Electronic Supplementary Material (ESI) for RSC Advances

Electronic Supplementary Information

Is the naked platinum nanocatalyst better than the analogous supported catalysts?

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1. General information

Preparation of cluster derived nano-materials and their subsequent manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures, distilled under nitrogen, and used immediately. Poly(diallyldimethylammoniumchloride) (PDADMAC, low mol. wt., 20 wt.% solution in water), sodium hexachloroplatinate and all other substrates were purchased from Sigma-Aldrich. Distilled water was used for the catalytic studies in water. Carbon monoxide (CO), oxygen (O_2) and hydrogen (H_2) were supplied by BOC, India. The synthetic procedures and characterization data of **2** and **3** have been reported in our earlier reports[S1-S3] and MCM-41 for **2** was synthesized according to the literature reported procedure.[S4]

Hydrogenation reactions were carried out in an autoclave. Conversions with different substrates were monitored by gas chromatographic technique (Shimadzu GC-14A with an FID detector) using a capillary column (SUPELCO-ASTEC-Chiraldex B-DM, fused silica, 50 m × 0.25 mm ×0.12 μm from Sigma). All products were initially identified by using authenticated commercial samples of the expected products. Thermo Nicolet 320 FT-IR was used for recording IR spectra. TEM experiments were performed using a Philips 1200 EX at 120 kV instrument. The histogram in Fig. S1b was made from around 2500 particles. Sonication in appropriate solvents in 1.5 L PCi Analytics Ultrasonic Bath Sonicators (60 W) was performed prior to all catalytic runs. All catalytic experiments were duplicated and reproducibility of conversion and *ee* were within ± 5%. A calibration graph of weight ratio versus area ratio in chromatographs of synthetic mixtures of methyl pyruvate and methyl lactate showed that linearity was maintained up to a molar ratio of 2.5. Outside this range cyclohexene was used as an external standard, if required. The analyses of other hydrogenated products were carried out by GC using n-dodecane as an external standard.

2. Synthesis of catalyst 1

Methanolic solution of $Na_2[Pt_{15}(CO)_{30}]$ was prepared from 100 mg of Na_2PtCl_6 by following the reported procedure.[S5] It was then precipitated out from the solution by adding excess $^tBu_4NI$. The solid mass was washed several times by methanol. The residue was subsequently dissolved in 25 mL DMF and distributed in five vials, 5 mL each. Each vial containing 5 mL above solution was heated at ~95°C for about 15 h in a conventional forced-convection drying oven. The resultant Pt-NP was washed with ethanol several times to remove excess reagents and finally it was dried in the drying oven. The difference in weight between vial containing Pt-NP and the empty vial was considered as the net amount of Pt-NP for any catalytic run and was within the range of 5 to 10 milligrams.

3. Generalized procedure for catalytic hydrogenation

Hydrogenation reactions were carried out in an autoclave under 50 bar hydrogen pressure at 300 K. In a typical experiment catalyst **1** was taken in 5 mL of solvent in a glass-vial and substrate was added to it at respective ratios with chiral modifier, wherever applicable. The resulting mixture was kept under 50 bar hydrogen pressure in the autoclave at 300 K for a specified time under vigorous stirring condition (≥900 rpm). The product was then recovered via decantation and/or solvent extraction and subsequently analyzed by GC.

4. Generalized procedure for catalytic oxidation

A mixture of catalyst **1** and the substrate methyl lactate with appropriate ratios were taken in 5 mL of solvent in a round-bottom flask with chiral modifier, where required. The mixture was stirred at 80°C under a steady flow of oxygen gas at atmospheric pressure for a specific time. After cooling the reaction mixture was extracted with ethyl acetate. The extract was dried over magnesium sulfate and analyzed by GC (Fig. S8). Similar experimental procedures

were followed for all other used commercially available catalysts, Pt/C, Pt/Al_2O_3 and Pt/TiO_2. The comparisons between the catalysts are based on their relative turnover numbers, i.e., for a fixed substrate to platinum molar ratio, the product to platinum molar ratios are compared.

