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Supporting information

An efficient proline-based homogeneous organocatalyst with recyclability.

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1. Apparatus and reagents

All the chemicals were purchased and used without any further purification. The preparation of cyclodextrin-modified Fe_3O_4@SiO_2 inclusion complex magnetic nanoparticles were synthesized as scheme 1 according to the ref. 14. Progress of the reaction was monitored by thin layer chromatography (TLC). Column chromatography was performed using forced flow of the indicated solvent on basic aluminum oxide (Shanghaixincheng Chemical Ltd). FTIR spectra were recorded on Perkin-Elmer Model GX Spectrometer using KBr pellet method with polystyrene as a standard. XRD were carried out on a XRD-7000S/L instrument Cu-K α radiation. The magnetic hysteresis loops were measured on a Quantum Design SQUID-MPMS-XL magnetic property measurement system. SEM was performed using an SII: SPI3800N microscope (Japan). ^{1}H and ^{13}C NMR spectra were measured using a Bruker AV-400 spectrometer at 400 MHz in DMSO and $CDCl_3$ with tetramethylsilane as the internal standard (US). Mass spectra were measured using an Axima CFR MALDI-TOF mass spectrometer (US). The enantiomeric excessed were determined by HPLC using a chiral OD column (hexyl hydride/isopropyl alcohol=9/1) under 25℃, 254nm and 1mL/min conditions.

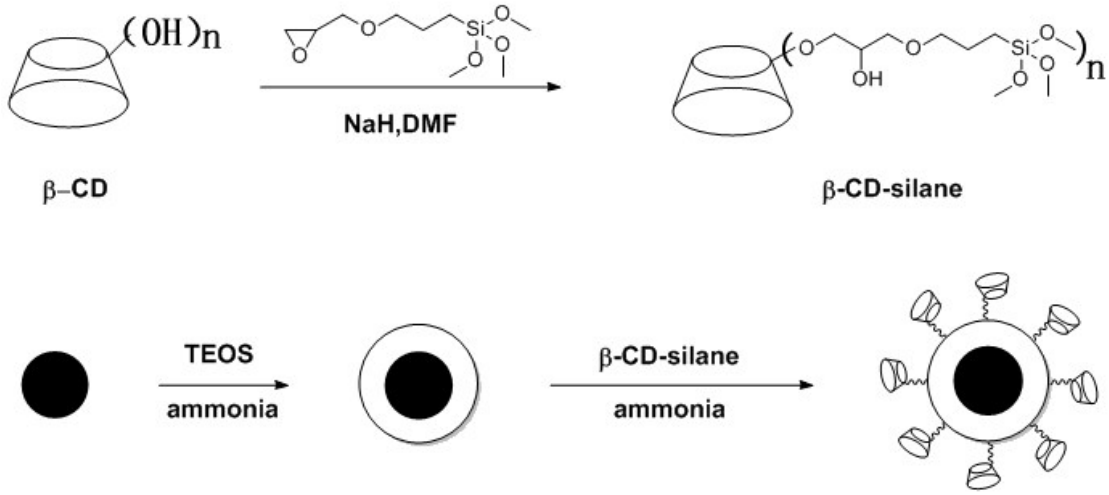
2. The preparation and characterization of MNPs

According to the literature [15], showing as the scheme. 1, $FeCl_3 \cdot 6H_2O$ (1.35g, 5mmol) was dissolved in glycol (40mL) adding NaAc (3.6g, 44mmol) stirring for 30min. Then the mixture was put into high pressure reactor with 200℃ for 12h. After that, magnetic microspheres (0.5g), TEOS (2ml) was mixed uniformly, dropwising 20ml H_2O, 6ml ammonia (25%) and 25ml ethanol with ultrasonic duly. The product was obtained through centrifugation, separated magnetically. β-CD (2.5g) was dissolved in 50ml DMF, then added 0.5g NaH. The mixture was filtered to get colatuie in which we added 4ml GTMS (KH560) stirring at 90℃ under N_2. After 5h, 1g magnetic sillica microspheres and 1.5ml ammonia (25%) was added stirring for 12h fiercely. The product was separated by magnet and dried in oven at 60℃ for 12h.

The magnetic hysteresis loop of the catalyst MNPs as Figure. S1a demonstrated that the samples have low coercivity and no obvious hysteresis, which indicated that the MNPs have superparamagnetism (measured at T= 300 K). When the outer magnetic field withdraws, there is no residual magnetism in the nanoparticles without the aggregation of MNPs. The saturation magnetization (Ms) values for the Fe_3O_4 nanoparticles and catalyst MNPs are 80.33 and 28.26 emu/g, respectively. The decrease in the Ms of catalyst MNPs could be attributed to the increasing amount of non-magnetic materials (organic ligands and silica shell) on the particle surface, which quenched the magnetic moment. However, the catalyst MNPs inherit the strong magnetic properties from the Fe_3O_4 which can be separated completely within 30s after the self-assembly process. The crystal structure of the as-synthesized Fe_3O_4 nanocrystals and the Fe_3O_4@MNPs was investigated using X-ray diffraction. As the Figure. S1b Shown, six discernible diffraction peaks can be indexed to (220), (311), (400), (422), (511) and (440), matching well with those on the database in the JCPDS file for magnetite indicating that the included Fe_3O_4 MNPs retain their crystalline structure. In addition, there is a more noteworthy XRD peak diffraction angle of the iron-oxide-SiO_2 core-shell, further confirmed the Fe_3O_4 MNPs were successfully coated and passivated with the SiO_2 shell.

