Supporting Information

Iron(II)-folded single-chain nanoparticle: a metalloenzyme mimicking sustainable catalyst for highly enantioselective sulfa-Michael addition in water

Weiying Wang, Jiajun Wang, Shiye Li, Chaoping Li, Rong Tan,* and Donghong Yin

National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources; Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education); Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, No.36, South Lushan Road, Changsha, Hunan 410081 (P. R. China)

* Corresponding author. E-mail: yiyangtanrong@126.com.

Number of pages: 29 (from S1 to S29)

Number of Figures: 38
CONTENT:

1. Identification of copolymer precursors of \( \text{PN}_x\text{O}_y \) (\( \text{PN}_{120}\text{O}_4 \), \( \text{PN}_{150}\text{O}_3 \), and \( \text{PN}_{210}\text{O}_3 \)) and the corresponding intermediate.

2. Synthesis and identification of \( \alpha, \beta \)-unsaturated ketones (chalcone, benzylidene acetone, 4-methoxychalcone, 4-methoxybenzylidene acetone, and 4-nitrochalcone).

3. Identification of obtained chiral \( \beta \)-thioketones ((\( S \))-3-(propylthio)-1,3-diphenylpropan-1-one (1), (\( S \))-4-(propylthio)-4-phenylbutan-2-one (2), (\( S \))-3-(propylthio)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (3), (\( S \))-4-(propylthio)-4-(4-methoxyphenyl)butan-2-one (4), (\( S \))-3-(propylthio)-3-(4-nitrophenyl)-1-phenylpropan-1-one (5), (\( S \))-3-(4-chloro-benzylthio)-1,3-diphenylpropan-1-one (6), (\( S \))-3-(4-chloro-benzylthio)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (7), (\( S \))-4-(4-chlorobenzylthio)pentan-2-one (8), and (\( S \))-3-(4-chlorophenylthio)-1,3-diphenylpropan-1-one (9)).
1. Identification of copolymer precursors of \( \text{PN}_2\text{O}_3 \) (\( \text{PN}_{120}\text{O}_4 \), \( \text{PN}_{150}\text{O}_3 \), and \( \text{PN}_{210}\text{O}_3 \)) and the corresponding intermediate

*Chiral 4-benzyl-2-vinyl oxazoline*

![Structure of chiral 4-benzyl-2-vinyl oxazoline](image)

Calc. for \((\text{C}_{12}\text{H}_{13}\text{NO})\): C, 76.98; H, 7.00; N, 7.48; O, 8.54%. Found: C, 76.59; H, 7.02; N, 7.37; O, 9.02%. The structure of chiral 4-benzyl-2-vinyl oxazoline was identified by \(^1\)H NMR spectrum (see Fig. S1). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm): 7.34-7.22 (m, 5 H, \( \text{Ph-CH}_2\text{-oxazoline} \)), 6.30-5.90 (m, 3 H, \( \text{CH}_2\text{-CH-oxazoline} \)), 4.25-4.23 (m, 1 H, \( \text{O-CH}_2\text{-CH-N in oxazoline} \)), 4.22-4.16 (m, 2 H, \( \text{O-CH}_2\text{-CH-N in oxazoline} \)), 3.03-2.86 (m, 2 H, \( \text{Ph-CH}_2\text{-oxazoline} \)). FT-IR (KBr): \( \gamma_{\text{max}}/\text{cm}^{-1} \) 3418, 3290, 3084, 3032, 2972, 2929, 2790, 1720, 1663, 1629, 1549, 1409, 1299, 1262, 1207, 1108, 1061, 1033, 983, 924, 885, 808, 752, 705, 603, 567, 477.

