



HAL
open science

Asymmetric hydrogenation of ethyl pyruvate over aqueous dispersed Pt nanoparticles stabilized by a cinchonidine-functionalized β -cyclodextrin

Sébastien Noël, Eleonora Caronia, Hervé Bricout, Iveta Chena Tichá, Stephane Manuel, Anne Ponchel, Sébastien Tilloy, Alessandro Galia, Eric Monflier, Jindřich Jindřich, et al.

► To cite this version:

Sébastien Noël, Eleonora Caronia, Hervé Bricout, Iveta Chena Tichá, Stephane Manuel, et al.. Asymmetric hydrogenation of ethyl pyruvate over aqueous dispersed Pt nanoparticles stabilized by a cinchonidine-functionalized β -cyclodextrin. *Catalysis Communications*, 2021, 150, pp.106272. 10.1016/j.catcom.2020.106272 . hal-03139645

HAL Id: hal-03139645

<https://hal.science/hal-03139645>

Submitted on 3 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Asymmetric hydrogenation of ethyl pyruvate over aqueous dispersed Pt nanoparticles stabilized by a cinchonidine-functionalized β -cyclodextrin

Sébastien Noël,^[a] Eleonora Caronia,^[b] Hervé Bricout,^[a] Iveta Chena Tichá,^[c] Stéphane Menuel,^[a] Anne Ponchel,^[a] Sébastien Tilloy,^[a] Alessandro Galia,^[b] Éric Monflier,^[a] Jindřich Jindřich,^[c] and Bastien Léger*^[a]

[a] Dr. S. Noël, Dr. H. Bricout, Dr. S. Menuel, Prof. Dr. A. Ponchel, Prof. Dr. S. Tilloy, Prof. Dr. E. Monflier, Dr. B. Léger

Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181

Unité de Catalyse et de Chimie du Solide (UCCS)

62300 Lens, France

[b] E. Caronia, Prof. Dr. A. Galia

Dipartimento di Ingegneria

Università degli Studi di Palermo, Viale delle Scienze, Ed. 6 90128, Palermo, Italy

[c] I. Chena Tichá, Prof. Dr. J. Jindřich

Department of Organic Chemistry

Faculty of Science, Charles University, Hlavova 8, 128 43, Prague 2, Czech Republic

* Corresponding author

Phone: 33 (0)3 21 79 17 49

Fax: 33 (0)3 21 79 17 55

E-mail: bastien.leger@univ-artois.fr

Abstract

Cinchonidine-functionalized β -cyclodextrin was used as stabilizing agent for platinum nanoparticles dispersed in water, but also as chiral modifier for the asymmetric hydrogenation of ethyl pyruvate at 30 °C under 40 bar of hydrogen. This functionalized cyclodextrin allowed getting more stable, more catalytically active and also more enantioselective Pt nanoparticles compared to control catalytic systems. NMR and MALDI-MS analyses clearly showed the reduction of the vinyl group of the cinchonidine graft during the nanoparticles preparation. Under hydrogen pressure, the hydrogenation of the quinolinic moiety was also proven and can be responsible for the difficulties encountered during the recycling study.

Keywords

Metal nanoparticles, Asymmetric hydrogenation, Cyclodextrin, Cinchonidine

1. Introduction

Since the second half of the 20th century, asymmetric hydrogenation has always been a challenging research area [1,2]. Most of the efficient catalytic systems are based on the use of molecular metal catalysts with well-defined chiral ligands [3] or supported metal catalysts in the presence of a chiral modifier [4,5], which creates a crucial enantio-differentiating interaction between the substrate and the chiral modifier on the metallic surface. Among the numerous reviews concerning enantioselective hydrogenation, the most studied chiral modifiers are cinchona derived compounds with good to excellent enantiomeric excesses (*ee*) for metal-based catalytic systems [5]. Despite a large number of publications, the clear identification of the key parameters to get the highest *ee* seems to be difficult. Different parameters such as the solvent, the substrate, the metal - support interactions or the metal source can deeply influence the catalytic results in terms of enantioselectivity.

Solvent dispersed metal nanoparticles (NPs) have received considerable attention for the twenty past years especially in catalysis [6], because they provide a high surface area of catalytically active metal thanks to a large fraction of surface-exposed metal atoms and a high number of edges and defects. While providing long-term stability of the dispersed particles, the choice of a capping agent is critical as it helps to control the size and shape of the particles as well as the accessibility of active surface sites to the reactants. Moreover, in the case of asymmetric hydrogenation, a critical condition is to find the most advantageous interactions between the metal NP, the chiral modifier and the substrate.

To the best of our knowledge, only few metal nanocatalysts modified by chiral ligands and dispersed in organic or aqueous media have been described in the hydrogenation of prochiral molecules [7–12]. In aqueous medium, Roucoux group synthesized platinum nanoparticles stabilized by *N,N*-dimethyl-*N*-hexadecyl-*N*-(2-hydroxyethyl) ammonium chloride (HEA₁₆Cl) [9], known as an efficient metal NPs stabilizer [13]. This colloidal suspension was evaluated

in the ethyl pyruvate hydrogenation in the presence of cinchonidine and led to high enantiomeric excesses. To constrain the different parts of the catalyst to be close to each other, Roucoux has also described a series of optically active amphiphilic compounds as efficient stabilizers of rhodium NPs in water but low *ee* were obtained [14,15].

Among the water soluble capping agents, cyclodextrins [16], that are cyclic oligosaccharides composed of six (α -), seven (β -) or eight (γ -) α -D-glucopyranose units connected by α -(1,4)-linkage have proven to be effective stabilizers of metal NPs in water. They have also demonstrated their potential for catalytic applications in aqueous phase, such as for the hydrogenation of petro and biosourced substrates [17,18]. In particular, amino acid-functionalized cyclodextrins were used as chiral stabilizers of ruthenium nanoparticles dispersed in water for the asymmetric hydrogenation of methyl-2-acetamidoacrylate, ethyl pyruvate, acetophenone and *m*-methylanisole [19]. Promising results were obtained in terms of catalytic activity but no enantioselectivity was noticed.

Considering the best results with supported catalysts in the presence of a chiral modifier, a cinchonidine-functionalized cyclodextrin used as both NP stabilizer and chiral modifier was considered. We reported that cinchonidine-functionalized- β -cyclodextrin (β -CD-trz-Cin) could be used for the platinum nanoparticles synthesis in aqueous medium using sodium borohydride as reducing agent. Then, the catalytic activity of these obtained Pt NPs was evaluated in the hydrogenation of ethyl pyruvate at 30 °C under 40 bar of hydrogen. The recyclability study of these Pt NPs was also considered. Finally, NMR and MALDI-MS analyses were performed to understand this catalytic system.

2. Experimental Section

2.1. Chemicals and reagents

Native β -cyclodextrin, abbreviated as β -CD, was kindly supplied by Roquette Frères (Lestrem, France). All chemicals were purchased from Aldrich Chemicals or Acros Organics and were used without further purification. Chloroplatinic acid hexahydrate (38-40 wt% Pt) was supplied by Strem Chemicals.

