Supporting Information

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

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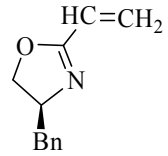
CONTENT:

1. Identification of copolymer precursors of PN_xO_y ($PN_{120}O_4$, $PN_{150}O_3$, and $PN_{210}O_3$) and the corresponding intermediate

Chiral 4-benzyl-2-vinyloxazoline



Calc. for ($C_{12}H_{13}NO$): 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-vinyloxazoline was identified by ^{1}H NMR spectrum (see Fig. S1). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.34-7.22 (m, 5 H, *Ph*-CH_2-oxazoline), 6.30-5.90 (m, 3 H, C*H*$_2$=C*H*-oxazoline), 4.25-4.23 (m, 1 H, O-CH_2-C*H*-N in oxazoline), 4.22-4.16 (m, 2 H, O-C*H*$_2$-CH-N in oxazoline), 3.03-2.86 (m, 2 H, Ph-C*H*$_2$-oxazoline). FT-IR (KBr): γ_{max}/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.

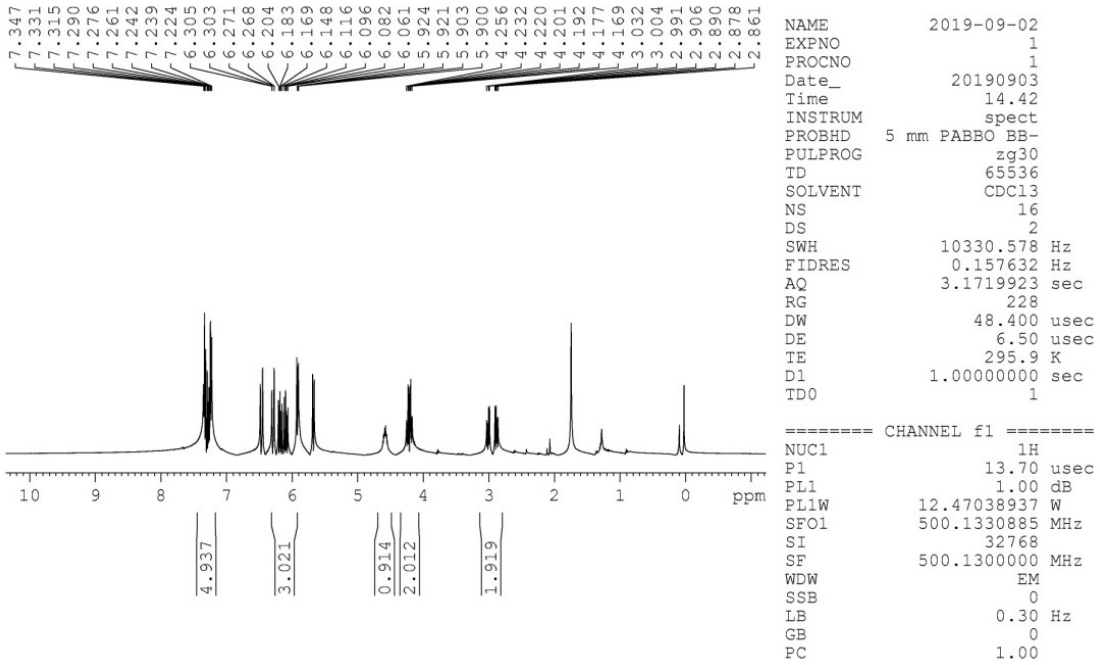
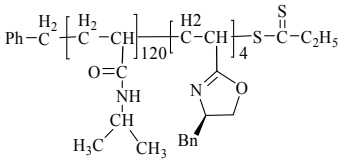


Fig. S1 ^{1}H NMR of chiral 4-benzyl-2-vinyloxazoline

$PN_{120}O_4$



The structure of $PN_{120}O_4$ was identified by ^{1}H NMR spectrum (see Fig. S2). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.39-7.08 (m, 25 H, *Ph*-CH_2-oxazoline and *Ph*-CH_2-CH_2-CH- in backbone chain), 6.59-6.27 (m, 120 H, O=C-N*H*-CH in NIPAAm), 4.01-3.89 (m, 126 H, -C*H*-CH_2- of backbone chain in NIPAAm, -C*H*-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-C*H*-CH_3 in NIPAAm, Ph-CH_2-oxazoline, -O-CH_2-CH-N- in oxazoline and Ph-CH_2-CH_2-CH- 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): γ_{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.

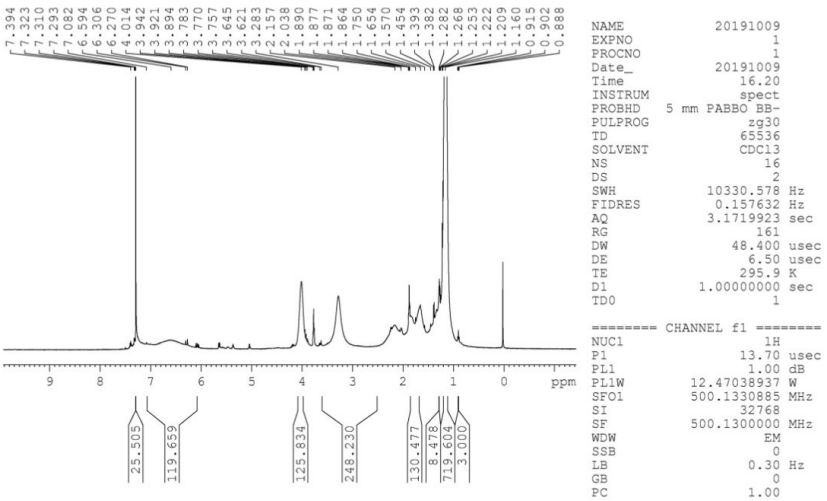
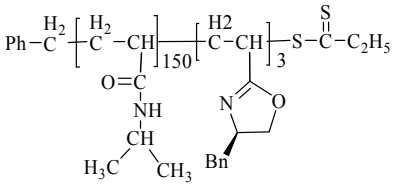


Fig. S2 ^{1}H NMR of $PN_{120}O_4$

$PN_{150}O_3$



The structure of $PN_{150}O_3$ was identified by ^1H NMR spectrum (see Fig. S3). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.50-7.08 (m, 20 H, *Ph*-CH_2-oxazoline and *Ph*-CH_2-CH_2-CH- in backbone chain), 6.78-6.04 (m, 150 H, O=C-N*H*-CH in NIPAAm), 4.77-4.02 (m, 154 H, -C*H*-CH_2- of backbone chain in NIPAAm, -C*H*-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-C*H*-CH_3 in NIPAAm, Ph-CH_2-oxazoline, -O-CH_2-CH-N- in oxazoline, and Ph-CH_2-CH_2-CH- 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): γ_{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.

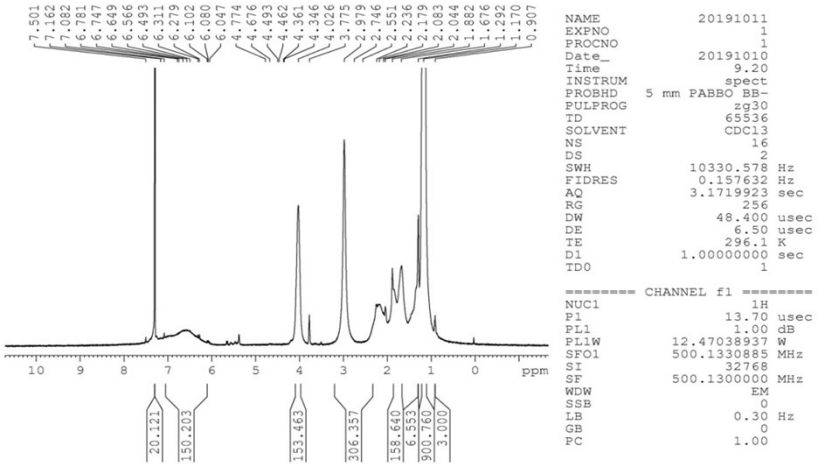
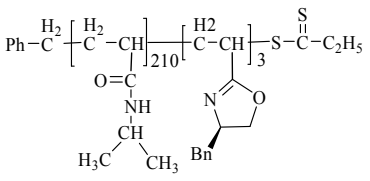


Fig. S3 ^1H NMR of $PN_{150}O_3$

$PN_{210}O_3$



The structure of $PN_{210}O_3$ was identified by ^1H NMR spectrum (see Fig. S4). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.29-6.69 (m, 20 H, *Ph*-CH_2-oxazoline and *Ph*-CH_2-CH_2-CH- in backbone chain), 6.69-6.62 (m, 210 H, O=C-N*H*-CH in NIPAAm), 4.00-3.68 (m, 215 H, -C*H*-CH_2- of backbone chain in NIPAAm, -C*H*-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-C*H*-CH_3 in NIPAAm, Ph-CH_2-oxazoline, -O-CH_2-CH-N- in oxazoline and Ph-CH_2-CH_2-CH- 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, CH_3-CH-CH_3 in NIPAAm), 1.19-1.14 (m, 3 H, S=C-CH_2-CH_3 in backbone chain). FT-IR (KBr): γ_{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.

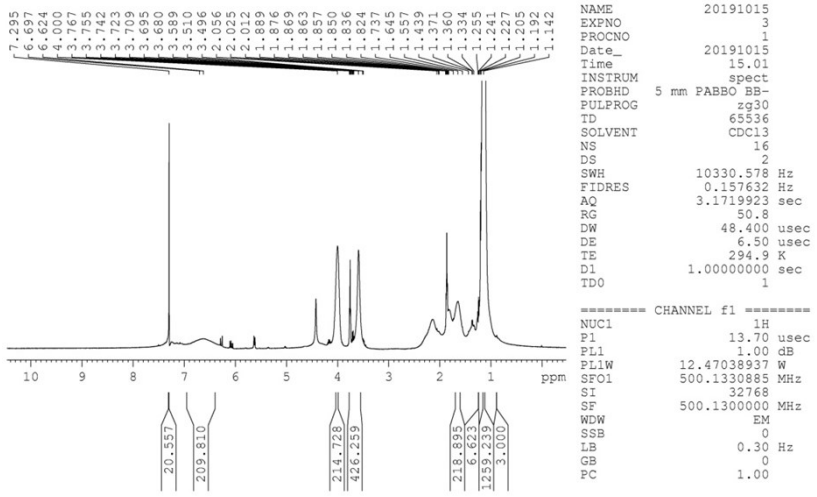


Fig. S4 ^1H NMR of $PN_{210}O_3$

2. Synthesis and identification of *α, β*-unsaturated ketones (chalcone, benzylidene acetone, 4-methoxychalcone, 4-methoxybenzylidene acetone, and 4-nitrochalcone)

Michael acceptors of *α, β*-unsaturated ketones were synthesized by the aldol condensation under alkaline condition.[1] In the typical process, acetone or acetophenone (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 *α, β*-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, $CDCl_3$): δ (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-C*H*-CH-), 7.45-7.44 (m, 3 H, *Ph*-CH-CH- and *Ph*-CH-C*H*-).

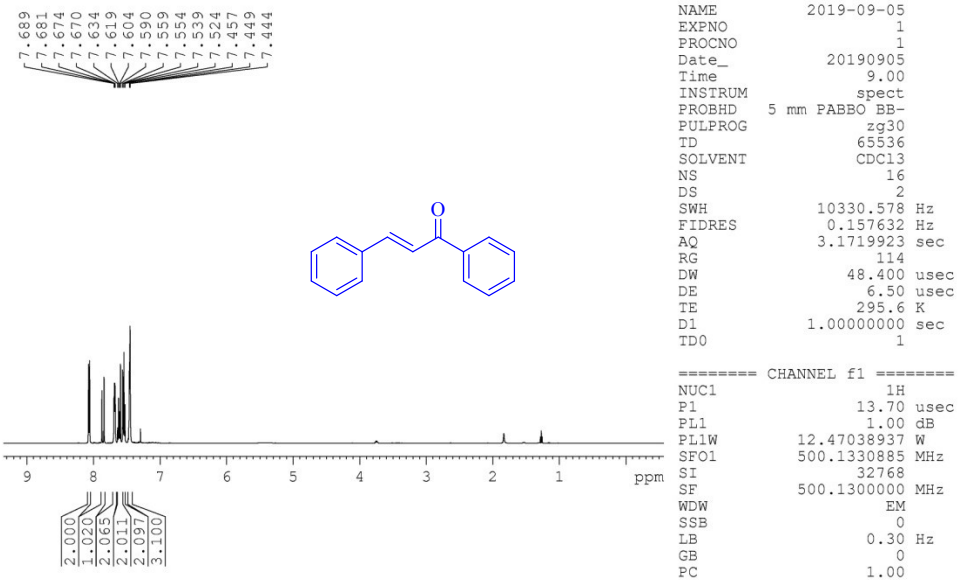


Fig. S5 ^{1}H NMR of chalcone

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, $CDCl_3$): δ (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-C*H*-), 6.77-6.74 (m, 1 H, -CH-C*H*-CO-), 2.42 (s, 3 H, -CO-CH_3).