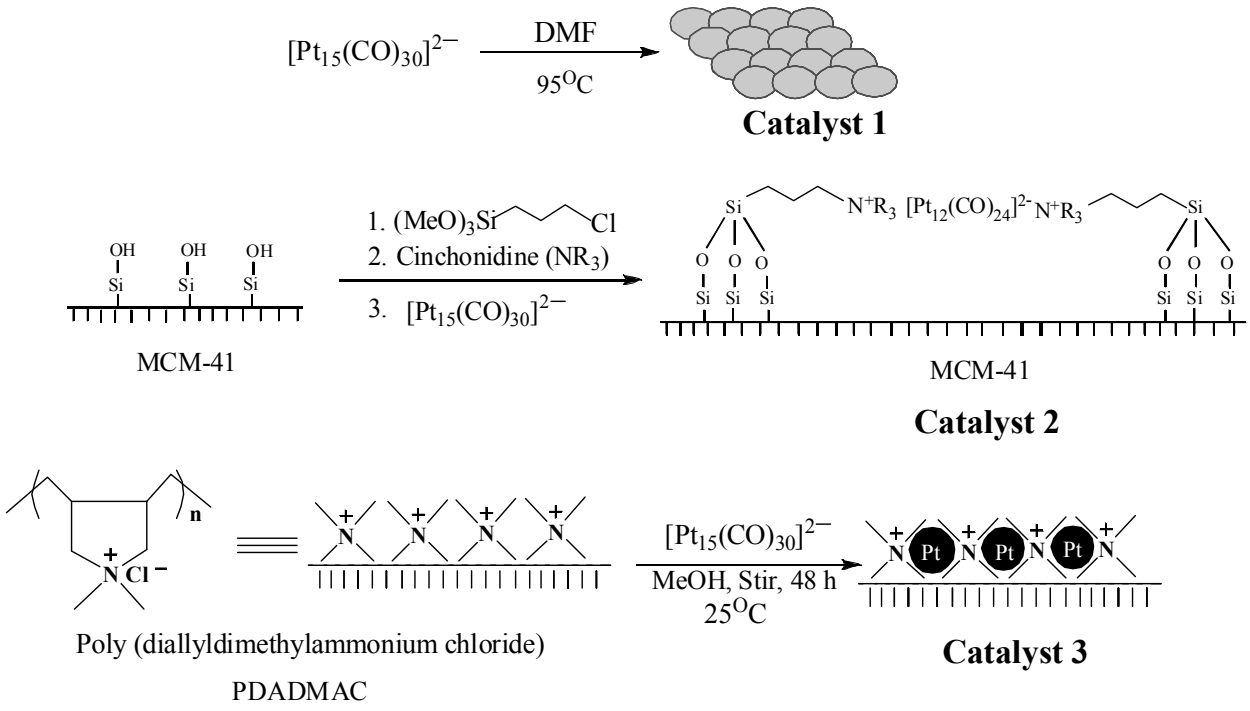
5. Additional mechanistic aspects of enantioselective Orito reaction

It is therefore reasonable to assume that the generally accepted molecular level enantioselection mechanism for Orito reaction would also apply to catalyst **1**.[S6] The anchoring of chiral modifier Cd onto the Pt-NP generates a "chiral footprint" which essentially acts as an active catalyst and induces enantiodifferentiation.[S6] In view of the observations, it is reasonable to believe that either π-stacking interaction between Pt-NP and quinoline ring or π-donation of quinoline nitrogen to platinum is operational (Fig. S4).

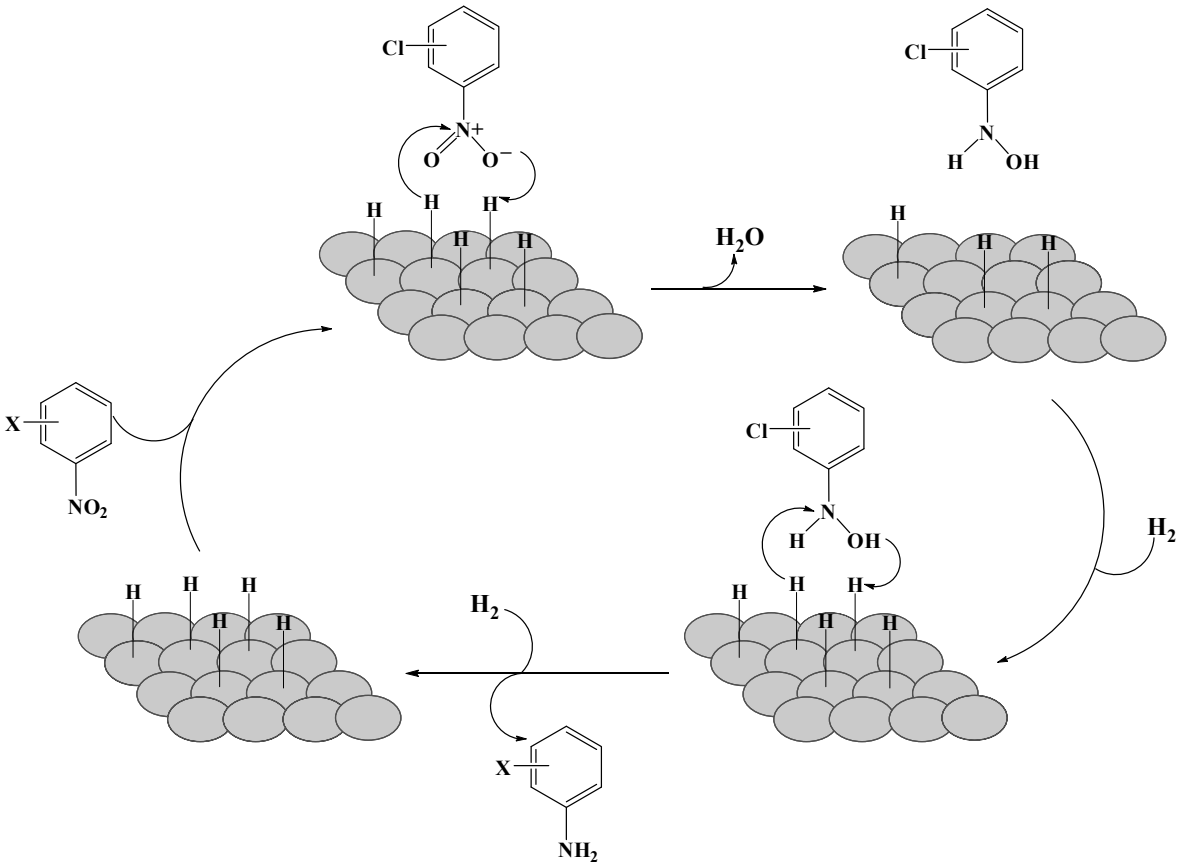
The presence of -OMe group on quinoline ring of quinidine and quinine may somehow prevent any of those interactions[S6] and hence, no enantioselectivity is observed with those chiral modifiers. The interaction between such chiral active catalyst and the incoming reactant is the origin of the observed enantiodifferentiation. In aprotic solvent such as toluene quinuclidine is not protonated, the keto group of methyl pyruvate interacts with the active catalyst via either of the two following proposals: (i) hydrogen bonded interaction of O···H–O or (ii) a N···H–O hydrogen bond involving a half-hydrogenated state of the methyl pyruvate (Fig. S5).[S6] Almost similar catalytic activity in absence of Cd suggests the crucial role of hydroxyl group during enantioselection (Fig. S5).

