

Osmium catalyzed asymmetric dihydroxylation of methyl *trans*-cinnamate in ionic liquids, followed by supercritical CO₂ product recovery

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Received 16 February 2005; accepted 12 April 2005

Available online 8 June 2005

Abstract

In this work, osmium-catalyzed asymmetric dihydroxylation (AD) of methyl *trans*-cinnamate was studied. Osmium and chiral ligand catalysts were immobilized in ionic liquid only, without any other reaction solvents, while the recovery of the product was performed by extraction with supercritical CO₂, and compared with results obtained by extractions with organic solvents such as hexane and diethyl ether. In supercritical CO₂ extraction experiments, optimal extraction pressure was found and ionic liquid chosen, so that the highest reaction yields coupled with lowest osmium content in the crude product can be achieved. Finally, recycle experiments of the same (ionic liquid + catalytic system) mixture were successfully conducted. Application of ionic liquids and supercritical CO₂ in osmium catalyzed AD allows for the isolation of the diol basically without contamination with osmium, in high yield and enantiomeric excess, and it makes possible the efficient reuse of ionic liquid solvent and the catalytic system.

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Keywords: Asymmetric dihydroxylation; Ionic liquids; Supercritical CO₂; Taxol side chain; Catalyst reuse; Osmium contamination

1. Introduction

N-Benzoyl-(2*R*,3*S*)-3-phenylisoserine **3** is an important unit of the C-13 side chain of the taxol (paclitaxel) family for the antitumor activity [1]. The synthesis of **3** has become of high interest [2], and a considerable number of asymmetric oxidation methodologies on the substrate *trans*-cinnamate unit have been applied [3].

Among them, the Sharpless asymmetric dihydroxylation (AD) and aminohydroxylation (AA) are the most

advantageous for the efficient synthesis of **3** [3a]. The Sharpless asymmetric dihydroxylation is a very robust methodology for the synthesis of a diverse range of chiral 1,2-diols in one step from the corresponding olefins [4]. However, the extension of this reaction to large-scale processes still suffers from several drawbacks – the high cost of the osmium and chiral ligands and the high toxicity of the osmium, which can contaminate the chiral product [5].

Several approaches have been developed in order to reuse the catalytic system [6], such as immobilization of chiral ligands onto soluble and insoluble polymers. However, this approach has shown the need of long synthesis of each chiral ligand, reduction of the enantioselectivity, and/or uncompleted recovery and reuse of the osmium-ligand catalytic system, due to the occurrence

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of osmium leaching [7]. Other efficient approaches have been described: microencapsulation of osmium catalyst in polystyrene [8], polyurea (achiral version) [9], anchoring in poly(ethylene glycol) matrixes [10], silica tetrasubstituted olefins [11], ion exchangers [12], nanocrystalline magnesium oxide [13] anchoring in Amberlite containing residual vinyl groups [14], gold colloids [15], biphasic system containing dendrimer-bound (achiral version) [16] or fluoros (achiral version) [17] osmium catalyst.

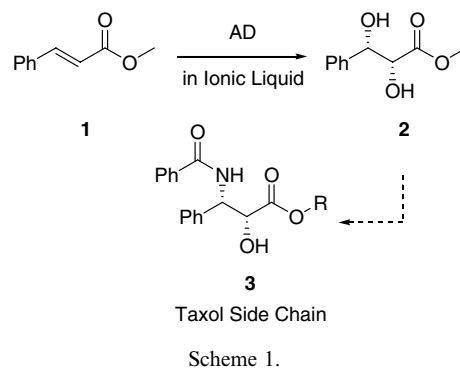
More recently, another simple and efficient approach for the immobilization of the (non-chiral) osmium [18] and chiral ligand [19] has been reported by using room temperature ionic liquids (ILs) as co-solvents to the traditional reaction solvent systems, consisting of *t*-BuOH/water or acetone/water, including the use of H₂O₂ as co-oxidant in the presence of OsO₄, *N*-methylmorpholine oxide (NMO) and flavin as the catalyst system [20]. Moreover, extensive research of osmium catalyst immobilization in ionic liquids only, without any other reaction solvents, followed by supercritical CO₂ extraction, has been conducted in our laboratories [21].