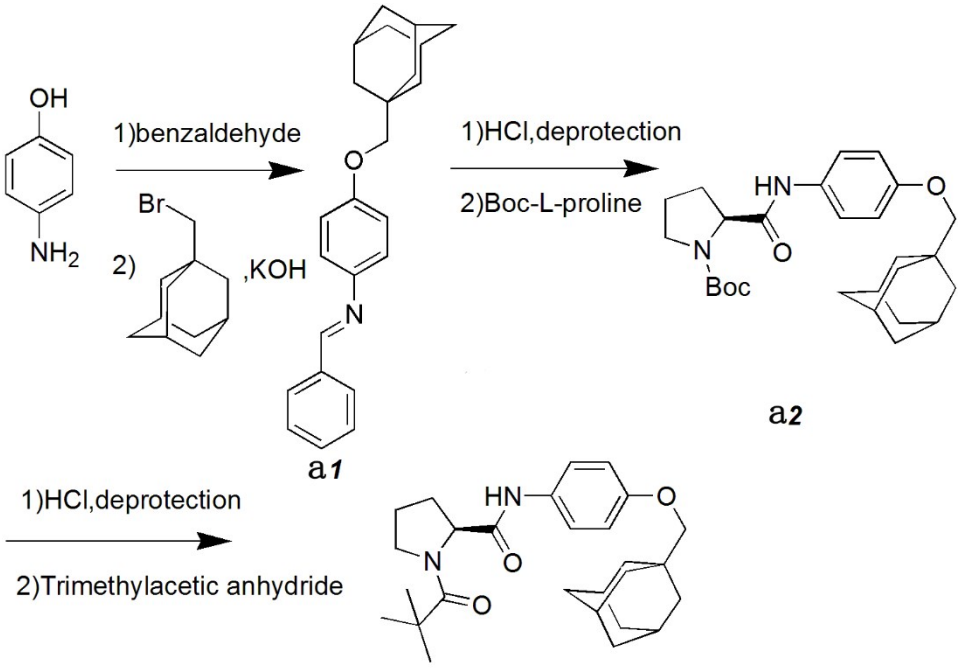
SEM and TEM images show the morphology of catalyst/Fe_3O_4@SiO_2-β-CD nanoparticles as Figure. S2 with a smooth surface and being quite uniform in size with no aggregation. The diameter of the embedded Fe_3O_4 is 310 nm and the thickness of the SiO_2 shell is 35 nm. TEM image showed distinct solid structures of the microspheres and suggested that the solid spheres possess excellent mechanical property that can provide the stability in the process of self-assembly.

Scheme. 1



3. Synthesis of Adamantane-modified L-proline derivative a

In a flask (50ml), 1.97g (10mmol) protected 4-Hydroxyaminobenzene, 2.28g (10mmol) 1-Bromomethyl-adamantane, 1.12g KOH and 0.16g KI were added into DMF (20ml). After that the mixture was stirred at 90℃ for 12h under N_2. Then the residue was purified by flash column chromatography and eluted with n-hexane/ethyl acetate (v/v=10/1) to give 3.0g (8.7mmol) ***a1*** (90% yield) as white crystals. After deprotection of ***a1*** with HCl, the 2.57g (10mmol) product, 2.15g (10mmol) Boc-Lproline and 1.91g (10mmol) EDCI were added into anhydrous 50ml CH_2Cl_2, stirring at room temperature for 12h. The residue was purified by flash column chromatography and eluted with n-hexane/ethyl acetate (v/v=10/1) to give 4g (8.8mmol) **a*2*** (88% yield) as white crystals. After deprotection of ***a2*** using HCl (g), the 3.54g (10mmol) product was dissolved into anhydrous 50ml CH_2Cl_2, then dropwise Trimethylacetic anhydride at 0℃ for 6h. The mixture was then added to sodium carbonate solution and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, concentrated in vacuo. The residue was purified by flash column chromatography and eluted with n-hexane/ethyl acetate (v/v=10/3) to give 4.2g (9.5mmol) ***a3*** (96% yield) as white crystals.