![Fig. S1 \(^1\)H NMR of chiral 4-benzyl-2-vinyl oxazoline](image)
The structure of PN$_{120}O_4$ was identified by $^1$H NMR spectrum (see Fig. S2). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.39-7.08 (m, 25 H, Ph-CH$_2$-oxazoline and Ph-CH$_2$-CH$_2$-CH$_2$- in backbone chain), 6.59-6.27 (m, 120 H, O=C-NH-CH in NIPAAm), 4.01-3.89 (m, 126 H, -CH-CH$_2$- of backbone chain in NIPAAm, -CH-CH$_2$- of backbone chain in oxazoline and S=C-CH$_2$-CH$_3$ in backbone chain), 3.78-2.03 (m, 248 H, -CH-CH$_2$- of backbone chain in NIPAAm and -O-CH$_2$-CH-N- in oxazoline), 1.89-1.57 (m, 130 H, CH$_3$-CH-CH$_3$ in NIPAAm, Ph-CH$_2$-oxazoline, -O-CH$_2$-CH-N- in oxazoline and Ph-CH$_2$-CH$_2$-CH$_2$- in backbone chain), 1.45-1.38 (m, 8 H, -CH-CH$_2$- of backbone chain in oxazoline), 1.28-1.16 (m, 720 H, CH$_3$-CH-CH$_3$ in NIPAAm), 0.91-0.88 (m, 3 H, S=C-CH$_2$-CH$_3$ in backbone chain). FT-IR (KBr): $\gamma_{max}$/cm$^{-1}$ 3533, 3440, 3310, 3068, 2973, 2946, 2892, 1663, 1538, 1458, 1368, 1342, 1261, 1172, 1131, 1079, 977, 927, 880, 838, 660, 504.

![Fig. S2 $^1$H NMR of PN$_{120}O_4$](image-url)
The structure of PN$_{150}$O$_3$ was identified by $^1$H NMR spectrum (see Fig. S3). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.50-7.08 (m, 20 H, Ph-CH$_2$-oxazoline and Ph-CH$_2$-CH$_2$-CH$_2$- in backbone chain), 6.78-6.04 (m, 150 H, O=C-NH-CH in NIPAAm), 4.77-4.02 (m, 154 H, -CH-CH$_2$- of backbone chain in NIPAAm, -CH-CH$_2$- of backbone chain in oxazoline and S=C-CH$_2$-CH$_3$ in backbone chain), 2.97-2.55 (m, 306 H, -CH-CH$_2$- of backbone chain in NIPAAm and -O-CH$_2$-CH-N- in oxazoline), 2.23-2.17 (m, 158 H, CH$_3$-CH-CH$_3$ in NIPAAm, Ph-CH$_2$-oxazoline, -O-CH$_2$-CH-N- in oxazoline, and Ph-CH$_2$-CH$_2$-CH$_2$- in backbone chain), 2.08-1.88 (m, 6 H, -CH-CH$_2$- of backbone chain in oxazoline), 1.29-1.67 (m, 900 H, CH$_3$-CH-CH$_3$ in NIPAAm), 1.17-0.91 (m, 3 H, S=C-CH$_2$-CH$_3$ in backbone chain). FT-IR (KBr): $\gamma_{\text{max}}$/cm$^{-1}$ 3533, 3438, 3312, 3068, 2974, 2945, 2897, 1663, 1542, 1460, 1367, 1340, 1261, 1172, 1129, 1068, 981, 934, 876, 838, 663, 505.