Room temperature ionic liquids are a relatively new and peculiar media that has been intensely studied during the last decade and applied in different areas, such as electrochemical transformations, fuel cells, solar cells, analytical and preparative separation and nanochemistry [22]. ILs are also appealing as reaction media in organic chemistry, with special focus in organometallic catalysis, organocatalysis and biocatalysis [23]. During the last years, it has been demonstrated that ILs are in fact a unique alternative reaction media for a considerable range of catalytic reactions [23], with many examples of similar or better enantioselectivities to the ones in traditional organic solvents.

Their non-volatility, as well as the possibility to modulate the solubility properties relative to either common organic solvents, water, catalysts, organic reactants or products by appropriate combination of the cation and anion, allow for a very simple, robust and efficient method for catalyst reuse, simply by immobilizing the catalyst in the IL under homogeneous conditions.

For the success of this approach, it is necessary that the catalyst has a strong affinity to the IL phase, while very low or no affinity for the solvent (including *sc*CO₂ [24] or membrane technology [25]) used to extract the product from the IL phase. It is also crucial for the catalyst to be effective in the IL reaction medium, especially in the case of asymmetric catalysis.

Supercritical CO₂ (*sc*CO₂) is the most commonly used supercritical fluid, due to its advantageous properties – relatively low and easily reachable critical parameters (*t*_c = 31 °C, *p*_c = 73.8 bar), non-flammability, low cost and low toxicity (threshold limit value – TLV = 5000 ppm). One of the most distinctive properties of a supercritical gas is that the density is very sensitive even to slight pressure and temperature changes. Since the



solvent power is a function of density, it is possible to tune it by a small modification of those variables. This property, combined with other advantages mentioned above, makes *sc*CO₂ attractive for solubility-based separation processes. At least two major reviews and a book have recently been published on *sc*CO₂ application in chemical synthesis and processing [26].

The combination of supercritical CO₂ with ionic liquids as alternative reaction medium has recently become an intensive focus of research [27]. In fact, the remarkable properties of both solvents can bring numerous advantages to chemical processes. Due to their ionic nature and negligible vapour pressure, ionic liquids exhibit no appreciable solubility in *sc*CO₂; at the same time, *sc*CO₂ is remarkably soluble in most ionic liquids, and can be used to extract numerous organic substances from them without any IL contamination in the final product [28].

Several reactions with organometallic catalysts have been performed in IL-*sc*CO₂ systems [29]. We reported for the first time this system being used for osmium catalyzed AD reaction [21].

In line with our ongoing interest in the development of new ILs [30], their application in separation technology [27c,31], and their use as an efficient reaction medium for catalyst immobilization [19a,c,32], and encouraged by the results obtained for the AD reaction on the model substrate 1-hexene [21], we applied this methodology to the important substrate methyl *trans*-cinnamate **1**. The importance of this substrate lies in the fact that it allows for the preparation of the diol **2**, a known efficient precursor for the synthesis of the taxol side chain **3** (Scheme 1).

2. Results and discussion

Herein, we present the extension of the research performed previously by our group, which proved the advantages of running AD reaction in ILs only, followed by extraction of the product with *sc*CO₂. The model substrate in these studies was 1-hexene. In this work, we performed a series of experiments of AD

Table 1
Asymmetric dihydroxylation of methyl *trans*-cinnamate **1** using ionic liquids as solvent and co-solvent^a

| Solvent system | Yield (%) (e.e. (%)) ^b | | | |
|---|------------------------------------|------------------|------------------|------------------|
| | K ₃ Fe(CN) ₆ | | NMO | |
| | PHAL | PYR | PHAL | PYR |
| [C ₄ mim]PF ₆ /H ₂ O (1:2) | 95 (81) | 78 (93) | 66 (62) | 60 (61) |
| [C ₈ mim]PF ₆ /H ₂ O (1:2) | 85 (68) | 67 (73) | 82 (83) | 70 (92) |
| [C ₈ mim]PF ₆ /H ₂ O/ <i>t</i> -BuOH (1:1:2) | 82 (75) | 83 (66) | 86 (91) | 65 (79) |
| [C ₈ mim]PF ₆ /H ₂ O/ <i>t</i> -BuOH (1:1:2) | 80 (70) | 87 (62) | 83 (92) | 80 (79) |
| [C ₄ mim]PF ₆ | 88 (83) | 68 (90) | 85 (72) | 70 (76) |
| [C ₈ mim]PF ₆ | 94 (84) | 78 (85) | 79 (66) | 93 (78) |
| [C ₄ mim][NTf ₂] | 83 (66) | 87 (79) | 82 (69) | 84 (66) |
| [C ₄ mim]BF ₄ | 65 (80) | 65 (91) | 83 (62) | 81 (65) |
| [bdmim]BF ₄ | 51 (76) | 66 (92) | 87 (80) | 84 (72) |
| <i>t</i> -BuOH/H ₂ O (1:2) | 88 (80) | 85 (84) | 86 (87) | 89 (89) |