2.2. Characterization techniques

Transmission Electron Microscopy (TEM) was performed on a Tecnai microscope (200 kV). A drop of the colloidal suspension was deposited onto a carbon coated copper grid. Metal particle size distributions have been determined from the measurement of around 200 particles found in arbitrarily chosen area of the images using ImageJ software. NMR spectra were recorded at 298 K on a Bruker Avance III HD 300 NanoBay spectrometer equipped with a 5 mm broadband probe BBFO with Z-gradients, operating at 7.05 T field strength at 300 MHz for ^1H nuclei. DMSO- D_6 (99.80 % isotopic purity) and D_2O (99.92 % isotopic purity) were purchased from Euriso-Top. Mass spectra were recorded on a MALDI-TOF/TOF Bruker Daltonics Ultraflex II in positive reflectron mode with 2,5-DHB as matrix.

2.3. Synthesis of water dispersed Pt NPs stabilized by cinchonidine-functionalized β -CD

In a typical experiment, the colloidal suspension was prepared as follows at ambient temperature. 12 mg of β -CD-trz-Cin (8 μmol) were dissolved in 5 mL of HPLC water. Besides this solution, 4 mg of H_2PtCl_6 hexahydrate (8 μmol) were diluted in 3 mL of water and were added to the previous solution. The mixture was kept under constant stirring at room

temperature for 30 minutes before the quick addition of 1.5 mg of sodium borohydride (0.04 mmol, 5 molar equivalents with respect to platinum) dispersed in 4 mL of HPLC water. The color of the reaction medium changes upon addition of NaBH₄ from yellow to dark brown due to the reduction of Pt (IV). The resulting colloidal dispersion was visually stable as shown by the absence of observed metal sedimentation after 18 hours of stirring at room temperature.

2.4. Catalytic test

All hydrogenation experiments have been performed using a Parker-Autoclave Engineers stainless steel autoclave containing a glass vessel which was charged with 6 mL of standard platinum colloidal suspension and 232 mg of ethyl pyruvate (2 mmol, 500 eq.). Hydrogen was fed to the system at constant pressure up to 40 bar. The mixture was heated up to 30 °C with a thermostated oil bath and stirred at 1000 rpm. The reaction was monitored by analyzing an aliquot of the reaction mixture after 1.5 h of reaction with a Shimadzu GC-2010 Plus gas chromatograph, equipped with a capillary column in polyethylene glycol (30 m x 0.25 mm x 0.25 μm) and a flame ionization detector using decane as an external standard. Enantiomeric excesses were determined with a Perkin Elmer Clarus 590 gas chromatograph, equipped with a capillary column CHIRALDEX β-CD (30 m × 0.25 mm × 0.12 μm) and a flame ionization detector.

2.5. Recyclability study

At the end of the reaction, all organic compounds were extracted using chloroform. After decantation and chloroform removal, the aqueous phase containing the catalyst was reused for another run by reloading with ethyl pyruvate and fed with hydrogen.

3. Results and Discussion

The synthesis of β -CD-trz-Cin has already been described in a previous publication [20]. Briefly, this compound was obtained by copper catalyzed coupling between 6^l-azido-6^l-deoxy- β -CD (β -CD-N₃) and *O*-propargyl cinchonidine in DMF (Figure 1).

< please insert Figure 1 >

Concerning the synthesis of the platinum NPs, the procedure is very similar to those previously reported by our team [21,22]. In short, the synthesis involves a one-step reduction of the platinum (IV) salt, in the presence of controlled amounts of β -CD-trz-Cin and an excess of sodium borohydride, in water and at room temperature. Contrary to our previous studies, the use of 10 molar equivalents of stabilizing agent with respect to platinum did not allow the reduction of the platinum precursor (no colour change of the solution during the reduction step and no Pt particles observed by TEM). This singular behaviour could be explained by the presence of the triazole group, which is known to interact strongly with the metal species.[23] Knowing that the solubility of β -CD-trz-Cin is very low (lower than 1 mg.mL⁻¹) and being sure that the cyclodextrin derivative is totally soluble [20], the best compromise was to work with a cyclodextrin/metal molar ratio of one, which was a sufficient but also a necessary amount to obtain Pt NPs. Several analyses were performed to characterize the platinum NPs in the liquid phase. First, we have checked by ¹H NMR if the cinchonidine-functionalized cyclodextrin structure (called **L**) was kept after the reduction step with sodium borohydride (Figure 2).

<please insert Figure 2>

The first ¹H NMR experiment (Figure 2a) was performed in DMSO-D₆. The obtained signals were consistent with those previously described in the literature for **L** [20]. To get a precise

assignment of the ethylenic methyne proton **c**, D₂O was added for the isotopic exchange of the cyclodextrin hydroxyl protons. This way, the NMR signal of the internal proton **c** of the vinyl group could also be clearly observed at 5.8 ppm (Figure 2b). After the addition of NaBH₄, reduction of the platinum precursor has occurred but changes were observed both in the ethylenic protons (4.8-6 ppm) and in the aliphatic protons regions (0.5-2 ppm). The **c** proton signal has disappeared and a triplet at 0.8 ppm (**b**¹) has grown, proving the reduction of the vinyl group (Figure 2c). The platinum NPs are finally not stabilized by β-CD-trz-Cin (named **L**), but by the reduced vinyl form (named **L**¹). The C=C double bond reduction during metal NPs synthesis by chemical reduction using sodium borohydride has already been observed.[21] The double bond reduction was confirmed by MALDI mass spectrometry as the signals of reduced β-CD-trz-Cin have been detected (see supporting information, Figure S8).

The existence and the morphology of Pt NPs stabilized by **L**¹ were then characterized by Transmission Electron Microscopy (Figure 3).

<please insert Figure 3>

According to the transmission electron micrograph at a magnification of × 200000 and to the size distribution, we observed that platinum NPs were spherical and assembled in non-ordered structure with a mean diameter of 2.3 nm ± 0.4 nm. This kind of dispersion has already been observed in previous studies concerning metal NPs stabilized by cyclodextrins [18].

The catalytic activity of the platinum colloidal suspension stabilized by **L**¹ was evaluated in the aqueous biphasic hydrogenation of ethyl pyruvate (Table 1). Catalytic tests were performed at 30 °C under 40 bar of hydrogen with a substrate/metal molar ratio of 500. The reaction was monitored by gas chromatography analyses. For comparison, control experiments were also carried out considering the same reaction conditions.

<please insert Table 1>

The use of **L**¹ (formed *in situ*, during the catalyst synthesis) appeared to be an efficient protective agent for the production of stable Pt colloidal suspension during the catalytic reaction (entry 1) and no trace of aggregation or aging of the particles was observed. The complete ethyl pyruvate conversion into ethyl lactate within 15 min was obtained with a good enantiomeric excess value of 63 % towards the (*R*)-ethyl lactate. To show the positive effect of this stabilizing agent, we have first checked if cinchonidine alone was able to stabilize Pt NPs in aqueous medium (entry 2). Under our concentration conditions (one molar equivalent of cinchonidine with respect to platinum), a total metal sedimentation has occurred after the reducing step.

