Electronic Supplementary Information (ESI) for

Thermoregulated phase transfer chiral Pt nanocatalyst for enantioselective hydrogenation of α-ketoesters

Pu Chen, Yanhua Wang*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, P. R. China
**Corresponding author: Tel/Fax: +86-411-84986033; E-mail: yhuawang@dlut.edu.cn*

1. Experimental section

1.1 Chemicals

Methyl benzoylformate (99%), isoamyl pyruvate (97%), and ethyl 3-chlorobenzoylformate (96%) were purchased from J&K Chemical. Cinchonidine (CD, 99%), $PtCl_4$ (99.9%, metals basis) were from Alfa Aesar. Ethyl 4-methyl-2-oxopentanoate (95%) was purchased from Ark. Pyruvic acid (Z)-3-hexenyl ester (95%) was from TCI. (*R*)-methyl 2-hydroxy-2-phenylacetate was purchased from Adamas. *n*-Pentanol, *n*-hexanol, cyclohexanol, toluene, glacial acetic acid, *n*-heptane, cyclohexane were purchased from Kermel. All these chemical agents were analytical reagent and without further purification. ^1H and ^{13}C NMR were recorded on a Varian (400 MHz) and Bruker Avance spectrometer (125 MHz), respectively. Chiral GC analyses were carried out on Fuli 9790 GC instrument equipped with an Agilent CP-Chirasil-Dex (25 m × 0.25 mm × 0.25 μm) and an FID detector (N_2 as a carrier gas). Transmission electron microscopic analyses (TEM) were carried out by using a Tecnai G^2 20 S-TWIN (200 kV) instrument. Inductively coupled plasma atomic emission spectrometer (ICP-AES) was performed on Optima 2000 DV.

1.2 Synthesis of CIL_{TPT}

The CIL_{TPT} was synthesized via a three-step procedure (Fig. S1). The methylsulfonyl chloride (0.010 mol) was added dropwise to a toluene (100 mL) solution of **S1** (0.010 mol) and triethylamine (0.010 mol) under an ice-water bath. The reaction mixture was stirred overnight at room temperature, and then filtered to remove the triethylamine hydrochloride precipitate. The filtrate was concentrated under reduced pressure and dried under vacuum to remove the volatile materials to give a white waxy solid **S2** [1]. Cinchonidine (CD, 0.012 mol) was added to a toluene solution (60 mL) of **S2**.

The mixture was refluxed for 48 h. After being cooled to 10 ºC, the excess CD was removed by filtration. The organic filtrate was extracted with anhydrous diethyl ether (60 mL × 3) to remove possible byproducts [2, 3]. The claret slurry was then dried under vacuum to afford **S3** in 86% yield. KPF_6 (0.010 mol) was added into the aqueous solution of **S3** (0.010 mol), and stirred for 2 h at room temperature [4]. Then, the mixed solution was extracted two times with dichloromethane (50 mL × 2). The solution was distilled to remove dichloromethane and vacuum dried to afford the $\mathbf{CIL_{TPT}}$ as viscous liquid in 83% yield.

