Journal of Molecular Catalysis A: Chemical 366 (2013) 17–21

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

The first example of asymmetric hydrogenation of imines with $Co_2(CO)_8$/(R)-BINAP as catalytic precursor

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ARTICLE INFO

Article history:
Received 28 May 2012
Received in revised form 20 August 2012
Accepted 21 August 2012
Available online 30 August 2012

Keywords:
Phosphine ligand
Dicobalt octacarbonyl
Asymmetric hydrogenation
Imines
Cobalt catalysis

ABSTRACT

The first example of asymmetric hydrogenation of imines using $Co_2(CO)_8$/(R)-BINAP/H_2/CO system was developed. The reaction conditions were screened with a wide range of N-aryl benzophenone ketimines, obtaining products with excellent yields and good enantiomeric excess. Moreover, a pathway is suggested based on the isolation and characterization of several catalyst intermediates.

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1. Introduction

Asymmetric catalysis is one of the most important tools for the synthesis of enantiopure chemicals [1], due to its high atom economy when compared to methods based on the resolution of racemates. In this context, the enantioselective reduction of prochiral ketimines is among the most reliable and efficient approaches to obtain the corresponding optically active amines [2–4], which are themselves found in various natural or medicinal compounds [5–8]. Likewise, several methodologies have been developed for the enantioselective reduction of imines [9–28], the asymmetric hydrogenation of functionalized imines such as acyclic aromatic N-aryl imines [29], α-fluorinated iminoesters [30,31] and acyclic imines [32], with a variety of complexes of Ir [32,33], Ru [34], Rh [19] and organocatalysts [35,36] have been employed in asymmetric hydrogenations and/or transfer hydrogenations of imines. Noteworthy, $Co_2(CO)_8$/modified phosphine complexes have never been used as catalysts in asymmetric hydrogenation of imines, even though, phosphine dicobalt octacarbonyl derivatives play an important role as catalytic promotors in other organic transformations, for example: hydroformylation of alkenes (also known as oxo process discovered in 1938 by Otto Roelen) [37,38], amidocarbonylation reaction [39,40], synthesis of quinolines [41], synthesis of β-lactams [42] and the Pauson–Khand reaction (PKR) [43–45]. Overall, the last reaction was applied in the synthesis of asymmetric 2-cyclopentanones using $Co_2(CO)_8$ modified with chiral bidentade phosphines as catalytic precursor. Furthermore, in 2003, Gibson's group studied the PKR mechanism of $Co_2(CO)_8$/BINAP system using the synthesis of bicyclic cyclopentenones; based on their results (they reported yields above 80% and ee up to 70%), postulated the existence of (BINAP)(CO)Co-μ-$(CO)_2$-$Co(CO)_3$ as catalyst precursor [46] and the isolation of a cobalt hydride (BINAP)$(CO)_2$CoH [47]. Therefore, we became interested in using of this hydride as a precursor in the reduction of prochiral imines, leading us to the first example of the catalytic asymmetric hydrogenation of imines with $Co_2(CO)_8$/(R)-BINAP.

2. Experimental

2.1. General

All reactions and manipulations were carried out under nitrogen atmosphere by using Schlenk-type techniques. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were obtained on a JEOL GX300 Bruker-Avance 300, Varian Unity 300 (300, 75 and 121 MHz respectively) spectrometers in $CDCl_3$ as solvent at 25 °C. IR spectra were recorded on a Nicolet FTIR Magna 750 spectrophotometer. Optical rotations were measured on a Perkin–Elmer 343 spectropolarimeter. Mass spectra were obtained using a JEOL JMS-SX102A instrument with m-nitrobenzyl alcohol as the matrix (FAB^+ mode). Elemental analyses for some compounds were obtained on an Elemental Analyzer CE-440. HPLC analyses were performed on a Hewlett Packard 1100 system with UV-DAD. Separations were achieved on a

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http://dx.doi.org/10.1016/j.molcata.2012.08.019

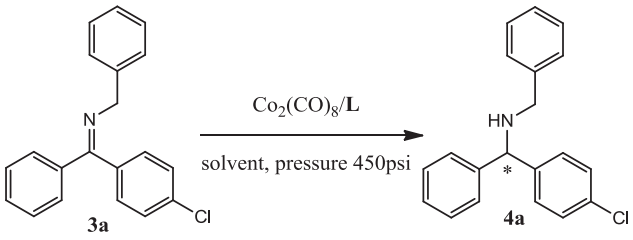
Daicel Chiracel OD-H (25 mm × 4.6 mm) column. X-ray determination was collected on a Bruker SMART APEX CCD area diffractometer by the ω-scan method.