The theoretical model assumed that enantiodifferentiation can be originated due to the different stability of the diastereomeric complexes formed between Cd anchored to the Pt catalyst and methyl pyruvate adsorbed in its two enantiofacial forms (*via re*- and *si*-faces), leading to *S*- and *R*-methyl lactate, respectively, upon hydrogenation (Fig. S6).[S6] Basically, the anchored chiral Cd modifier adopts an "open" conformation upon substrate addition where the basic quinuclidine nitrogen atom points away from the aromatic quinoline ring as shown in Fig. S6. The decrease of enantioselection after first run can be attributed to (i) the

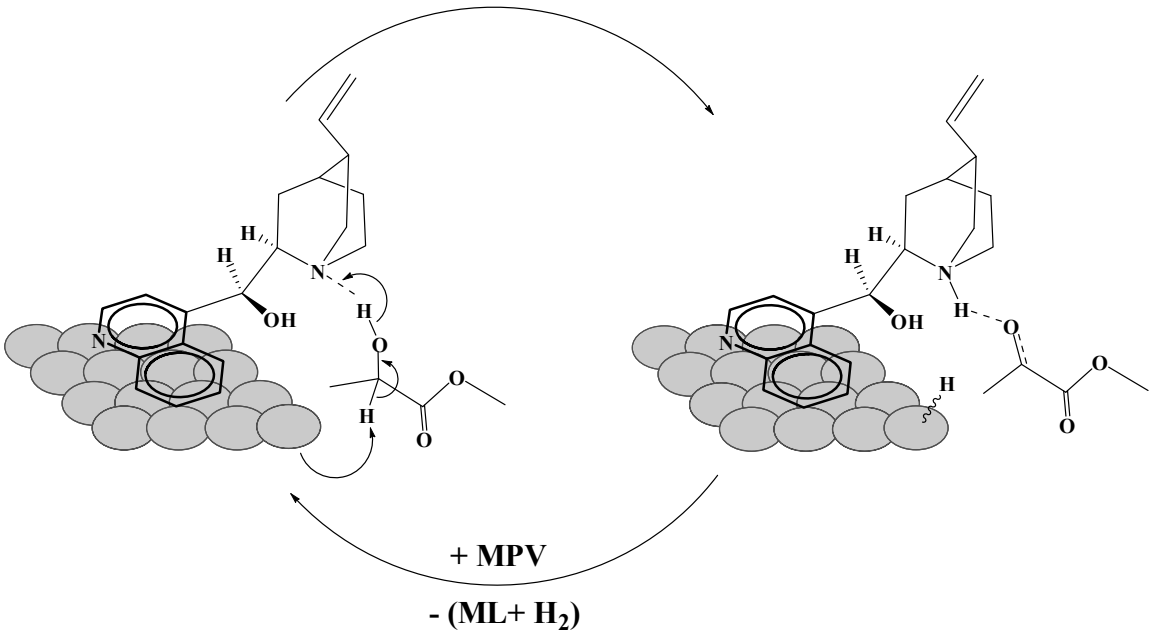
loss of Pt(111) face from the active catalytic sites (Fig. S1-S2), (ii) increase in particle size (5-6 nm after the first run) and (iii) change in morphology.