Fig. S3 $^1$H NMR of PN$_{150}$O$_3$
The structure of PN$_{210}$O$_3$ was identified by $^1$H NMR spectrum (see Fig. S4). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.29-6.69 (m, 20 H, Ph-CH$_2$-oxazoline and Ph-CH$_2$-CH$_2$-CH$_2$- in backbone chain), 6.69-6.62 (m, 210 H, O=C-NH-CH in NIPAAm), 4.00-3.68 (m, 215 H, -CH-CH$_2$- of backbone chain in NIPAAm, -CH-CH$_2$- of backbone chain in oxazoline and S=C-CH$_2$-CH$_3$ in backbone chain), 3.58-3.49 (m, 426 H, -CH-CH$_2$- of backbone chain in NIPAAm and -O-CH$_2$-CH-N- in oxazoline), 2.05-1.82 (m, 218 H, CH$_3$-CH-CH$_3$ in NIPAAm, Ph-CH$_2$-oxazoline, -O-CH$_2$-CH-N- in oxazoline and Ph-CH$_2$-CH$_2$-CH$_2$- in backbone chain), 1.73-1.43 (m, 6 H, -CH-CH$_2$- of backbone chain in oxazoline), 1.33-1.20 (m, 1260 H, C$_3$H$_7$-CH-C$_3$H$_7$ in NIPAAm), 1.19-1.14 (m, 3 H, S=C-CH$_2$-C$_3$H$_7$ in backbone chain). FT-IR (KBr): $\gamma_{\text{max}}$/cm$^{-1}$ 3533, 3437, 3310, 3071, 2977, 2949, 2897, 1663, 1540, 1459, 1368, 1341, 1261, 1172, 1133, 1075, 979, 930, 879, 841, 662 504.

2. Synthesis and identification of $\alpha, \beta$-unsaturated ketones (chalcone, benzylidene acetone, 4-methoxychalcone, 4-methoxybenzylidene acetone, and 4-nitrochalcone)
Michael acceptors of \(\alpha,\beta\)-unsaturated ketones were synthesized by the aldol condensation under alkaline condition. In the typical process, acetone or acetylphenone (10 mmol) was dissolved in ethanol (20 mL), and then cooled to 0 °C. Sodium hydroxide (40 mmol, 1.60 g) in water (10 mL) was added dropwise. After being stirred at 0 °C for 0.5 h, aromatic aldehyde (10 mmol) in ethanol (20 mL) was slowly added. The mixture was stirred at room temperature for 12 h, and then was filtered. Drying the filter residue in vacuo provided \(\alpha,\beta\)-unsaturated ketones as follows.

**Chalcone** (1.89 g, yield: 91%, canary yellow powder). Calc. for \((C_{15}H_{12}O)\): C, 86.51; H, 5.81; O, 7.68 %. Found: C, 86.40; H, 5.82; O, 7.78 %. The structure of chalcone was identified by \(^1\)H NMR spectrum (see Fig. S5). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 8.07-8.05 (m, 2 H, \(Ph-CO-\)), 7.87-7.83 (m, 1 H, \(Ph-CO-\)), 7.69-7.67 (m, 2 H, \(Ph-CO-\)), 7.63-7.59 (m, 2 H, \(Ph-CH-CH-\)), 7.56-7.52 (m, 2 H, \(Ph-CH-CH-\) and \(Ph-CH-CH-\)), 7.45-7.44 (m, 3 H, \(Ph-CH-CH-\) and \(Ph-CH-CH-\)).

**Benzylidene acetone** (1.24 g, yield: 85%, yellow powder). Calc. for \((C_{10}H_{10}O)\): C, 82.16; H, 6.89; O, 10.94 %. Found: C, 82.21; H, 6.83; O, 10.96 %. The structure of benzylidene acetone was identified by \(^1\)H NMR spectrum (see Fig. S6). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.66-7.65 (m,
1 H, Ph-CH-), 7.46-7.45 (m, 2 H, Ph-CH-), 7.45-7.44 (m, 2 H, Ph-CH-), 7.14 (s, 1 H, Ph-CH-), 6.77-6.74 (m, 1 H, -CH-CH-CO-), 2.42 (s, 3 H, -CO-CH3).