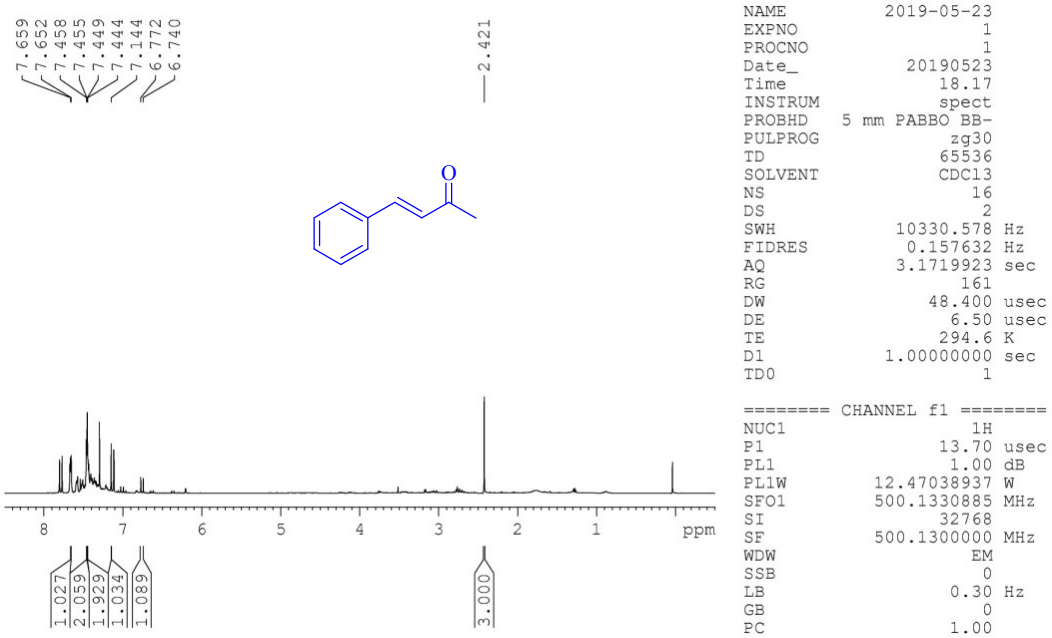


Fig. S6 ^{1}H NMR of benzylidene acetone

4-Methoxychalcone (2.19 g, yield: 92%, yellow powder). Calc. for ($C_{16}H_{14}O_2$): 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 ^{1}H NMR spectrum (see Fig. S7). ^{1}H NMR (500 MHz, $CDCl_3$): 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 CH_3O-*Ph*-CH-), 7.54-7.51 (m, 2 H, CH_3O-*Ph*-CH-), 7.46-7.43 (m, 1 H, CH_3O-*Ph*-CH-), 6.98-6.96 (m, 2 H, Ph-C*H*-C*H*-CO-), 3.88 (s, 3 H, CH_3O-Ph-CH-).

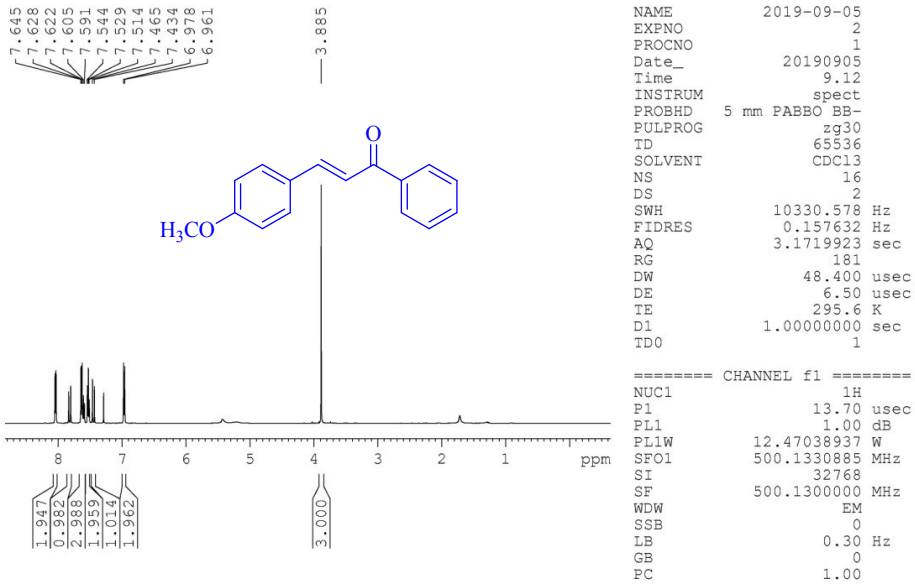


Fig. S7 [1]H NMR of 4-methoxychalcone

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-C*H*-C*H*-CO-), 5.27 (s, 3 H, -CO-CH_3), 3.88 (s, 3 H, CH_3O-Ph-CH-).

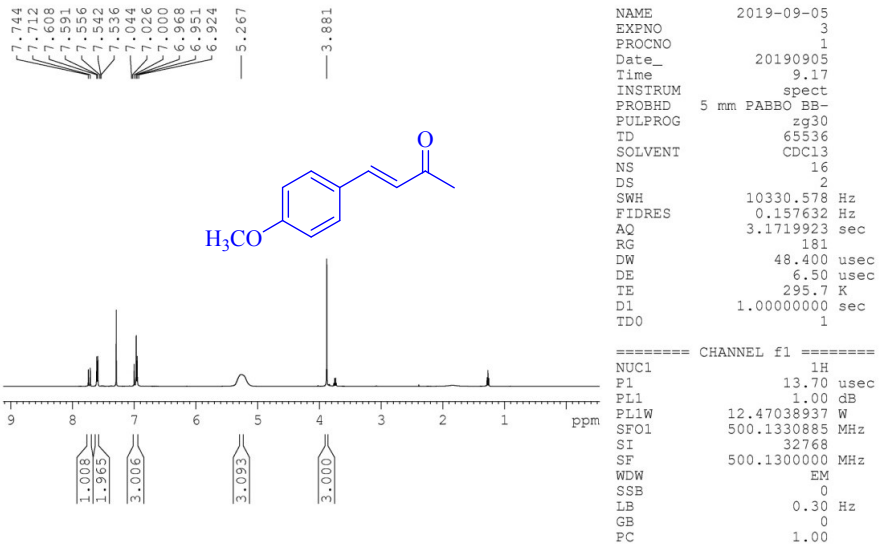


Fig. S8 [1]H NMR of 4-methoxybenzylidene acetone

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, $CDCl_3$): δ (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-C*H*-C*H*-CO-).

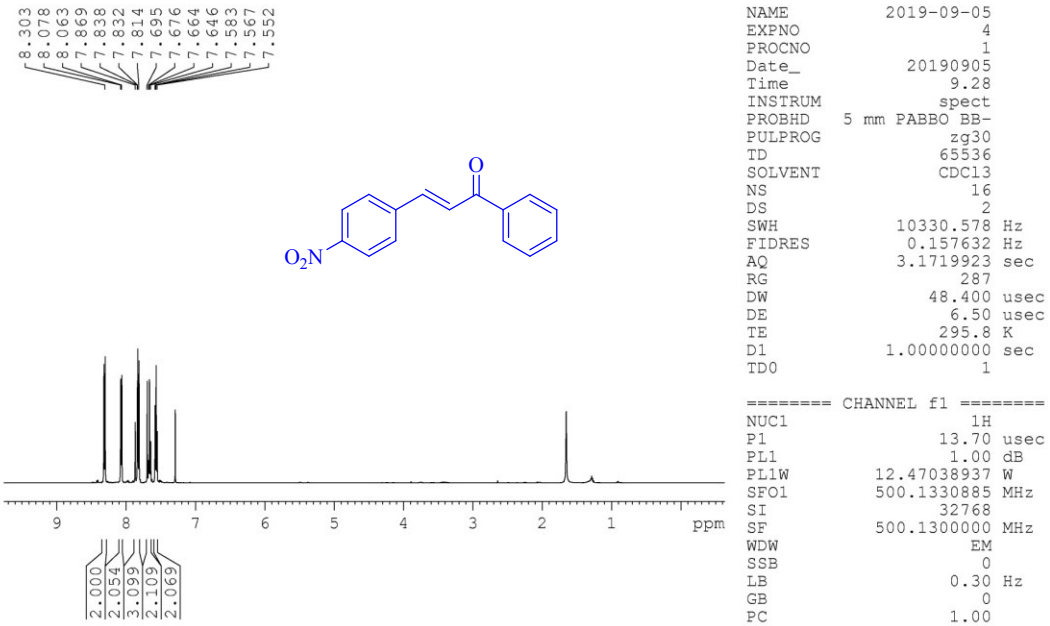
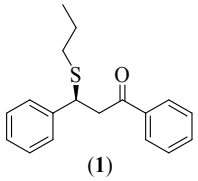


Fig. S9 ^{1}H NMR of 4-nitrochalcone

3. Identification of obtained chiral β-thioketones.

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



(**1**)

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): δ (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

H, C*H*-CH_2-CO-), 3.57-3.56 (d, 2 H, CH-CH_2-CO-), 2.41-2.23 (m, 2 H, -S-CH_2-CH_2-), 1.60-1.49 (m, 2 H, S-CH_2-CH_2-CH_3), 0.94-0.91 (m, 3 H, S-CH_2-CH_2-CH_3). Ee value: 96%, determined by HPLC (^{i}PrOH/*n*-hexane = 10:90 (v/v)), flow rate = 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, major enantiomer t_S = 5.75 min, minor enantiomer t_R = 4.82 min (Fig. S11-S14).

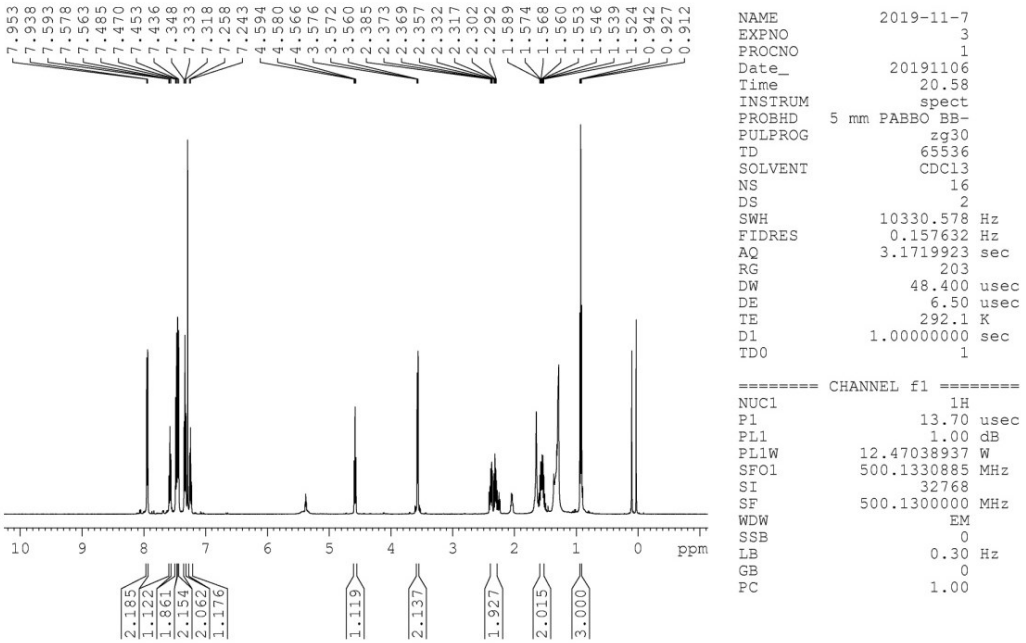


Fig. S10 ^{1}H NMR of the as-obtained product **1**

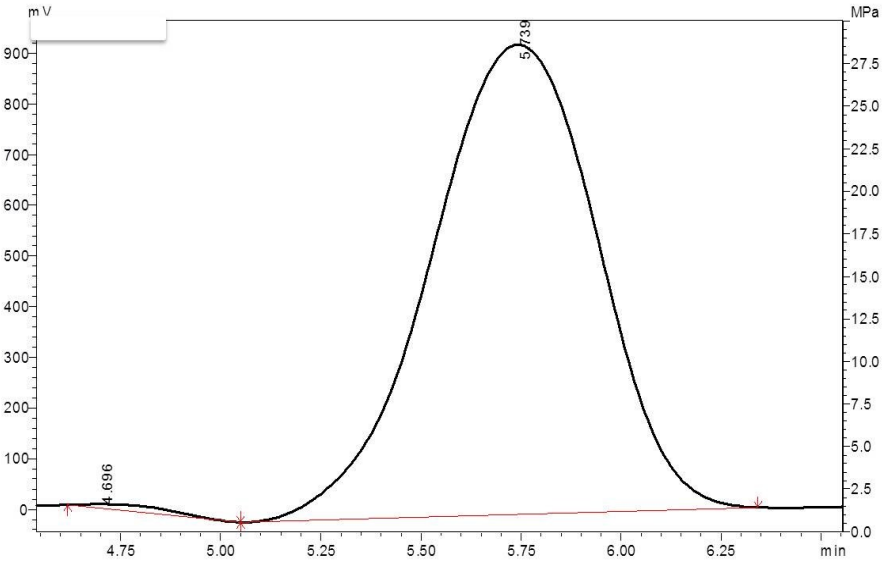


Fig. S11 HLPC of product **1** obtained over **Fe^{II}-$PN_{120}O_4$** (ee value = 99%)

