self-assembly of **$PN_{427}A_{10}$-C** in aqueous system was demonstrated by ^{1}H NMR spectrum carried out in D_2O (see Fig. S3). ^{1}H NMR (500 MHz, D_2O) δ (ppm): 3.92 (m, 427 H, CH_3-C*H*-CH_3 in NIPAAm), 2.75 (m, 2 H, S-CH_2-CH_2-NH). 2.59 (m, 2 H, S-CH_2-CH_2-), 2.15-

2.04 (m, 427 H, CH_2-C*H*- in NIPAAm), 1.74-1.60 (m, 854 H, -CH_2-CH- in NIPAAm), 1.17 (s, 2562 H, CH_3-CH-CH_3 in NIPAAm).

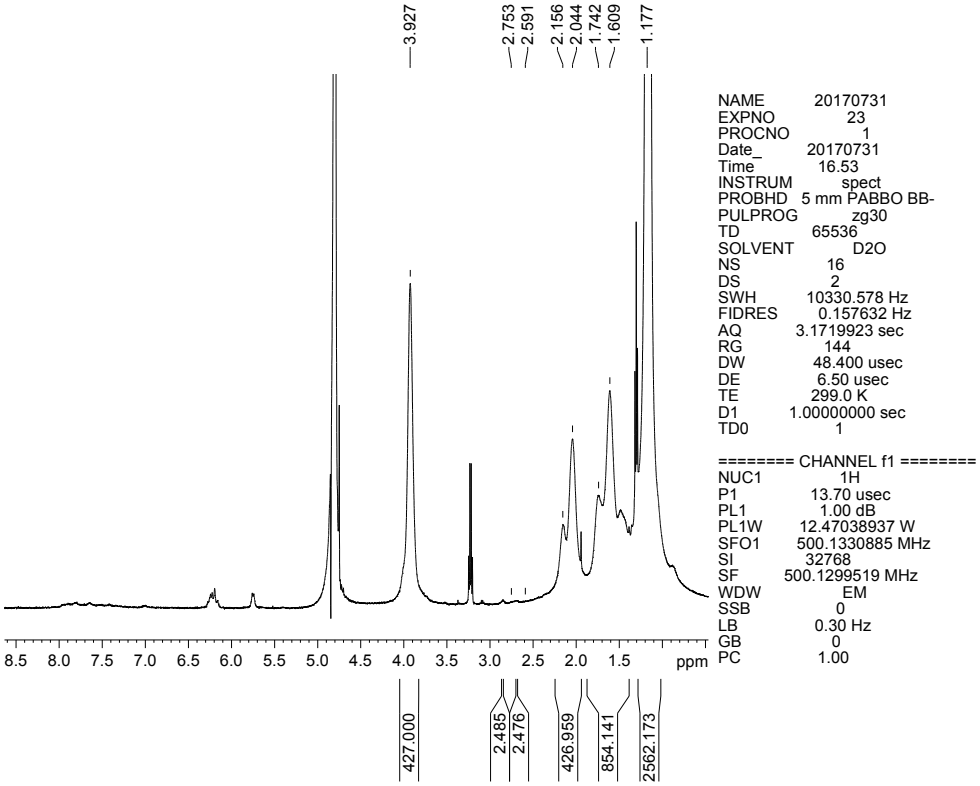

Fig. S3 ^{1}H NMR spectrum of dark-adapted **PN$_{427}$A$_{10}$-C** in D_2O.

PN$_{429}$A$_5$-C in DMSO-d_6: The structure and chemical composition of **PN$_{429}$A$_5$-C** were identified by ^{1}H NMR spectrum carried out in DMSO-d_6 (see Fig. S4). ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 7.90 (s, 2 H, Ph-*H* in Ti(salen)), 7.84 (m, 22 H, -N=N-Ph-*H* and Ph-*H* in Ti(salen)), 7.55 (m, 10 H, -NH-Ph-*H*), 7.52 (m, 15 H, N=N-Ph-*H*), 7.19 (m, 434 H, O=C-N*H*-CH and O=C-N*H*-Ph), 3.84 (m, 429 H, CH_3-C*H*-CH_3 in NIPAAm), 3.57 (m, 2 H, cyclohexyl-*H*), 2.63 (m, 2 H, S-CH_2-CH_2-NH_2), 2.36 (m, 2 H, S-CH_2-CH_2-NH), 2.17 (m, 2 H, CH_3-C*H*-CH_3 of ^{i}PrO- in Ti(salen)) 1.96 (m, 434 H, CH_2-C*H*-, CH_2-C*H*- in NIPAAm and *N*-azo-acrylamide), 1.43-1.34 (s, 868 H, -CH_2-CH- in NIPAAm and *N*-azo-acrylamide), 1.22 (m, 8 H, cyclohexyl-*H*), 1.17 (m, 39 H, -CH_3 of *t*-Bu and ^{i}PrO- in Ti(salen)), 1.04 (s, 2574 H, CH_3-CH-CH_3).

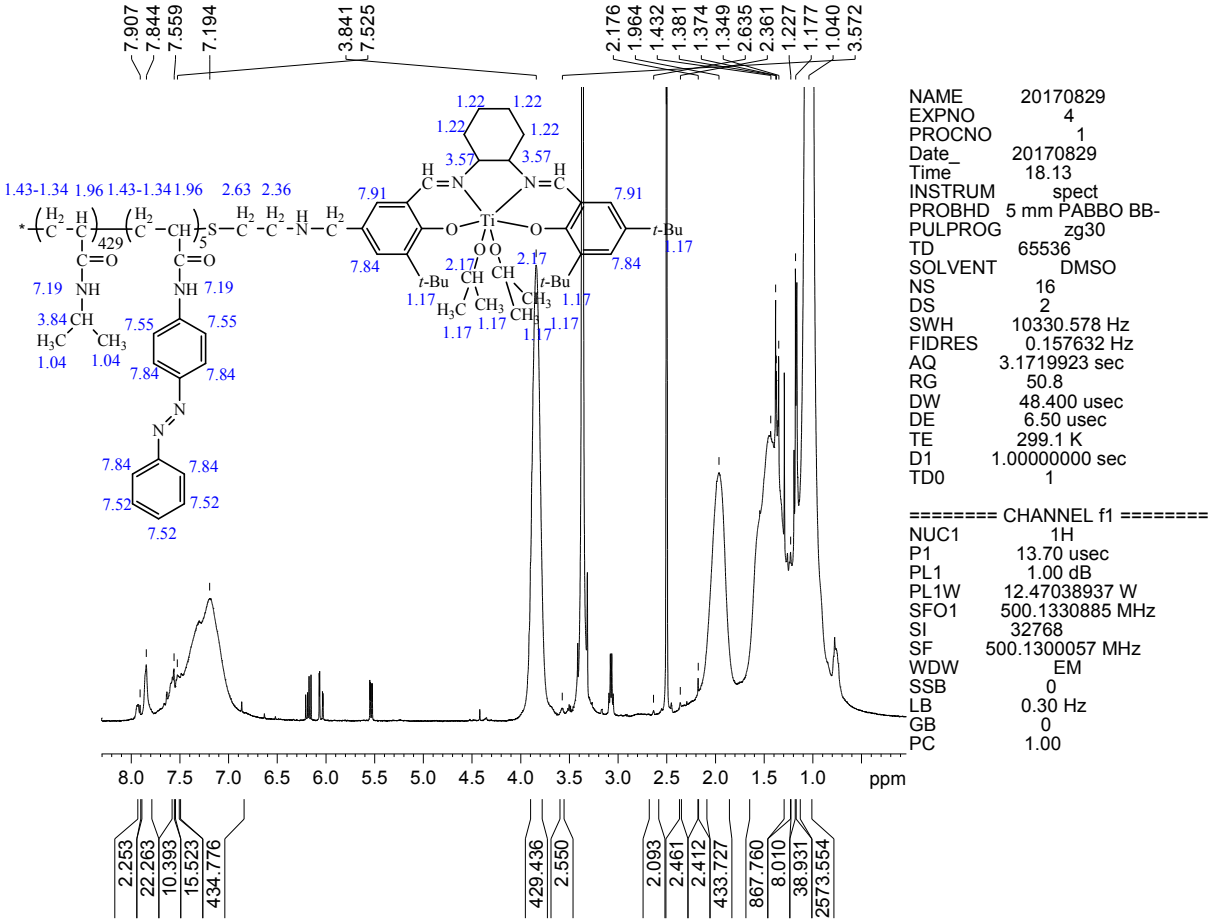

Fig. S4 ^{1}H NMR spectrum of dark-adapted **PN$_{429}$A$_5$-C** in DMSO-d_6.

