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# NJC

#### Supporting Information

### Asymmetric Hydrogenation of $\alpha$ -ketoesters on Pt (111) Surface

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### Table of Contents

## 1. Experiment

- 1.1 Reagents
- 1.2 General procedure for the synthesis of Pt HNC/C composites
- 1.3 General procedure for the asymmetric hydrogenation reaction

## 2. Characterization

- 2.1 Catalysts characterisation
  - 2.1.1 XRD analysis
  - 2.1.2 SEM analysis
  - 2.1.3 FTIR analysis
  - 2.1.4 CV analysis
  - 2.1.5 TGA analysis
  - 2.1.6 TEM analysis
  - 2.1.7 AFM analysis

## 3. Optimization of hydrogenation reaction

- 4. Product characterisation
  - 4.1 HPLC analysis
  - 4.2 FTIR analysis
  - 4.3 UV-Vis analysis
  - 4.4 NMR analysis

## 5. Possible interaction between cinchonine and catalyst surface

- 6. Recyclability
  - Reference

## 1. Experiment

## 1.1 Reagents

Carbon nanotubes (90% carbon basis) and Graphene (91% carbon basis) were purchased from Sigma Aldrich and Reinste Nano Ventures respectively while carbon fiber and activated carbon were commercially available. Ethyl pyruvate (98%), ethyl 3-bromo-2 oxopropanoate (90%, Aldrich), ethyl 3-methyl-2-oxobutanoate (97%, Aldrich), ethyl 2-oxo-4-phenylacetate (95%, Aldrich), ethyl 2-oxo-4-phenylbutanoate, cinchonine (CN,  $\geq$ 98%), and tetraoctyl ammonium bromide (98%) were received from Sigma Aldrich. Tetrabutyl ammonium bromide (99%, Spectrochem), tetrapropyl ammonium bromide (99%, Spectrochem), (1-octyl) trimethyl ammonium bromide ( $\geq$ 98%, Alfa Aesar) and docyl ammonium bromide (98%, Spectrochem) are received commercially. Acetic acid (99.8%), toluene, tetrahydofurane and ethyl alcohal were purchased from local source.

## 1.2 General procedure for the synthesis of Pt HNC/C catalyst

A typical preparation experiment for Pt HNC/MWNTs has been carried out as described below and similar procedure was adopted for other carbon materials. First, the activation process was carried out in which MWNTs (10 g) were refluxed under constant stirring in HNO<sub>3</sub> (500 mL, 68 wt %) at 140 °C, and extracted by centrifugation at 3000 rpm. MWNTs were washed several times with water (till pH reaches to 6.5-7 of supernatant) followed by ethanol. Resultant MWNTs were dried at 80 °C for 4 h under argon. The process starts with addition of  $H_2PtCl_6$  (0.5

mmol; 0.210 g) in 5 mL water to make a clear yellowish solution that was added to 5 ml toluene in a 15 ml glass bottle. The solution was thoroughly shook for 5 min followed by adding Tw20 (2 mL) to this solution and, further shook until toluene layer turned to yellowish (Pt-organic precursor). The Pt-organic precursor layer was separated and added dropwise to a suspended ethanol solution of functionalized MWNT (2 g, 20 mL) under sonication for over a period of 1 h. The resultant Pt-Org-MWNT solution was drop casted to a preheated glass disc at 130°C and maintained for 24 h under air. The dried solid substance was washed with deionised water and ethanol to remove residual Tw20 (Fig. S2a). The Pt loaded MWNT catalyst was dried at 50°C and calcinated at 180 °C for 24 h to obtained Pt HNC/MWNT (1.9 g). A typical procedure of preparing Pt HNC/MWNT pictorially presented in fig. S2a.



Tween 20

Figure S1. Structure of Tween 20 (X+W+Y+Z = 20)



(a)



**Fig.** S2. Pictorial representation of phase transfer process by using (a) Tw20 phase transfer reagent for preparing Pt HNC/MWNT (b) Other Phase transfer reagent like (1) Tetrabutyl ammonium bromide, (2) Tetrapropyl ammonium bromide, (3) (1-octyl) trimethyl ammonium bromide, (4) CTAB (Cetyl trimethylammonium bromide) and (5) Docyl ammonium bromide.