Scheme S1 Synthetic outlines for catalysts **1-3**

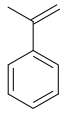
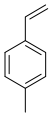
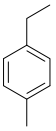
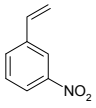
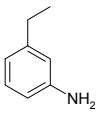
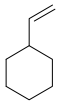
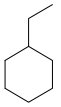
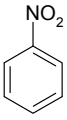
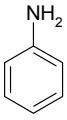
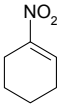
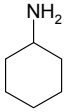


Scheme S2 The proposed catalytic cycle for the hydrogenation of chloronitrobenzenes by catalyst **1**



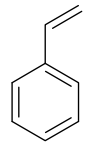
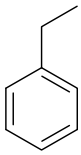
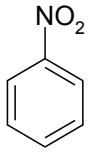
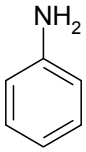
Scheme S3 The proposed route for oxidation of methyl lactate by catalyst **1**

Table S1 Additional hydrogenation data by catalyst **1**[a]

Substrate	Product	% Conversion	TOF (h^{-1})
		100	666
		100	666
		100	666
		100	666
		100	666
		100	666

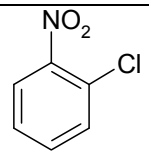
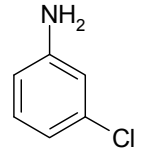
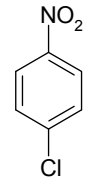
[a] Reaction condition: Catalyst **1**: substrate = 1:1000, solvent: MeOH, hydrogen pressure: 50 bar, temperature: 298 K, sonication time: 30 min, reaction time: 90 min, analyzed by GC using n-doecane as an external standard, TOF=turnover frequency (turnover number/time).

Table S2 Recycling experiments with catalyst **1**[a]

Substrate	Product	Number of cycle	% Conversion
		1	100
		2	92
		3	85
		1	100
		2	95
		3	79

[a]Reaction condition: Catalyst **1**:substrate = 1:1000, solvent: MeOH, hydrogen pressure: 50 bar, temperature: 298K, sonication time: 30 min, reaction time: 90 min, analyzed by GC using n-doecane as external standard.

Table S3 Catalytic hydrogenation study of chloronitrobenzenes by catalyst **1**[a]

Substrate	% Conversion	% Conversion			
		Chloroaniline	Nitrobenzene	Aniline	Chlorobenzene
	100	88	7	4	<1
	67	60	5	<1	<1
	100	92	4	2.5	<1

[a]Reaction condition: catalyst **1**:substrate = 1:1000, solvent: MeOH, hydrogen pressure: 50 bar, temperature: 298K, sonication time: 30 min, reaction time: 90 min, analyzed by GC using dodecane as external standard.