2.2. Hydrogenation of imines

Imines were synthesized according to a literature procedure [48]. Typical procedure: in a Schlenk tube under nitrogen atmosphere, a solution of imine (100 mg), $Co_2(CO)_8$ (1 mol%) and (R)-BINAP (2 mol%) in THF (10 mL) was transferred to a 45 mL stainless Steel Parr vessel which was pressurized at 450 psi with a H_2/CO mixture in a 1/3 ratio. The reactor was placed in a preheated oil bath at 120° with magnetic stirring for 15 h. The reaction mixture was purified by column chromatography using hexane and ethyl acetate as eluents.

3. Results and discussion

In our preliminary studies, we determined the influence of solvent, temperature, and carbon monoxide pressure, in the hydrogenation of imine **3a** (Eq. (1)) with $Co_2(CO)_8$/*rac*-BINAP (Table 1). The reduction of **3a** was not observed when working only with hydrogen (H_2) (entry 1), however, in the presence of CO/H_2 mixtures (3:1) (entries 2–4 and 7) good yields were obtained, behavior that suggests the stabilization of the catalytic species by CO partial pressure [40].



(1)

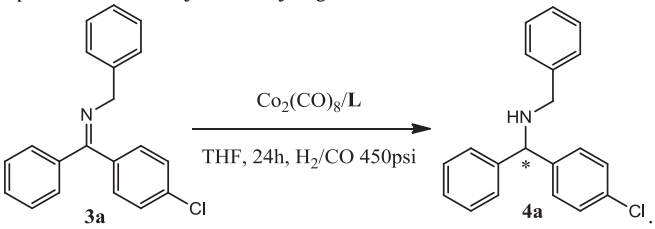
At room temperature, the hydrogenation product was not observed (entry 5) but, a temperature increase (120 °C) favored conversion and reaction yields (entries 4 and 6). The use of a coordinating solvent (THF) led to the best enantiomeric excess (95%ee) (entry 11), that contrasts with lower values obtained when carrying out the reaction in other solvents such as: toluene (67%ee), benzene (75%ee) and methylene chloride (52%ee) (entries 8–10).

Table 1
Effect of the H_2/CO ratio, solvent and temperature in hydrogenation of imine **3a**.[a]

Entry	Temperature (°C)	H_2/CO ratio	Yields (%)[b]	ee%[g]
1	120	1/0	0	0
2	120	1/1	0	0
3	120	1/2	0	0
4	120	1/3	87	0
5	25	1/3	0	0
6	100	1/3	20	0
7	120	1/4	73	0
8[c]	120	1/3	91	67
9[d]	120	1/3	75	75
10[e]	120	1/3	80	52
11[f]	120	1/3	86	95

[a] Reaction time 24 h and 450 psi pressure, 100 mg of imine **3a**, 5 mol% $Co_2(CO)_8$/*rac*-BINAP (1/2) and dry tetrahydrofuran (THF, 10 mL) as solvent.
[b] Isolated yield.
[c] The reaction was carried out in dry toluene (10 mL) as solvent and (R)-BINAP.
[d] The reaction was carried out in dry benzene (10 mL) as solvent and (R)-BINAP.
[e] The reaction was carried out in dry methylene chloride (10 mL) as solvent and (R)-BINAP.
[f] The reaction was carried out in dry THF as solvent and (R)-BINAP.
[g] Determined by HPLC.