2. LCST determination of the copolymers (PN$_{422}$A$_{25}$-C, PN$_{427}$A$_{10}$-C, and PN$_{429}$A$_5$-C)

The LCST of these copolymers were measured *via* UV–visible spectrophotometry by determining the turbidity of corresponding aqueous solutions at various temperatures. The copolymer concentration was 0.8 mg. mL^{-1}, and the heating rate was 2 ◦C/min. The copolymer solution was stirred and kept at the same temperature for 1 min before each measurement. The turbidimetry curves was drawn by measuring the transmittance of the aqueous polymer solution (max = 440 nm) as a function of temperature, as shown in Fig. S5. Sharp decrease in transmittance pointed to the characteristic temperature of corresponding LCST. Therefore, the LCST of **PN$_{422}$A$_{25}$-C**, **PN$_{427}$A$_{10}$-C**, and **PN$_{429}$A$_5$-C** were determined as *ca.* 14, 26, and 28 ◦C. It was logical

that decreased hydrophobic block in PNIPAAm-based copolymer led to increase in the LCST.[1]

Apparently, **$PN_{422}A_{25}$-C** with the LCST (14 °C) lower than room temperature (25 °C) couldn't fulfill the demand of aqueous asymmetric sulfoxidation, since it would become hydrophobic and precipitate from the aqueous system at reaction temperature (25 °C). For **$PN_{429}A_{5}$-C**, although its LCST (28 °C) fitted for the aqueous asymmetric sulfoxidation, few amount of photo-responsive azobenzene moiety in the copolymer was unfavorable to finely control the aqueous asymmetric sulfoxidation by UV light. With these points in mind, more azobenzene-containing **$PN_{427}A_{10}$–C** whose LCST (26 °C) was close to room temperature was chose as the suitable catalyst for photo-controlled catalysis of asymmetric sulfoxidation in water at room temperature (25 °C). The selected **$PN_{427}A_{10}$–C** indeed made the photo-controlled asymmetric catalysis in water come true, and also could be recovered for efficient reuse at mild temperature (slightly higher than room temperature).

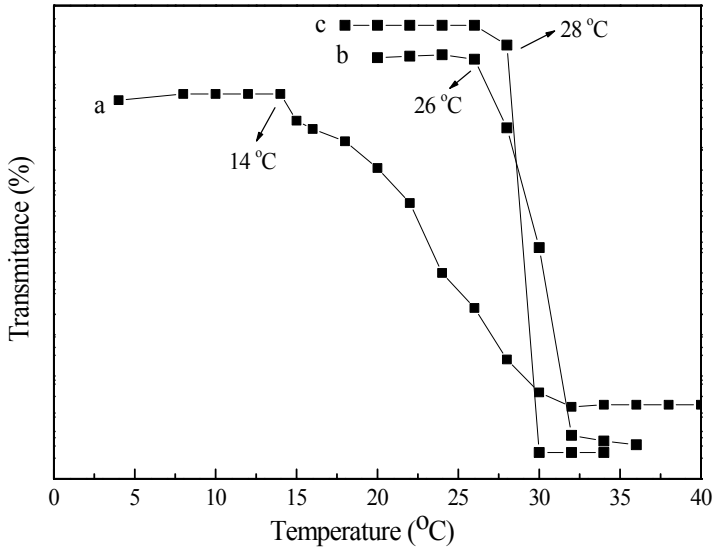

Fig. S5 Plot of changes in solution transmittance (at 440 nm) as a function of temperature for aqueous solutions of **PN_xA_y-C** (concentration: 0.8 mg mL^{-1}).

[1] T. Sun, G. Qing, *Adv. Mater.* **2011,** *23,* 57–77.

3. Identity of the obtained chiral sulfoxide.

Methyl phenyl sulfoxide: The product has been identified by ^{1}H and ^{13}C NMR spectra (see Fig. S6 and S7). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 7.44-7.42 (m, 2 H, Ar*H*), 7.29-7.27 (m, 3 H, Ar*H*), 2.49 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 43.1 (S*C*H_3), 122.8, 128.6, 130.3, 144.9 (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 = 5: 5 (v/v)); flow rate = 1.0 mL· min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 4.4 min, minor enantiomer t_S = 5.2 min (see Fig. S8, S9 and S10).

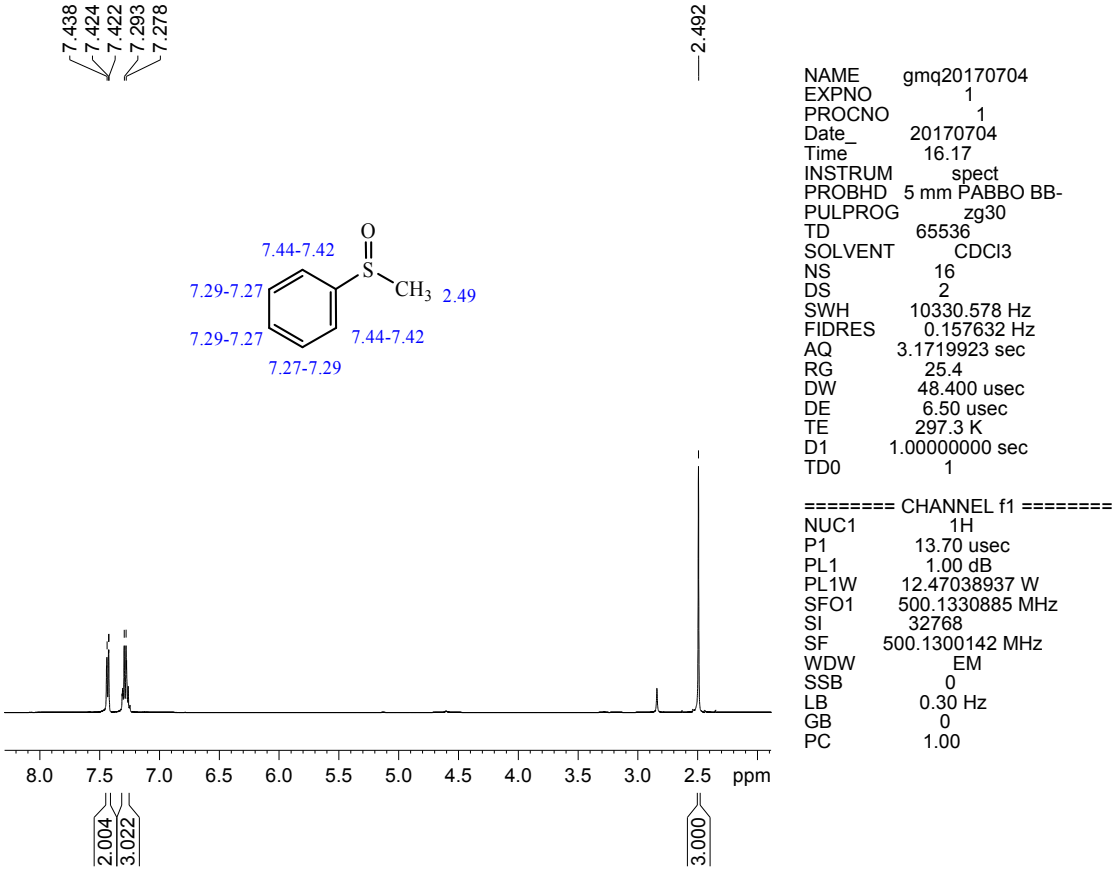

Fig. S6 ^{1}H NMR of methyl phenyl sulfoxide.