To show the beneficial effect of the covalent link between the cyclodextrin and cinchonidine, the Pt NPs synthesis was performed using a physical mixture corresponding to **L** (β -CD-trz-CH₂OH and cinchonidine) (entry 3). Unfortunately, the resulting colloidal suspension was unstable. As in the case of cinchonidine alone, total metal sedimentation was observed.

We decided to change the synthesis procedure by first synthesizing Pt NPs stabilized with β -CD-trz-CH₂OH followed by the addition of cinchonidine, 24 h later (entry 4). However, this catalytic system was not stable during the hydrogenation reaction due to the platinum sedimentation in the bottom of the glass reactor. The enantiomeric excess did not exceed 15 %. This enantiomeric excess was essentially due to the cinchonidine ring, *ee* with Pt NPs stabilized just by β -CD-trz-CH₂OH being negligible (< 5%). All these controls emphasized the beneficial effect of the cyclodextrin-functionalized cinchonidine in terms of stability, catalytic activity but also enantioselectivity. The same experiments were performed with β -CD but led to unstable colloidal suspensions during the preparation step (entries 5 and 6).

The results obtained with the Pt NPs stabilized by **L**¹ were compared to those described in the literature with other cinchonidine-based Pt NPs, showing that the developed system gave relatively good values of activity and enantioselectivity in ethyl pyruvate hydrogenation (see supporting information, IV., Table S2).

The reusability of **L**¹ stabilized Pt NPs was further investigated keeping ethyl pyruvate as substrate (Figure 4), under the same catalytic conditions. After 15 minutes, products were extracted with chloroform and a second run could occur.

<please insert Figure 4>

According to the experiments, catalytic activity and enantiomeric excess both decreased as runs progressed. Please note that a small metal sedimentation was observed after the third run, that means a NPs agglomeration in the aqueous layer involved in runs 3, 4 and 5. Leading to black platinum visible to the naked eye, this colloidal suspension instability was thought to be directly responsible of the observed catalytic activity decrease. A Pt NPs leaching, which could also occur during the extraction of ethyl lactate and residual ethyl pyruvate after each run, seems less probable. Indeed, stirring each organic layer obtained along the recycling experiments with added ethyl pyruvate (1 mmol) and in the reaction conditions (30 °C, 40 bar of H₂), showed no evolution in the sample composition even after 24 h. To understand what could be the origin of the instability of the aqueous colloidal suspension, which seemed to also undergo an enantioselectivity decrease along the recycling experiments, ¹H NMR of the aqueous phase was performed after the fifth run in order to check if the structure of the stabilizing agent **L**¹ was kept. According to the ¹H NMR spectrum, the aromatic region (7-9 ppm) deeply changed (see supporting information, Figure S4).

To rationalize this data, the platinum NPs stabilized by **L**¹ were analyzed by ¹H NMR and MALDI spectroscopies, after being placed under catalytic conditions (40 bar of hydrogen, 30 °C) during different times (15, 30, 60 and 120 minutes) but without ethyl pyruvate. A blackening of the solution followed by a progressive metal sedimentation were observed with time. Moreover, NMR analyses (Figure 5) and MALDI experiments (see supporting information, III.) proved that the quinoline moiety of **L**¹ was hydrogenated with time in two steps: benzene ring hydrogenation and then pyridine ring hydrogenation.

<please insert Figure 5>

These successive hydrogenations of the cyclodextrin graft leading to the transformation of **L**¹ to **L**³ and then to **L**⁶ can be quantified by the NMR spectra integrations (see supporting information, II.5) showing for example that, after 1 hour under 40 bar of H₂ and without ethyl pyruvate, **L**¹ has led to 55 % of **L**³ and 45 % of **L**⁶ (Figure 6).

<please insert Figure 6>

The same yields of 55 % and 45 % for **L**³ and **L**⁶ were estimated after five runs of Pt_**L**¹ NPs catalyzed ethyl pyruvate hydrogenation, showing that the cyclodextrin graft hydrogenation was a little bit slower in the presence of the ethyl pyruvate substrate as a competitor (see supporting information, Figure S5). Nevertheless, this denaturation of the chiral inductor graft is probably responsible for the less efficient both stabilizing and enantioselective properties observed with time. Contrary to the quinoline part, the triazole ring was perfectly stable in these hydrogenation conditions. This result is consistent with a perfect integrity of β-CD-trz-CH₂OH under hydrogen at 30 °C (see supporting information, Figure S7).

4. Conclusion

In this paper, we showed that a cinchonidine-functionalized β -cyclodextrin synthesized by crosslinking mono azido- β -CD with *O*-propargyl cinchonidine was a good candidate for the synthesis of catalytically active platinum nanoparticles for the asymmetric hydrogenation of ethyl pyruvate in water. The chemical reduction of Pt (IV) species by sodium borohydride provided stable Pt colloidal suspensions organized into non-ordered superstructures with narrow size distributions. Control experiments have clearly shown the beneficial effect of the covalently linkage between cyclodextrin and cinchonidine. The platinum NPs were catalytically active towards ethyl pyruvate hydrogenation, with 63 % of enantiomeric excess. Nevertheless, the recovery and the recycling of the platinum NPs were difficult to realize, due to the instability of the stabilizing agent in presence of Pt NPs under high hydrogen pressure. Other metals are under investigation to avoid the aromatic reduction.

Acknowledgements

The TEM facility in Lille (France) is supported by the Conseil Regional des Hauts de France, and the European Regional Development Fund (ERDF). The authors are grateful to Dr. Ahmed Addad (UMET, University of Lille 1) for technical assistance in TEM measurements. We thank Dr. Nicolas Kania and D. Prévost for the technical assistance and Dr. Jérémy Ternel for NMR spectroscopy experiments. We also thank Johan Hachani (Plateau technique de protéomique et de spectrométrie de masse de l'Université d'Artois) for his help with mass spectrometry analysis.