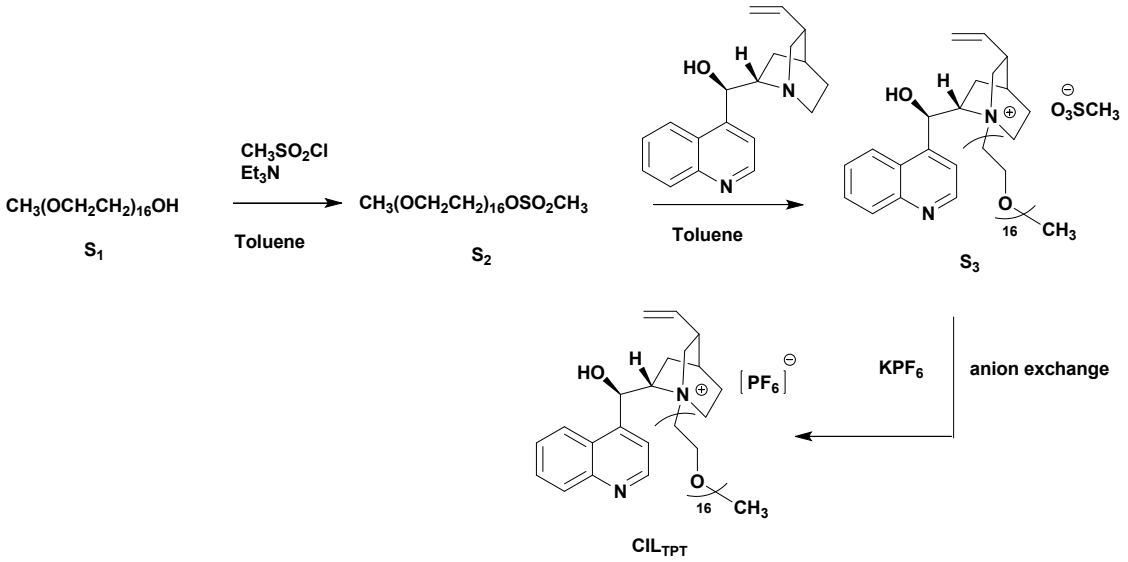


Fig. S1 Typical procedure for the synthesis of CIL_{TPT}

1.3 Determination of Cp

An appropriate amount of CIL_{TPT} was added into a Schlenk tube containing deionized water under vigorously stirred. After stirring for a certain time, the clear CIL_{TPT} solution was obtained. Then, the Schlenk tube was moved to a temperature-controlled oil bath. The Cp was determined by the turbidity temperature (visual observation) at which the solution became obviously turbid. The determination was repeated three times and averaged.

1.4 Preparation of chiral Pt nanocatalyst

As a typical example, a H_2O (0.400 g) solution of $PtCl_4$ (0.60 mg, 1.78×10^{-3} mmol), ethanol (0.200 g) and CIL_{TPT} (31.32 mg, 2.67×10^{-2} mmol) was added to a 75 mL stainless-steel autoclave. The autoclave was flushed for three times with 2.0 MPa H_2 and then inflated to 4.0 MPa with H_2. After being stirred at 70 ºC for 6 h, the reactor was cooled to room temperature and depressurized. The

color of the mixture changed from claret to black, indicating of the formation of chiral Pt nanocatalyst. Then, the solvents were removed prior to a catalytic run. The preparation of other Pt nanocatalyst with different ratios of CIL_{TPT} to Pt was carried out according to the same procedure.

1.5 Enantioselective hydrogenation of α-ketoesters

The hydrogenation of methyl benzoylformate (MBF) serves as a standard model reaction. The reaction was carried out in a 75 mL Teflon-lined standard stain-steel autoclave and stirred in a thermostatic oil bath. The autoclave was charged with the as-prepared Pt nanocatalyst, H_2O (1.000 g), *n*-pentanol (2.000 g), glacial acetic acid (0.600 g), cyclohexane (0.050 g, internal standard). The mixture was stirred for 30 min at 40 ^oC, and then MBF (substrate/Pt = 150:1) was added. The autoclave was flushed three times with 2 MPa H_2. The reactor was pressurized with H_2 up to the required pressure and held at the scheduled temperature with magnetic stirring for a fixed reaction time. After reaction, the reactor was cooled in an ice-water bath and depressurized. The upper *n*-pentanol phase was separated and analyzed by chiral GC. The enantiomeric excess (ee%) was calculated with the formula ee% = |[R]- [S]|/([R]+ [S]) × 100.