#### 1.3 General procedure for the asymmetric hydrogenation reaction

Catalysts were prehydrogentated at 300°C for 3 h in hydrogen atmosphere before hydrogenation reaction. In a typical procedure, asymmetric hydrogenation reaction was carried out in a high pressure vessel (Berghof HR-100) equipped with a Teflon container. A reaction mixture of 30 mg catalysts, 75  $\mu$ L  $\alpha$ -ketoester, 4 mg (0.01 M) CN and 1.5 mL (17.5 M) acetic acid were added. Vacuum was created in vessel followed by purging hydrogen gas under the maintained pressure of 10 bars for 12 h at room temperature. The reaction mixture was centrifuged to obtain the crude product. The product was purified via bulb to bulb distillation (Glass Oven B-585 Kugelrohr). The yield was calculated by weighing the finally obtained purified product; using balance (Mettlar Toledo-ML204) with accuracy of 0.1 mg. Reaction conversion and enantiomeric excess were monitored by NMR and HPLC spectroscopy, respectively.

### 2. Characterisation

An X-ray diffractometer (XRD), D8 advance (Bruker, U.S.A.) using Cu K $\alpha$ 1 ( $\lambda$  = 1.54056 Å) as a radiation source was used to ascertain the quality and crystalline nature of carbon materials with tube current and voltage 40 mA and 40 kV, respectively. Morphology and elemental analysis of Pt HNC/C composites were determined using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX, EVO18 Ziess) with an accelerating voltage of 20 KeV. Thermogravimetric analysis (TGA) were performed on TGA-6000 thermal analyzer (Perkin Elmer) under a nitrogen atmosphere (19.8 mL/min flowing nitrogen, temperature range of 30-900°C, at rate of 10 °C/min and pressure 3 bar) and a heating rate of 10 °C min<sup>-1</sup>. High resolution transmission electron microscopy (HRTEM) was carried out in a FEI Tecnai-G2 T20. Atomic force microscopy (AFM) images were recorded on XE-70 (park system). The electrochemical activity of Pt HNC/C catalyst was analysed in oxygen reduction reaction by cyclic voltammetry (CV) at room temperature in a three compartment electrochemical cell (CH Instruments, electrochemical workstation). Diffuse reflectance spectroscopy (DRS) and UV-vis spectra were recorded on Varian Cary 4000 in the range of 200-800 nm. Fourier-transform infrared spectra (FTIR) of the samples were recorded on a Vertex 70 v spectrometer (Bruker) in the range of 400-4000 cm<sup>-1</sup> using KBr pallets. Surface area and pore size measurements were carried out on a standard adsorption equipment (ASAP 2010, Micromeritics Instruments Inc., Norcross, GA, USA) using N2 gas with 99.99% purity. Nuclear magnetic resonance spectra (1H NMR) were recorded on a Bruker 500 spectrometer operating at 500 MHz in CDCl3. High performance liquid chromatography (HPLC) from WATERS, Ireland was used to analyse catalytic products. The chiral columns CHIRALPAK IA, IC, ID AND QD-AX were used to find out % ee under isocratic and isothermal (at 30 °C) conditions using respective mixture of nhexane/iso-propanol/buffer as the mobile phase (see supporting information for details). Specific rotation was measured from Rudolph polarimeter (APII/2W).

#### 2.1 Catalysts characterisation

### 2.1.1 XRD analysis

Material spectrum range is  $\lambda$  = 20-80 with 0.02 increment. Pt 111 % have been calculated for every Pt supported carbon materials and found that MWNT have maximum % of Pt 111 (Fig. S3). Pt 111 % has been calculated by following formula.

$$Pt(111)\% = \frac{Pt(111)}{(Pt(111) + Pt(200) + Pt(220))} * 100$$



Fig. S3. XRD spectra of different Pt loaded carbon materials.