Table 2
Optimization of the asymmetric hydrogenation of imine **3a**.[a]

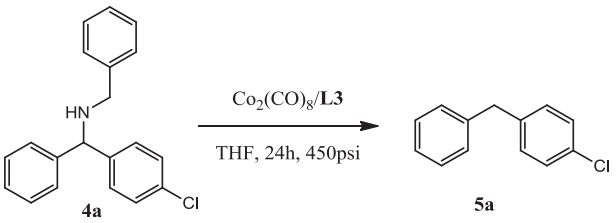


Entry	$Co_2(CO)_8$ (mol%)	Ligand	Yield (%)[b]	ee (%)[c]
1	5	**L1**	31	–
2	2	**L1**	30	–
3	5	**L2**	79	–
4	3	**L2**	80	–
5	2	**L2**	79	–
6	1	**L2**	81	–
7	1	**L3**	86	93
8	1	**L4**	83	53
9	1	**L5**	40	5
10	1	**L6**	34	1
11[d]	1	**L3**	89	92
12[e]	1	**L3**	95	93
13[f]	1	**L3**	82	90
14[g]	1	**L3**	95	63

[a] Reaction conditions: imine **3a** (100 mg), 1 mol% $Co_2(CO)_8$/ligand (1/2) in dry THF (10 mL), 24 h, 450 psi with a 1/3 ratio (H_2/CO), ligand: PPh_3 **L1**, *rac*-BINAP **L2**, (R)-BINAP **L3**, (R)-Tol-BINAP **L4**, (S-S)-Me-DUPHOS **L5**, (S,S)-DIOP **L6**.
[b] Isolated yield.
[c] Determined by HPLC.
[d] 20 h.
[e] 15 h.
[f] 12 h.
[g] $Co_2(CO)_8$/ligand (ratio: 1/1), 15 h.

Our initial evaluation began with hydrogenation of imine **3a** as the model substrate, finding an optimal H_2/CO ratio (1:3) in THF. Afterwards, we tested the influence of different monodentate and bidentate phosphine ligands in the conversion yields; the results are summarized in Table 2.

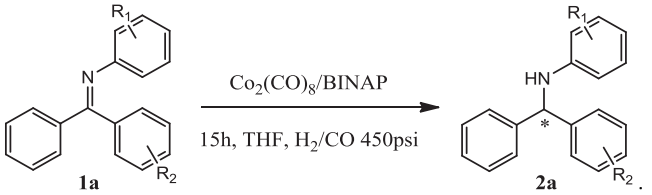
The use of monophosphine ligand **L1** resulted in poor yields (entries 1 and 2), unlike the biphosphine ligands **L2**–**L6**, we found that low catalyst loading (1%) did not affect the conversion of **3a** (entries 3–6). However, low yields were obtained when using Me-DUPHOS **L5** or DIOP **L6** ligands (entries 9 and 10), compared to those observed for **L4** (entry 8) and (R)-BINAP **L3**, which achieved the best result (entry 7). After 24 h we found in this reaction a lower concentration of the by-product **5a** (less than 6%), which was isolated and fully characterized (Eq. (2)), same results were obtained using the fluorinated imine **2b** as substrate in catalytic amounts of $Co_2(CO)_8$/**L3** (1 mol%). Moreover, when we used previously prepared amine **4a** in the same reaction conditions, we found again the product **5a** (25%). Finally when this last reaction was carried out in the absence of $Co_2(CO)_8$/**L3** we did not find by-product **5a**. This by-product was not formed when the reaction time was reduced to 15 h (entries 11–13).



(2)

Noteworthy, the use of an equimolar mixture of $CO_2(CO)_8$/ligand resulted in good reaction yield but low enantioselectivity (entry 14), this lack of selectivity could be related to the existence of two hydride species, $HCo(CO)_4$ and $HCo(CO)_2$–BINAP

Table 3
Asymmetric hydrogenation of imines from substituted anilines.[a]



Entry	R_1	R_2	Product	Yield (%)[b]	ee (%)[c]
1	4-Me	4-Cl	**2a**	98	81
2	4-Me	4-F	**2b**	96	78
3	4-MeO	4-Cl	**2c**	99	83
4	4-MeO	4-F	**2d**	97	70
5	2-MeO	4-Cl	**2e**	98	7
6	3-Cl	4-Cl	**2f**	98	4
7	3-Cl	4-F	**2g**	94	4
8	3-Cl	4-Me	**2h**	95	91

[a] Reaction conditions: 100 mg of imine, 1 mol% $Co_2(CO)_8$/(R)-BINAP (1/2), dry THF (10 mL), 15 h, 450 psi with a 1/3 ratio (H_2/CO).
[b] Isolated yield.
[c] Determined by HPLC.