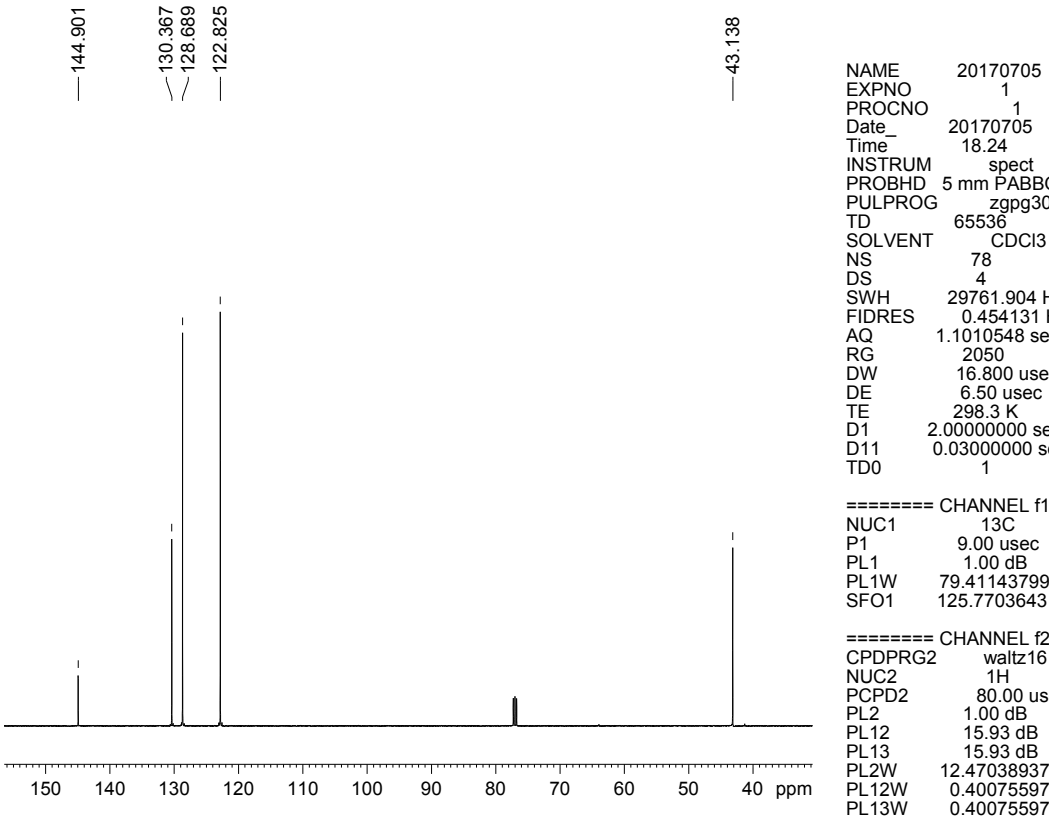

Fig. S7 ^{13}C NMR of methyl phenyl sulfoxide.

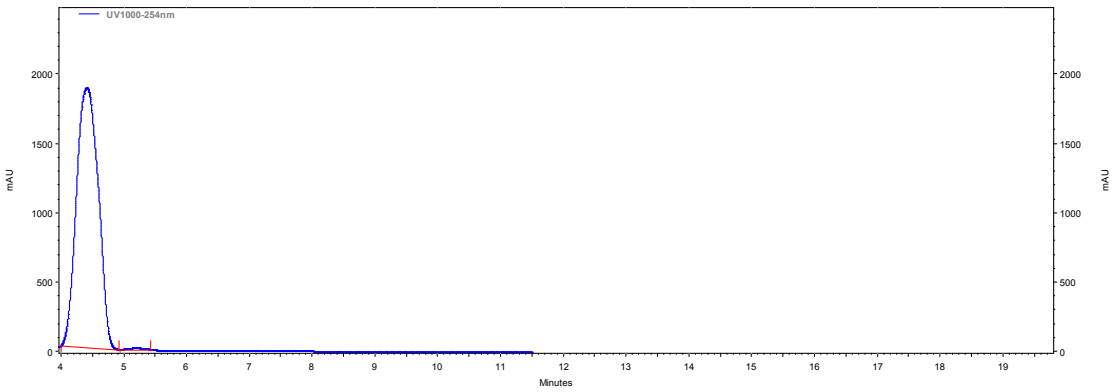

Fig. S8 HLPC of methyl phenyl sulfoxide obtained over **$PN_{427}A_{10}$-C** after 60 s of UV irradiation (ee value = 99%).

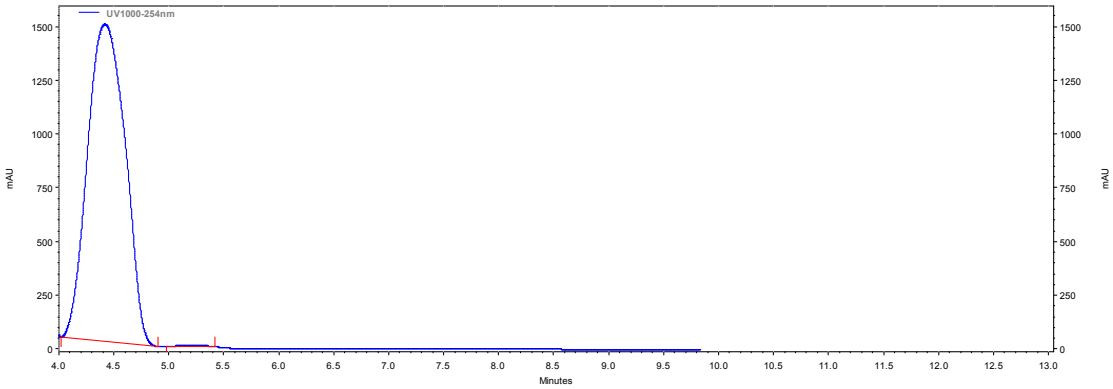

Fig. S9 HLPC of methyl phenyl sulfoxide obtained over dark-adapted **$PN_{427}A_{10}$-C** (ee value = 99%).