#### 2.1.2 SEM analysis

The morphology of the carbon materials/silver nanocomposites is explored. EDX images of samples confirm the presence of Pt nanoparticles on the surface of carbon materials and weight % graph shows the approximately percentages of Pt present in the sample. Five different samples have been analysed for EDX and average Pt loading % calculated (Fig. S4d & e).





Fig. S4. SEM image of Pt loaded on (a) CF (b) Graphene (c) MWNT (d, e) Catalyst loading of five samples (f) EDX of Pt peaks and Pt weight%.

### 2.1.3 FTIR analysis

IR (KBr) 699.23 cm<sup>-1</sup> (C-H bending), 1547.07 (C-C Stretching), 1696.21 (six member C=O stretching), 2356 (carboxylic O-H stretching) and 3600-3700 (O-H) cm<sup>-1</sup>. Fig. S5 (b) 839.86 cm<sup>-1</sup> and 1056.02 cm<sup>-1</sup> (interaction between the Pt HNC and the functionalize carbon), 1727.52 cm<sup>-1</sup> (aromatic C=C stretching), and 3331.11 cm<sup>-1</sup> (O-H stretching) Fig.S5 (a).



Fig. S5. FTIR spectra of (a) functionalised C (b) Pt HNC/C.

### 2.1.4 CV analysis

Electrochemical activities were compared between blank glass electrodes, functionalised carbon materials and Pt HNC/C (Fig. S6). Background of cyclic voltammetry was collected in 0.5 M H<sub>2</sub>SO<sub>4</sub> (saturated with oxygen) for blank glass electrode. Solution has been made of carbon materials and Pt HNC/C with nafion and pasted it on glass electrode. The activities were scanned between -0.21 and 1.2 V potential for functionalised carbon materials and Pt HNC/C at 50 mV/s, where Pt HNC/C showed maximum electrochemical activity.



Fig. S6. Cyclic voltammetry of plane electrode, functionalised carbon materials and Pt/C.

### 2.1.5 TGA analysis

Carbon materials start decomposing earlier than the pristine carbon materials due to functionalization and defects. The decomposition temperature of carbon materials also decrease (200-400  $^{\circ}$ C) after loading of Pt on carbon materials (due to increased defects). A temperature loss of 150-200  $^{\circ}$ C for Pt HNC/C was observed in figure S7.



Fig. S7. TGA analysis of functionalised C and Pt HNC/C.

### 2.1.6 TEM analysis

The average size, diameters, miller index and loading state of Pt HNC were also determined from TEM analysis at 1 to 100 nm (Fig. S8). TEM images indicated the surface of the nanotubes coated, decorated or embedded with the hexagonal nanocrystals. Dispersed Pt nanoparticles on carbon nanotube showed in figure S8. The size of Pt HNC are 2 to 8 nm for those particles which were found inside the MWNT. The particles placed outside surface of MWNT have 2-20 nm size.



Fig. S8. TEM image of Pt HNC/ MWNT.

#### 2.1.7 AFM analysis

The sample was prepared sample via drop casting, in which well sonicated homogeneous solution was dropped on mica followed by dehydrated at 60°C. Fig. S9 (a, b) gives us information about the length of nanotubes, approximate valuation of the bundles diameter and attachment of metal particles. It was impossible to determine

accurate value of diameter of nanotube, because some of nanotubes didn't attach directly on mica. Graphene layered structure was seen by AFM in fig. S9 (c, d). In case of carbon fiber, metal particles stacked on fiber surface. All the parameter recorded in non contact mode (Fig. S9g).



Fig. S9. AFM image of Pt HNC loaded on (a, b) Carbon nanotube (c, d) Graphene (e,f) Carbon fiber (g) Analysis parameters.

### 3. Optimization of hydrogenation reaction

 Table S1. Asymmetric catalytic hydrogenation reaction with Pt HNC/MWNT.