Fig. S6 1H NMR of benzylidene acetone

4-Methoxychalcone (2.19 g, yield: 92%, yellow powder). Calc. for (C16H14O2): C, 80.65; H, 5.92; O, 13.43 %. Found: C, 80.57; H, 5.59; O, 13.84 %. The structure of 4-methoxychalcone was identified by 1H NMR spectrum (see Fig. S7). 1H NMR (500 MHz, CDC13): δ (ppm): 8.05-8.03 (m, 2 H, Ph-CO-), 7.83-7.80 (m, 1 H, Ph-CO-), 7.64-7.59 (m, 3 H, Ph-CO- and CH3O-Ph-CH-), 7.54-7.51 (m, 2 H, CH3O-Ph-CH-), 7.46-7.43 (m, 1 H, CH3O-Ph-CH-), 6.98-6.96 (m, 2 H, Ph-CH-CH-CO-), 3.88 (s, 3 H, CH3O-Ph-CH-).
4-Methoxybenzylidene acetone (1.50 g, yield: 85%, yellow powder). Calc. for (C_{11}H_{12}O_{2}): C, 74.98; H, 6.86; O, 18.16 %. Found: C, 75.02; H, 6.79; O, 18.19 %. The structure of 4-methoxybenzylidene acetone was identified by $^1$H NMR spectrum (see Fig. S8). $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm): 7.74-7.60 (m, 1 H, Ph-CH-), 7.59-7.53 (m, 2 H, Ph-CH-), 7.04-6.92 (m, 3 H, Ph-CH- and Ph-CH-CH-CH-CO-), 5.27 (s, 3 H, -CO-CH$_3$), 3.88 (s, 3 H, CH$_3$O-Ph-CH-).
4-Nitrochalcone (2.03 g, yield: 81%, brown powder). Calc. for (C_{15}H_{11}NO_3): C, 71.14%; H, 4.38;
N, 5.53%; O, 18.95 %. Found: C, 70.98%; H, 4.42%; N, 5.47%; O, 19.13 %. The structure of 4-
nitrochalcone was identified by $^1$H NMR spectrum (see Fig. S9). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$
(ppm): 8.32-8.30 (m, 2 H, NO$_2$-Ph-CH-), 8.08-8.06 (m, 2 H, NO$_2$-Ph-CH-), 7.87-7.81 (m, 3 H,
Ph-CO-), 7.70-7.66 (m, 3 H, Ph-CO-), 7.58-7.55 (m, 2 H, Ph-CH-CH-CO-).

![Fig. S9 $^1$H NMR of 4-nitrochalcone](image)

3. Identification of obtained chiral $\beta$-thioketones.

(S)-3-(Propylthio)-1,3-diphenylpropan-1-one (I)

Yield: 95%, determined by isolated yield after column chromatography. The structure of as-

obtained product 1 was identified by $^1$H NMR spectrum (see Fig. S10). $^1$H NMR (CDCl$_3$, 500
MHz): $\delta$ (ppm): 7.95-7.46 (m, 5 H, Ph-CO-CH$_2$-), 7.45-7.15 (m, 5 H, Ph-CH-S-), 4.59-4.56 (m, 1
Ph-CO-), 7.70-7.66 (m, 3 H, Ph-CO-), 7.58-7.55 (m, 2 H, Ph-CH-CH-CO-).
H, CH-CH₂-CO-), 3.57-3.56 (d, 2 H, CH-CH₂-CO-), 2.41-2.23 (m, 2 H, -S-CH₂-CH₂-), 1.60-1.49 (m, 2 H, S-CH₂-CH₂-CH₃), 0.94-0.91 (m, 3 H, S-CH₂-CH₂-CH₃). Ee value: 96%, determined by HPLC (PrOH/n-hexane = 10:90 (v/v)), flow rate = 1.0 mL·min⁻¹, 25 °C, λ = 254 nm, major enantiomer tₛ = 5.75 min, minor enantiomer tᵣ = 4.82 min (Fig. S11-S14).