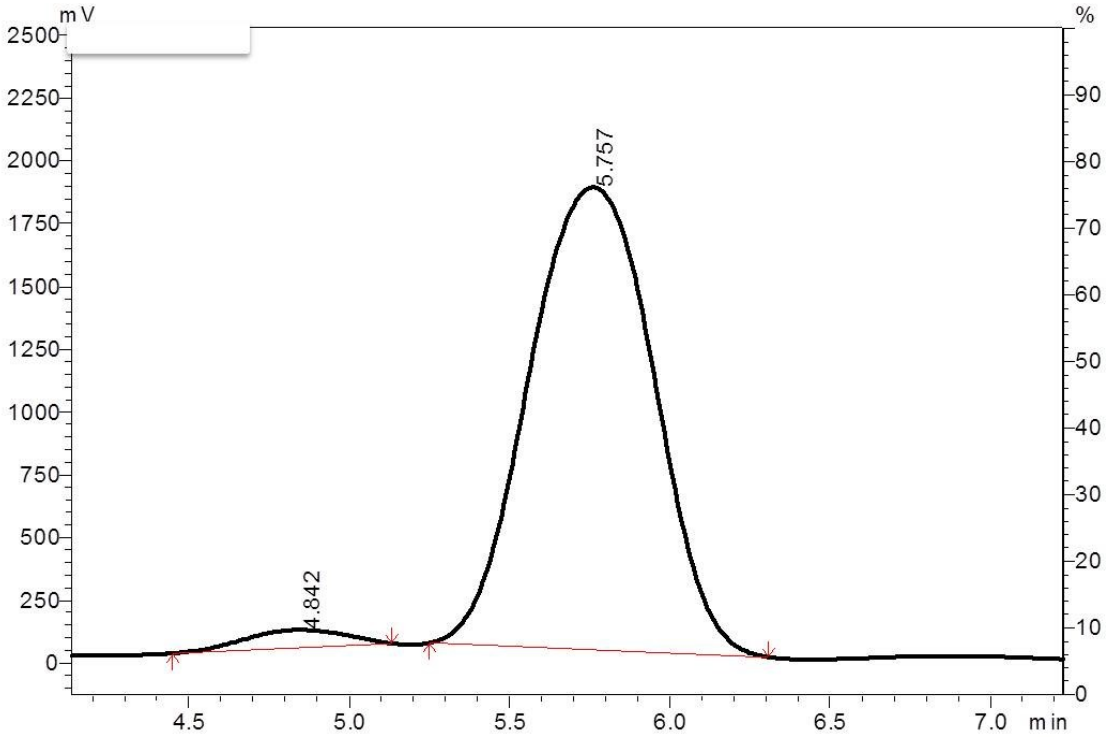


Fig. S12 HLPC of product **1** obtained over **Fe^{II}-$PN_{150}O_3$** (ee value = 96%)

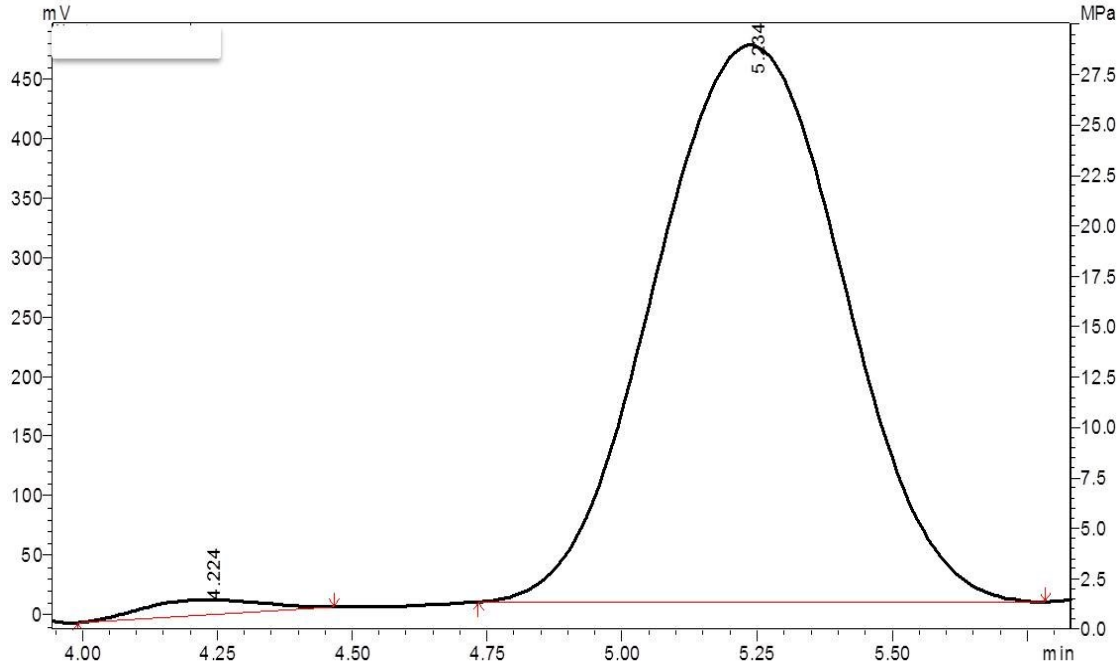


Fig. S13 HLPC of product **1** obtained over **Fe^{II}-$PN_{210}O_3$** (ee value = 96%)

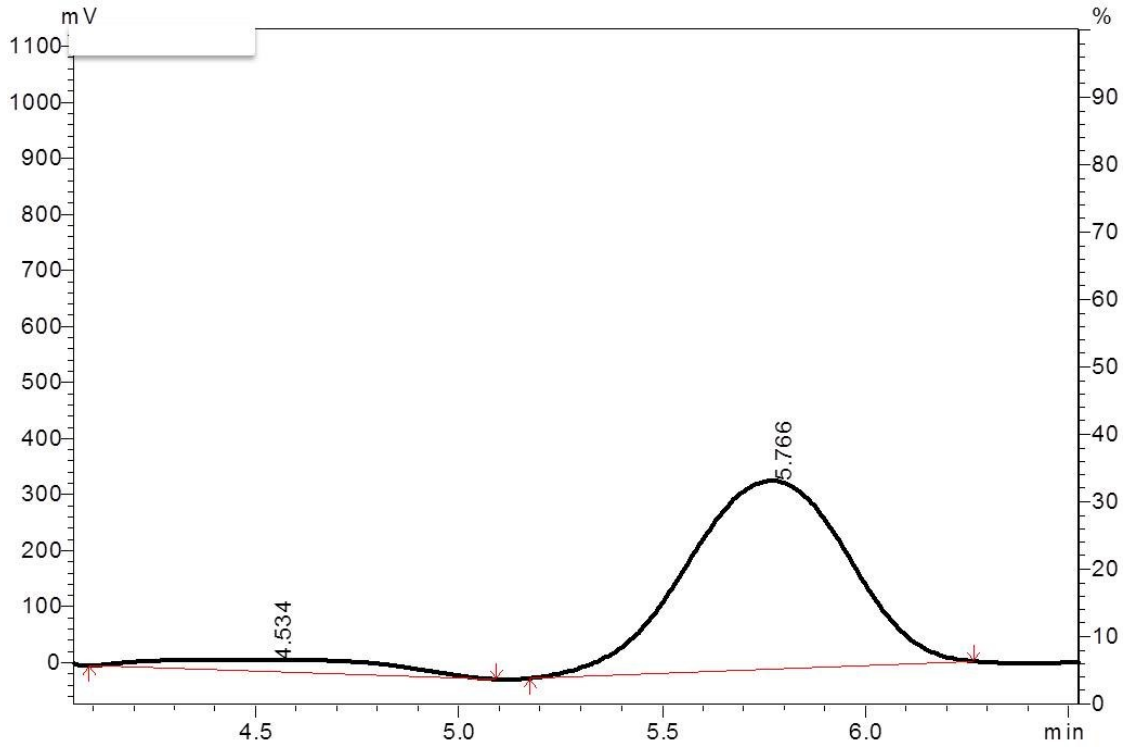
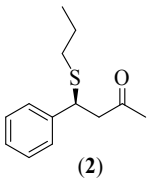


Fig. S14 HLPC of product **1** obtained over **Neat-C** (ee value = 83%)

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



(**2**)

Yield: 96%, determined by isolated yield after column chromatography. The structure of as-obtained product **2** was identified by ^{1}H NMR spectrum (see Fig. S15). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.55-7.31 (m, 5 H, *Ph*-CH-S-), 4.49-4.46 (m, 1 H, C*H*-CH_2-CO-), 3.25-3.24 (d, 2 H, CH-C*H*$_2$-CO-), 2.39-2.23 (m, 2 H, -S-C*H*$_2$-CH_2-CH_3), 1.57-1.53 (m, 2 H, -S-CH_2-C*H*$_2$-CH_3), 1.36 (s, 3 H, -CO-C*H*$_3$), 0.96-0.91 (m, 3 H, -S-CH_2-CH_2-C*H*$_3$). Ee value: 99%, determined by HPLC (^{i}PrOH/*n*-hexane = 20:80 (v/v)), flow rate = 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, major enantiomer t_S = 6.12 min, minor enantiomer t_R = 4.74 min (see Fig. S16 and S17).