References

- [1] H.-U. Blaser, Heterogeneous catalysis for fine chemicals production, *Catal. Today*. 60 (2000) 161–165. [https://doi.org/10.1016/S0920-5861\(00\)00332-1](https://doi.org/10.1016/S0920-5861(00)00332-1).
- [2] H. Blaser, C. Malan, B. Pugin, F. Spindler, M. Studer, Selective Hydrogenation for Fine Chemicals: Recent Trends and New Developments, *Adv. Synth. Catal.* 345 (2003) 103–151. [10.1002/adsc.200390000](https://doi.org/10.1002/adsc.200390000).
- [3] W. Zhang, Y. Chi, X. Zhang, Developing Chiral Ligands for Asymmetric Hydrogenation, *Acc. Chem. Res.* 40 (2007) 1278–1290. <https://doi.org/10.1021/ar7000028>.
- [4] F. Meemken, A. Baiker, Recent Progress in Heterogeneous Asymmetric Hydrogenation of C = O and C = C Bonds on Supported Noble Metal Catalysts, *Chem. Rev.* 117 (2017) 11522. [10.1021/acs.chemrev.7b00272](https://doi.org/10.1021/acs.chemrev.7b00272).
- [5] M. Studer, H.U. Blaser, C. Exner, Enantioselective Hydrogenation Using Heterogeneous Modified Catalysts: An Update, *Adv. Synth. Catal.* 345 (2003) 45–65. <https://doi.org/10.1002/adsc.200390029>.
- [6] A. Roucoux, J. Schulz, H. Patin, Reduced Transition Metal Colloids: A Novel Family of Reusable Catalysts?, *Chem. Rev.* 102 (2002) 3757–3778. <https://doi.org/10.1021/cr010350j>.
- [7] H. Bönemann, G.A. Braun, Enantioselective Hydrogenations on Platinum Colloids, *Angew. Chemie Int. Ed. English.* 35 (1996) 1992–1995. [https://doi.org/https://doi.org/10.1002/anie.199619921](https://doi.org/10.1002/anie.199619921).
- [8] X. Zuo, H. Liu, D. Guo, X. Yang, Enantioselective hydrogenation of pyruvates over polymer-stabilized and supported platinum nanoclusters, *Tetrahedron*. 55 (1999) 7787–7804. [https://doi.org/https://doi.org/10.1016/S0040-4020\(99\)00415-9](https://doi.org/https://doi.org/10.1016/S0040-4020(99)00415-9).

- [9] V. Mévellec, C. Mattioda, J. Schulz, J.-P. Rolland, A. Roucoux, Enantioselective hydrogenation of ethyl pyruvate in biphasic liquid–liquid media by reusable surfactant-stabilized aqueous suspensions of platinum nanoparticles, *J. Catal.* 225 (2004) 1–6. <https://doi.org/https://doi.org/10.1016/j.jcat.2004.03.017>.
- [10] J. Keilitz, S. Nowag, J.-D. Marty, R. Haag, Chirally Modified Platinum Nanoparticles Stabilized by Dendritic Core-Multishell Architectures for the Asymmetric Hydrogenation of Ethyl Pyruvate, *Adv. Synth. Catal.* 352 (2010) 1503–1511. <https://doi.org/https://doi.org/10.1002/adsc.201000128>.
- [11] F. Kirby, C. Moreno-Marrodan, Z. Baán, B.F. Bleeker, P. Barbaro, P.H. Berben, P.T. Witte, NanoSelect Precious Metal Catalysts and their Use in Asymmetric Heterogeneous Catalysis, *ChemCatChem.* 6 (2014) 2904–2909. <https://doi.org/https://doi.org/10.1002/cctc.201402310>.
- [12] W. Yu, L.-L. Lou, K. Yu, S. Li, Y. Shi, S. Liu, Pt nanoparticles stabilized by thermosensitive polymer as effective and recyclable catalysts for the asymmetric hydrogenation of ethyl pyruvate, *RSC Adv.* 6 (2016) 52500–52508. <https://doi.org/10.1039/C6RA06277F>.
- [13] J. Schulz, S. Levigne, A. Roucoux, H. Patin, A. Nowicki, V. Le Boulaire, A. Roucoux, Aqueous Rhodium Colloidal Suspension in Reduction of Arene Derivatives in Biphasic System: a Significant Physico-chemical Role of Surfactant Concentration on Catalytic Activity, *Adv. Synth. Catal.* 349 (2007) 266–269. <https://doi.org/10.1002/adsc.200700208>.
- [14] E. Guyonnet Bilé, A. Denicourt-Nowicki, R. Sassine, P. Beaunier, F. Launay, A. Roucoux, N-Methylephedrium Salts as Chiral Surfactants for Asymmetric Hydrogenation in Neat Water with Rhodium(0) Nanocatalysts, *ChemSusChem.* 3

- (2010) 1276–1279. <https://doi.org/10.1002/cssc.201000206>.
- [15] E. Guyonnet Bilé, E. Cortelazzo-Polisini, A. Denicourt-Nowicki, R. Sassine, F. Launay, A. Roucoux, Chiral Ammonium-Capped Rhodium(0) Nanocatalysts: Synthesis, Characterization, and Advances in Asymmetric Hydrogenation in Neat Water, *ChemSusChem*. 5 (2012) 91–101. <https://doi.org/10.1002/cssc.201100364>.
- [16] G. Crini, Review: A History of Cyclodextrins, *Chem. Rev.* 114 (2014) 10940–10975. <https://doi.org/10.1021/cr500081p>.
- [17] R. Herbois, S. Noël, B. Léger, L. Bai, A. Roucoux, E. Monflier, A. Ponchel, Cyclodextrins as growth controlling agents for enhancing the catalytic activity of PVP-stabilized Ru(0) nanoparticles, *Chem. Commun.* 48 (2012). <https://doi.org/10.1039/c2cc17355g>.
- [18] A. Nowicki, Y. Zhang, B. Leger, J.-P. Rolland, H. Bricout, E. Monflier, A. Roucoux, Supramolecular shuttle and protective agent: a multiple role of methylated cyclodextrins in the chemoselective hydrogenation of benzene derivatives with ruthenium nanoparticles, *Chem. Commun.* 42 (2006) 296–298. <http://dx.doi.org/10.1039/B512838B>.
- [19] N.T.T. Chau, J.-P. Guégan, S. Menuel, M. Guerrero, F. Hapiot, E. Monflier, K. Philippot, A. Denicourt-Nowicki, A. Roucoux, β -Cyclodextrins grafted with chiral amino acids: A promising supramolecular stabilizer of nanoparticles for asymmetric hydrogenation?, *Appl. Catal. A Gen.* 467 (2013) 497–503. <https://doi.org/10.1016/j.apcata.2013.08.011> (accessed November 6, 2013).
- [20] I.C. Tichá, S. Hybelbauerová, J. Jindřich, New α - and β -cyclodextrin derivatives with cinchona alkaloids used in asymmetric organocatalytic reactions, *Beilstein J. Org.*

Chem. 15 (2019) 830–839. <https://doi.org/10.3762/bjoc.15.80>.

- [21] R. Herbois, S. Noël, B. Léger, S. Tilloy, S. Menuel, A. Addad, B. Martel, A. Ponchel, E. Monflier, Ruthenium-containing β -cyclodextrin polymer globules for the catalytic hydrogenation of biomass-derived furanic compounds, *Green Chem.* 17 (2015) 2444–2454. <https://doi.org/10.1039/C5GC00005J>.
- [22] S. Noël, D. Bourbiaux, N. Tabary, A. Ponchel, B. Martel, E. Monflier, B. Léger, Acid-tolerant cyclodextrin-based ruthenium nanoparticles for the hydrogenation of unsaturated compounds in water, *Catal. Sci. Technol.* 7 (2017). <https://doi.org/10.1039/c7cy01687e>.
- [23] D. Astruc, L.Y. Liang, A. Rapakousiou, J. Ruiz, Click Dendrimers and Triazole-Related Aspects: Catalysts, Mechanism, Synthesis, and Functions. A Bridge between Dendritic Architectures and Nanomaterials, *Acc. Chem. Res.* 45 (2012) 630. <https://doi/10.1021/ar200235m>.