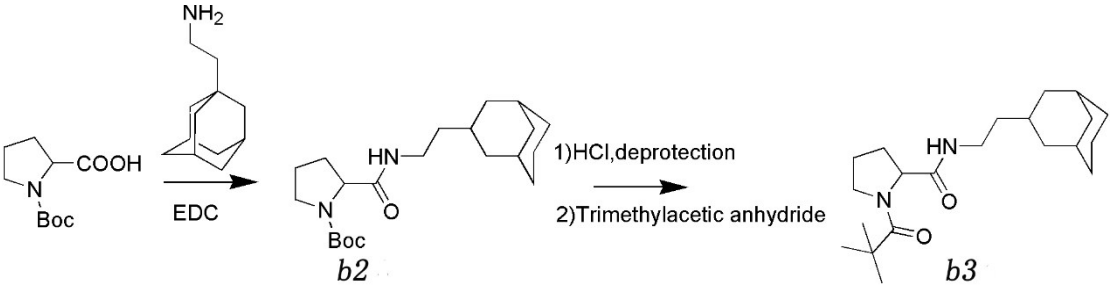
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.39 (d, *J* = 7.7 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 4.82 (d, *J* = 7.8 Hz, 1H), 3.87 – 3.62 (m, 2H), 3.46 (s, 2H), 2.43 (d, *J* = 3.7 Hz, 1H), 2.17 (s, 1H), 2.00 (s, 4H), 1.79 – 1.57 (m, 13H), 1.27 (d, *J* = 17.8 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.48 (s), 169.50 (s), 156.30 (s), 131.23 (s), 121.21 (s), 114.67 (s), 78.68 (s), 62.28 (s), 48.37 (s), 39.42 (d, *J* = 15.1 Hz), 39.34 (s), 37.16 (s), 33.84 (s), 28.22 (s), 27.59 (s), 27.14 (s), 25.91 (s).

ESI-MS (m/z): $[M+H]^+$ calcd for $[C_{27}H_{39}N_2O_3]^+$, 441.3079; found, 441.3112.

4. Synthesis of Adamantane-modified L-proline derivative b

Boc-L-proline (2.15g, 10mmol), rimantadine (1.9g, 11mmol) and EDCI (1.91g, 10mmol) were added into anhydrous CH_2Cl_2 (50ml), stirring at room temperature for 12h. The residue was was purified by flash column chromatography and eluted with n-hexane/ethyl acetate (v/v=10/1) to give 3.4g (9mmol) ***b2*** (90%yield) as white crystals. After deprotection of ***b2*** using HCl (g), the product (3.4g, 12.3mmol) was dissolved into anhydrous CH_2Cl_2 (50ml), then added Trimethylacetic anhydride at 0℃ for 6h. The mixture was then added to sodium carbonate solution and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, concentrated in vacuo. The residue was purified by flash column chromatography and eluted with n-hexane/ethyl acetate (v/v=10/3) to give 3g (8.3mmol) ***b3*** (83%yield) as white crystals.



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (d, *J* = 6.8 Hz, 1H), 3.74 (dd, *J* = 17.4, 7.8 Hz, 1H), 3.61 (d, *J* = 7.4 Hz, 2H), 2.48 – 2.36 (m, 1H), 2.12 (s, 1H), 1.96 (s, 4H), 1.76 – 1.40 (m, 13H), 1.27 (d, *J* = 11.4 Hz, 9H), 1.00 (d, *J* = 6.8 Hz, 3H).

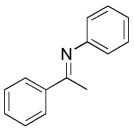
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.89, 170.57, 77.36, 77.04, 76.72, 61.39, 53.06, 48.14, 39.29, 38.28, 37.11, 35.79, 28.33, 27.64, 14.41.

ESI-MS (m/z): $[M+H]^+$ calcd for $[C_{22}H_{37}N_2O_2]^+$, 361.2850; found, 361.2852.

5. General procedure for synthesis of imines

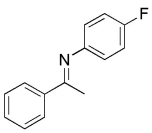
To a mixture of ketone (10 mmol) and amine (12 mmol) in toluene (25mL) was added molecular sieves 4 A (5 g) and p-toluenesulfonic acid monohydrate (950 mg, 5 mmol) at room temperature. The suspension was warmed to 100℃ and stirred for 12 h. The reaction mixture was then filtered through a pad of Celite. The filtrate was concentrated in vacuo. The residue was purified by column chromatography on basic silica gel with hexane/ethyl acetate (90:10) as an eluent to give the desired product **1**.

5. 1. N-(1-Phenylethylidene) aniline (**1a**).[1]



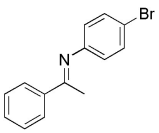
Yield 70%, 1.372g, yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.95 (dd, *J* = 23.5, 6.7 Hz, 2H), 7.49 (d, *J* = 6.8 Hz, 3H), 7.38 – 7.29 (m, 2H), 7.07 (dd, *J* = 17.3, 9.8 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 2H), 2.20 (s, 3H).

5. 2. N-(1-Phenylethylidene)-4-fluoroaniline (**1b**).[2]



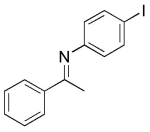
Yield 70%, 1.491g, white crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.95 (d, *J* = 6.9 Hz, 2H), 7.53 – 7.39 (m, 3H), 7.16 (t, *J* = 8.8 Hz, 2H), 6.79 (dd, *J* = 8.5, 5.1 Hz, 2H), 2.17 (s, 3H).