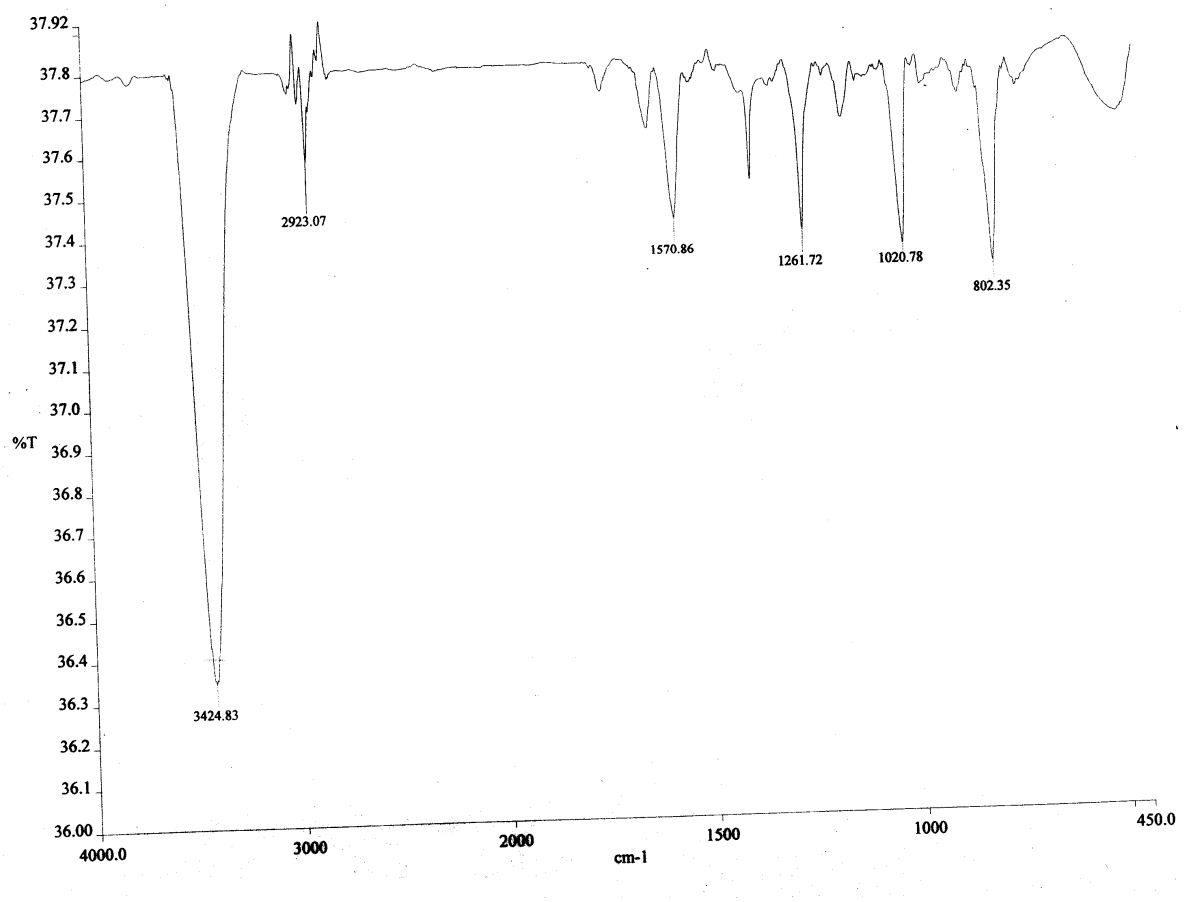
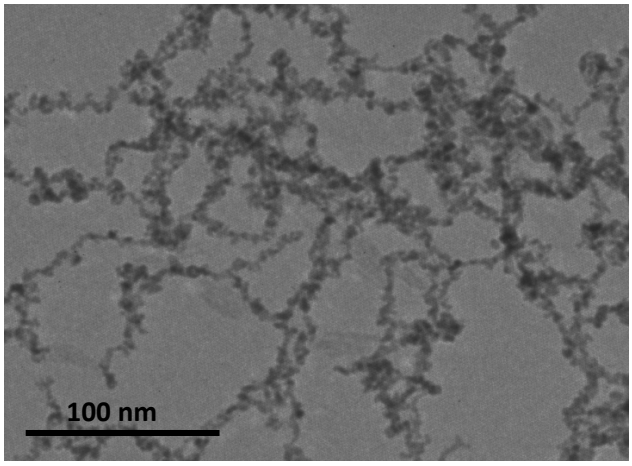
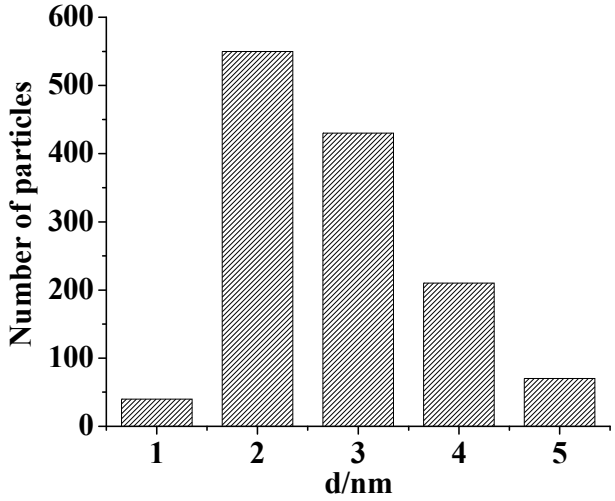


Fig. S1 IR spectrum (in KBr) of fresh catalyst **1**. The absence of any vibration in the region of 1800-2150 cm^{-1} reveals the non-existence of metal carbonyl species. The IR spectrum of parent $[Pt_{15}(CO)_{30}]^{2-}$ (ν_{IR}: 2055, 1850 and 1870 cm^{-1}) is available in Figure 2 of Ref. S5 for comparison.

(a)



(b)



(c)

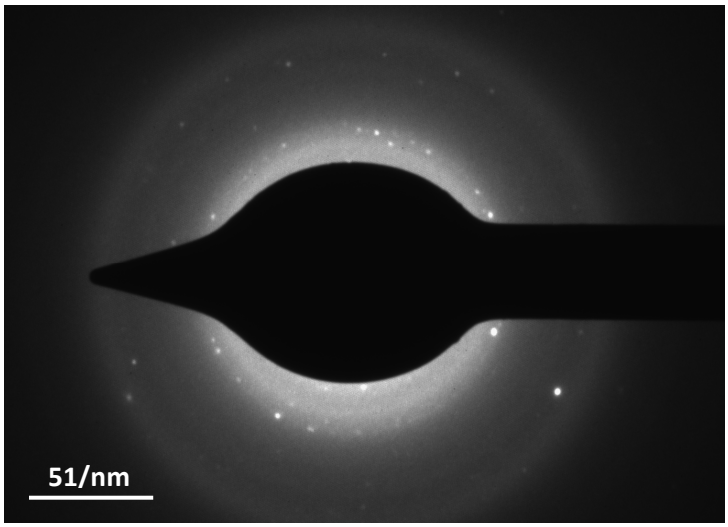


Fig. S2 (a) TEM micrograph; (b) histogram and (c) diffraction pattern for catalyst **1**.