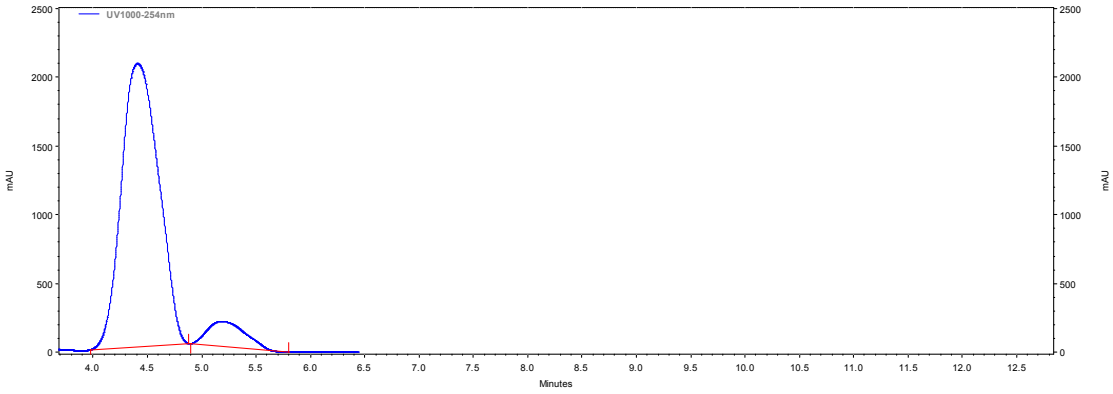

Fig. S10 HLPC of methyl phenyl sulfoxide obtained over neat complex (ee value = 83%).

Ethyl phenyl sulfoxide: The product has been identified by ^{1}H and ^{13}C NMR spectra (see Fig. S11 and S12). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 7.59-7.53 (m, 2 H, Ar*H*), 7.52-7.47 (m, 3 H, Ar*H*), 2.92-2.72 (m, 2 H, -C*H*$_2$-), 1.19-1.16(m, 3 H, Me); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 5.91 (*C*H$_3$), 50.24 (S*C*H$_2$), 124.13, 129.09, 130.88, 143.25 (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 °C, the column temperature was 180 °C, $t_{ethyl\ phenyl\ sulfoxide}$ = 2.5 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 = 6.4 min and minor enantiomer t_S =8.2 min (see Fig. S13, S14 and S15).

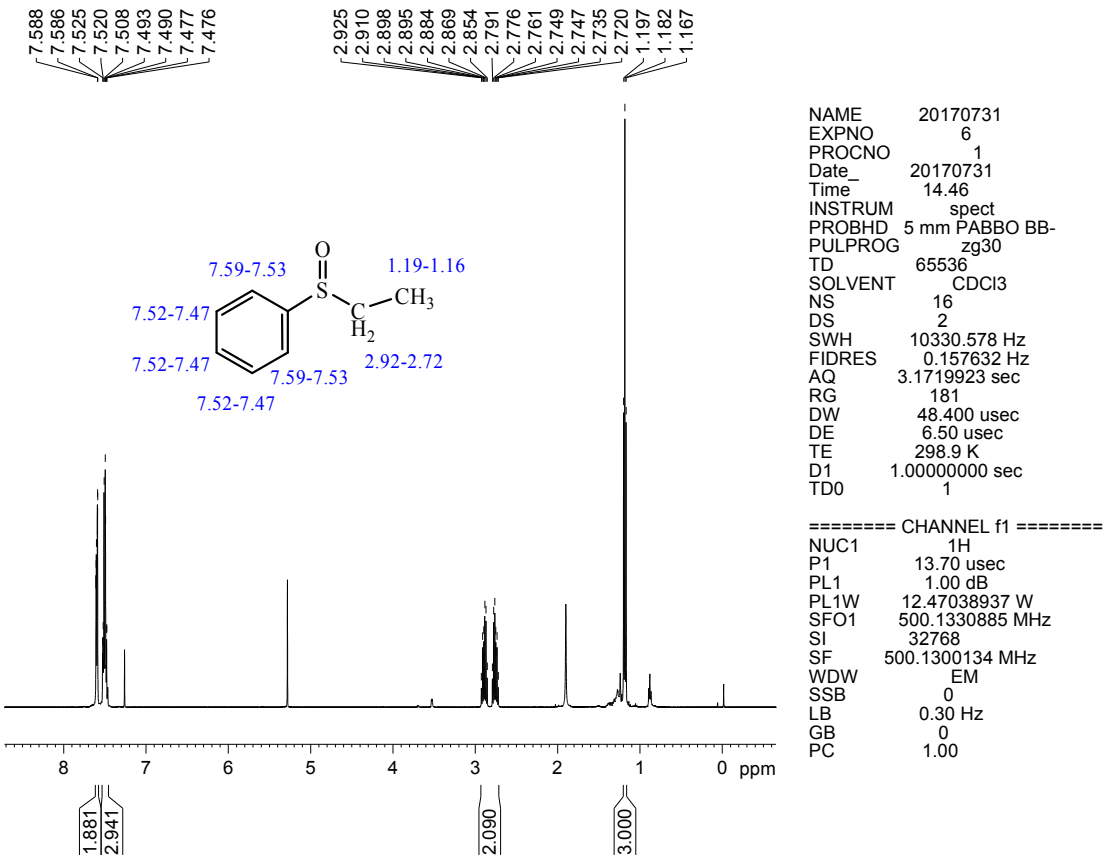

Fig. 11 ^{1}H NMR of ethyl phenyl sulfoxide.

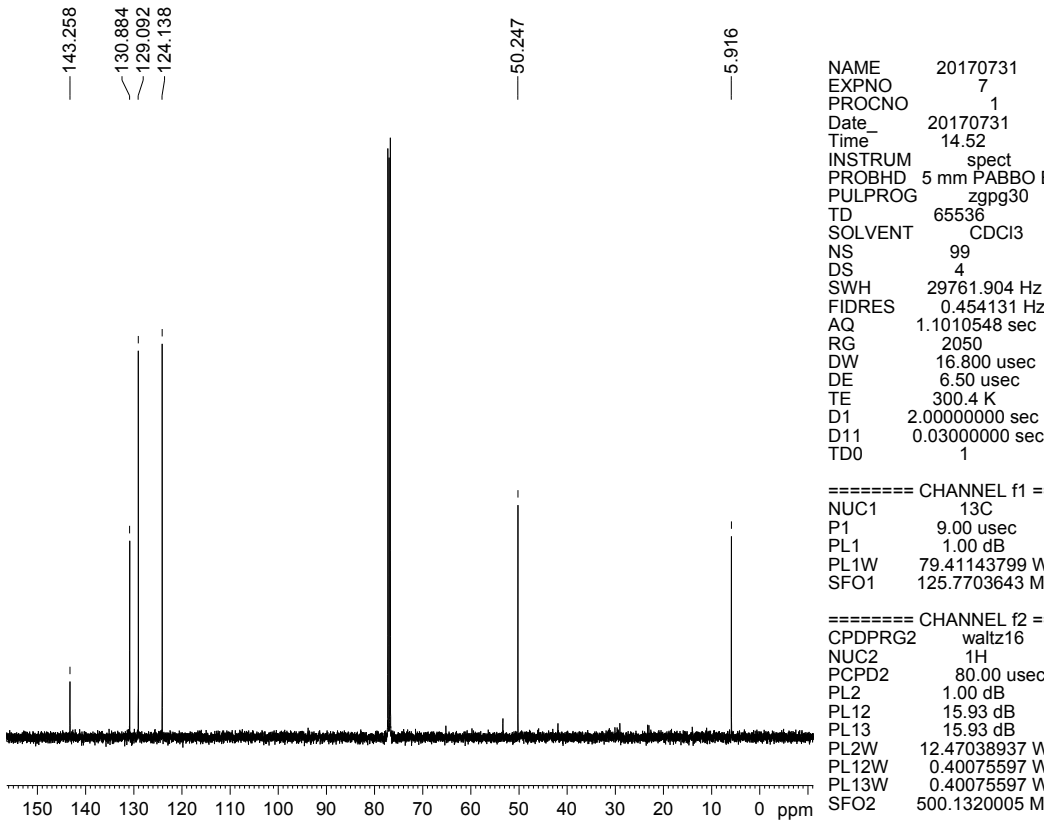

Fig. 12 ^{13} NMR of ethyl phenyl sulfoxide.