5. 3. N-(1-Phenylethylidene)-4-bromoaniline (**1c**).[1]



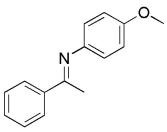
Yield 50%, 1.365g, yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.98 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.59 – 7.38 (m, 5H), 6.83 – 6.69 (m, 2H), 2.21 (s, 3H).

5. 4. N-(1-Phenylethylidene)-4-iodoaniline (**1d**).[3]



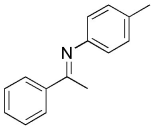
Yield 50%, 1.605g, yellow crystals. ^{1}H NMR (500 MHz, DMSO) δ 8.04 – 7.92 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.42 (m, 3H), 6.64 (d, *J* = 8.4 Hz, 2H), 2.21 (s, 3H).

5. 5. N-(1-Phenylethylidene)-4-methoxyaniline (**1e**).[1]



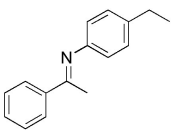
Yield 72%, 1.62g, yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.95 (t, *J* = 15.3 Hz, 2H), 7.55 – 7.39 (m, 3H), 6.92 (dd, *J* = 15.5, 12.1 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 3.73 (d, *J* = 17.4 Hz, 3H).

5. 6. N-(1-Phenylethylidene)-4-methylaniline (**1f**).[4]



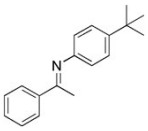
Yield 82%, 1.713g, white crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.97 (d, *J* = 6.2 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 8.1 Hz, 2H), 2.29 (s, 3H), 2.19 (s, 3H).

5. 7. N-(1-Phenylethylidene)-4-ethylaniline (**1g**).[5]



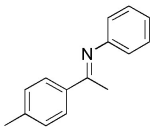
Yield 85%, 1.895g, yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.97 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.53 – 7.43 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 8.2 Hz, 2H), 2.60 (q, *J* = 7.5 Hz, 2H), 2.20 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H).

5. 8. N-(1-Phenylethylidene)-4-*t*-Bu aniline (**1h**).[5]



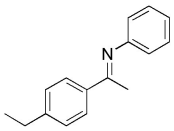
Yield 75%, 1.882g yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.97 (d, *J* = 6.5 Hz, 2H), 7.55 – 7.43 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 2.20 (s, 3H), 1.30 (s, 9H).

5. 9. N-(1-(4-methylphenyl) ethylidene) aniline (**1i**).[2]



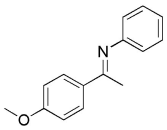
Yield 70%, 1.463g, yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 2H), 2.37 (s, 3H), 2.17 (s, 3H).

5. 10. N-(1-(4-ethylphenyl) ethylidene) aniline (**1j**).[6]



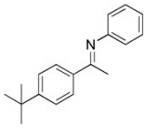
Yield 70%, 1.561g, yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.28 (m, 4H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 2H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.17 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H).

5. 11. N-(1-(4-methoxyphenyl) ethylidene) aniline (**1k**).[7]



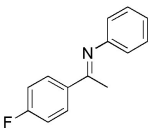
Yield 40%, 0.9g, white crystals. ^{1}H NMR (300 MHz, dmso) δ 8.03 – 7.87 (m, 2H), 7.43 – 7.26 (m, 2H), 7.15 – 6.94 (m, 3H), 6.82 – 6.65 (m, 2H), 3.82 (s, 3H), 2.15 (s, 3H).

5. 12. N-(1-(4-*t*-Buphenyl) ethylidene) aniline (**1l**).[6]



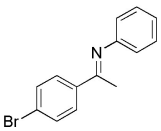
Yield 70%, 1.757g, yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.90 (t, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 8.9 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.12 – 7.02 (m, 1H), 6.76 (d, *J* = 7.7 Hz, 2H), 2.17 (s, 3H), 1.31 (d, *J* = 5.0 Hz, 9H).

5. 13. N-(1-(4-Fluorophenyl) ethylidene) aniline (**1m**).[2]



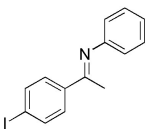
Yield 65%, 1.384g, white crystals. ^{1}H NMR (500 MHz, DMSO) δ 8.10 – 7.98 (m, 2H), 7.42 – 7.25 (m, 4H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.85 – 6.71 (m, 2H), 2.19 (s, 3H).

5. 14. N-(1-(4-Bromophenyl) ethylidene) aniline (**1n**).[7]



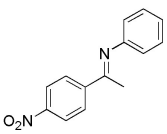
Yield 75%, 2.047g, yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 2.19 (s, 3H).

5. 15. N-(1-(4-iodophenyl) ethylidene) aniline (**1o**).[3]



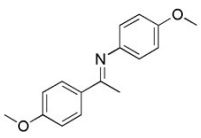
Yield 80%, 2.568g, white crystals. ^{1}H NMR (500 MHz, DMSO) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.13 – 7.04 (m, 1H), 6.78 (d, *J* = 7.5 Hz, 2H), 2.17 (s, 3H).