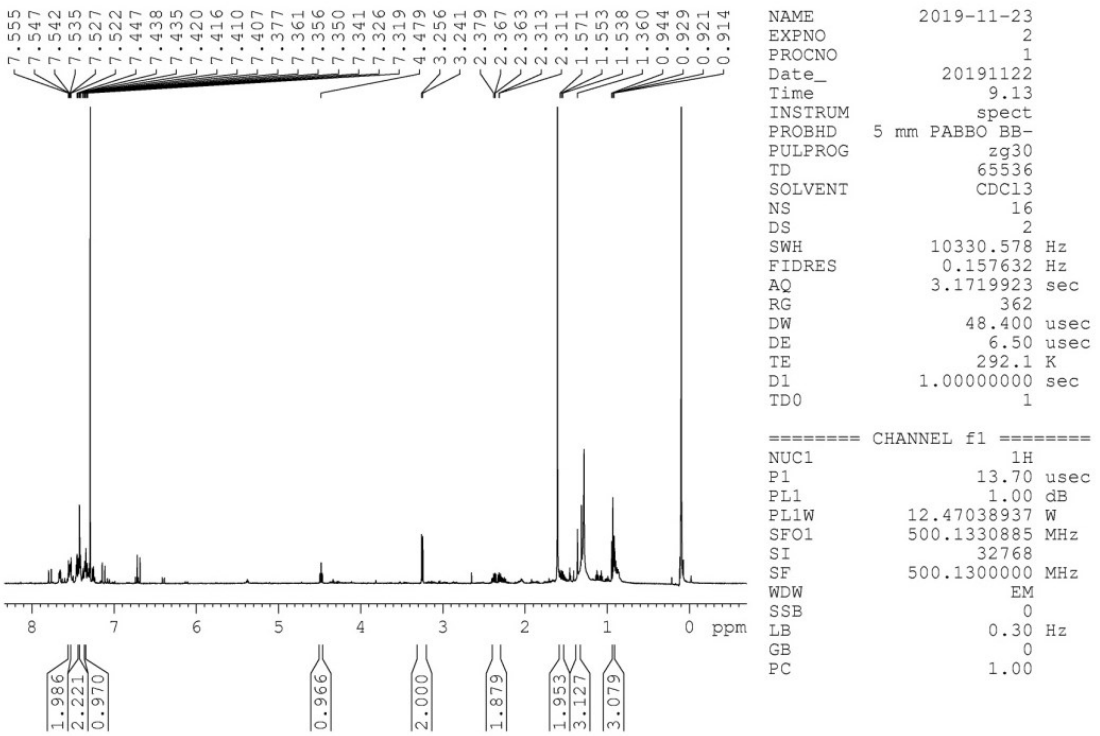


Fig. S15 ^{1}H NMR of as-obtained product **2**

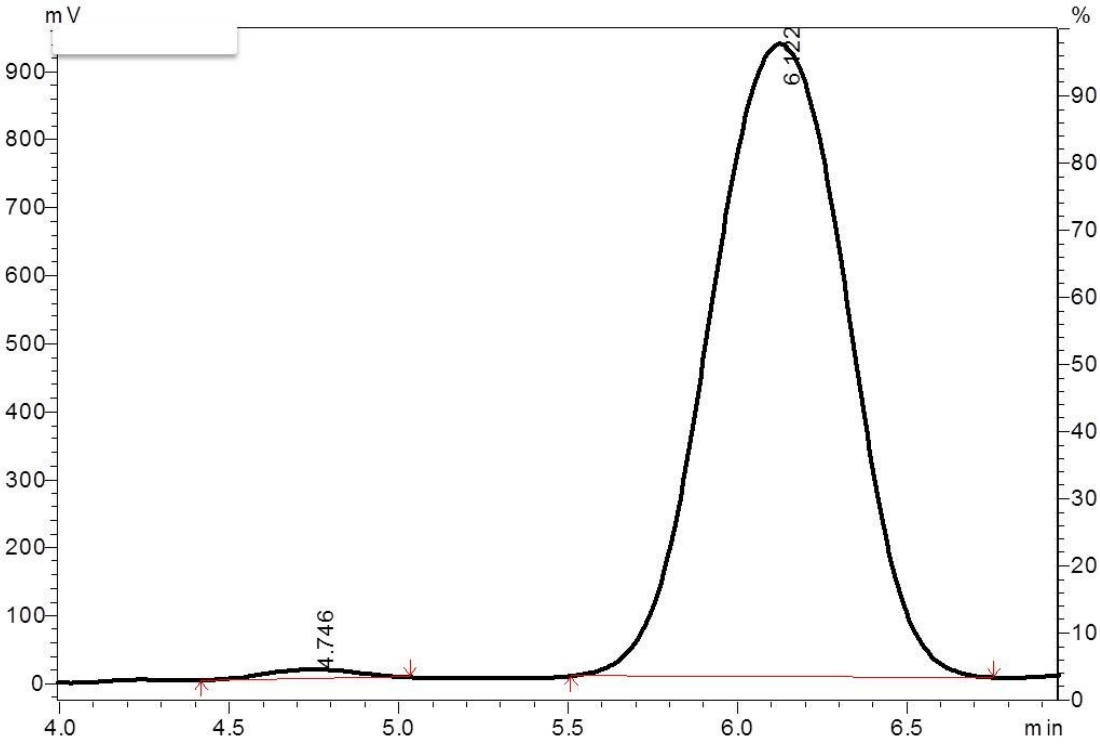


Fig. S16 HLPC of product **2** obtained over $\mathbf{Fe^{II}\text{-}PN_{150}O_3}$ (ee value = 99%)

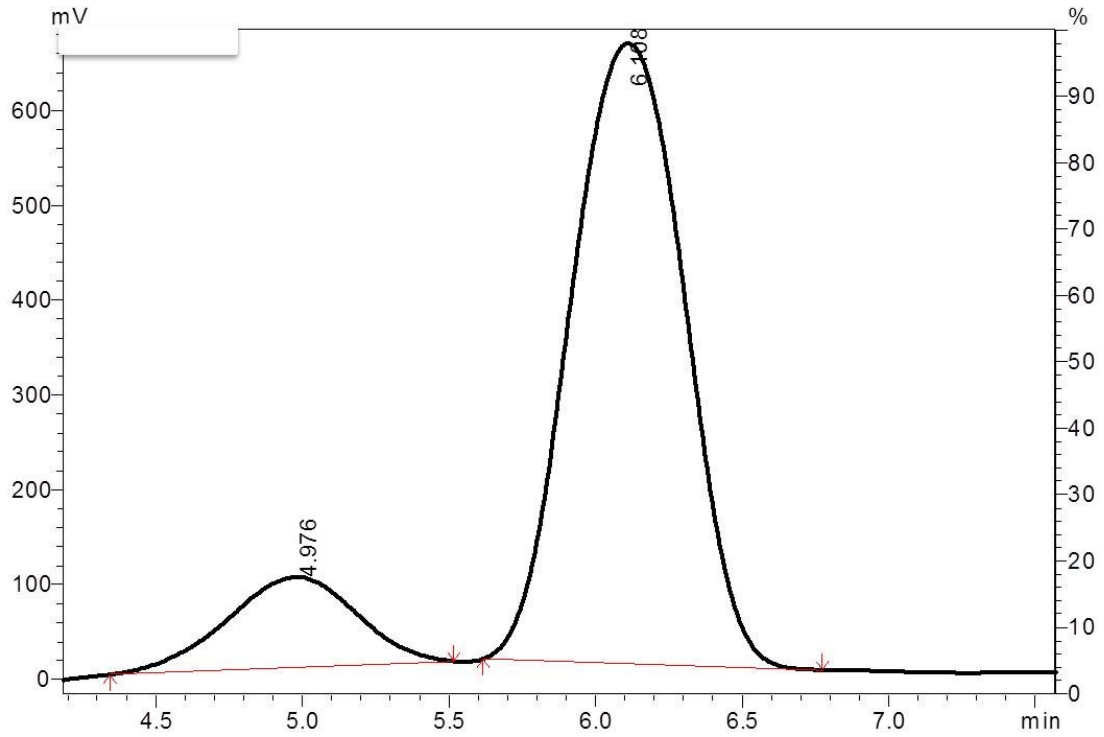
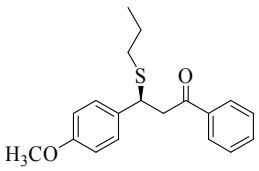


Fig. S17 HLPC of product **2** obtained over **Neat-C** (ee value = 70%)

*(S)-3-(Propylthio)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (**3**)*



(**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): δ (ppm): 7.94-7.43 (m, 5 H, *Ph*-CO-CH_2-), 7.39-6.82 (m, 4 H, CH_3O-*Ph*-CH-), 4.56-4.53 (m, 1 H, C*H*-CH_2-CO-), 3.81 (s, 3 H, C*H*$_3$O-Ph-CH-), 3.57-3.48 (d, 2 H, CH-C*H*$_2$-CO-), 2.38-2.23 (m, 2 H, -S-C*H*$_2$-CH_2-CH_3), 1.60-1.49 (m, 2 H, -S-CH_2-C*H*$_2$-CH_3), 0.97-0.88 (m, 3 H, -S-CH_2-CH_2-C*H*$_3$). Ee value: 98%, determined by HPLC (^{i}PrOH/*n*-hexane = 20:80 (v/v)), flow rate = 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, major enantiomer t_S = 12.32 min; minor enantiomer t_R = 10.08 min (see Fig. S19 and S20).

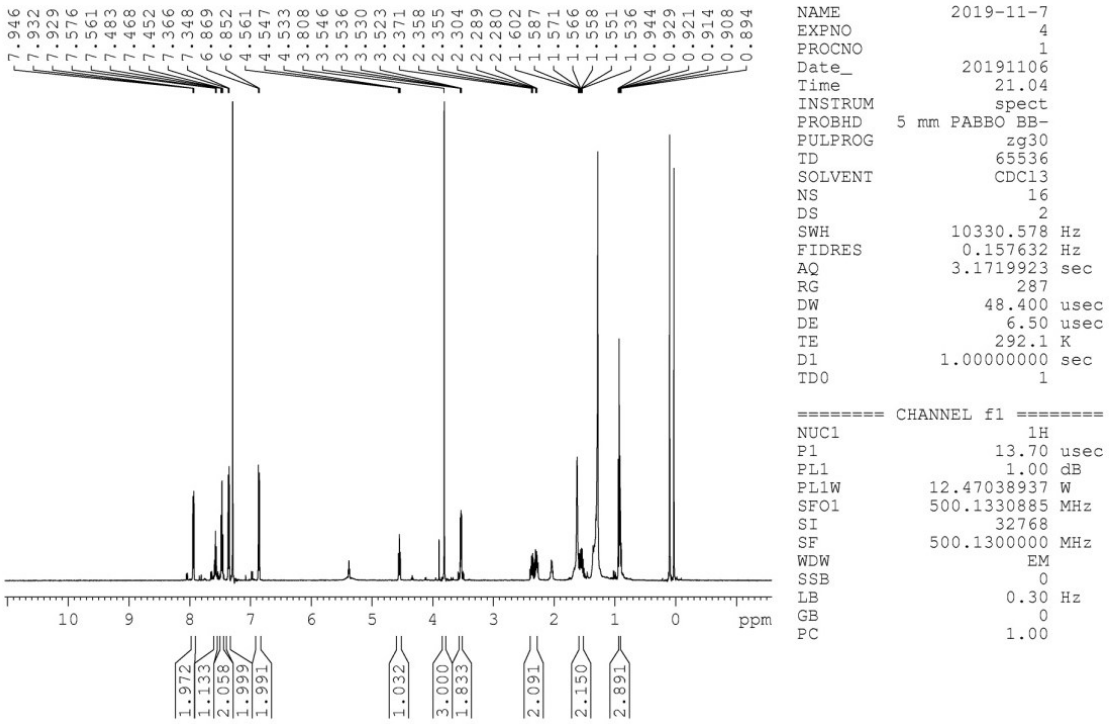


Fig. S18 ^{1}H NMR of as-obtained product **3**

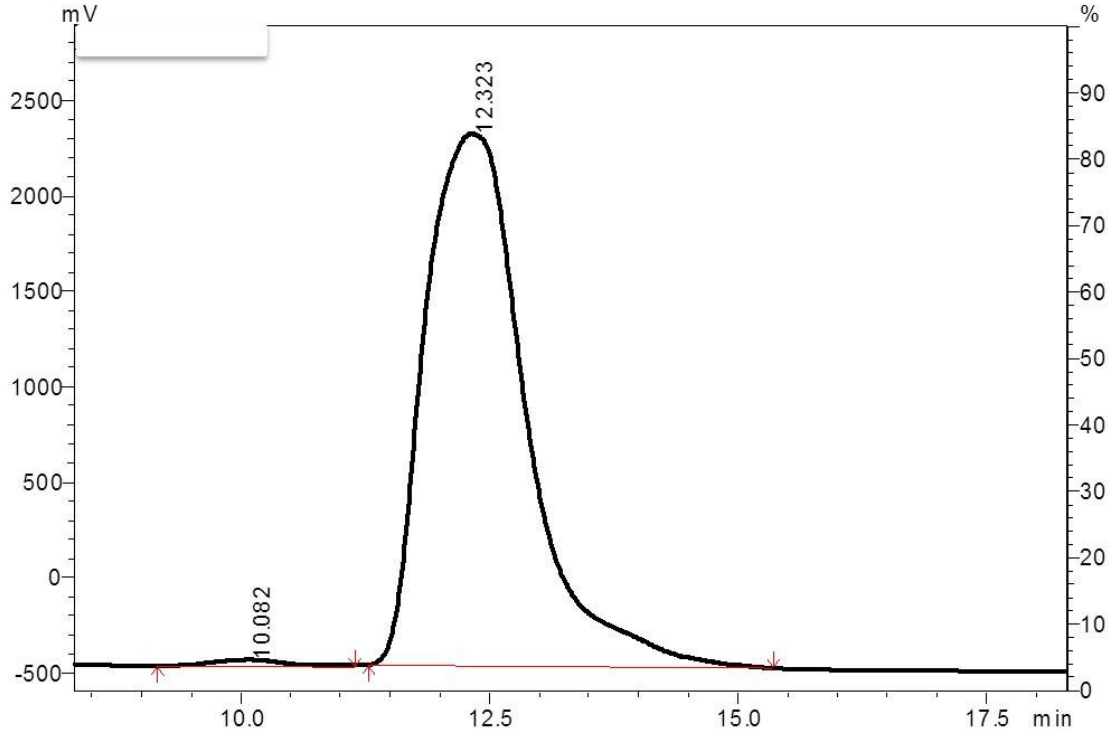


Fig. S19 HLPC of product **3** obtained over **Fe^{II}-$PN_{150}O_3$** (ee value = 98%)