^a Reaction conditions: **1** (0.55 mmol), K₃Fe(CN)₆ (3 mol equiv.) or NMO (1.3 mol equiv.), K₂OsO₂(OH)₄ (0.5 mol%), (DHQD)₂PHAL or (DHQD)₂PYR (1 mol%), solvent system (1–2 mL), RT, 24 h.

^b Isolated yield (%) and enantiomeric excess (%) (e.e. in brackets) of the diol **2**; in bold are presented the best three results using IL as solvent or co-solvent.

reactions for the substrate methyl *trans*-cinnamate **1**, with ionic liquids acting either as co-solvent or only solvent. The reaction is followed by extraction of the product by either organic solvents or supercritical CO₂.

Ionic liquids [C₄mim]PF₆, [C₄mim]BF₄, [C₄mim][NTf₂], [C₈mim]PF₆ and [bdmim]BF₄ were selected as potential candidates for further experiments, on the basis of previous study of the AD reaction in ILs for a range of aryl and alkyl-olefins [21].

In Table 1, the results obtained for methyl *trans*-cinnamate **1** are presented, using K₂OsO₂(OH)₄ (0.5 mol%), two chiral ligands (DHQD)₂PHAL or (DHQD)₂PYR (1.0 mol%), and the co-oxidants K₃Fe(CN)₆ or *N*-methylmorpholine oxide (NMO).

For systems consisting of IL as a co-solvent (IL/water or IL/water/*t*-BuOH), higher yields were obtained using K₃Fe(CN)₆ as co-oxidant, while higher enantiomeric excesses were generally observed using NMO. When IL was used as the only solvent, the results clearly show that the observed yields and enantiomeric excesses (e.e.s) are more dependent on the combination of IL, chiral ligand and co-oxidant. However, for each chiral ligand and co-oxidant, similar or even better yield and e.e. was obtained than in the case of the conventional *t*-BuOH/H₂O (1:2) solvent (results in bold vs. last row).

In our previous study of AD of 1-hexene in ionic liquid as co-solvent, we were able to reuse the IL and the osmium-chiral ligand catalytic system for nine times with low reduction of the yield (8%) and enantioselectivity (e.e., 5%) by careful extraction of the reaction media with the appropriate organic solvent. Under those conditions the osmium content in the recovered chiral diol was always less than 3% of initial amount [19a,c].

The use of NMO instead of K₃Fe(CN)₆ is advantageous for the removal of the reaction products from the IL, since all products can be removed using non-aqueous solvents. In case of the co-oxidant K₃Fe(CN)₆

it is also necessary to extract the IL with water in order to remove the inorganic salts, which implies additional leaching of the osmium catalyst [19c].

AD reaction can also be efficiently performed using IL as the only solvent used, giving better or similar yields and e.e.s for a range of substrates to those reported using the optimised solvent system consisting of organic solvent/water [4] or IL as a co-solvent [19]. In our previous experiments with 1-hexene, the IL and the catalytic system was reused for 14 times by extraction with diethyl ether without considerable loss of yield (6%) and e.e. (4%) and the osmium content in the product was in the range of 1–2% of the initial amount of the osmium catalyst. Additionally, when NMO was used as a co-oxidant, high e.e.s were observed by adding the olefin at once, which is due to low solubility of the olefin in the IL [21], allowing to suppress the secondary catalytic cycle [4a,33].