2. Supporting table and figures

Table S1. The effect of the CIL_{TPT} concentration on the Cp

Entry	CIL_{TPT} (wt%)	Cp (°C)
1	1.0	78
2	1.5	70
3	2.0	65
4	3.0	62
5	4.0	59

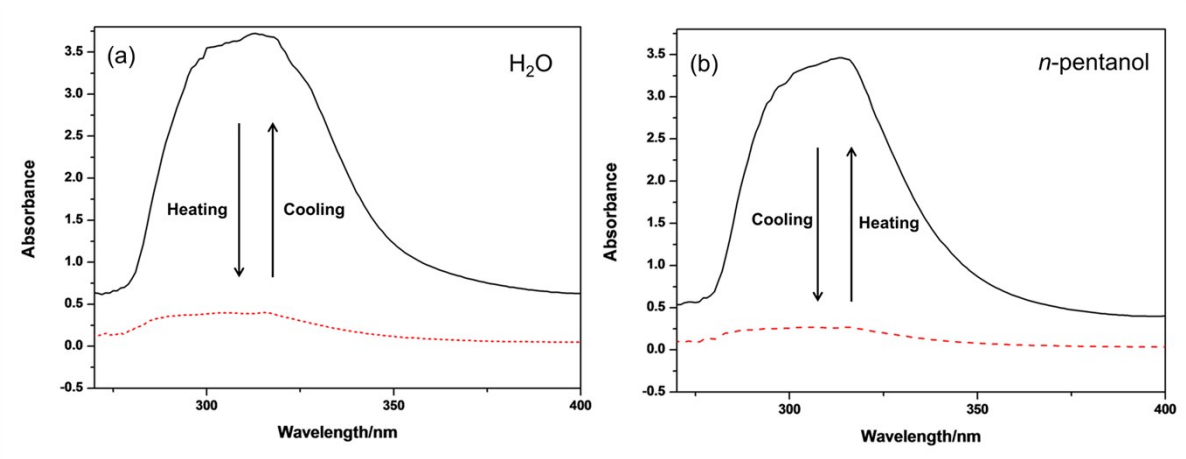


Fig. S2 UV-vis spectra of CIL_{TPT} before and after phase transfer in H_2O/*n*-pentanol biphasic system upon heating and cooling (the original concentration of CIL_{TPT} in H_2O was 1.5 mg/mL)

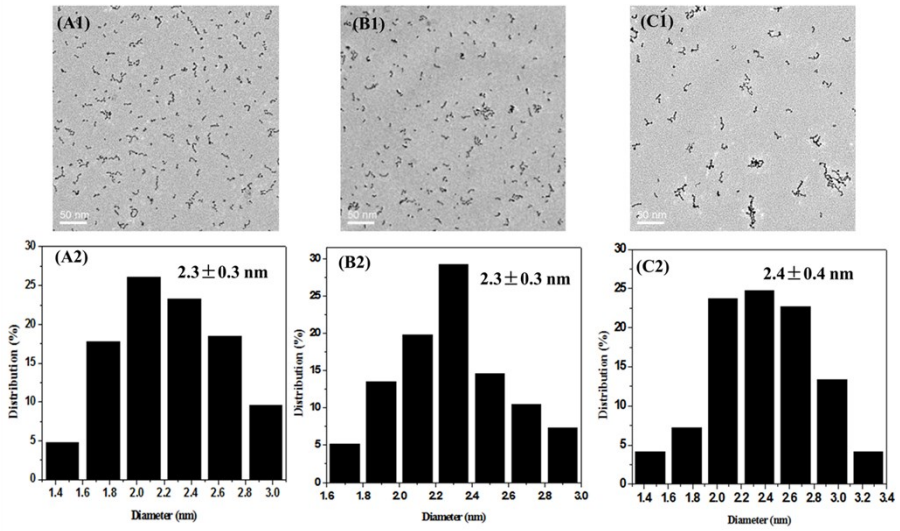


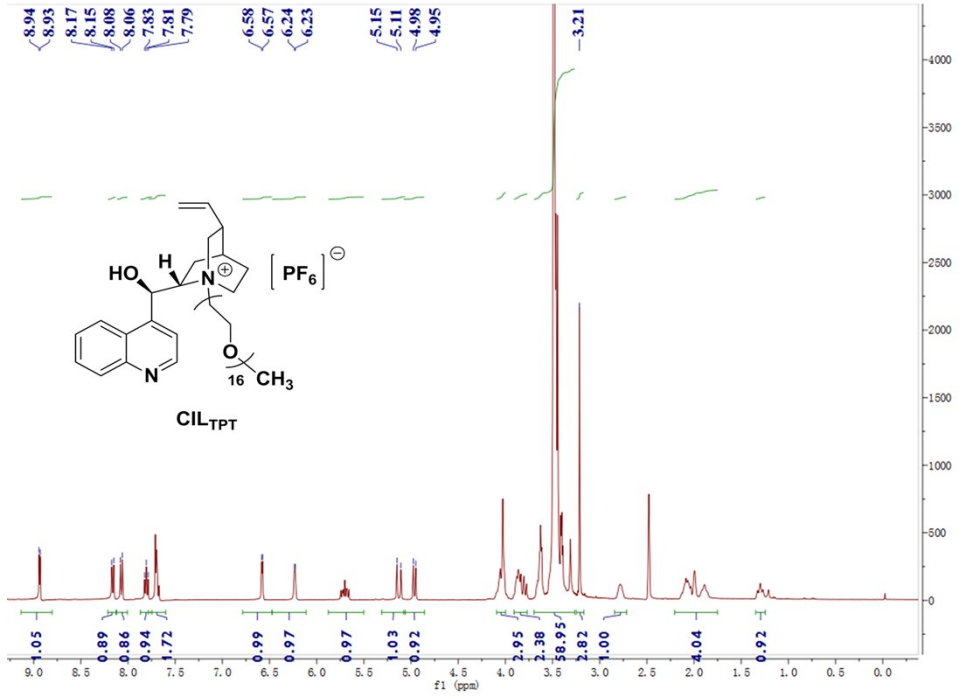
Fig. S3 TEM micrographs and particle size histograms of chiral Pt nanocatalyst: freshly prepared (A1-2), after one cycle (B1-2) and after five cycles (C1-2) of heating and cooling, respectively.