5. 16. N-(1-(4-Nitrophenyl) ethylidene) aniline (**1p**).[7]



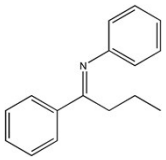
Yield 80%, 1.920g, yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 8.27 (d, *J* = 39.8 Hz, 4H), 7.39 (s, 2H), 7.13 (s, 1H), 6.83 (s, 2H), 2.27 (s, 3H).

5. 17. N-(1-(4-methoxyphenyl) ethylidene)-4-methoxyaniline (**1q**).[8]



Yield 40%, 1.020g, white crystals. ^{1}H NMR (300 MHz, dmso) δ 7.98 – 7.89 (m, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 6.97 – 6.88 (m, 2H), 6.77 – 6.68 (m, 2H), 3.83 (d, *J* = 6.4 Hz, 3H), 3.75 (s, 3H), 2.18 (s, 3H).

5. 18. N-(1-Phenylbutylidene) aniline (**1r**).[9]



Yield 70%, 1.561g, white crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.94 (dd, *J* = 5.5, 1.5 Hz, 2H), 7.54 – 7.46 (m, 3H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.04 (dd, *J* = 15.4, 8.1 Hz, 1H), 6.73 (d, *J* = 7.4 Hz, 2H), 2.65 – 2.53 (m, 2H), 1.72 – 1.57 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H).

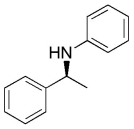
6. General procedure for reduction

Imine 1**a** (48mg, 0.25mmol) and catalyst **a** (10.9 mg, 0.025mmol) were dissolved in CH_2Cl_2 (1.5mL) and cooled to -30℃. Then Trichlorosilane (76μL, 0.75mmol) was then added. The synthesis method of other amines **2b**-**r** was similar.

After 48 h, saturated $NaHCO_3$ was added and extracted with CH_2Cl_2 (3 X). The combined organic phases were dried over $MgSO_4$, and concentrated in vacuo. The residue was dissolved by a little CH_3OH, then 0.23g MNPs was added according to figure. S4 that 98% of catalyst can be recycled measured by RP-HPLC as Figure. S3 shown. Deionized water dropwised, monitoring by TLC till the catalyst **a** was rare in the solution. The L-proline derivative/MNPs was separated magnetically. Then, the catalyst will be washed and released from MNPs with CH_2Cl_2 to process the next run.

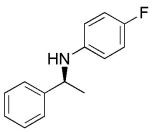
The solution was extracted with CH_2Cl_2 (3 X), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on basic silica gel with hexane/ethyl acetate as an eluent to give the desired product **2a**. The enantiomeric excess was determined by chiral-phase HPLC analysis.

6. 1. (S)-N-Phenyl-1-phenylethylamine (**2a**).[1]



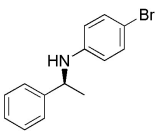
Yield 96%, 47.28mg, yellow crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 2H), 6.55 – 6.41 (m, 3H), 6.13 (d, *J* = 6.8 Hz, 1H), 4.46 (p, *J* = 6.7 Hz, 1H), 1.42 (d, *J* = 6.7 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=6.2 min; minor isomer(R isomer): t_R=7.7min.

6. 2. (S)-N-(4-fluorophenyl)-1-phenylethylamine (**2b**).[2]



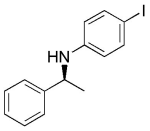
Yield 92%, 49.519mg, yellow syrup. ^{1}H NMR (400 MHz, DMSO) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.81 (t, *J* = 8.9 Hz, 2H), 6.46 (dd, *J* = 8.9, 4.6 Hz, 2H), 6.10 (d, *J* = 6.6 Hz, 1H), 4.40 (p, *J* = 6.6 Hz, 1H), 1.39 (d, *J* = 6.7 Hz, 3H). HPLC (Daicel CHRALCEL AD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=6.253min; minor isomer(R isomer): t_R=5.762min.

6. 3. (S)-N-(4-Bromophenyl)-1-phenylethylamine (**2c**).[1]



Yield 81%, 55.89mg, white crystals. ^{1}H NMR (300 MHz, dmso) δ 7.40 – 7.22 (m, 4H), 7.22 – 7.14 (m, 1H), 7.14 – 7.02 (m, 2H), 6.49 – 6.33 (m, 3H), 4.42 (p, *J* = 6.9 Hz, 1H), 1.38 (t, *J* = 8.3 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=5.376min; minor isomer(R isomer): t_R=4.492min.

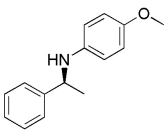
6. 4. (S)-N-(4-Iodophenyl)-1-phenylethylamine (**2d**).[10]



Yield 70%, 56.525mg, yellow syrup. ^{1}H NMR (500 MHz, DMSO) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J*

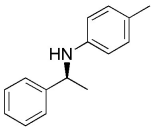
= 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.14 (m, 4H), 7.12 (t, *J* = 7.1 Hz, 1H), 4.37 (s, 1H), 1.34 (d, *J* = 6.7 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=8.153min; minor isomer(R isomer): t_R=7.092min.