Figure captions

- Figure 1** Synthesis of β -CD-trz-Cin by click chemistry between azido- β -CD and propargyl cinchonidine.
- Figure 2** ^1H NMR spectra of (a) β -CD-trz-Cin in $\text{DMSO-}D_6$, (b) β -CD-trz-Cin in $\text{DMSO-}D_6/\text{D}_2\text{O}:70/30$, (c) β -CD-trz-Cin after 18 h at RT in water with H_2PtCl_6 and NaBH_4 ($\text{DMSO-}D_6/\text{D}_2\text{O}:70/30$).
- Figure 3** Transmission electron micrograph at a magnification of $\times 200000$ and its corresponding size distribution of $\text{Pt-}L^1$ NPs.
- Figure 4** Reusability of $\text{Pt-}L^1$ in the hydrogenation of ethyl pyruvate. Reaction conditions: Pt (4 μmol), ethyl pyruvate (2 mmol), hydrogen pressure (40 bar), temperature (30 $^\circ\text{C}$), stirring rate (1000 rpm), water (6 mL), reaction time (15 min).
- Figure 5** ^1H NMR spectrum of (a) β -CD-trz-Cin after 18 h with H_2PtCl_6 and NaBH_4 at RT and then after (b) 15 min, (c) 30 min, (d) 60 min and (e) 120 min at 30 $^\circ\text{C}$ under 40 bar of H_2 (DMSO-

D₆/D₂O: 70/30; 300 MHz).

Figure 6 Platinum catalyzed transformation of **L**¹ into **L**³ and then **L**⁶ with time under 40 bar of hydrogen, at 30°C.

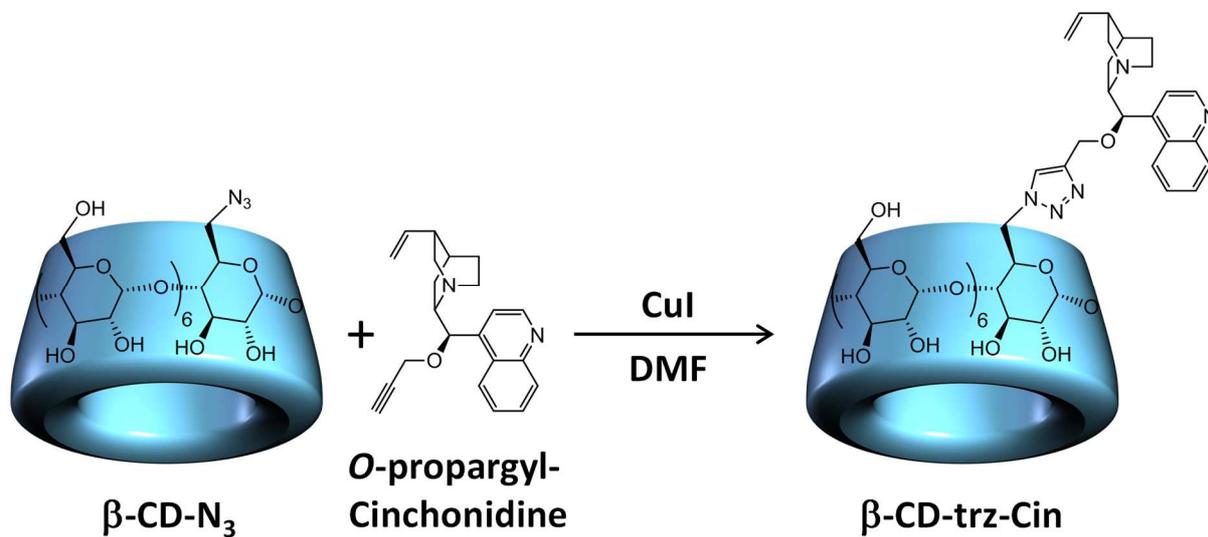


Figure 1. Synthesis of β -CD-trz-Cin by click chemistry between azido- β -CD and propargyl cinchonidine.