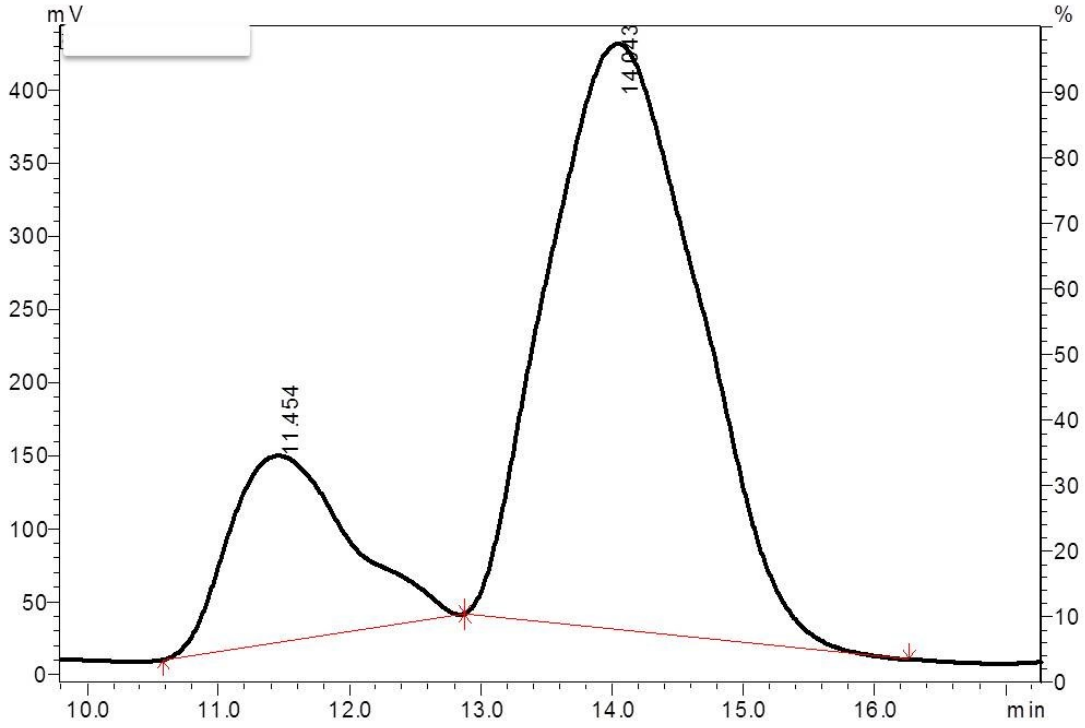
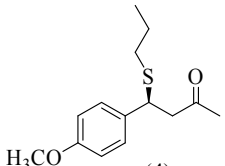


Fig. S20 HLPC of product **3** obtained over **Neat-C** (ee value = 60%)

*(S)-4-(Propylthio)-4-(4-methoxyphenyl) butan-2-one (**4**)*



(**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): δ (ppm): 7.75-6.91 (m, 4 H, CH_3O-*Ph*-CH-), 4.40-4.30 (m, 1 H, C*H*-CH_2-CO-), 3.92-3.87 (d, 2 H, CH-CH_2-CO-), 2.64 (s, 3 H, CH_3O-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 (^{i}PrOH/*n*-hexane = 10:90 (v/v)), flow rate = 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, major enantiomer t_S = 11.04 min, minor enantiomer t_R = 8.11 min (see Fig. S22 and S23).

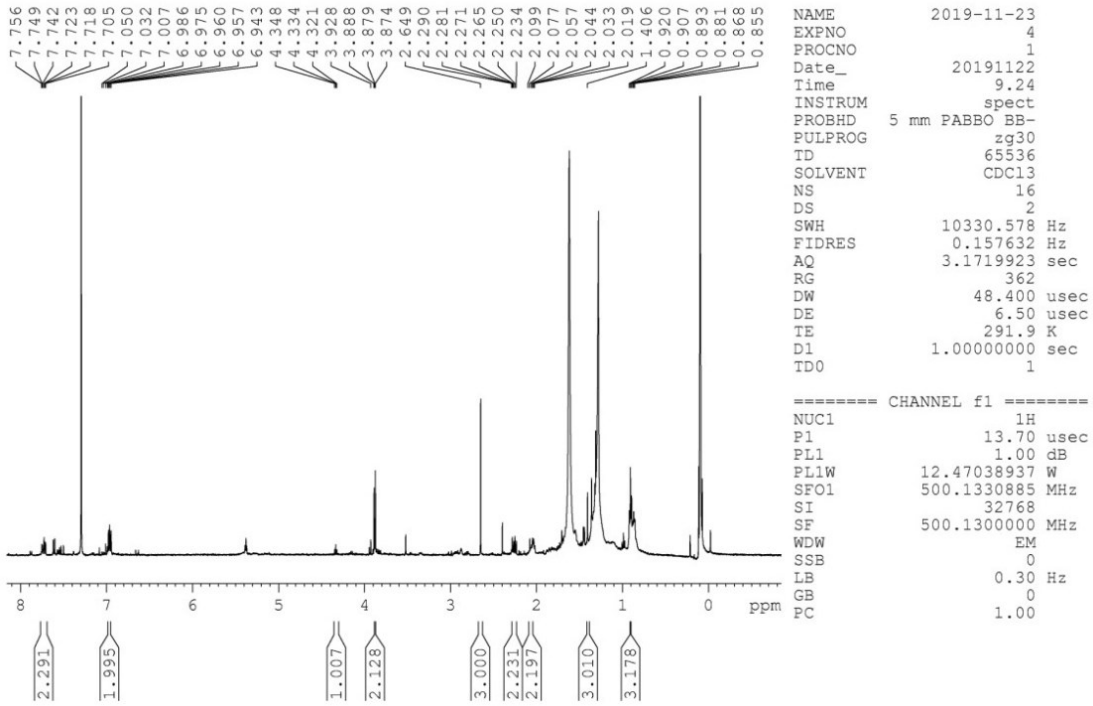


Fig. S21 ^{1}H NMR of as-obtained product **4**

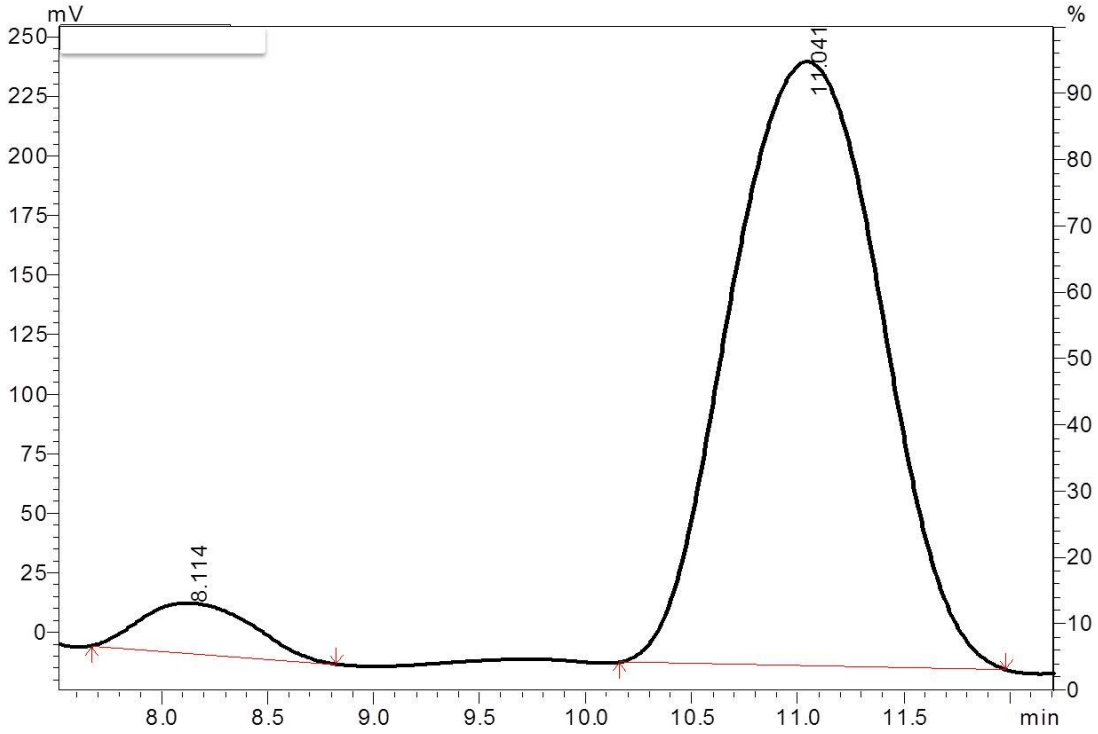


Fig. S22 HLPC of product **4** obtained over $\mathbf{Fe^{II}\text{-}PN_{150}O_3}$ (ee value = 90%)

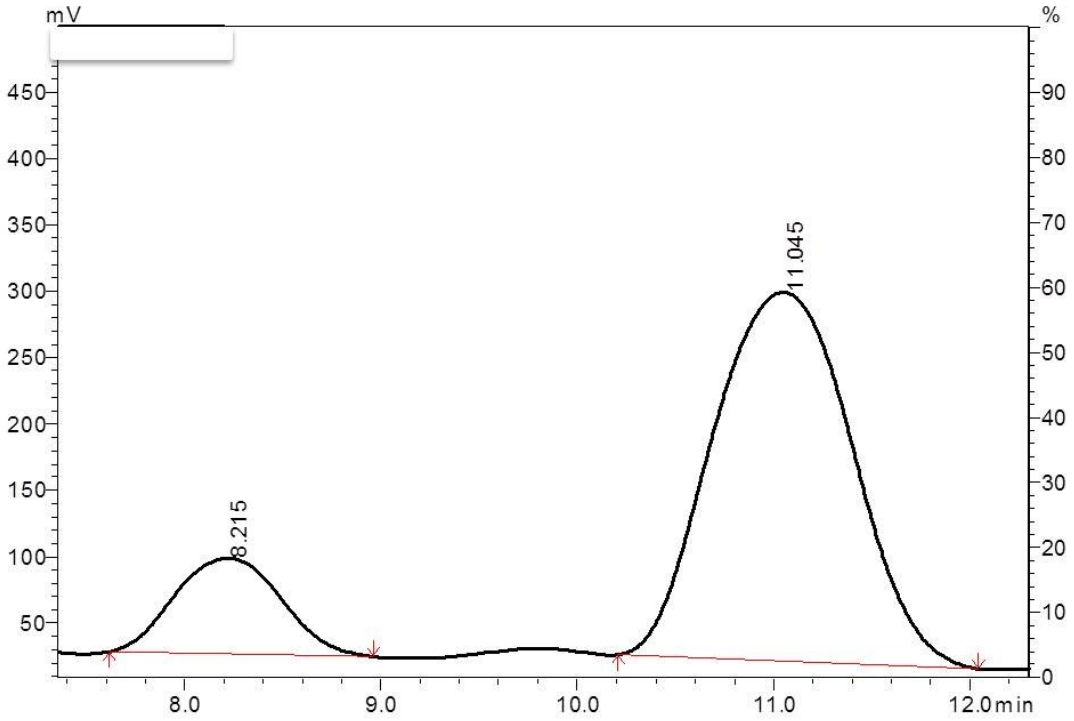
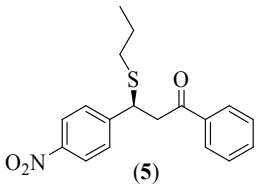


Fig. S23 HLPC of product **4** obtained over **Neat-C** (ee value = 67%)

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



(**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): δ (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, C*H*-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 (^{i}PrOH/*n*-hexane = 30:70 (v/v)), flow rate = 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, major enantiomer t_S = 11.78 min, minor enantiomer t_R = 10.01 min (see Fig. S25 and S26).