6. 5. (S)-N-(4-Methoxyphenyl)-1-phenylethylamine (**2e**).[1]



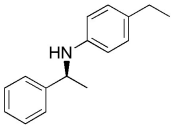
Yield 80%, 45.4mg, yellow syrup. ^{1}H NMR (300 MHz, dmso) δ 7.39 – 7.31 (m, 2H), 7.31 – 7.22 (m, 2H), 7.20 – 7.10 (m, 1H), 6.64 – 6.55 (m, 2H), 6.49 – 6.37 (m, 2H), 5.74 (dd, *J* = 9.5, 3.9 Hz, 1H), 4.37 (p, *J* = 6.7 Hz, 1H), 3.56 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=8.046min; minor isomer(R isomer): t_R=7.466min.

6. 6. (S)-N-(4-methylphenyl)-1-phenylethylamine (**2f**).[11]



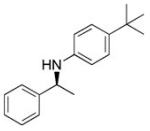
Yield 92%, 48.53mg, white crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 2H), 6.39 (d, *J* = 8.4 Hz, 2H), 5.91 (d, *J* = 7.1 Hz, 1H), 4.40 (p, *J* = 6.8 Hz, 1H), 4.40 (p, *J* = 6.8 Hz, 1H), 2.07 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=6.912min; minor isomer(R isomer): t_R=6.348min.

6. 7. (S)-N-(4-ethylphenyl)-1-phenylethylamine (**2g**).[12]



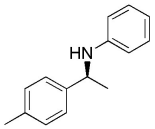
Yield 91%, 51.19mg, yellow syrup. ^{1}H NMR (400 MHz, DMSO) δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 8.4 Hz, 2H), 5.94 (d, *J* = 6.9 Hz, 1H), 4.41 (p, *J* = 6.7 Hz, 1H), 2.37 (q, *J* = 7.6 Hz, 2H), 1.39 (d, *J* = 6.7 Hz, 3H), 1.05 (t, *J* = 7.6 Hz, 3H). HPLC (Daicel CHRALCEL AD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R= 5.328min; minor isomer(R isomer): t_R=4.719min.

6. 8. (S)-N-(4-*t*-Buphenyl)-1-phenylethylamine (**2h**).[13]



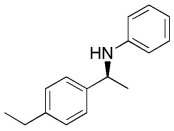
Yield 87%, 55.03mg, yellow syrup. ^{1}H NMR (400 MHz, DMSO) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.42 (d, *J* = 8.6 Hz, 2H), 5.96 (d, *J* = 6.9 Hz, 1H), 4.40 (p, *J* = 6.7 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.15 (s, 9H). HPLC (Daicel CHRALCEL AD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=4.934min; minor isomer(R isomer): t_R=4.487min.

6. 9. (S)-N-phenyl-1-(4-methylphenyl) ethyl amine (**2i**).[2]



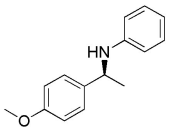
Yield 96%, 50.64mg, white crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.95 (t, *J* = 7.8 Hz, 2H), 6.51 – 6.39 (m, 3H), 6.07 (d, *J* = 6.9 Hz, 1H), 4.39 (p, *J* = 6.7 Hz, 1H), 2.24 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H). HPLC (Daicel CHRALCEL AD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=5.774min; minor isomer(R isomer): t_R=6.804min.

6. 10. (S)-N-phenyl-1-(4-ethylphenyl) ethyl amine (**2j**).[6]



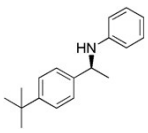
Yield 97 %, 54.56mg, yellow syrup. ^{1}H NMR (400 MHz, DMSO) δ 7.25 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.94 (t, *J* = 7.6 Hz, 2H), 6.57 – 6.36 (m, 3H), 5.99 (s, 1H), 4.45 – 4.32 (m, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 1.40 (d, *J* = 6.7 Hz, 3H), 1.15 (t, *J* = 7.6 Hz, 3H). HPLC (Daicel CHRALCEL AD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=5.385 min; minor isomer(R isomer): t_R=6.514 min.

6. 11. (S)-N-phenyl-1-(4-Methoxyphenyl) ethyl amine (**2k**).[7]



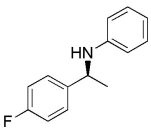
Yield 90%, 51.08mg, white crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.96 (t, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.55 – 6.37 (m, 3H), 6.04 (d, *J* = 6.8 Hz, 1H), 4.39 (p, *J* = 6.7 Hz, 1H), 3.70 (s, 3H), 1.36 (t, *J* = 12.1 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=7.956min; minor isomer(R isomer): t_R=9.908min.

6. 12. (S)-N-phenyl-1-(4-*t*-Buphenyl) ethyl amine (**2l**).[6]



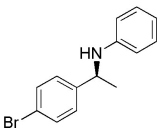
Yield 91%, 57.56mg, white crystals. ^{1}H NMR (300 MHz, dmso) δ 7.33 – 7.24 (m, 4H), 7.02 – 6.90 (m, 2H), 6.53 – 6.39 (m, 3H), 6.12 (t, *J* = 9.0 Hz, 1H), 4.41 (p, *J* = 6.7 Hz, 1H), 1.38 (d, *J* = 6.8 Hz, 3H), 1.24 (s, 9H). HPLC (Daicel CHRALCEL AD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=5.265min; minor isomer(R isomer): t_R=6.562min.