Fig. S10 ¹H NMR of the as-obtained product 1

Fig. S11 HPLC of product 1 obtained over Fe⁹⁺-PN₁₂₀O₄ (ee value = 99%)
Fig. S12 HPLC of product 1 obtained over Fe^{II}-PN_{150}O_3 (ee value = 96%)

Fig. S13 HPLC of product 1 obtained over Fe^{II}-PN_{210}O_3 (ee value = 96%)
**Fig. S14** HLPC of product 1 obtained over Neat-C (ee value = 83%)

(S)-4-(Propylthio)-4-phenylbutan-2-one (2)

\[
\text{Yield: 96%, determined by isolated yield after column chromatography. The structure of as-}
\text{obtained product 2 was identified by } ^1\text{H NMR spectrum (see Fig. S15). } ^1\text{H NMR (CDCl}_3, 500}
\text{MHz): } \delta \text{ (ppm): 7.55-7.31 (m, 5 H), 4.49-4.46 (m, 1 H), 3.25-3.24 (d, 2 H), 2.39-2.23 (m, 2 H), 1.57-1.53 (m, 2 H), 1.36 (s, 3 H), 0.96-0.91 (m, 3 H). Ee value: 99%, determined by HPLC (PrOH/n-hexane = 20:80 (v/v)), flow rate = 1.0 mL·min}^{-1}, 25 ^\circ\text{C, } \lambda = 254 \text{ nm, major enantiomer } t_s = 6.12 \text{ min, minor enantiomer } t_R = 4.74 \text{ min (see Fig. S16 and S17).}
Fig. S15 ¹H NMR of as-obtained product 2

Fig. S16 HLPC of product 2 obtained over Fe⁶⁺-PN₃₅O₃ (ee value = 99%)
(S)-3-(Propylthio)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (3)

Yield: 92%, determined by isolated yield after column chromatography. The structure of as-obtained product 3 was identified by $^1$H NMR spectrum (see Fig. S18). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.94-7.43 (m, 5 H, Ph-CO-CH$_2$-), 7.39-6.82 (m, 4 H, CH$_3$O-Ph-CH-), 4.56-4.53 (m, 1 H, C$_3$H$_7$-CH$_2$-CO-), 3.81 (s, 3 H, C$_3$H$_3$O-Ph-CH-), 3.57-3.48 (d, 2 H, CH-CH$_2$-CO-), 2.38-2.23 (m, 2 H, -S-CH$_2$-CH$_2$-CH$_3$), 1.60-1.49 (m, 2 H, -S-CH$_2$-CH$_2$-CH$_3$), 0.97-0.88 (m, 3 H, -S-CH$_2$-CH$_2$-CH$_3$). Ee value: 98%, determined by HPLC (iPrOH/n-hexane = 20:80 (v/v)), flow rate = 1.0 mL·min$^{-1}$, 25 °C, $\lambda = 254$ nm, major enantiomer $t_S = 12.32$ min; minor enantiomer $t_R = 10.08$ min (see Fig. S19 and S20).
Fig. S18 $^1$H NMR of as-obtained product 3

Fig. S19 HPLC of product 3 obtained over Fe$^{II}$-PN$_{150}$O$_3$ (ee value = 98%)
Fig. S20 HLPC of product 3 obtained over Neat-C (ee value = 60%)

\((S)-4-(\text{Propylthio})\)-4-(4-methoxyphenyl) butan-2-one (4)

Yield: 95%, determined by isolated yield after column chromatography. The structure of as-obtained product 4 was identified by \(^1\)H NMR spectrum (see Fig. S21). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) (ppm): 7.75-6.91 (m, 4 H, CH\(_3\)O-Ph-CH\(-\)), 4.40-4.30 (m, 1 H, CH-CH\(_2\)-CO-), 3.92-3.87 (d, 2 H, CH-CH\(_2\)-CO-), 2.64 (s, 3 H, CH\(_3\)O-Ph-CH\(-\)), 2.28-2.23 (m, 2 H, -S-CH\(_2\)-CH\(_2\)-CH\(_3\)), 2.09-2.01 (m, 2 H, -S-CH\(_2\)-CH\(_2\)-CH\(_3\)), 1.40 (s, 3 H, -CO-CH\(_3\)), 0.92-0.85 (m, 2 H, -S-CH\(_2\)-CH\(_2\)-CH\(_3\)).