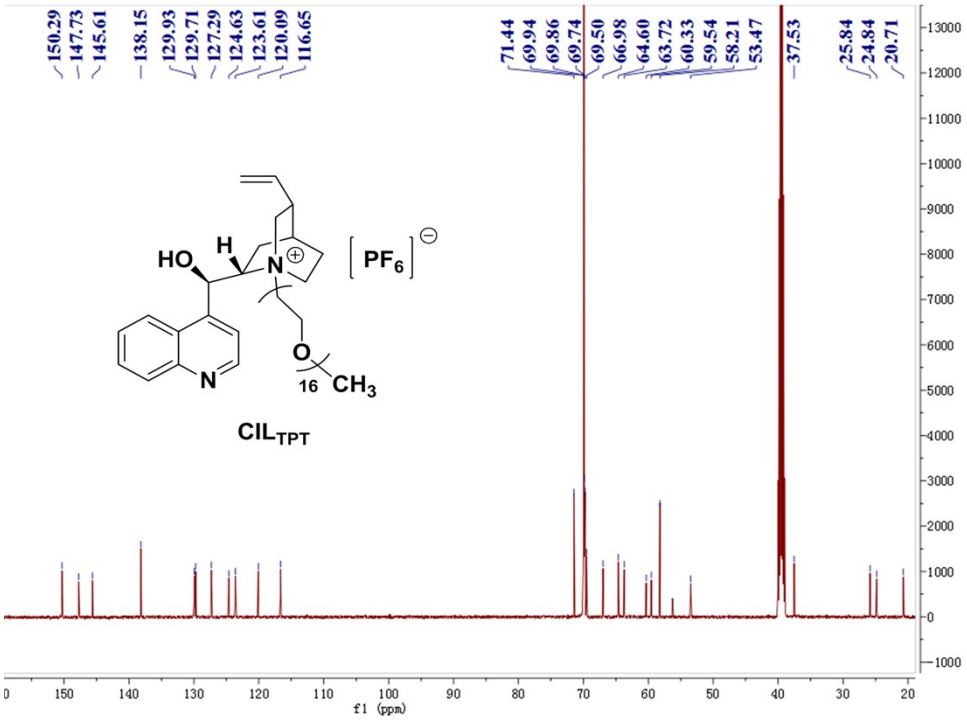
3. Characterization Data

CIL_{TPT}: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.94 (d, J = 4.5 Hz, 1H), 8.16 (d, J = 8.6 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.81 (t, J = 7.7 Hz, 1H), 7.76-7.62 (m, 2H), 6.58 (d, J = 4.2 Hz, 1H), 6.23 (d, J = 4.0 Hz, 1H), 5.70 (m, 1H), 5.13 (d, J = 17.3 Hz, 1H), 4.96 (d, J = 10.3 Hz, 1H), 4.12-3.77 (m, 5H), 3.71-3.30 (m, 59H), 3.21 (s, 3H), 2.86-2.72 (m, 1H), 2.17-1.80 (m, 4H), 1.37-1.24 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 150.29, 147.73, 145.61, 138.15, 129.93, 129.71, 127.29, 124.63, 123.61, 120.09, 116.65, 71.44, 69.94, 69.50, 66.98, 64.60, 63.72, 60.33, 59.54, 58.21, 53.47, 37.53,

25.84, 24.84, 20.71.