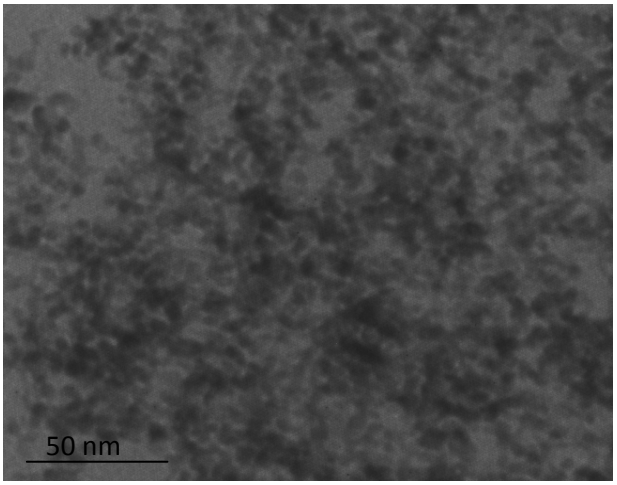


Fig. S3 TEM micrograph of used catalyst **1** after hydrogenation.

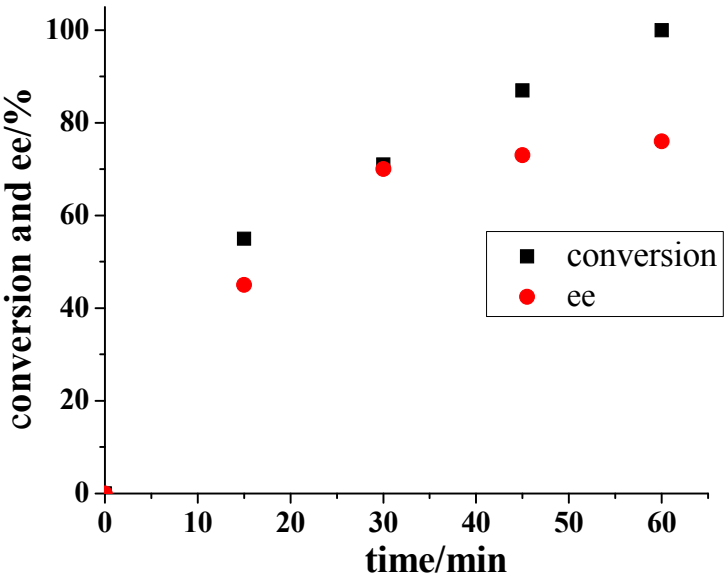


Fig. S4 Time monitored enantioselective hydrogenation of MPV by catalyst **1** [Reaction conditions*:* hydrogen pressure:50 bar, temperature:300K, sonication time:30 min, substrate:**1**=100:1, **1:**Cd=1:10, solvent=methanol, time:60 min].

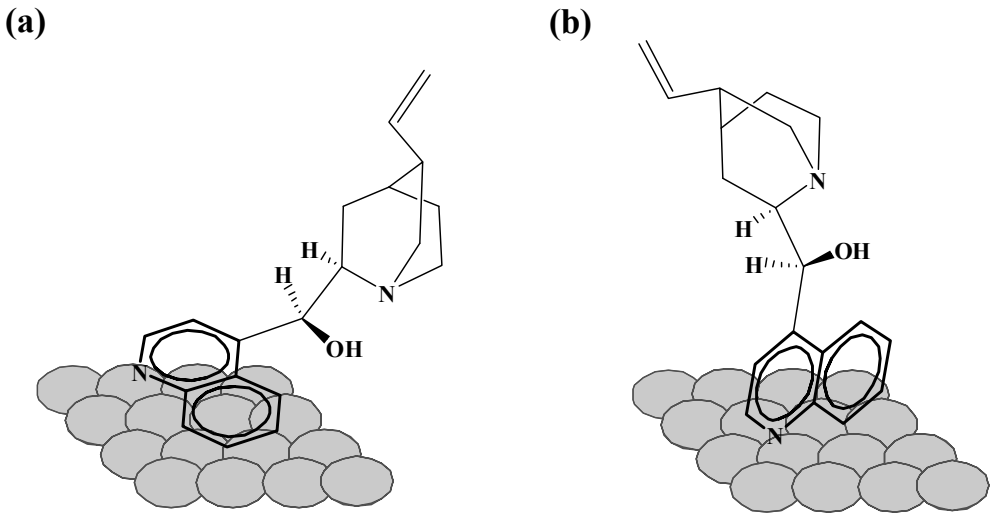


Fig. S5 The possible interaction mode between Pt-NP and Cd via (a) π-stacking of quinoline moeity and (b) π-donation from quinoline nitrogen.