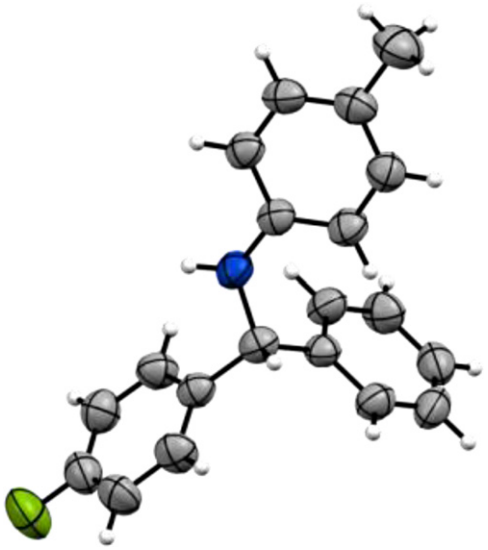
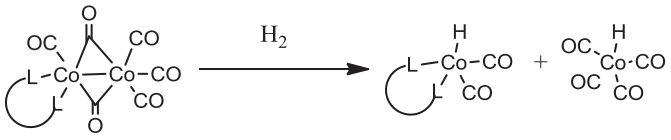


Fig. 1. Crystallographic structure of compound **2b** [49].

(Eq. (3)), which are competing in the hydrogenation step.



(3)

Under the optimized reaction conditions [$Co_2(CO)_8$/(R)-BINAP, THF, 15 h, H_2/CO (1:3) 450 psi], a wide variety of imines were tested to examine the reaction scope, starting with the synthesis of imines derived from anilines with different substituents. Thus, the presence of different arylic groups attached to the nitrogen atom in the imine can be tolerated with excellent yields (entries 1–8, 94–98%), as shown in Table 3.

These substrates indicate a substituent effect on enantioselectivity, thus, the presence of *p*-Cl or *p*-F substituents on the benzophenone moiety and *p*-Me or *p*-MeO groups on the amine moiety, resulted in good enantioselectivities (entries 1–4, 70–83%ee), but a lower value was obtained when *o*-MeO was substituted on the aromatic ring in R_1 (entry 5, 7%ee). The reduction of enantioselectivity may be attributed to the steric hindrance of the *ortho* substituent in the substrate. Furthermore, the inclusion of a *m*-Cl substituent in the R_1 resulted in low enantioselectivity (entries 6 and 7, 4%ee), however, the introduction of a *p*-methyl group on the aromatic ring in R_2 led to an increase in enantioselectivity (entry 8, 91%ee). In this context, we were able to determine the structure of amine **2b** by X-ray diffraction studies (Fig. 1).

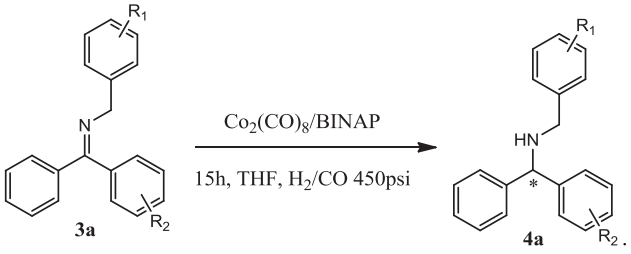
This methodology was also applied to the asymmetric hydrogenation of imines from benzylamines derivatives. The first attempts resulted in excellent yields and good enantiomeric excesses; the results are shown in Table 4.

As mentioned before, the conversion of all substrates resulted in excellent yields (93–98%), although, the influence of the substituents affected the enantiomeric excess. Thus, the presence of *p*-Cl, *p*-F or *p*-Me groups on the benzophenone moiety gave excellent enantioselectivities (entries 1–3, 73–95%ee), meanwhile, when R_1 is a *methyl* group, slightly higher enantioselectivities were obtained (entries 4–6, 96–99%ee). The variation of the substituent attached to the benzylamine moiety for *p*-Cl, *p*-CF_3 or *m*-CF_3 groups resulted in a negative effect on the enantioselectivities, which may be ascribed to both steric and electronic effects (entries 7–9, 41–72%ee). Moderated 36–58%ee were achieved with R_1 = *m*-F or *para* and *meta* CF_3 groups in conjunction with *p*-F and *p*-Cl on the benzophenone moiety (entries 10–13, 36–58%ee). Noteworthy, the *methyl* group on the aromatic ring in R_1 or R_2 leads again to an increase in enantioselectivity (entries 4–6 and 9).