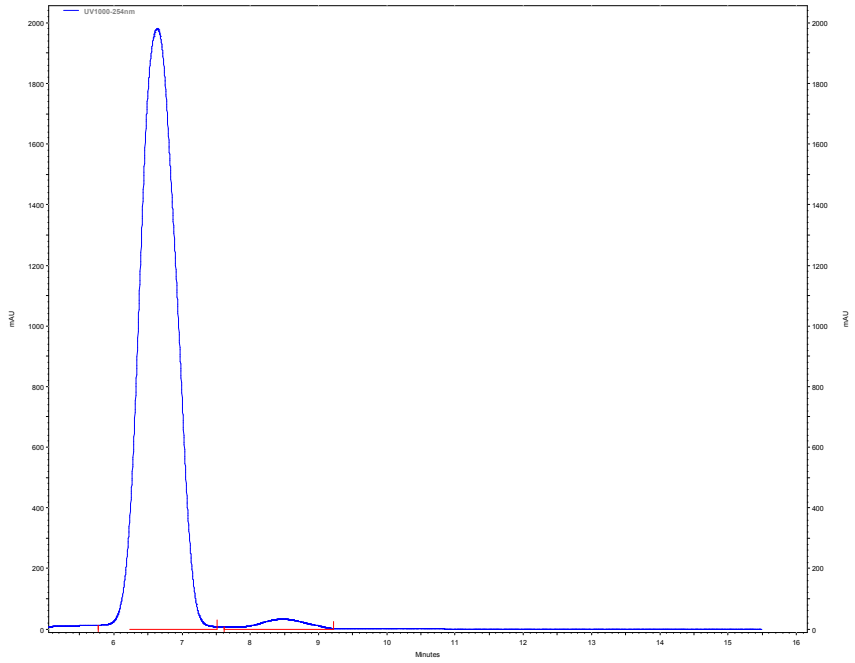

Fig. 13 HLPC of ethyl phenyl sulfoxide obtained over $\mathbf{PN_{427}A_{10}}$**-C** after 60 s of UV irradiation (ee value = 97%).

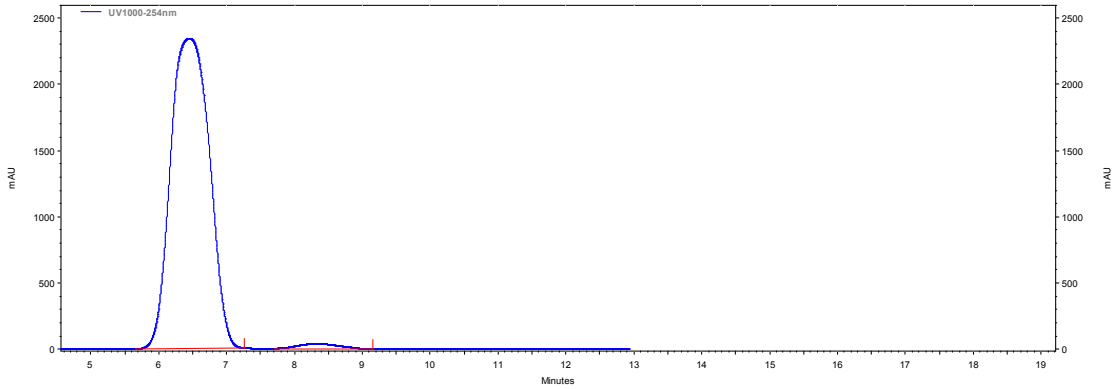

Fig. 14 HLPC of ethyl phenyl sulfoxide obtained over dark-adapted $\mathbf{PN_{427}A_{10}}$**-C** (ee value = 97%).

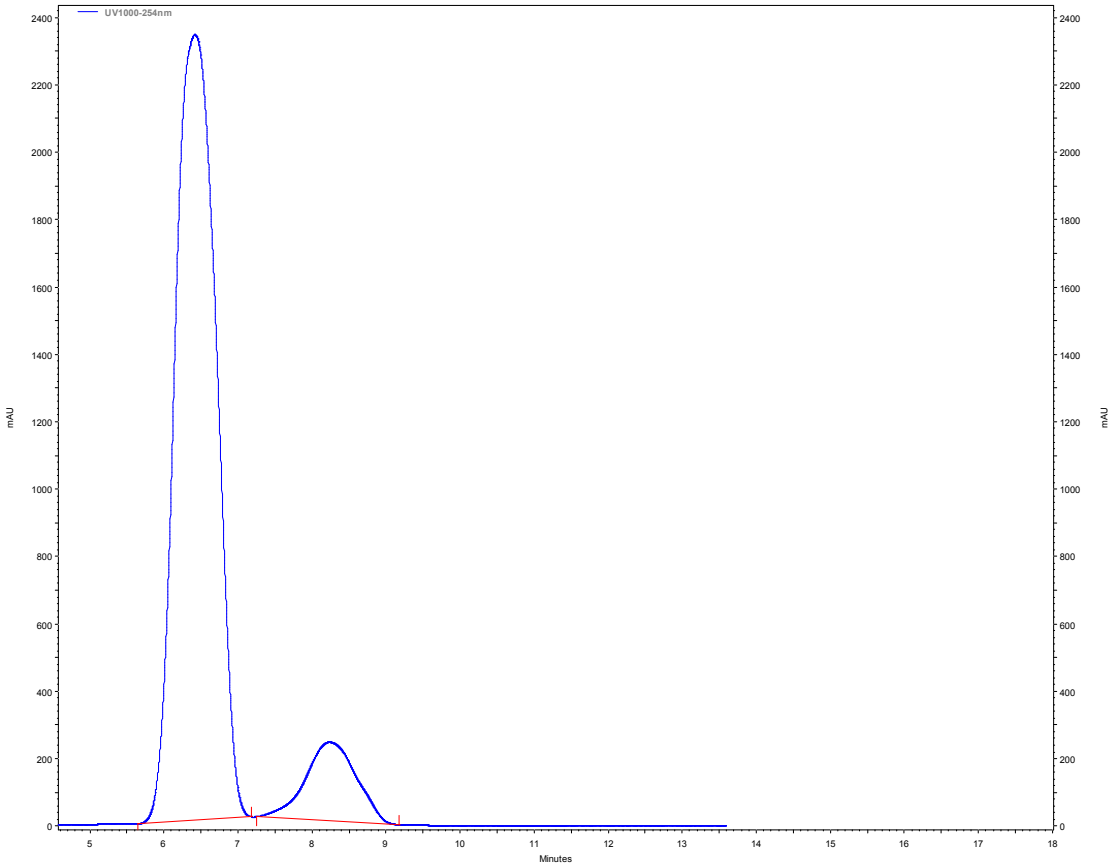

Fig. 15 HLPC of ethyl phenyl sulfoxide obtained over **neat complex** (ee value = 82%).