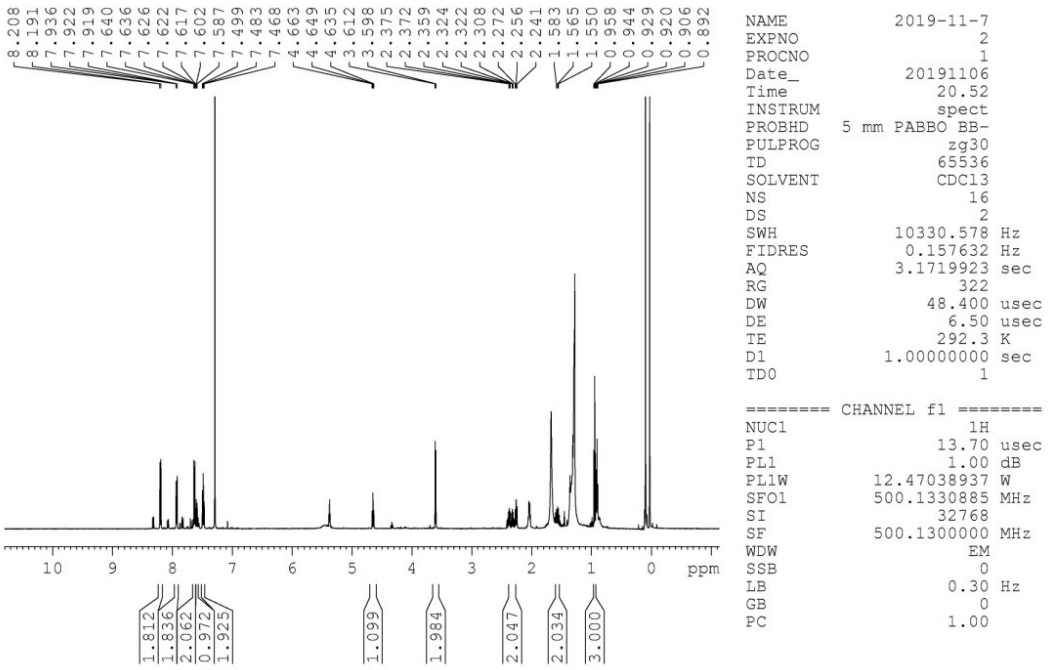


Fig. S24 ^{1}H NMR of as-obtained product **5**

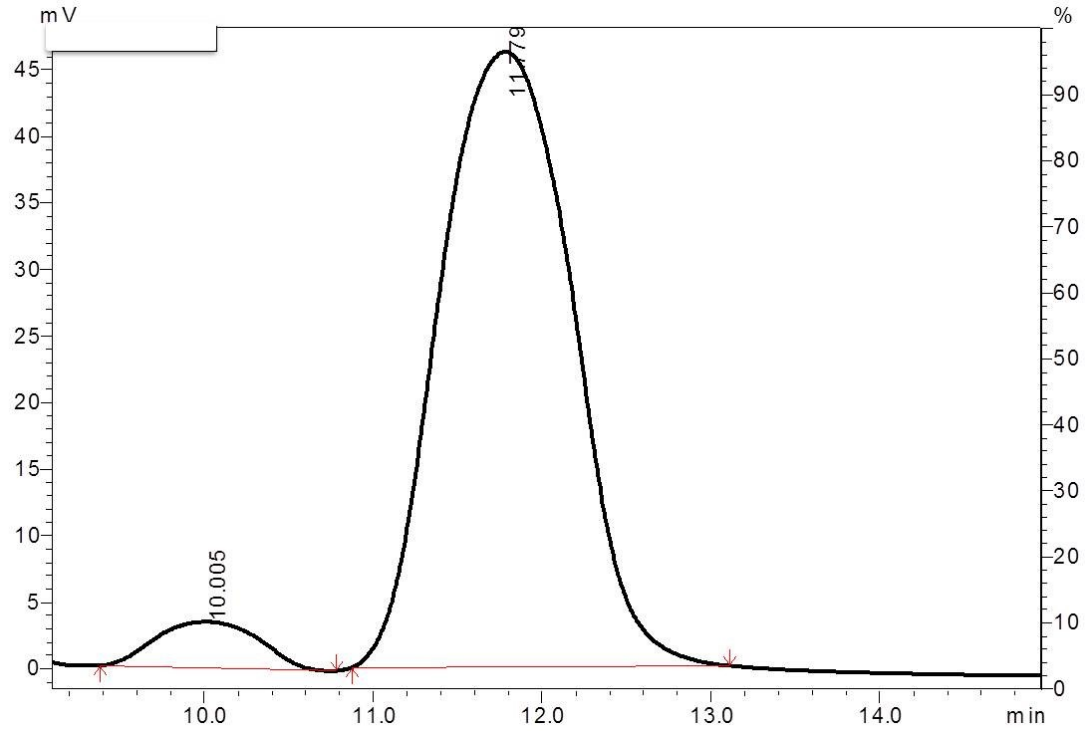


Fig. S25 HLPC of product **5** obtained over **Fe^{II}-$PN_{150}O_3$** (ee value = 89%)

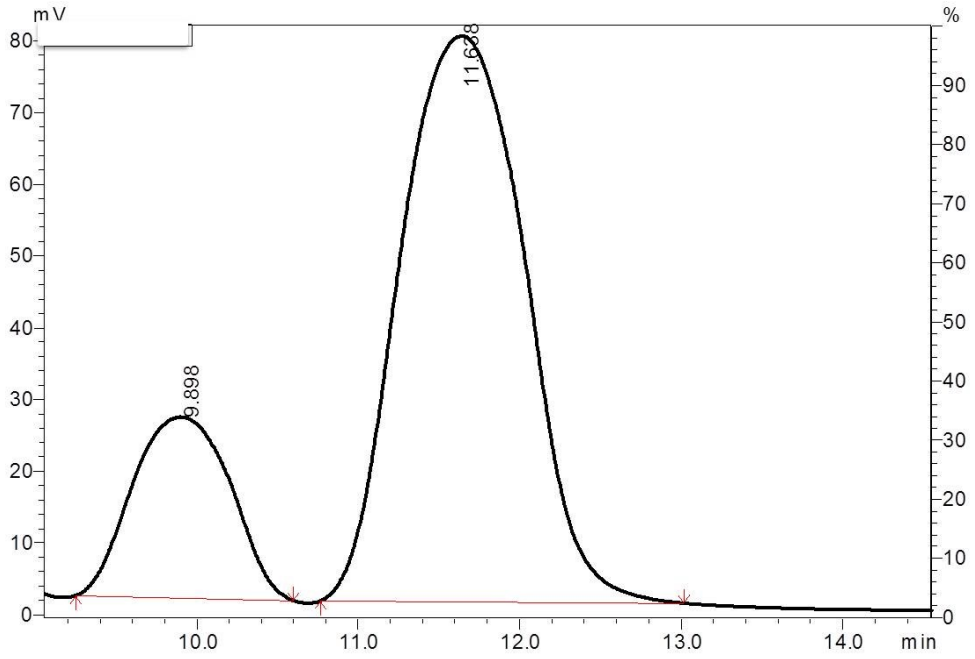
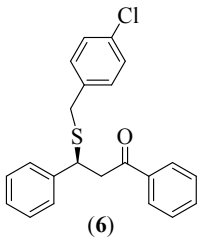


Fig. S26 HLPC of product **5** obtained over **Neat-C** (ee value = 59%)

*(S)-3-(4-Chlorobenzylthio)-1,3-diphenylpropan-1-one (**6**)*



(**6**)

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-CH_2-Ph), 3.51-3.44 (m, 2 H, CH-CH_2-CO-). Ee value: 95%, determined by HPLC (^{i}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]

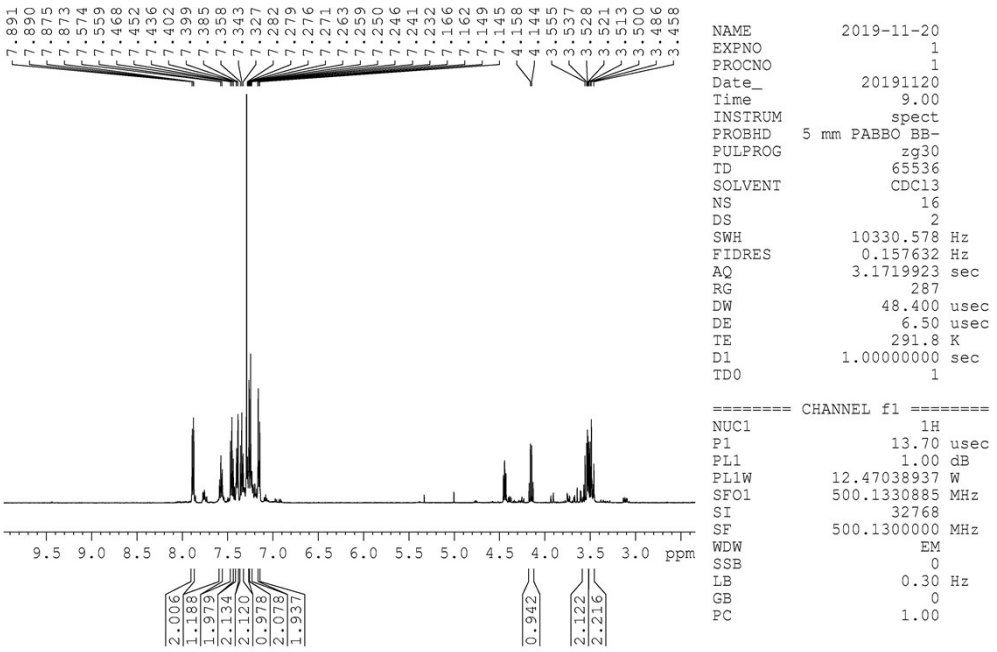


Fig. S27 ^{1}H NMR of as-obtained product **6**

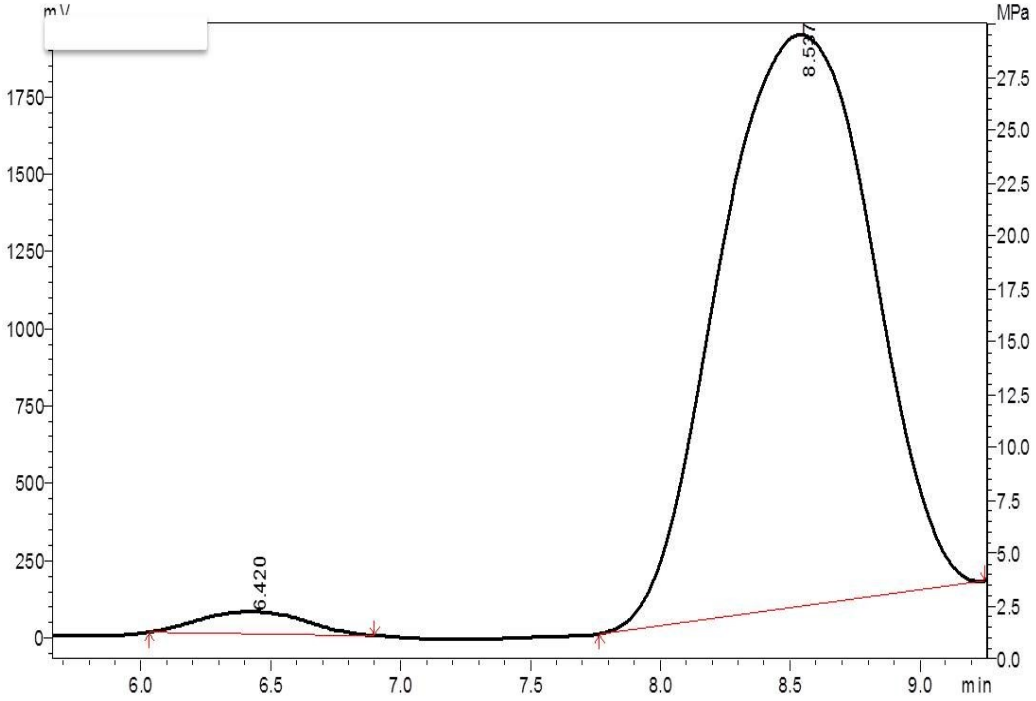


Fig. S28 HLPC of product **6** obtained over **Fe^{II}-$PN_{150}O_3$** (ee value = 95%)

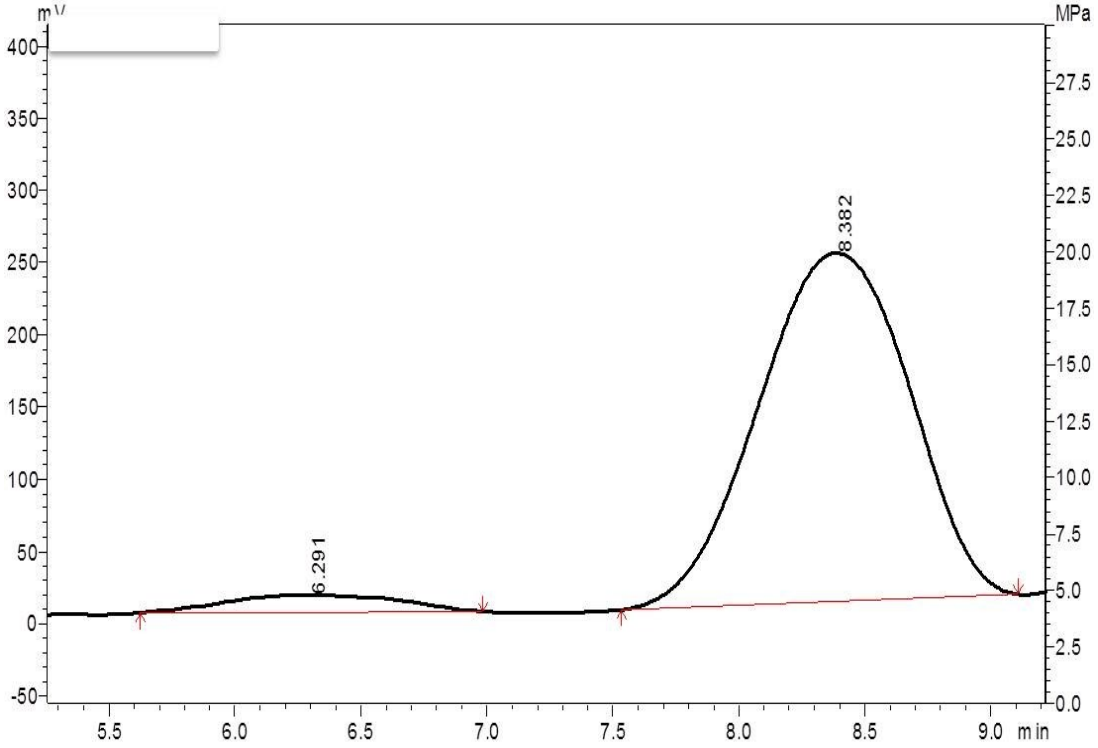
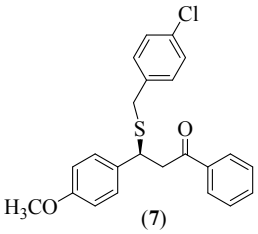


Fig. S29 HLPC of product **6** obtained over **Neat-C** (ee value = 87%)

(S)-3-(4-Chlorobenzylthio)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (7)



(**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): δ (ppm): 7.33-7.17 (m, 13 H, Cl-*Ph*-CH_2-, CH_3O-*Ph*-CH-, and *Ph*-CO-CH_2-), 4.17-4.15 (m, 1 H, C*H*-CH_2-CO-), 4.14-4.13 (m, 2 H, Cl-Ph-CH_2-S-), 3.60 (s, 3 H, CH_3O-Ph-CH-), 2.99-2.91 (m, 2 H, CH-CH_2-CO-). Ee value: 96%, determined by HPLC (^{i}PrOH/*n*-hexane = 3:97 (v/v)), flow rate = 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, major enantiomer t_S = 20.15 min, minor enantiomer t_R = 17.48 min (see Fig. S31 and S32).