4. Copies of NMR Spectra





5. GC charts

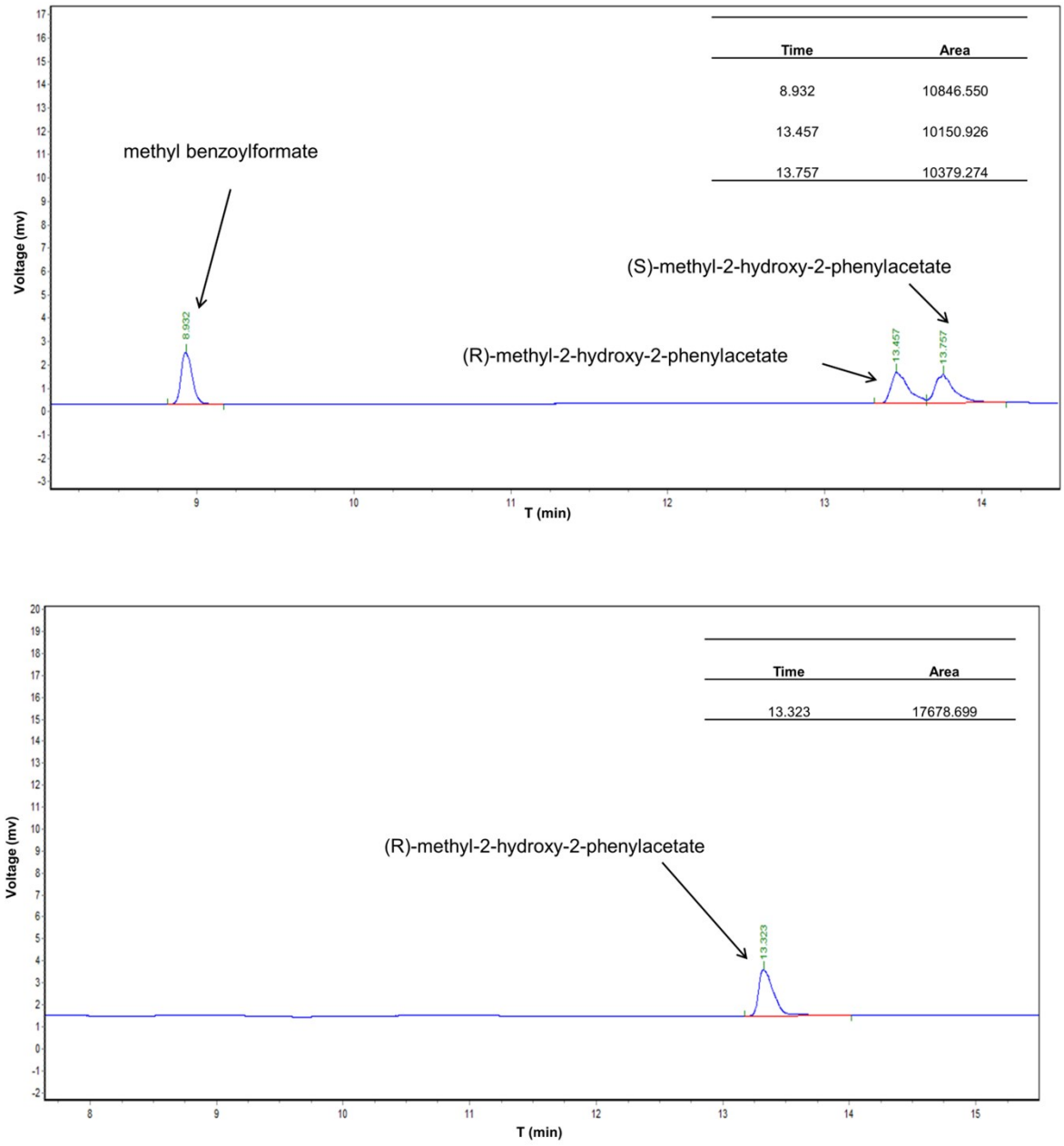


Fig. S4 GC chromatogram for the model reaction

Reference

[1] B. Tan, J. Jiang, Y. Wang, L. Wei, D. Chen, Z. Jin, *Appl. Organometal. Chem.*, 2008, **22**, 620-623.

[2] A. Indra, S. Basu, D. G. Kulkarni, C. S. Gopinath, S. Bhaduri, G.K. Lahiri, *Appl. Catal. A Gen.,* 2008, **344**, 124-130.

[3] Y. Wang, X. Xue, CN patent, 105777742, 2016.

[4] Q. Liu, Z. Tan, U. Welz-Biermann, X. Liu, *J. Chem. Thermodyn.,* 2014, **68**, 82-89.