Entry	Catalyst <sup>a</sup>	Time (h)	H <sub>2</sub> Pressure (bar)	Conversion(%)b	Solvent
1	Pt HNC/MWNT	24	1	20	Acetic acid
2	Pt HNC/MWNT	24	5	70.4	Acetic acid
3	Pt HNC/MWNT	24	10	99.9	Acetic acid
4	Pt HNC/MWNT	24	15	99.1	Acetic acid
5	Pt HNC/MWNT	24	20	98.5	Acetic acid
6	Pt HNC/MWNT	12	10	99.9	Acetic acid
7	Pt HNC/MWNT	6	10	82.2	Acetic acid
8	Pt HNC/MWNT	12	10	30.3	Tetrahydrofurane
9	Pt HNC/MWNT	12	10	45.8	Toluene
10	Pt HNC/MWNT	12	10	25.6	Ethyl alcohal
<sup>a</sup> Catalyst was prepared with 5 wt% metal loading. All the reactions were performed by taking 30 mg Pt HNC/MWNT and 75 μL ethyl pyruvate					

under different pressure in different solvent by varying time. <sup>b</sup>Conversions were investigated by NMR and HPLC.



Fig. S10. Enantioselectivity% and conversion% versus catalysts (a) Carbon materials (b) Pt HNC/MWNT (c) Pt HNC/Graphene (d) Pt HNC/AC (e) Pt HNC/CF.

### 4. Product characterisation

#### 4.1 FTIR analysis

FTIR spectrum of ethyl lactate has been given a broad peak at 3411 cm<sup>-1</sup>, which indicates hydroxyl groups. Absorption at 2856 and 2915 cm<sup>-1</sup> indicates C-H stretching and the peak at 1649 cm<sup>-1</sup> consists of C-H bending peaks. The presence of carbonyl and ester groups range among 1600-1800 cm<sup>-1</sup>.



Fig. **S11.** FTIR spectra of ethyl lactate produce from catalysts (a) Pt HNC/CF (b) Pt HNC/Graphene (c) Pt HNC/AC (d) Pt HNC/MWNT (e) Ethyl pyruvate.

#### 4.2 UV-Vis analysis



The formation of ethyl lactate obtained from different catalysts was confirmed by UV spectroscopy. In UV/Vis analysis ethyl lactate gives an absorbance peak around at 245 nm whereas, two absorbance peaks were observed at 245 nm and 345 nm for ethyl pyruvate.

Fig. S12. UV analyses of ethyl pyruvate and ethyl lactate produce from (a) Ethyl pyruvate mixed with Ethyl lactate (b) Pt HNC/MWNT (c) Pt HNC/AC (d) Pt HNC/Graphene (e) Pt HNC /CF (f) Ethyl pyruvate

### 4.3 HPLC analysis

Entry	Condition
Compound	EthylLactate
Catalysts	(a) Pt HNC/MWNT (b) Pt HNC/ Graphene (c) Pt HNC/AC (d) Pt HNC/CF
Column	DAICEL CORPORATION, CHIRALPAK ID 4.6mm
Solvent	n-hexane/iso-propanol, 90:10 with 0.1% Na <sub>2</sub> B <sub>2</sub> O <sub>7</sub> buffer, 1.0 ml/min,
Temperature	30°C
Wavelength	245 nm

S. No	Name	Retention Time	Area	% Area	Height
1	(R)-(+)-ethyl lactate	3.192	37625	0.17	9388
2	(S)-(-)-ethyl lactate	4.192	21901123	99.83	1581017





S. No	Name	Retention Time	Area	% Area	Height
1	(R)-(+)-ethyl lactate	3.197	53792	2.70	6708
2	(S)-(-)-ethyl lactate	4.369	1935804	97.30	147873



10



Fig. S13. HPLC of ethyl lactate from (a) Pt HNC/MWNT (b) Pt HNC/ Graphene (c) Pt HNC/AC (d) Pt HNC/CF.



Fig. S14. HPLC of methyl lactate





Fig. S15. HPLC of ethyl 2-hydroxy-3-methylbutanoate.

Height

30236

2062348



Fig. S16. HPLC of ethyl 2-hydroxy-2-phenylacetate.