Ee value: 90%, determined by HPLC (\(\text{iPrOH}/n\)-hexane = 10:90 (v/v)), flow rate = 1.0 mL·min\(^{-1}\), 25 °C, \(\lambda = 254\) nm, major enantiomer \(t_S = 11.04\) min, minor enantiomer \(t_R = 8.11\) min (see Fig. S22 and S23).
Fig. S21 ¹H NMR of as-obtained product 4

Fig. S22 HPLC of product 4 obtained over Fe^{II}-PN_{180}O_{3} (ee value = 90%)
Fig. S23 HLPC of product 4 obtained over Neat-C (ee value = 67%)

(S)-3-(Propylthio)-3-(4-nitrophenyl)-1-phenylpropan-1-one (5)

Yield: 10%, determined by isolated yield after column chromatography. The structure of as-obtained product 5 was identified by $^1$H NMR spectrum (see Fig. S24). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 8.20-7.81 (m, 4 H, NO$_2$-Ph-CH-), 7.75-7.46 (m, 5 H, Ph-CO-CH$_2$-), 4.79-4.50 (m, 1 H, CH-CH$_2$-CO-), 3.78-3.44 (d, 2 H, CH-CH$_2$-CO-), 2.50-2.18 (m, 2 H, -S-CH$_2$-CH$_2$-CH$_3$), 1.59-1.52 (m, 2 H, -S-CH$_2$-CH$_2$-CH$_3$), 0.95-0.89 (m, 3 H, -S-CH$_2$-CH$_2$-CH$_3$). Ee value: 89%, determined by HPLC (PrOH/n-hexane = 30:70 (v/v)), flow rate = 1.0 mL·min$^{-1}$, 25 °C, $\lambda$ = 254 nm, major enantiomer $t_S$ = 11.78 min, minor enantiomer $t_R$ = 10.01 min (see Fig. S25 and S26).
Fig. S24 1H NMR of as-obtained product 5

Fig. S25 HPLC of product 5 obtained over FeII-PN150O3 (ee value = 89%)
Yield: 93%, determined by isolated yield after column chromatography. The structure of as-obtained product 6 was identified by $^1$H NMR spectrum (see Fig. S27). $^1$H NMR (CDCl$_3$, 500 MHz): δ (ppm): 7.89-7.42 (m, 5 H, Ph-CO-CH$_2$-), 7.40-7.35 (m, 4 H, Cl-Ph-CH$_2$-), 7.28-7.14 (m, 5 H, Ph-CH-S-), 4.17-4.12 (m, 1 H, -S-C$_H$Ph), 3.59-3.51 (m, 2 H, -S-C$_H$$_2$-Ph), 3.51-3.44 (m, 2 H, CH-C$_H$$_2$-CO-). Ee value: 95%, determined by HPLC ($^t$PrOH/n-hexane = 20:80 (v/v)), flow rate = 1.0 mL·min$^{-1}$, 25 °C, λ = 254 nm, major enantiomer $t_S = 8.51$ min; minor enantiomer $t_R = 6.42$ min (see Fig. S28 and S29). $[a]_D^{25} = -137.3$ (c =0.14 in CHCl$_3$); lit: $[a]_D^{25} = +139.2$ (c =0.14 in CHCl$_3$) for $(R)$, 97% ee.$^2$

(S)-3-(4-Chlorobenzylthio)-1,3-diphenylpropan-1-one (6)
Fig. S27 $^1$H NMR of as-obtained product 6

Fig. S28 HPLC of product 6 obtained over Fe$^{II}$-PN$_{150}$O$_3$ (ee value = 95%)
(S)-3-(4-Chlorobenzylthio)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (7)