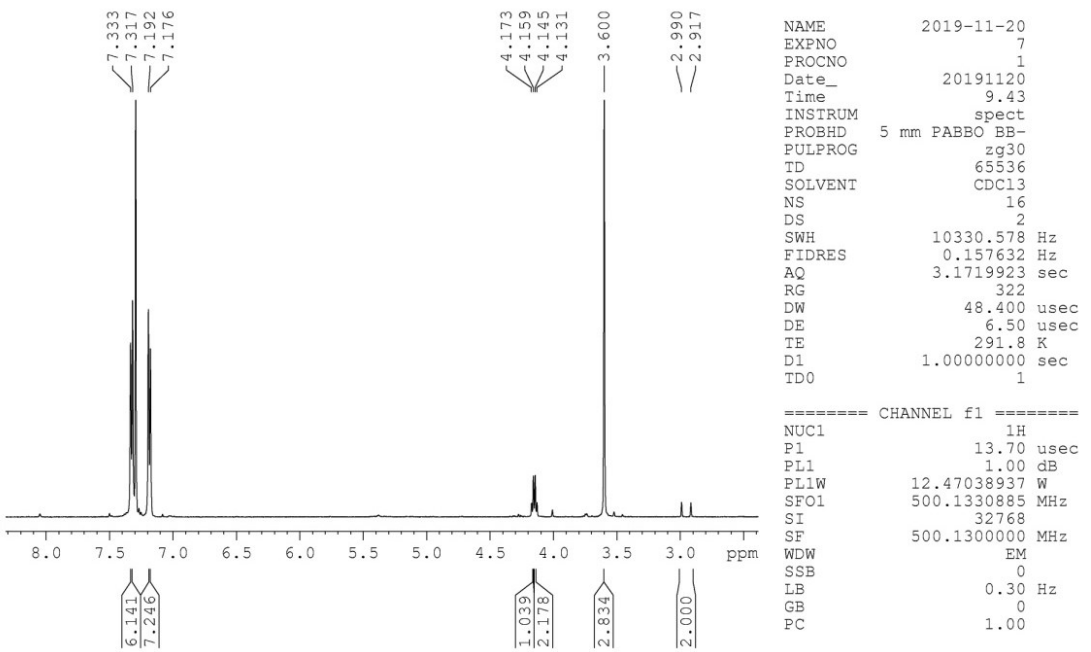


Fig. S30 ^{1}H NMR of as-obtained product **7**

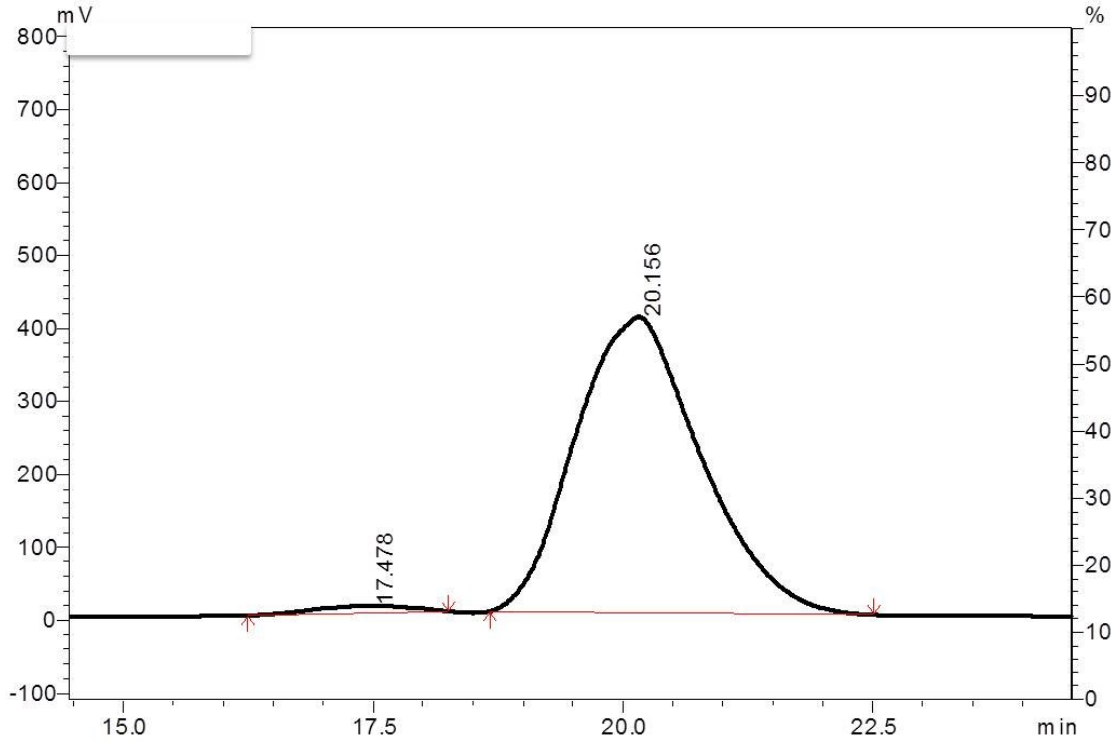


Fig. S31 HLPC of product **7** obtained over **Fe^{II}-$PN_{150}O_3$** (ee value = 96%)

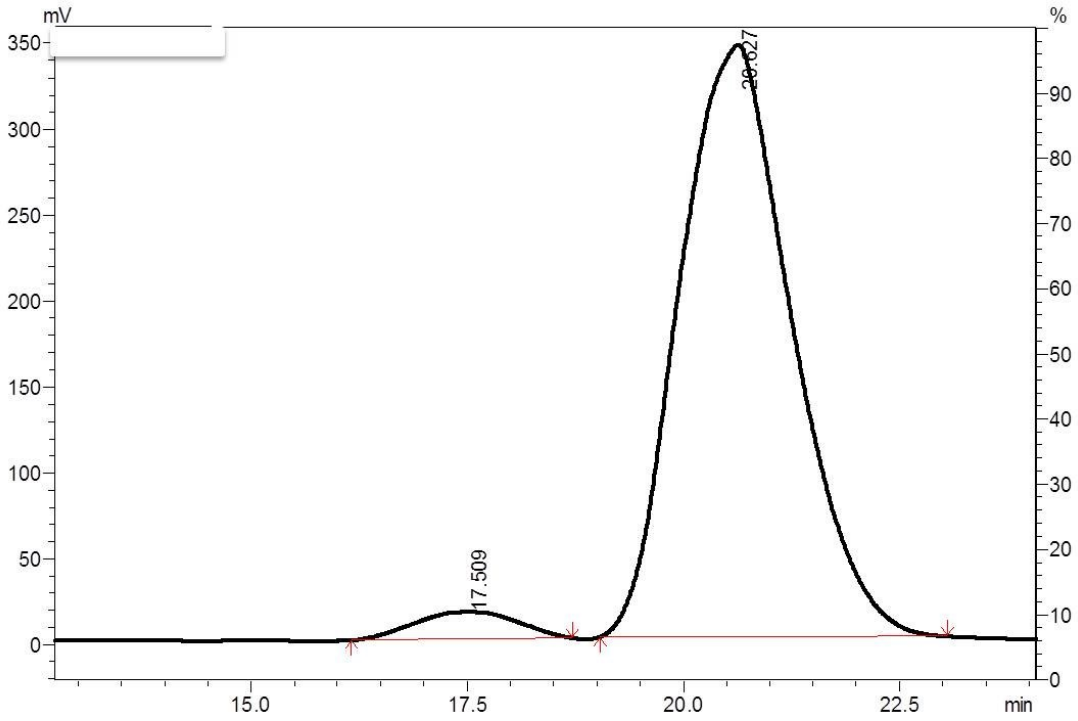
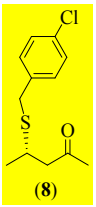


Fig. S32 HLPC of product **7** obtained over **Neat-C** (ee value = 90%).

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



(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): δ (ppm): ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.33-7.27 (m, 4 H, Cl-*Ph*-CH_2-), 3.75-3.74 (m, 2 H, Cl-Ph-C*H*$_2$-), 3.20-3.13 (m, 1 H, -S-C*H*-CH_3), 2.73-2.64 (m, 2 H, CH-C*H*$_2$-CO-), 2.14 (s, 3 H, -CO-C*H*$_3$), 1.64-1.52 (m, 3 H, C*H*$_3$-CH-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, λ = 254 nm, major enantiomer t_S = 6.07 min, minor enantiomer t_R = 4.99 min (see Fig. S34 and S35).

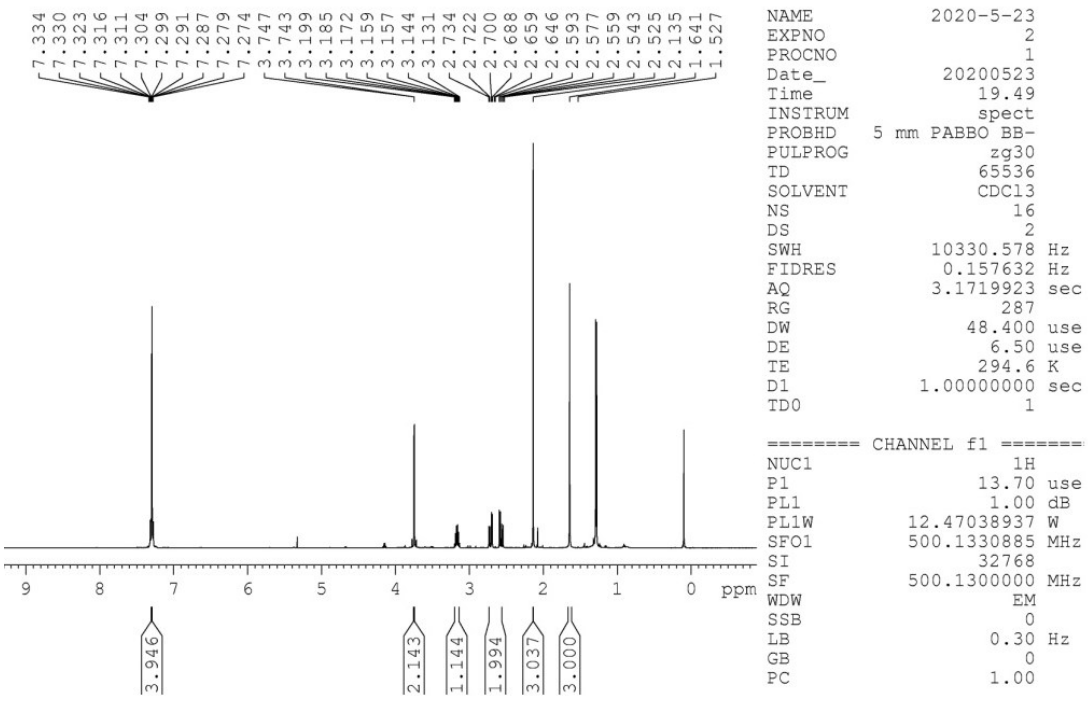


Fig. S33 ^{1}H NMR of the as-obtained product **8**

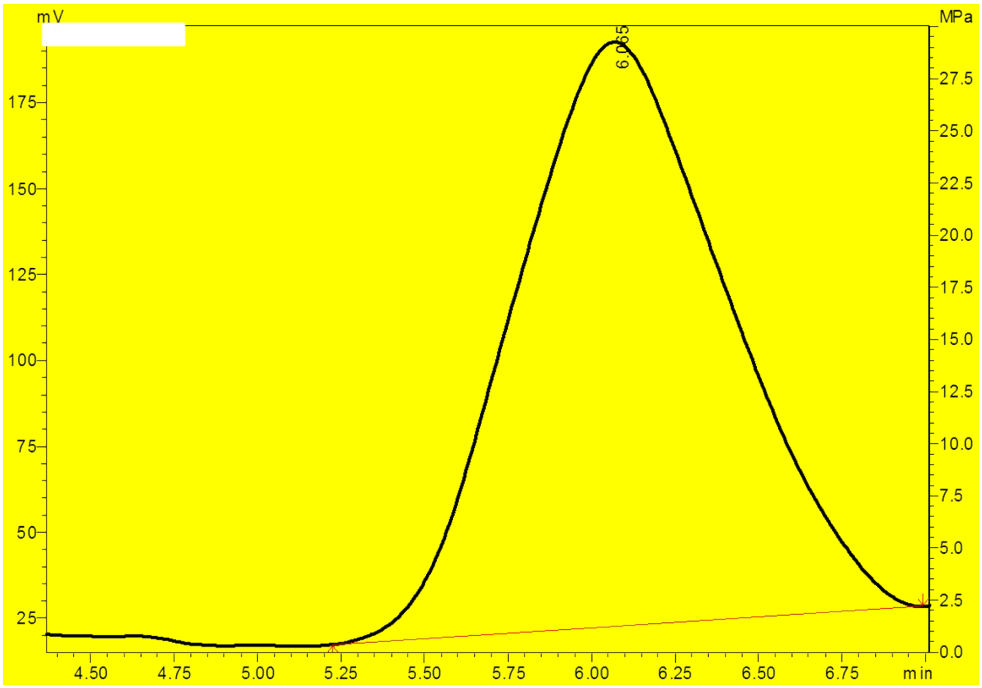


Fig. S34 HLPC of product **8** obtained over **Fe^{II}-$PN_{120}O_4$** (ee value = >99%)