Regarding the pathway of this reaction, we have developed several stoichiometric experiments and we found the species configuring the equilibrium shown in Scheme 1.

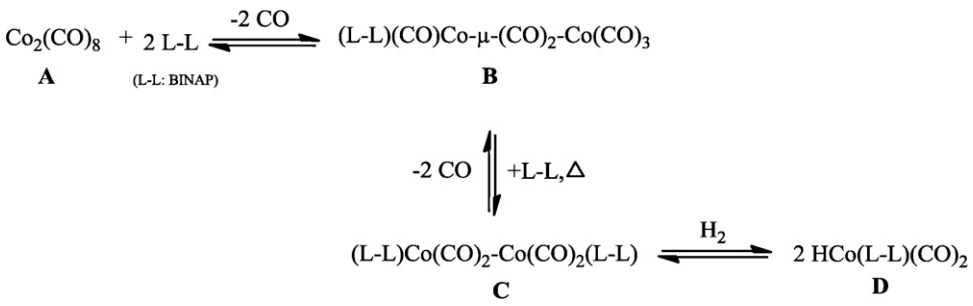
The reaction of $Co_2(CO)_8$ **A** with BINAP at room temperature in a stoichiometric 1:2 ratio results in the formation of **B** (Scheme 1) as a brown powder compound in good yield (91% respect to $Co_2(CO)_8$). Red crystals of **B** (this compound crystallizes with a THF molecule), suitable for X-ray studies, were grown from slowly diffusion of

Table 4
Asymmetric hydrogenation of imines from substituted benzylamines.[a]



Entry	R_1	R_2	Product	Yield (%)[b]	ee (%)[c]
1	H	4-Cl	**4a**	95	95
2	H	4-F	**4b**	96	94
3	H	4-Me	**4c**	98	73
4	4-Me	4-Cl	**4d**	94	99
5	4-Me	4-F	**4e**	96	99
6	4-Me	4-Me	**4f**	96	96
7	4-Cl	4-Me	**4g**	97	41
8	4-CF_3	4-Me	**4h**	94	44
9	3-CF_3	4-Me	**4i**	93	72
10	3-F	4-Cl	**4j**	97	37
11	4-CF_3	4-F	**4k**	93	36
12	3-CF_3	4-Cl	**4l**	93	45
13	3-CF_3	4-F	**4m**	95	58

[a] Reaction conditions: 100 mg of imine, 1 mol% $Co_2(CO)_8$/(R)-BINAP (1/2), dry THF (10 mL), 15 h, 450 psi in a 1/3 ratio (H_2/CO).
[b] Isolated yield.
[c] Determined by HPLC.



Scheme 1. Equilibriums found with the system $Co_2(CO)_8$/L-L/H_2/CO.

pentane into a solution of **B** in THF (Fig. 2). IR spectrum of **B** shows five absorptions for the CO stretching frequencies at 2042, 1967, 1916, 1868, 1787 cm^{-1}, this data is in accord with that reported by Gibson's group [46]. In the FAB^+ spectra of **B** the appropriate ions peaks are found, additionally, the ESI mass spectrum shows a characteristic fragmentation pattern of successive CO elimination. The ^{31}P NMR spectrum reveals a broad signal at 41.4 ppm, which is assigned to specie **B** [46].

In order to obtain compound **C**, a temperature was increased until reflux conditions favored **C** formation. The IR spectrum shows two absorption bands at 2011 and 2030 cm^{-1} for terminal CO ligands. In the FAB^+ and ESI mass spectra, the appropriate molecular ions peaks are found, while, the recorded ^{31}P NMR spectrum reveals a single resonance at δ 61.08 ppm. Compound **C** is thermally sensitive at atmosphere pressure and slowly decomposes in solution at 25 °C. The hydride complex **D** was prepared from **C** in hydrogenation conditions without substrate and it was possible to detect the hydride moiety of **D** by the appearance of a band at 2063 cm^{-1} in the IR spectra [50,51]. In addition, the ESI mass spectra showed a 710 *m*/*z* [M−CO] peak corresponding to [HCo(L-L)CO] moiety **E** (Scheme 2), even though, the molecular ion was not observed.