Methyl *p*-methoxyphenyl sulfoxide: The product has been identified by ^{1}H and ^{13}C NMR spectra (see Fig. S16 and S17). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 7.60-7.57 (d, 2 H, Ar*H*), 7.03-7.01 (d, 2 H, Ar*H*), 3.84 (s, 3 H, OCH_3), 2.69 (s, 3 H, SCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 43.9 (S*C*H_3), 55.5 (O*C*H_3), 114.8, 125.4, 136.6, 162.0 (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 = 4: 6 (v/v)); flow rate = 1.0 mL·min^{-1}; 25 °C; λ = 254 nm; major enantiomer t_R = 5.5 min and minor enantiomer t_S = 6.6 min (see Fig. S18, S19, and S20)

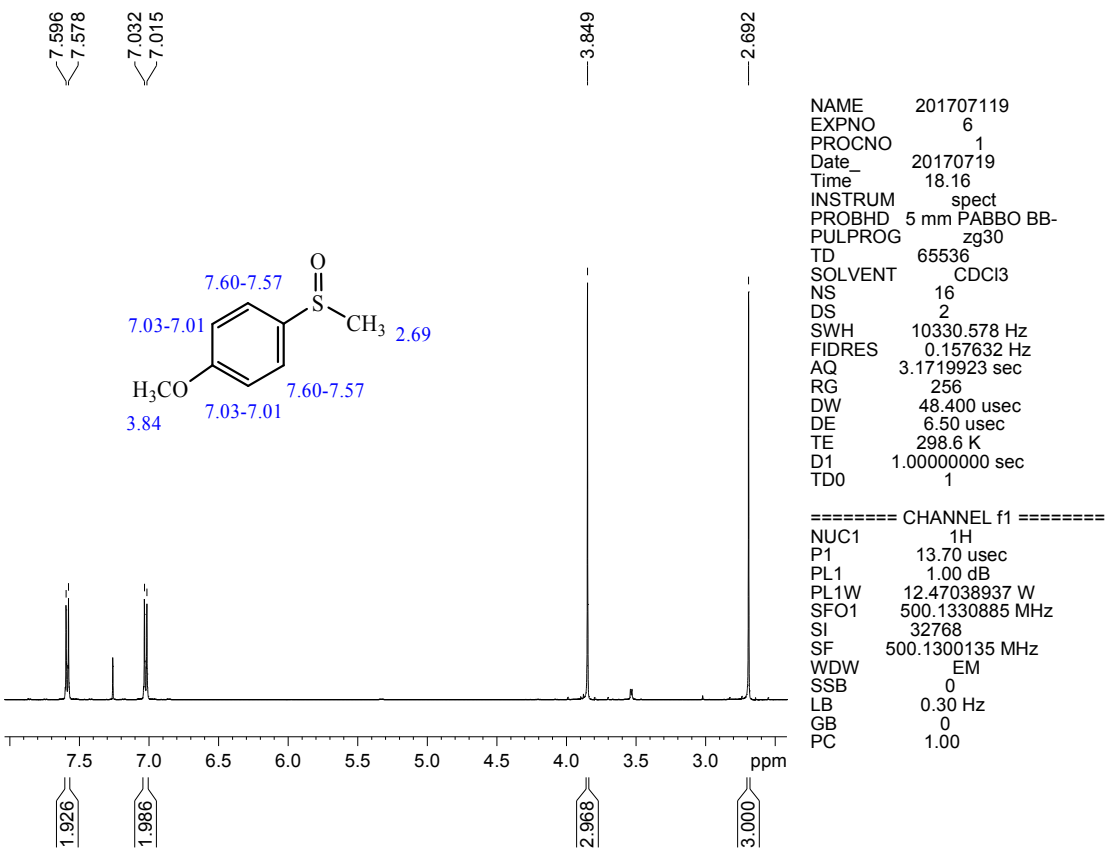

Fig. S16 ^{1}H NMR of methyl *p*-methoxyphenyl sulfoxide.

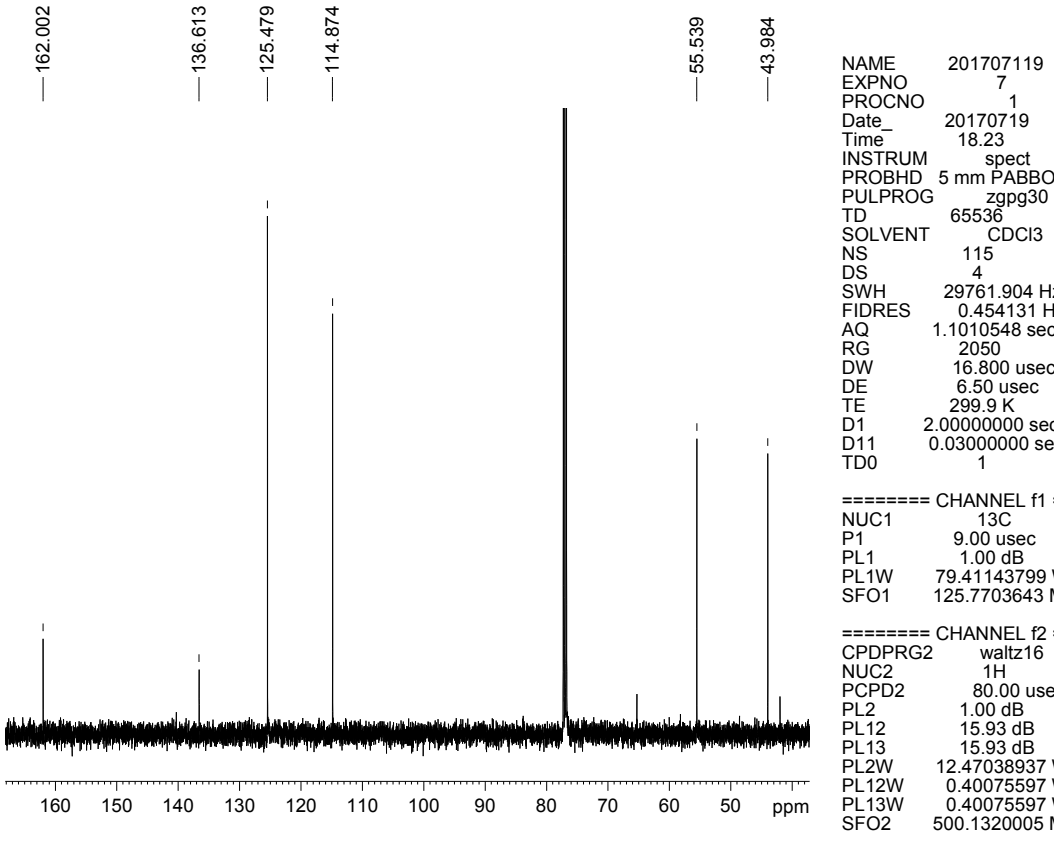

Fig. S17 ^{13}C NMR of methyl *p*-methoxyphenyl sulfoxide.