Fig. S17. HPLC of ethyl 3-bromo-2-hydroxypropanoate.



Fig. S18. HPLC of ethyl 2-hydroxy-4-phenylbutanoate.

#### 4.4 NMR analysis

Nuclear magnetic resonance spectra (<sup>1</sup>H NMR) were recorded on a Bruker 500 spectrometer operating at 500 MHz for <sup>1</sup>H (CDCl<sub>3</sub>). Chemical shift for <sup>1</sup>H NMR spectra are reported as  $\delta$  in parts per million (PPM) downfield from SiMe<sub>4</sub> ( $\delta$  0.0) and relative to the signal of chloroform-d ( $\delta$  7.26, singlet).

#### 4.4.1 Ethyl lactate

<sup>1</sup>H NMR;  $\delta_{H}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.28 (3 H, t, J 7.34Hz, *CH*<sub>3</sub>), 1.42 (3 H, d, J 6.90 Hz, *CH*<sub>3</sub>), 4.21 (2 H, q, J 7.09 Hz, *CH*<sub>2</sub>), 4.26 (1H, q, J 6.85 Hz, *CH*), ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 14.01, 20.6, 61.6, 66.7, 175.8 ppm; [ $\alpha$ ]<sub>D</sub><sup>20°C</sup> = +10 (c 0.1 in ethanol)<sup>1</sup>.





|| 0





Fig. S20. <sup>13</sup>C NMR of ethyl lactate.

 $\sum_{\substack{|1.3|5\\1.286}}^{1.432}$ 

<sup>4.4.2</sup> Ethyl 3-bromo-2-hydroxypropanoate

<sup>1</sup>H NMR;  $\delta_{H}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.21 (3 H, t, *J* 7.20 Hz, *CH*<sub>3</sub>), 3.17 (2 H, d, *J* 7.05 Hz, *CH*<sub>2</sub>), 4.06(2 H, q, *J* 7.27 Hz, *CH*<sub>2</sub>), 5.04 (1 H, t, *J* 7.17Hz, *CH*) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz): 13.9, 35.4, 60.6, 82.7, 170.8 ppm; [ $\alpha$ ]<sub>D</sub><sup>20°C</sup> = -19.01 (c 0.1 in chloroform).

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Fig. S22. <sup>13</sup>C NMR of ethyl 3-bromo-2-hydroxypropanoate.

<sup>1</sup>H NMR;  $\delta_{\text{H}}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.86 (6 H, d, *J* 7.15Hz, *CH*<sub>3</sub>), 1.36 (3 H, t, *J* 6.87 Hz, *CH*<sub>3</sub>), 3.26 (1 H, m, *J* 7.47 Hz, *CH*), 4.04 (1 H, d, *J* 3.53Hz, *CH*), 4.26(2 H, q, *J* 7.07 Hz, *CH*<sub>2</sub>), ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 14.1, 18.6, 32.1, 61.6, 75.6, 175.08 ppm; [ $\alpha$ ]<sub>D</sub><sup>20°C</sup> = -8.3 (c 0.1 in chloroform)<sup>2</sup>.



Fig. S23. <sup>1</sup>H NMR of ethyl 2-hydroxy-3-methylbutanoate.



Fig. S24. <sup>13</sup>C NMR of ethyl 2-hydroxy-3-methylbutanoate.

#### 4.4.4 Ethyl 2-hydroxy-2-phenylacetate

<sup>1</sup>H NMR;  $\delta_{H}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.21 (3 H, t, *J* 7.45 Hz, *CH*<sub>3</sub>), 4.21 (2 H, q, *J* 3.45 Hz, *CH*<sub>2</sub>), 5.19 (1 H, s, *CH*), 7.29 (5 H, m, *J* 6.85 Hz, *C*<sub>4</sub>*H*<sub>5</sub>), ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 14.0, 61.6, 72.8, 126.8, 127.5, 129.5, 138.2, 173.7 ppm;  $[\alpha]_{D}^{20^{\circ}C}$  = +10 (c 0.1 in chloroform).