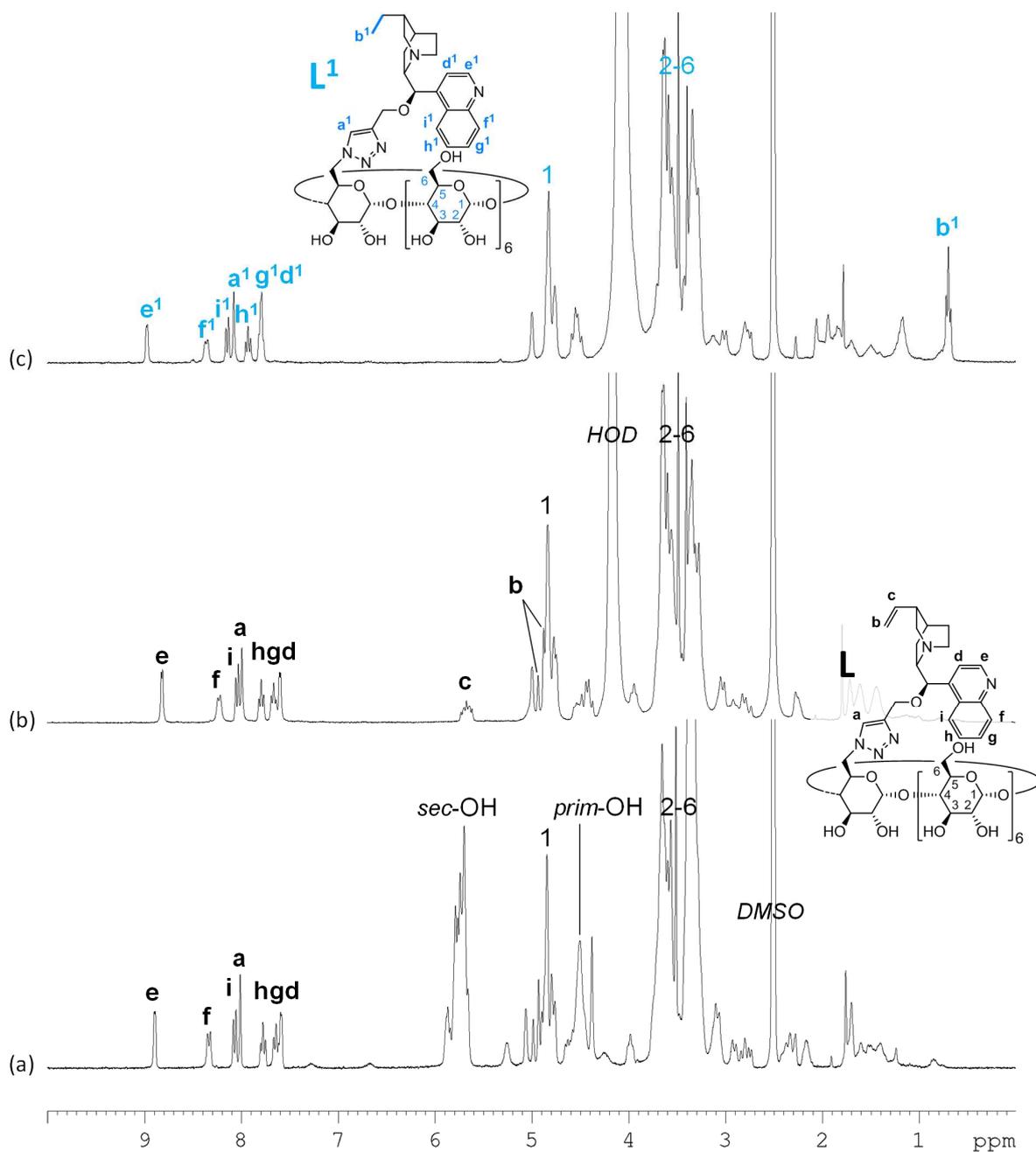


Figure 2. ^1H NMR spectra of (a) β -CD-trz-Cin in $\text{DMSO-}D_6$, (b) β -CD-trz-Cin in $\text{DMSO-}D_6/D_2O$: 70/30, (c) β -CD-trz-Cin after 18 h at RT in water with H_2PtCl_6 and NaBH_4 ($\text{DMSO-}D_6/D_2O$: 70/30).

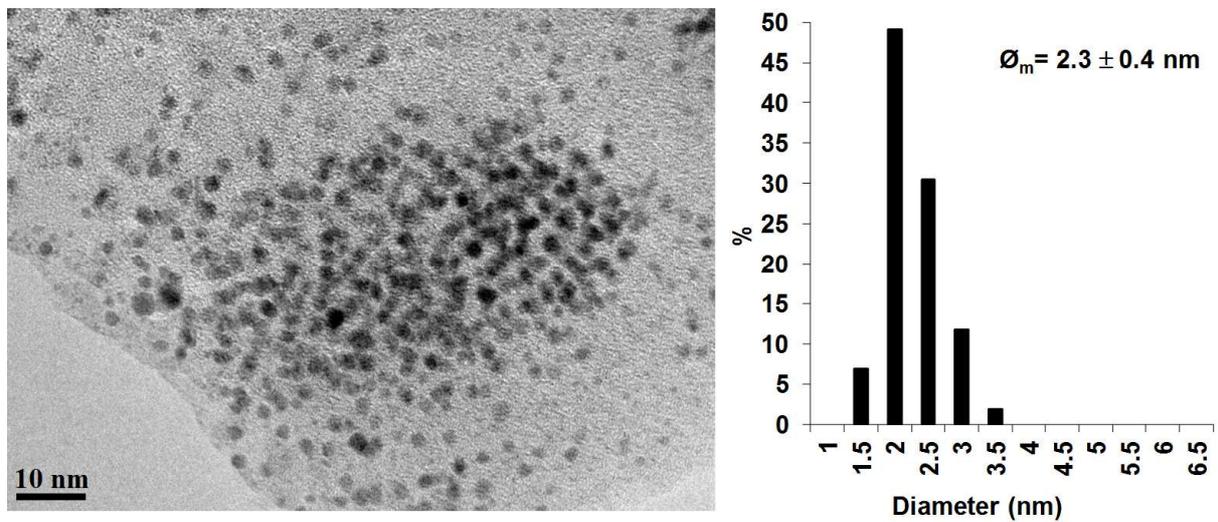


Figure 3. Transmission electron micrograph at a magnification of $\times 200000$ and its corresponding size distribution of Pt_L¹ NPs.

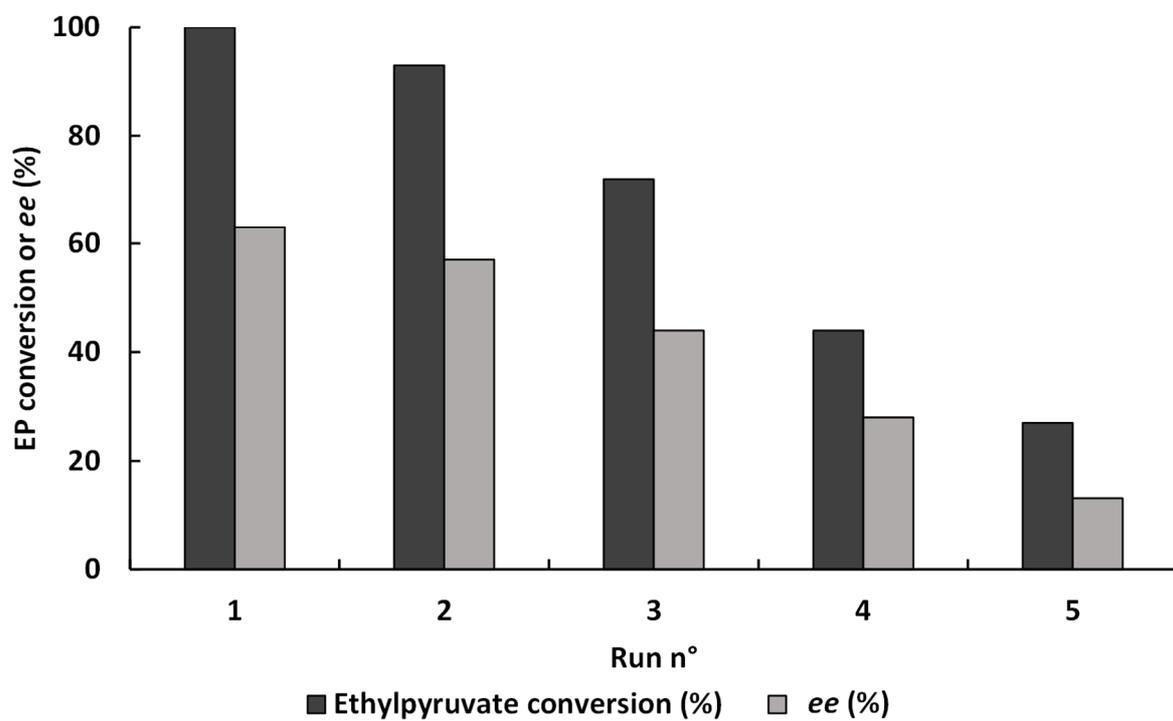


Figure 4. Reusability of Pt_L¹ in the hydrogenation of ethyl pyruvate. Reaction conditions: Pt (4 μ mol), ethyl pyruvate (2 mmol), hydrogen pressure (40 bar), temperature (30 °C), stirring rate (1000 rpm), water (6 mL), reaction time (15 min).