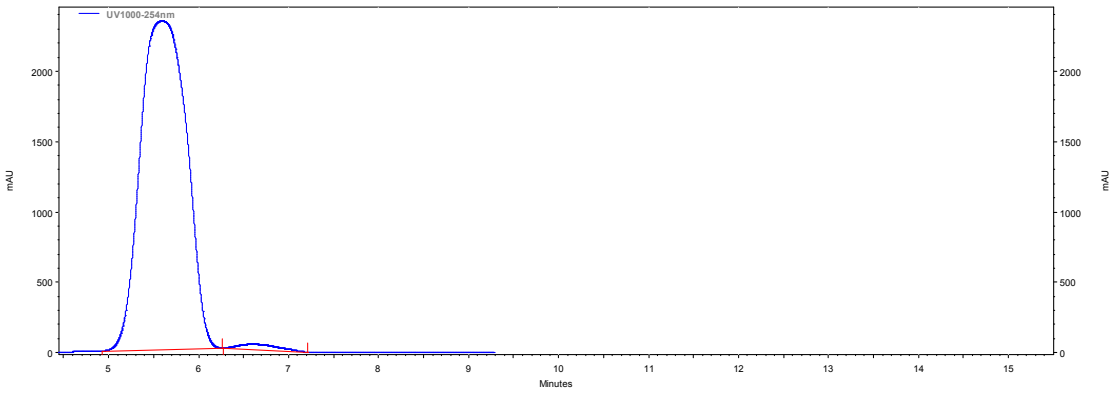

Fig. S18 HLPC of methyl *p*-methoxyphenyl sulfoxide obtained over **$PN_{427}A_{10}$-C** after 60 s of UV irradiation (ee value = 97%)

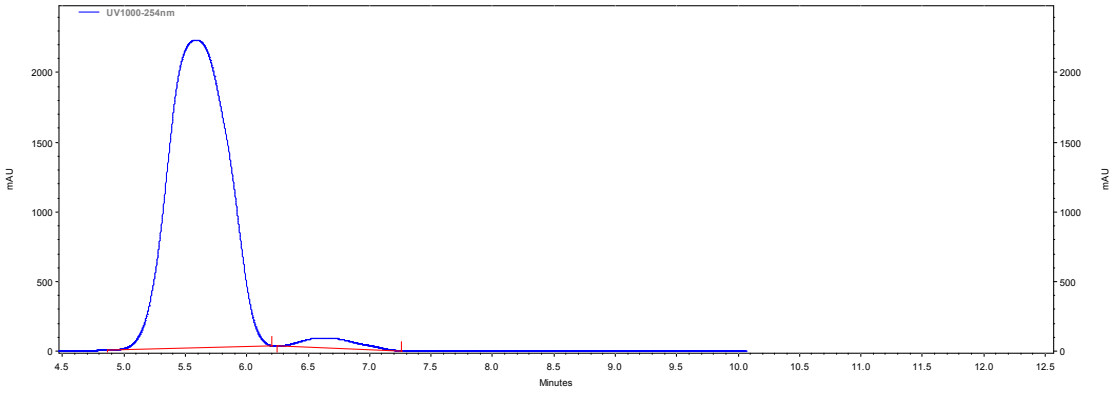

Fig. S19 HLPC of methyl *p*-methoxyphenyl sulfoxide obtained over dark-adapted **$PN_{427}A_{10}$-C** (ee value = 94%).

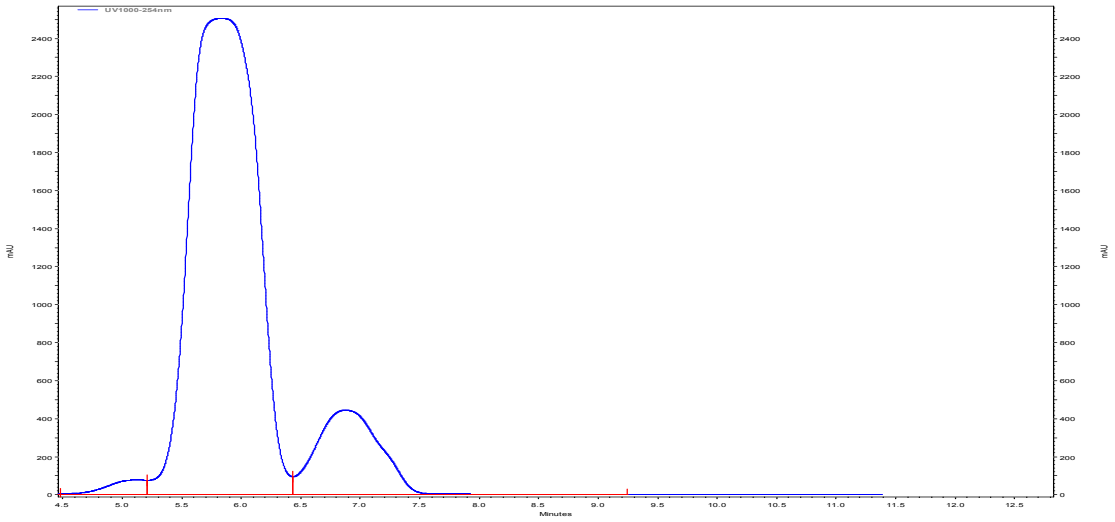

Fig. S20 HLPC of methyl *p*-methoxyphenyl sulfoxide obtained over neat complex (ee value = 70%)

Methyl *o*-methoxyphenyl sulfoxide: The product has been identified by ^{1}H and ^{13}C NMR spectra (see Fig. S21 and S22). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 7.82-7.80 (m, 1 H, Ar*H*), 7.46-7.42 (m, 1 H, Ar*H*), 7.19-7.16 (m, 1 H, Ar*H*), 6.92-6.90 (m, 1 H, Ar*H*), 3.87 (s, 3 H, OCH_3), 2.76 (s, 3 H, SCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 41.16 (SCH_3), 55.64 (OCH_3), 110.53, 121.65, 124.58, 131.89, 133.07, 154.76 (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 180 °C, $t_{methyl\ o\text{-}methoxyphenyl\ sulfoxide}$ = 9.8 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 = 4.8 min and minor enantiomer t_S =5.7 min (see Fig. S23, S24, and S25).

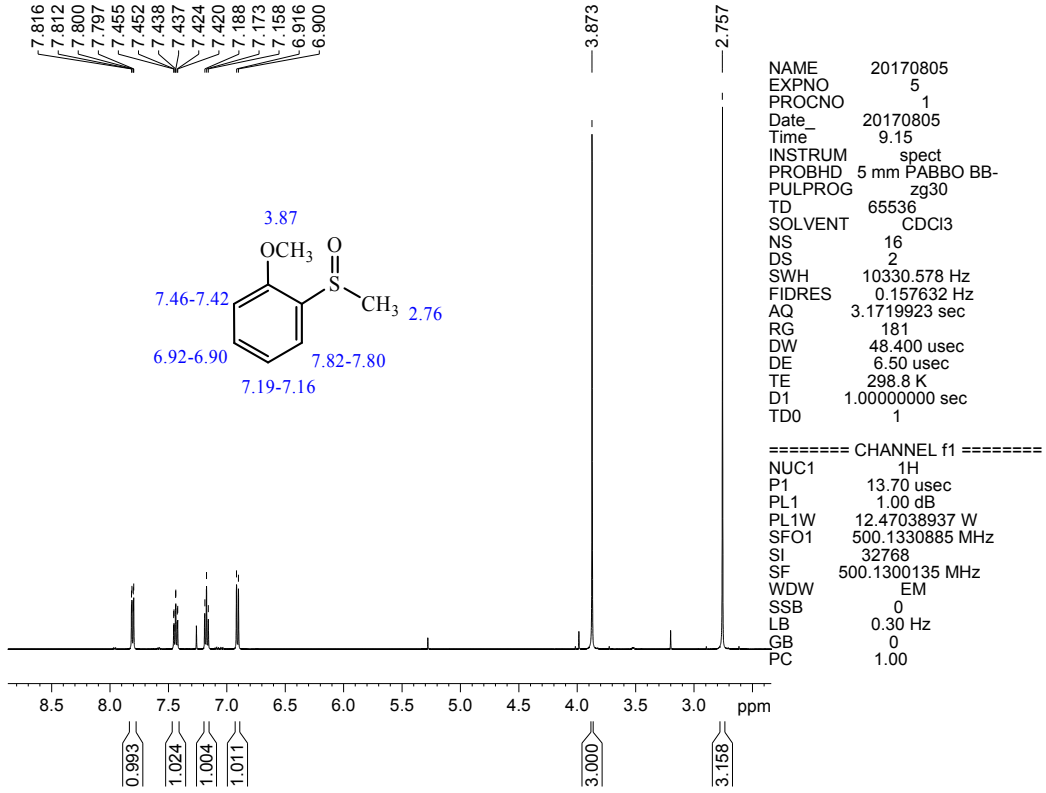

Fig. S21 ^{1}H NMR of methyl *o*-methoxyphenyl sulfoxide.