Yield: 90%, determined by isolated yield after column chromatography. The structure of as-obtained product 7 was identified by $^1$H NMR spectrum (see Fig. S30). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.33-7.17 (m, 13 H, Cl-Ph$_2$-, CH$_3$O-Ph-, and Ph-CO-CH$_2$-), 4.17-4.15 (m, 1 H, CH$_2$-CO-), 4.14-4.13 (m, 2 H, Cl-Ph$_2$S-), 3.60 (s, 3 H, CH$_3$O-Ph-), 2.99-2.91 (m, 2 H, CH-CH$_2$-CO-). Ee value: 96%, determined by HPLC (PrOH/n-hexane = 3:97 (v/v)), flow rate = 1.0 mL·min$^{-1}$, 25 °C, $\lambda$ = 254 nm, major enantiomer $t_S$ = 20.15 min, minor enantiomer $t_R$ = 17.48 min (see Fig. S31 and S32).
Fig. S30 $^1$H NMR of as-obtained product 7

Fig. S31 HLPC of product 7 obtained over Fe$^{II}$-PN$_{150}$O$_3$ (ee value = 96%)
Fig. S32 HLPC of product 7 obtained over Neat-C (ee value = 90%).

(S)-4-(4-Chlorobenzylthio)pentan-2-one (8)

Yield: 94%, determined by isolated yield after column chromatography. The structure of as-obtained product 8 was identified by $^1$H NMR spectrum (see Fig. S33). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.33-7.27 (m, 4 H, Cl-Ph-CH$_2$-), 3.75-3.74 (m, 2 H, Cl-Ph-C$_2$H$_5$), 3.20-3.13 (m, 1 H, -S-C$_2$H$_5$CH$_3$), 2.73-2.64 (m, 2 H, CH-CH$_2$-CO-), 2.14 (s, 3 H, -CO-C$_2$H$_3$), 1.64-1.52 (m, 3 H, CH$_2$-CH$_2$-CH$_2$). Ee value: >99%, determined by HPLC ($^i$PrOH/n-hexane = 10:90 (v/v)), flow rate = 1.0 mL·min$^{-1}$, 25 °C, $\lambda$ = 254 nm, major enantiomer $t_S$ = 6.07 min, minor enantiomer $t_R$ = 4.99 min (see Fig. S34 and S35).
**Fig. S33** $^1$H NMR of the as-obtained product 8

**Fig. S34** HLPC of product 8 obtained over Fe$^{II}$-PN$_{120}$O$_4$ (ee value = >99%)
Fig. S35 HPLC of product 8 obtained over Neat-C (ee value = 69%)

*(S)-3-(4-Chlorophenylthio)-1,3-diphenylpropan-1-one (9)*

![Chemical structure of (S)-3-(4-Chlorophenylthio)-1,3-diphenylpropan-1-one (9)](image)

Yield: 92%, determined by isolated yield after column chromatography. The structure of as-obtained product 9 was identified by ¹H NMR spectrum (see Fig. S36). ¹H NMR (CDCl₃, 500 MHz): δ (ppm): 7.44-7.41 (m, 5 H, Ph-CO-CH₂-), 7.32-7.29 (m, 9 H, Ph-CH-S- and Cl-Ph-S-), 2.05-2.03 (m, 1 H, CH₂-CO-), 1.60-1.58 (d, 2 H, CH₂-CO-). Ee value: 98%, determined by HPLC (PrOH/n-hexane = 20: 80 (v/v)), flow rate = 1.0 mL·min⁻¹, 25 °C, λ = 254 nm, major enantiomer tₛ = 10.34 min, minor enantiomer tᵣ = 8.34 min (see Fig. S37 and S38).
**Fig. S36** $^1$H NMR of as-obtained product 9

**Fig. S37** HPLC of product 9 obtained over Fe$^{II}$-PN$_{12}$O$_4$ (ee value = 98%).
Fig. S38 HLPC of product 9 obtained over Neat-C (ee value = 55%).

References

(1) S. Nidhi, K. Neeraj, R. Garima, S. Damini, S. Aarushi, T. Vartika, K. Sujata and C. Ramesh,  
ACS Omega, 2020, 5, 2267.