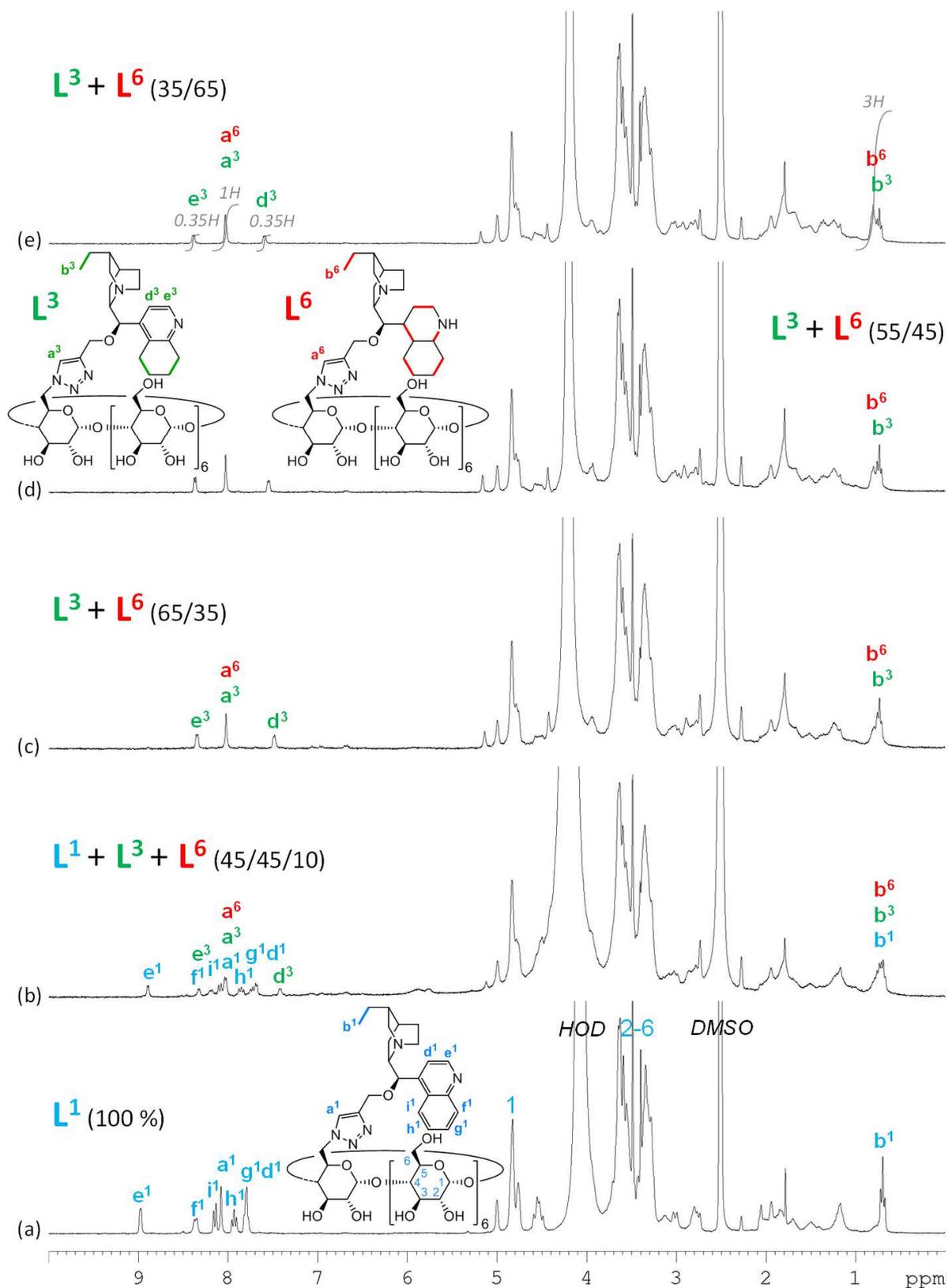


Figure 5. $^1\text{H-NMR}$ spectrum of (a) $\beta\text{-CD-trz-Cin}$ after 18 h with H_2PtCl_6 and NaBH_4 at RT and then after (b) 15 min, (c) 30 min, (d) 60 min and (e) 120 min at 30 $^\circ\text{C}$ under 40 bar of H_2 ($\text{DMSO-D}_6/\text{D}_2\text{O}$: 70/30; 300 MHz).

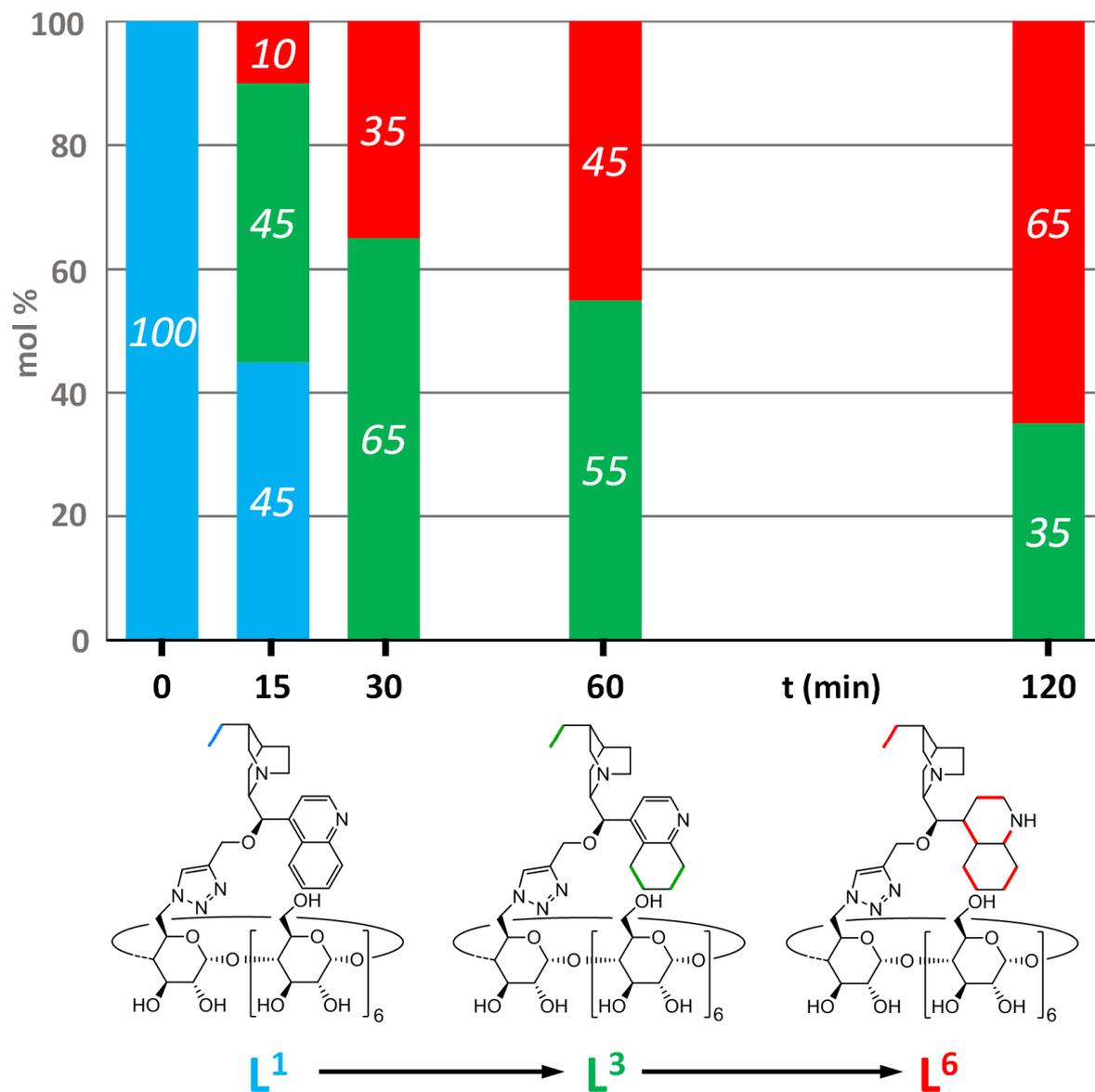
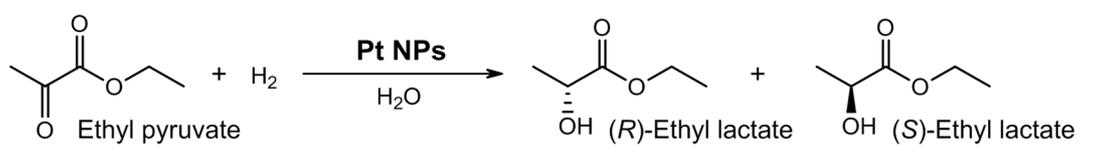