6. 13. (S)-N-phenyl-1-(4-Fluorophenyl) ethyl amine (**2m**).[2]



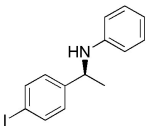
Yield 88%, 47.3mg, white syrup. ^{1}H NMR (500 MHz, DMSO) δ 7.39 (dd, *J* = 8.1, 5.9 Hz, 2H), 7.10 (t, *J* = 8.8 Hz, 2H), 6.97 (t, *J* = 7.7 Hz, 2H), 6.46 (dd, *J* = 18.6, 7.7 Hz, 3H), 6.12 (d, *J* = 6.9 Hz, 1H), 4.47 (p, *J* = 6.7 Hz, 1H), 1.39 (d, *J* = 6.7 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=7.765min; minor isomer(R isomer): t_R=10.714min.

6. 14. (S)-N-phenyl-1-(4-Bromophenyl) ethyl amine (**2n**).[7]



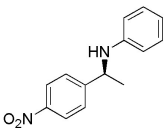
Yield 91%, 62.79mg, white crystals. ^{1}H NMR (300 MHz, dmso) δ 7.53 – 7.36 (m, 2H), 7.34 – 7.22 (m, 2H), 7.01 – 6.83 (m, 2H), 6.48 – 6.34 (m, 3H), 6.13 (d, *J* = 6.9 Hz, 1H), 4.39 (p, *J* = 6.8 Hz, 1H), 1.33 (d, *J* = 6.8 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=8.806min; minor isomer(R isomer): t_R=12.086min.

6. 15. (S)-N-phenyl-1-(4-Iodophenyl) ethyl amine (**2o**).[3]



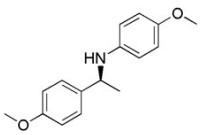
Yield 90%, 72.68mg, white crystals. ^{1}H NMR (500 MHz, DMSO) δ 7.70 – 7.58 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.96 (t, *J* = 7.8 Hz, 2H), 6.45 (t, *J* = 7.3 Hz, 3H), 6.14 (d, *J* = 6.9 Hz, 1H), 4.42 (p, *J* = 6.7 Hz, 1H), 1.38 (d, *J* = 6.7 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=9.368min; minor isomer(R isomer): t_R=12.871min.

6. 16. (S)-N-phenyl-1-(4-nitrophenyl) ethyl amine (**2p**).[7]



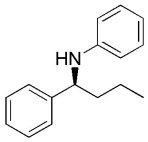
Yield 56%, 33.89mg, yellow syrup. ^{1}H NMR (300 MHz, dmso) δ 8.22 – 8.14 (m, 2H), 7.71 – 7.60 (m, 2H), 6.98 (dd, *J* = 9.5, 6.3 Hz, 2H), 6.47 (ddd, *J* = 3.9, 3.4, 1.4 Hz, 3H), 6.35 (d, *J* = 6.9 Hz, 1H), 4.64 (p, *J* = 6.7 Hz, 1H), 1.42 (t, *J* = 8.8 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=26.596min; minor isomer(R isomer): t_R=34.849min.

6. 17. (s)-N-(4-Methoxyphenyl)-1-(4-Methoxyphenyl) ethylamine (**2q**).[8]



Yield 95%, 61.04mg, white crystals. ^{1}H NMR (300 MHz, dmso) δ 7.29 – 7.19 (m, 2H), 6.89 – 6.75 (m, 2H), 6.65 – 6.54 (m, 2H), 6.48 – 6.37 (m, 2H), 5.65 (d, *J* = 6.0 Hz, 1H), 4.29 (dd, *J* = 20.7, 14.0 Hz, 1H), 3.69 (s, 3H), 3.57 (s, 3H), 1.35 (d, *J* = 6.7 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=9.819min; minor isomer(R isomer): t_R=9.126min.

6. 18. (S)-N-Phenyl-1-phenylbutylamine (**2r**).[9]



Yield 70%, 39.37mg, white syrup. ^{1}H NMR (400 MHz, DMSO) δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 2H), 6.52 (d, *J* = 7.9 Hz, 2H), 6.43 (t, *J* = 7.1 Hz, 1H), 6.12 (d, *J* = 7.4 Hz, 1H), 4.29 (dd, *J* = 14.0, 7.2 Hz, 1H), 1.84 – 1.71 (m, 1H), 1.61 (dt, *J* = 19.5, 6.3 Hz, 1H), 1.47 – 1.26 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). HPLC (Daicel CHRALCEL OD, hexane/ ^{i}PrOH=9/1, flow rate 1.0 mL/min, λ=254nm): major isomer(S isomer): t_R=4.737min; minor isomer(R isomer): t_R=5.594min.