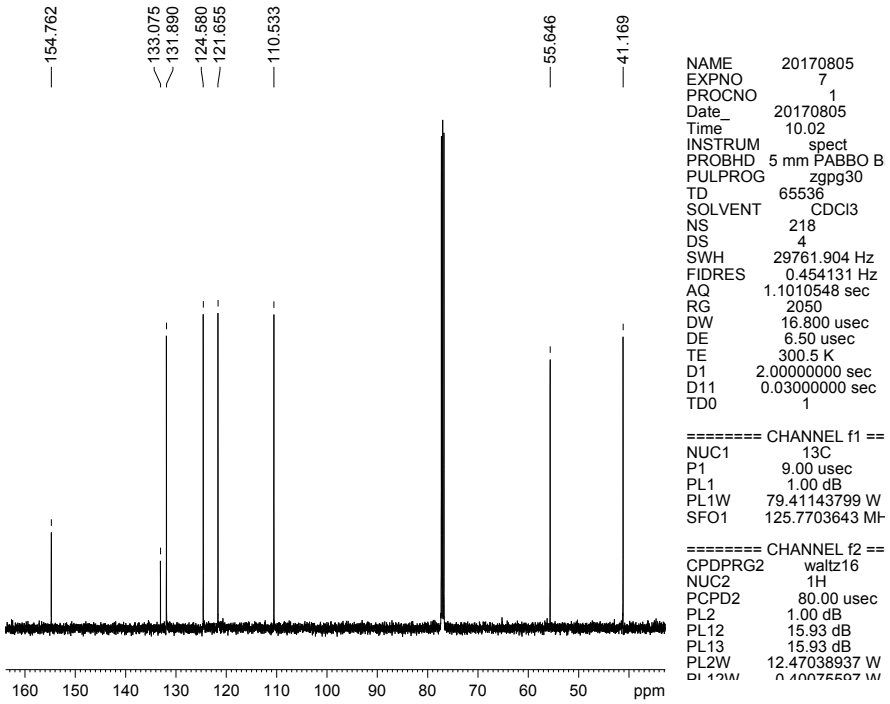

Fig. S22 ^{13}C NMR of methyl *o*-methoxyphenyl sulfoxide.

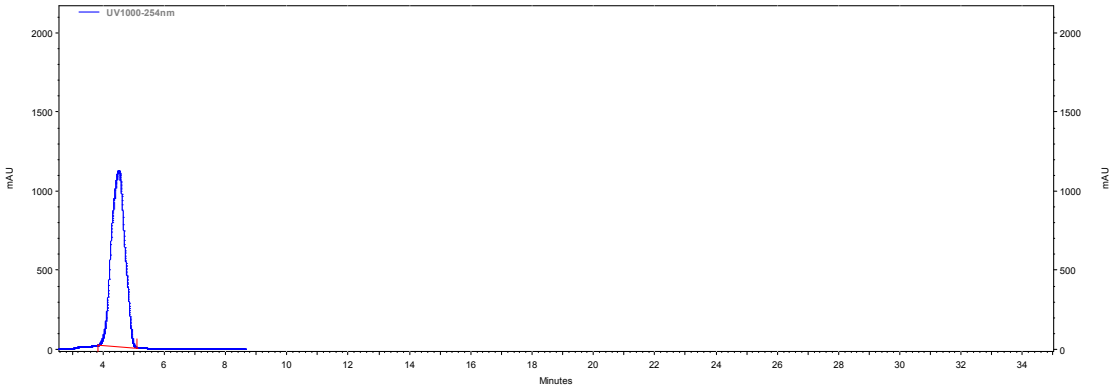

Fig. S23 HLPC of methyl *o*-methoxyphenyl sulfoxide obtained over **$PN_{427}A_{10}$-C** after 60 s of UV irradiation (ee value > 99%).

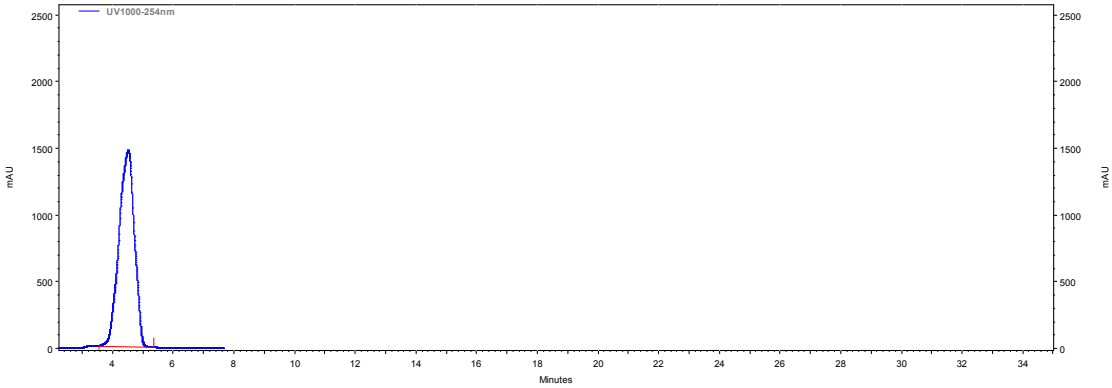

Fig. S24 HLPC of methyl *o*-methoxyphenyl sulfoxide obtained over dark-adapted **$PN_{427}A_{10}$-C** (ee value > 99%).

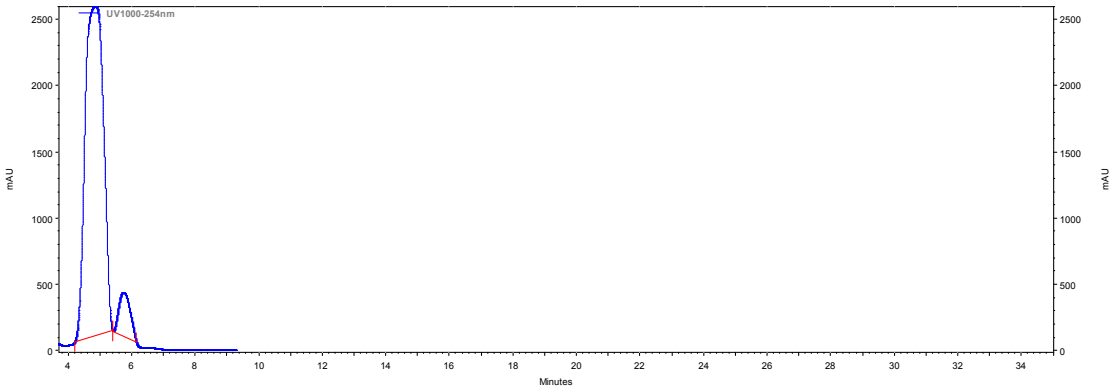

Fig. S25 HLPC of methyl *o*-methoxyphenyl sulfoxide obtained over neat complex (ee value = 76%).