The proposed mechanism sequence of this reaction is outlined in Scheme 2, the pathway is presumed in the absence of a more thorough study. As the reaction is conducted under CO atmosphere, carbon monoxide dissociation–association is likely to be reversible in many of these species (Scheme 1). The formation of a cobalt hydride **D** is the first reaction step, followed by the loss of a CO ligand from **D** giving species **E** (16e electrons), this species forms

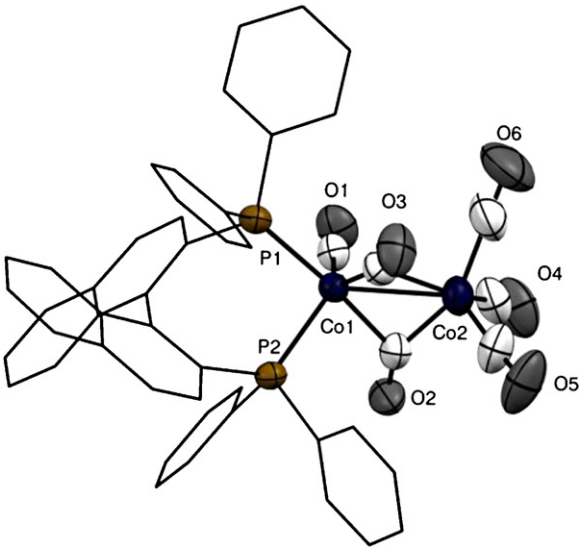
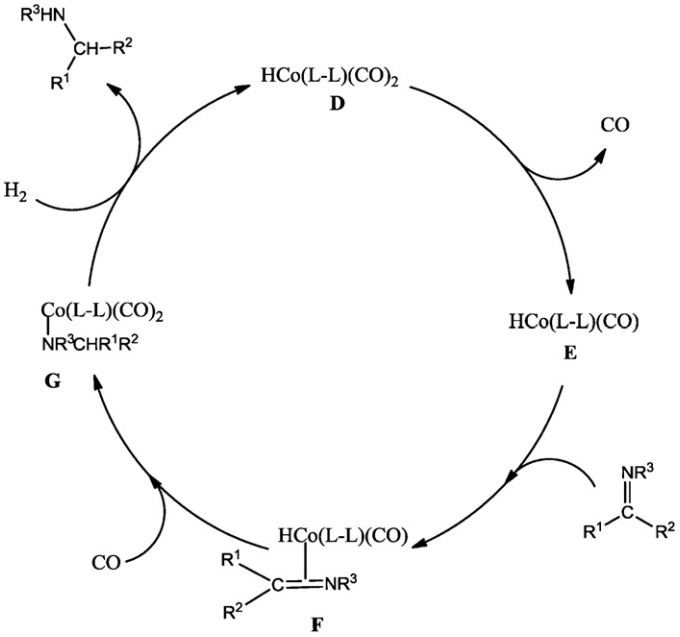


Fig. 2. Molecular structure of compound **B**. Hydrogen atoms are omitted for clarity [49].



Scheme 2. Proposed mechanism sequence.

the cobalt intermediate **F** by coordination of the imine moiety. Afterwards, an imine insertion into the Co—H bond would give an amino-cobalt species **G** [52] with concomitant binding of the CO ligand. The regeneration of the active species **D** could occur by different processes (hydrogenolysis, sigma-bond-metathesis reaction or even oxidative addition–reductive elimination) in the presence of H_2.

4. Conclusion

In summary, we reported for the first time the enantioselective reduction of imines using dicobalt octacarbonyl system modified with (R)-BINAP as ligand, where the *methyl* group substituent is a key feature for good enantioselectivity. In addition, a mechanism is suggested based on the isolation and characterization of several cobalt species. Therefore, this methodology provides an attractive alternative to imines reduction under mild conditions.

Acknowledgments

We thank DGAPA-UNAM for financial support (PAPIIT IN203209) and CONACyT (Fellowship 229448). Also, we gratefully acknowledge A. Toscano, S. Hernández-Ortega, J. Pérez, L. Velasco, Rocio Patiño Maya, Ma. Angeles-Peña, L.C. Marquez and E. Garcia for technical support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.08.019.

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