Fig. S26. <sup>13</sup>C NMR of ethyl 2-hydroxy-2-phenylacetate.

#### 4.4.5 Ethyl 2-hydroxy-4-phenylbutanoate

<sup>1</sup>H NMR;  $\delta_{H}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.36 (3H, t, *J* 7.11 Hz, *CH*<sub>3</sub>), 2.9 (2H, m, *J* 7.36 Hz, *CH*<sub>2</sub>), 3.16 (2H, t, *J* 7.15 Hz, *CH*<sub>2</sub>), 4.25 (2H, q, *J* 7.22Hz, *CH*<sub>2</sub>), 4.33 (1H, t, 7.52, *CH*), 7.19(5H, m, *J* 7.48 Hz, *C*<sub>4</sub>H<sub>5</sub>), ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz): 14.1, 35.8, 61.7, 70.0, 126.0, 128.3, 128.5, 141.1, 175.3, ppm; [ $\alpha$ ]<sub>D</sub><sup>20°C</sup> = +16.5 (c 0.1 in chloroform)<sup>3</sup>.







<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$ : 1.41 (d, 3 H, *J* = 7.05 Hz, CH<sub>3</sub>), 2.93 (d, 1 H, *J* = 5 Hz OH, D<sub>2</sub>O exchangeable), 3.79 (s, 3 H, CH<sub>3</sub>), 4.29 (q, 1 H, *J* = 6.94 Hz, CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$ : 20, 52.2, 66.7, 175.7;[ $\alpha$ ]<sub>D</sub><sup>20°C</sup> = -6.9 (c 0.1 in chloroform).



Figure S29. <sup>1</sup>H NMR of methyl lactate.



Fig. S30. <sup>1</sup>H NMR of methyl lactate. 5. Possible interaction between cinchonine and catalyst surface

Possible interaction model have been reported earlier (Fig. S31)<sup>4</sup>. It has been shown that the aromatic and aliphatic part of cinchonine interact with ethyl pyruvate. (Fig. S33).



Fig. S31. Probably interaction model.



Figure S32. Structure of CN.



Fig. S33. NMR data of interaction of CN and ethyl pyruvate.



Fig. S34. Comparative XRD spectra of Pt HNC/MWNT, Pt HNC/MWNT with CN and Pt HNC/MWNT with CN after catalytic reaction.

### 6. Recyclability

These catalysts are recoverable and reusable without significant loss of activity (Table S2), where the catalyst (Pt HNC/MWNT) was separated out by centrifugation and washed with acetic acid after each reaction cycle. Fresh reactant and modifier were added to the regenerated catalyst and steps were repeated for 10 consecutive cycles. Catalyst recycled at 20 fold scale (1.5 mL, ethyl pyruvare). The regenerated catalyst provided low enantioselectivity in absence of modifier. A relatively constant conversion and enantioselectivity was obtained in all cycles (Table S2). The HRTEM images of recycled catalyst (after ten cycles) revealed individuality of catalytic reaction centre that secured high enantioselectivity. The PXRD of recycled catalyst also supports the regeneration of active Pt(111) planes responsible for high selectivity.

Entry	Yield %	Ee%	
Cycle 1	99.9	99.6	
Cycle 2	99.9	99.6	
Cycle 3	99.9	99.6	
Cycle 4	99.9	99.6	
Cycle 5	99.9	99.5	
Cycle 6	99.9	99.2	
Cycle 7	99.8	99.2	
Cycle 8	99.5	99.2	
Cycle 9	99.5	99.0	
Cycle 10	99.3	99.0	
$^{a}\mbox{The}$ reaction were performed at room temperature and 10 bar $H_{2}$ with 5 wt% Pt			
HNC/MWNT in high pressure reactor.			

		<b>.</b>
Table S2.	Recyclability	v of catalvst <sup>a</sup>



Fig. S35. TEM image of Pt HNC/MWNT after 10 cycles.



Fig. S36. XRD of Pt HNC/MWNT after 10 cycles of catalytic reaction.



Fig. S37. Graph between Pt (111) % and enantioselectivity.

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