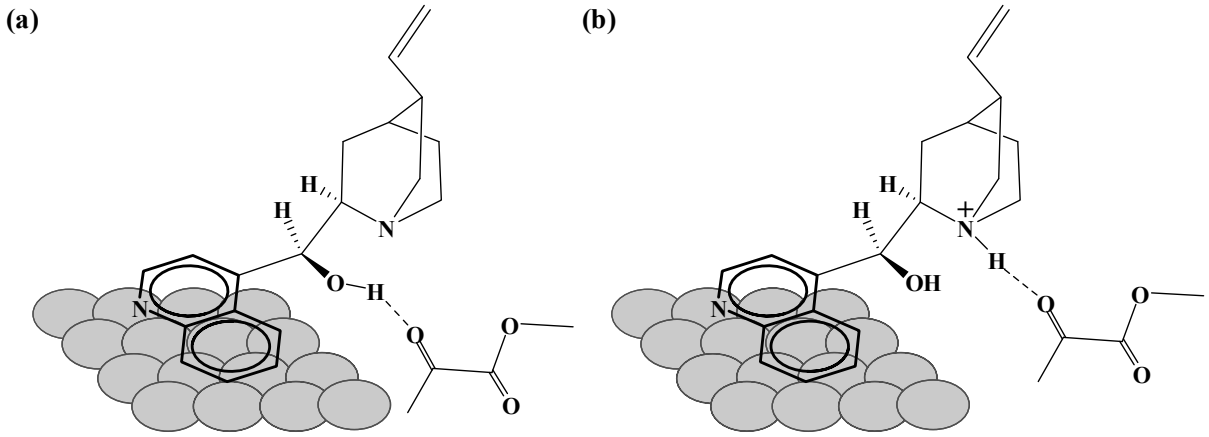


Fig. S6 The interaction between the absorbed modifier (Cd) and methyl pyruvate for the enantioselective hydrogenation: hydrogen bonded interaction (a) O···H–O and (b) N···H–O in a half-hydrogenated state.

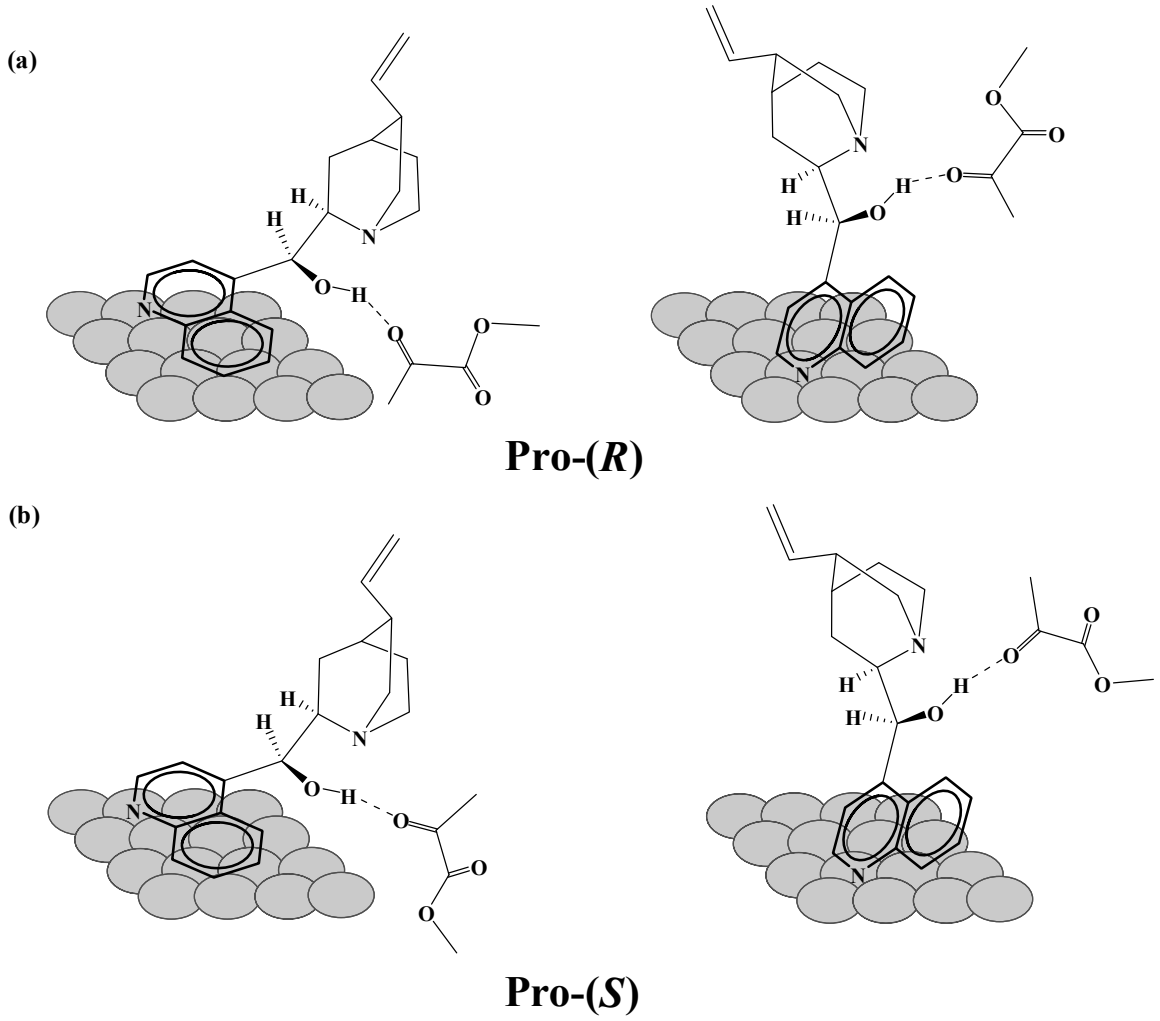


Fig. S7 The proposed 1:1 (Pt-NP:Cd) interaction model for the enantioselective hydrogenation of methyl pyruvate.