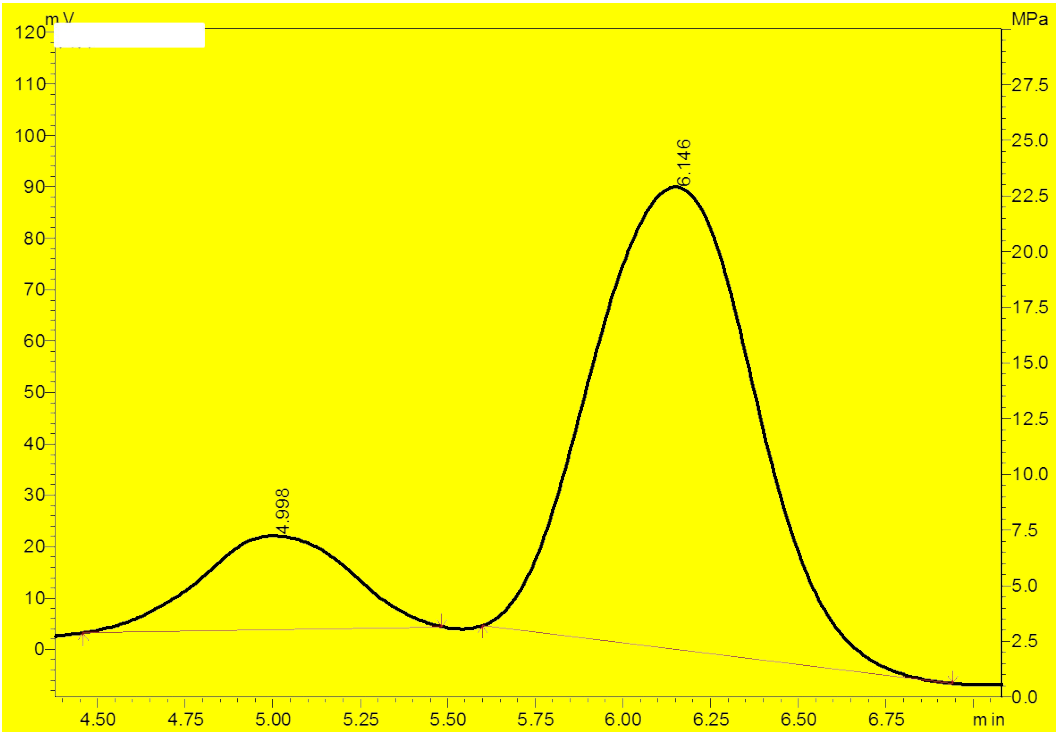
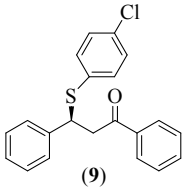


Fig. S35 HLPC of product **8** obtained over **Neat-C** (ee value = 69%)

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



(**9**)

Yield: 92%, determined by isolated yield after column chromatography. The structure of as-obtained product **9** was identified by ^{1}H NMR spectrum (see Fig. S36). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.44-7.41 (m, 5 H, *Ph*-CO-CH_2-), 7.32-7.29 (m, 9 H, *Ph*-CH-S- and Cl-*Ph*-S-), 2.05-2.03 (m, 1 H, C*H*-CH_2-CO-), 1.60-1.58 (d, 2 H, CH-CH_2-CO-). Ee value: 98%, determined by HPLC (^{i}PrOH/*n*-hexane = 20: 80 (v/v)), flow rate = 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, major enantiomer t_S = 10.34 min, minor enantiomer t_R = 8.34 min (see Fig. S37 and S38).

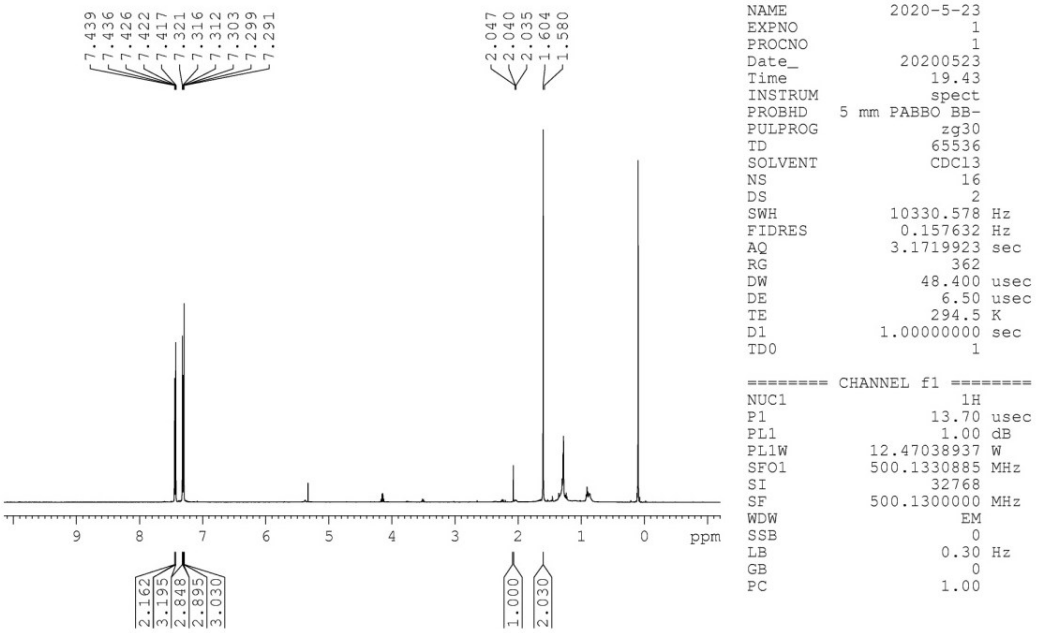


Fig. S36 ^{1}H NMR of as-obtained product **9**

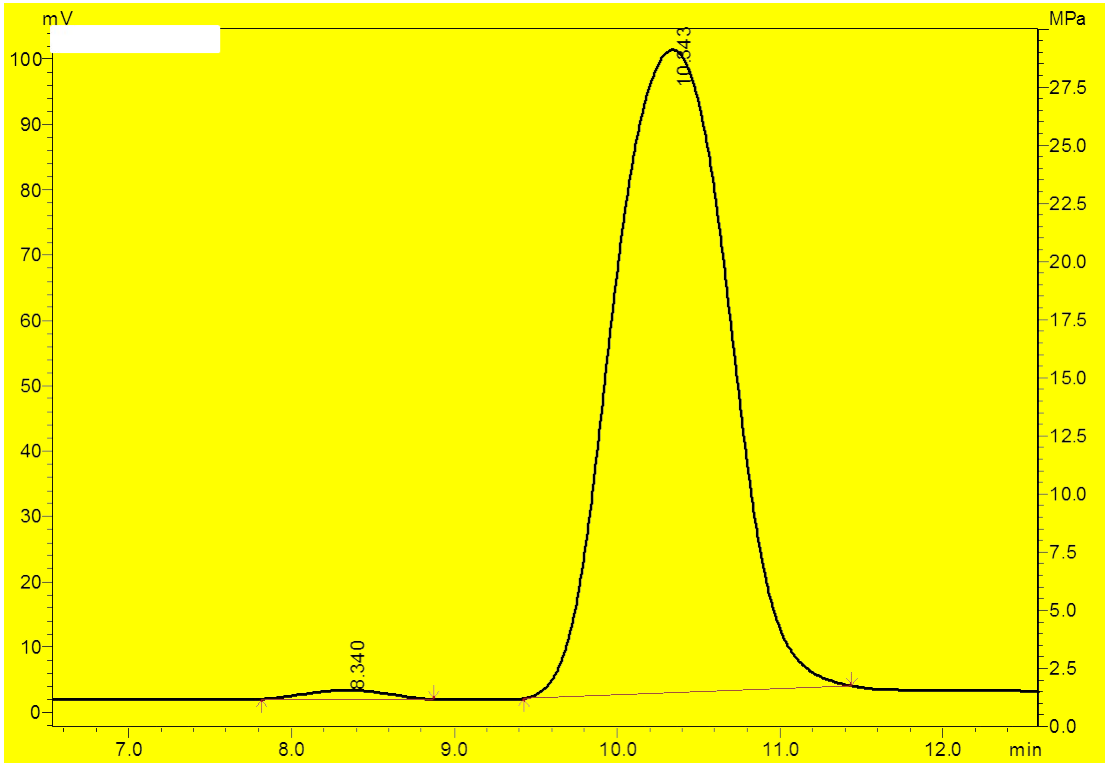


Fig. S37 HLPC of product **9** obtained over **Fe^{II}-$PN_{120}O_4$** (ee value = 98%).

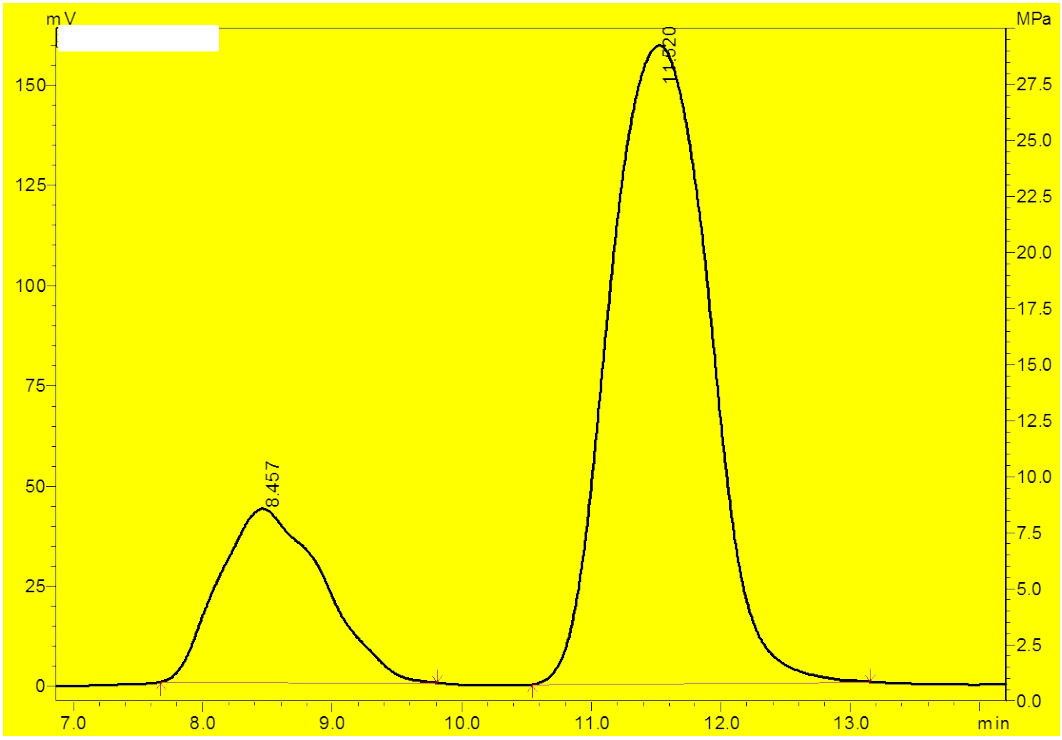


Fig. S38 HLPC of product **9** obtained over **Neat-C** (ee value = 55%).

References

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

(2) J. D. White and S. Shaw, *Chem. Sci.,* 2014, **5**, 2200.