Figure 6. Platinum catalyzed transformation of L¹ into L³ and then L⁶ with time under 40 bar of hydrogen, at 30°C.

Table captions

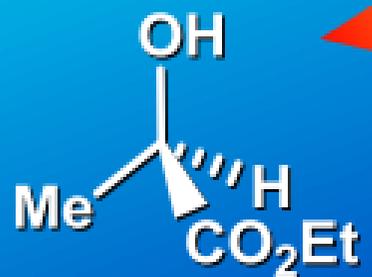
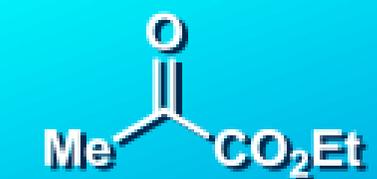
Table 1. Hydrogenation of ethyl pyruvate in the presence of Pt NPs^[a].



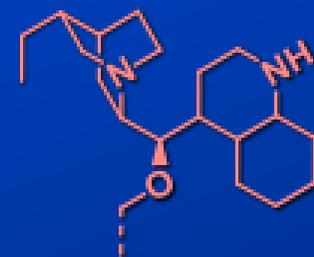
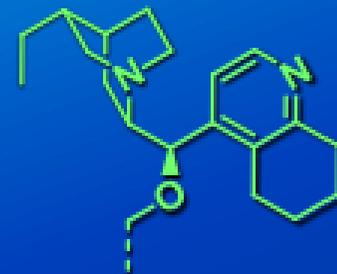
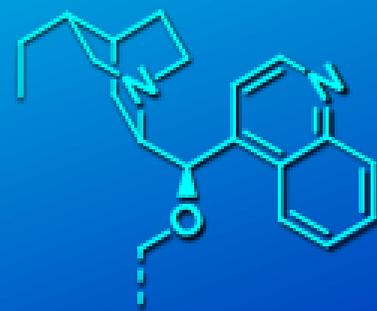
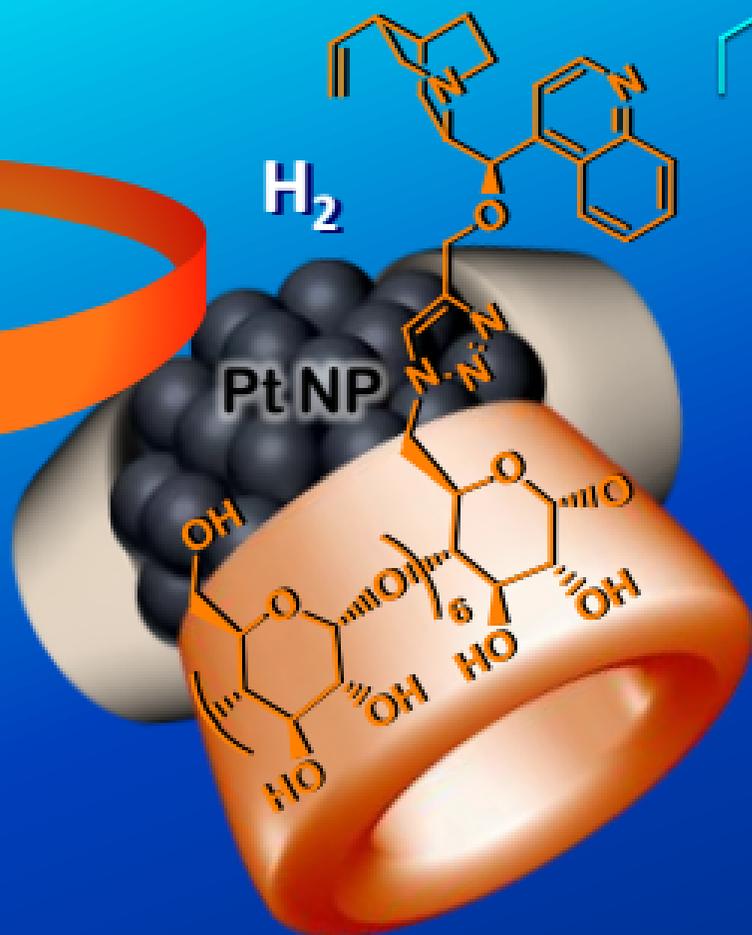
Ethyl pyruvate + H₂ $\xrightarrow[\text{H}_2\text{O}]{\text{Pt NPs}}$ (R)-Ethyl lactate + (S)-Ethyl lactate

Entry	Stabilizer	NPs stability		Conv. [%] ^[b]	<i>ee</i> [%] ^[b,c]
		<i>before catalysis</i>	<i>after catalysis</i>		
1	L ¹	Yes	Yes	100	63(<i>R</i>)
2 ^[d]	Cinchonidine (CN)	No	-	-	-
3 ^[e]	β-CD-trz-CH ₂ OH + CN	No	-	-	-
4 ^[f]	β-CD-trz-CH ₂ OH + CN	Yes	No	38	15(<i>R</i>)
5 ^[e]	β-CD + CN	No	-	-	-
6 ^[f]	β-CD + CN	No	-	-	-

[a] Reaction conditions: Pt (4 μmol), stabilizer (4 μmol), ethyl pyruvate (2 mmol), hydrogen pressure (40 bar), temperature (30 °C), stirring rate (1000 rpm), 6 mL water, reaction time (15 min). [b] conversion and enantiomeric excess were determined by GC analysis. [c] predominant configuration in brackets. [d] CN (4 μmol). [e] prepared by mixing cyclodextrin (4 μmol) and CN (4 μmol). [f] Pt NPs stabilized by cyclodextrin (4 μmol), followed by addition of CN (4 μmol), 24 h after the reducing step.



63% of *ee*



Cinchonidine-functionalized
 β -cyclodextrin

Water