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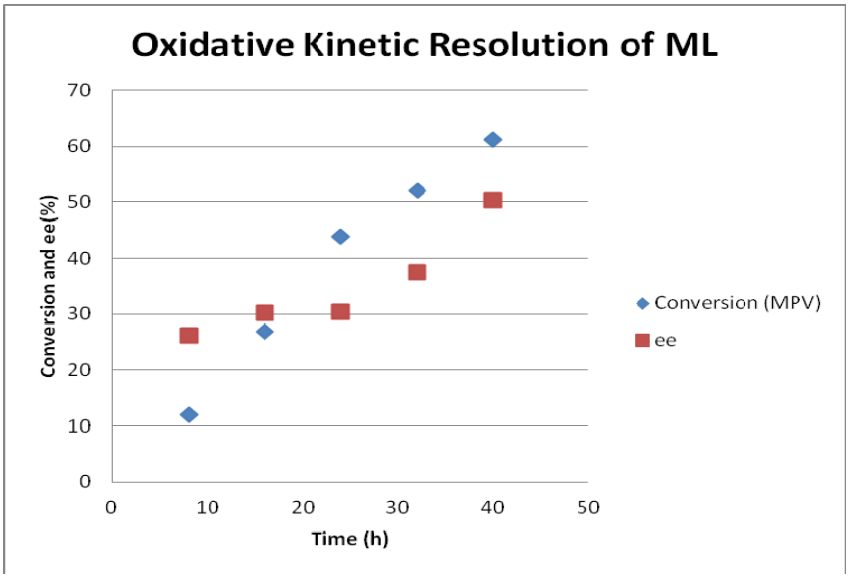
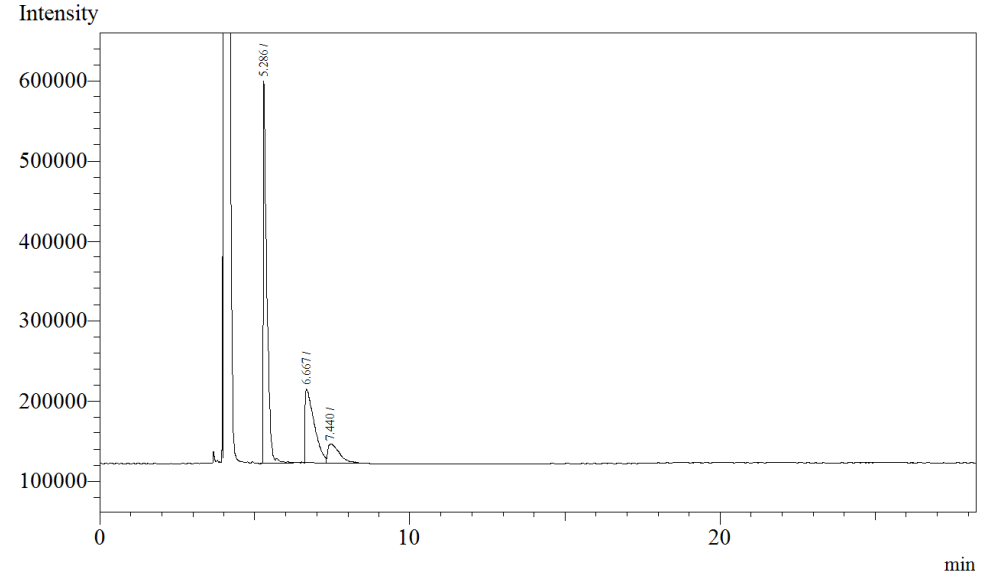


Fig. S8 Time monitored oxidative kinetic resolution of methyl lactate by **1** [Reaction conditions: Oxygen pressure:1 atm, temperature:353K, sonication time:30min, substrate:**1**=85:1, substrate:cinchonidine=10:1, solvent=water:methanol(5:1), time:40 h].

Sample Name : vial 1
Sample ID : vial 1
Sample Type : Unknown
Injection Volume :
ISTD Amount :

Data Name : C:\GCsolution\Work\SnapShot1_1222011131649.gcd
Method Name : C:\Documents and Settings\Administrator\Desktop\Untitled.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.286	3887648	476971	61.291				
2	6.667	1844898	91644	29.086				
3	7.440	610429	23562	9.624		V		
Total		6342975	592177					

Fig. S9 The representative chromatogram of kinetic resolution of methyl lactate [Peaks at 5.286, 6.667 and 7.440 correspond to methyl pyruvate, R-methyl lactate and S- methyl lactate, respectively].

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S5 G. Longoni and P. Chini, *J. Am. Chem. Soc.*, 1976, **98**, 7225.

S6 (*a*) T. Burgi and A. Baiker, *Acc. Chem. Res.*, 2004, **37**, 909; (*b*) E. N. Jacobsen, A. Pfaltz and H. Yamamoto, *Comprehensive Asymmetric Catalysis*, Springer: Berlin, 1999, Vols. 1-3.