7. The loss of catalyst

Three cuvettes for **A** (10.9mg catalyst **a** in 1.5ml CH_2Cl_2), **B** (10.9mg catalyst **a** and 0.5mmol $HSiCl_3$ in 1.5ml CH_2Cl_2), **C** (10.9mg catalyst **a** and 0.75mmol $HSiCl_3$ in 1.5ml CH_2Cl_2, self-assembly) and 0.23g MNPs according to Figure. S4 were prepared independently. Then the process of extraction was carried out for **A**, it was found that there was 2.7% loss of the catalyst measured by RP-HPLC as Figure. S3. For **B**, the hydrolysis of $HSiCl_3$ and process of extraction were carried out successively, then it was found that there was 5.7% loss of catalyst including 2.7% loss in the process of extraction and 3% loss for the inclusion interaction of SiO_2 formed in the hydrolysis of $HSiCl_3$. For system **C**, there was 7.4% loss of catalyst **a** measured by RP-HPLC.

8. Theoretical calculation

The *л-л* stacking and hydrogen bond interaction were investigated by the hybrid functional B3LYP-D3 and the basis set 6-311G (d, p) for all the atoms. The ma-def2-TZVP basis set was used to reach more accurate results by calculating the single-point energy of the optimized geometries. The geometrical optimizations and their single-point energy are performed by using the Gaussion 09 program package. The RDG (reduced density gradient) analysis was performed by Multiwfn. The visual pictures were made by VMD. The solvent effect of dichloromethane simulated by the polarized continuum model (PCM) was taken into account in the calculation of the weak interaction. In order to simplify the calculation, the huge alkyl was replaced by the methyl.

The irrelevant hydrogen atoms were omitted. The main geometric parameters of these complexes were summarized in **Table s1**. It is found that the phenyl of catalyst **a** and the N-phenyl of R_2 on imines kept face-to-face at a vertical distance of about 3.59Å in model A, which means there was *л-л* stacking. But the catalyst couldn't have face-to-face array when directly interacted with the imines like model B showed. The bond lengths of H_1-O and H_2-N_2 were 1.89 Å and 1.82 Å separately, meanwhile the hydrogen atoms always directed to the lonely-pair electrons of O and N_1. In comparison to the monomer, the N_1-C_1 and N_2-C_2 kept constant but N_1-H_1 decreased by 0.02 Å and O-H_2 increased by 0.03 Å. It indicated that the catalyst, water and substrate had hydrogen bond interaction each other in model A. But for model B, the bond length of H_1-N_2 was 2.02 Å, which increased 0.2 Å less than the bond H_2-N_2 in model A. It indicated that the hydrogen bond interaction in model B was weaker than that in model A. What is more, the total energy of the CWS (the abbreviation of catalyst, water and substrate) decreased by 28.2 kcal/mol when CWS were stacking like model A. When the imines was rotated 180 degrees compared to model A which was shown the model C as Figure S13, that was proposed in ref. 1, the total energy of the CWS decreased by 25.4 kcal/mol. In addition, it only decreased 14.0 kcal/mol without water serving as a bridge shown in model B. Therefore, on the basis of our findings, it can be concluded that the stacking model A is more stable than others. All the data of the energy are showed in **Table s2**.

9. Tables

Table s1. The geometrical parameters of the catalyst, water, substrate, model A and B

Bond Lengths(Å)	Catalyst	Water	Substrate	A	B
N_1-C_1	1.43			1.43	1.42

N_1-H_1	1.01			1.03	1.02
H_1-O				1.89	-
O-H_2		0.96		0.99	-
H_1-N_2					2.02
H_2-N_2				1.82	
N_2-C_2			1.40	1.41	1.41

Table s2. The energy of optimized geometrical structures of catalyst, water and substrate

	Energy (a.u.)	ΔE(kcal/mol)
Catalyst	-997.78578	
Water	-76.45357	
Substrate	-596.23826	
CWS-Sum[a]	-1670.47761	
A[a]	-1670.52252	28.2[b]
C[a]	-1670.51808	25.4[b]
CS-Sum[a]	-1594.02404	
B[a]	-1594.04636	14.0[b]

[a] CWS means the abbreviation of catalyst, water and substrate. CWS-Sum means the sum of the energy of catalyst, water and substrate. CS-Sum means the sum of the energy of catalyst and substrate. [b] The values of ΔE of A/C are acquired by the subtract of CWS-Sum and A/C. The value of ΔE of model B is acquired by the subtraction of CS-Sum and B.

Table s3. Recyclable performance of catalyst a

Entry[a]	Time[h]	Cat[%]	Yield[b][%]	ee[c][%]
1	48	100	97	92
2	72	92.6	94	92
3	72	85.2	91	91
4	96	77.9	87	90
5	96	70.5	86	85
6	96	63.2	76	82
7	48	100	96	92
8	48	92.7	95	91

[a] The reactions were performed using 0.25mmol of imine and 0.75mmol of trichlorosilane with catalyst **a** in -30℃.

[b] Isolated yields.

[c] Determined by chiral HPLC.

[d] No reaction

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