The reuse of the IL and catalytic system for the AD of methyl *trans*-cinnamate **1** was tested by performing extraction with either organic solvents hexane and diethyl ether, or *sc*CO₂. The co-oxidant used for these comparative experiments was NMO, while the ionic liquids chosen were [C₈mim]PF₆ and [bdmim]BF₄, those that gave the best performance in the preliminary studies. In the case of extraction with organic solvents, after each cycle the organic phases were removed, and more substrate **1** and co-oxidant NMO was added to the IL phase. The combined organic phases were equally divided in two parts. One part was used for the determination of the osmium content by ICP and the other was further purified by flash chromatography for the determination of the yield and e.e.

In Table 2, the observed results are presented. It is clear that the IL-catalytic system is also extremely robust for the substrate **1** (run 1, yield 79%, e.e. 78%; run 6, yield 79%, e.e. 81%). The isolated yields for each

Table 2

Reuse of the catalyst system for the AD reaction of methyl *trans*-cinnamate **1** in [C₈mim]PF₆ using NMO as co-oxidant and extraction with Et₂O or hexane^a

| Run | Et ₂ O | | Hexane | |
|-----|-----------------------------------|-----------------------------|-----------------------------------|-----------------------------|
| | Yield (%) ^b (e.e. (%)) | Os content (%) ^c | Yield (%) ^b (e.e. (%)) | Os content (%) ^c |
| 1 | 79 (78) | <0.05 | 41 (82) | <0.05 |
| 2 | 72 (79) | <0.05 | 45 (77) | <0.05 |
| 3 | 75 (83) | <0.05 | 48 (78) | <0.05 |
| 4 | 70 (81) | 0.08 | 64 (76) | <0.05 |
| 5 | 77 (85) | <0.05 | 67 (80) | <0.05 |
| 6 | 79 (81) | <0.05 | 61 (78) | <0.05 |
| | 52 ^d (82) | – | 142 ^d (77) | – |

^a Reaction conditions: **1** (0.55 mmol), NMO (1.3 mol equiv.), K₂OsO₂(OH)₄ (0.5 mol%), (DHQD)₂PYR (1 mol%), [C₈mim]PF₆ (2 mL), RT, 24 h, followed by extraction with Et₂O or hexane (2 × 5 mL), removed the organic solvent and reload with substrate **1** and NMO.

^b Isolated yield and enantiomeric excess (e.e. in brackets) of the diol **2** (%).

^c Percentage of osmium relative to initial amount detected by ICP in the combined organic phase (detection limit 0.05%).

^d After purification by flash chromatography, more diol **2** was isolated from the remaining ionic liquid (61 mg (52%) by extraction with Et₂O and 168 mg (142%) by extraction with hexane).

run obtained by extraction with Et₂O and hexane are for all cycles, respectively, 8.7% and 23.7% in average lower than the observed one when the product **2** was removed from the IL reaction mixture without solvent extraction (Table 1, yield of 93%). In fact, after solvent extraction of the last cycle, the IL retained 52% and 142% of diol **2**. This demonstrates that the AD reaction keeps the efficiency during the reuse experiments, but the removal of the product is not complete by extraction with Et₂O and very inefficient when using the less polar solvent hexane. However, very importantly, the osmium content in the crude organic phases of each cycle has been found below the detection limit (less than 0.05%), for reuse systems extracted with either Et₂O or hexane.

In the study with 1-hexene, *sc*CO₂ was proved a feasible solvent for product extraction, and the catalytic system was reused eight times [21a]. The erosion of yields and e.e.s was higher than when using diethyl ether as extraction solvent, but more importantly, the osmium content in the product was the lowest one reported (less than 0.4% of initial osmium catalyst amount).

The extraction of the AD reaction in ILs for substrate **1** by *sc*CO₂ was performed using the apparatus are presented in Figs. 1 and 2.

The initial round of *sc*CO₂ extraction experiments was performed in two different ionic liquids [bdmim]BF₄ and [C₈mim]PF₆, at 40 °C and two different pressures (100 and 125 bar). This was done in order to find optimal extraction pressure and choose ionic liquid for further recycle experiments, so that the highest reaction yields coupled with lowest osmium content can be achieved.

Provided that the AD reaction proceeds efficiently in ILs, the application of IL-*sc*CO₂ concept requires that *sc*CO₂ will be selective towards the reaction products, and that it will not extract the catalyst. Selectivity of supercritical CO₂ as an extraction medium can be tuned by changing operating pressure. At higher pressures,

*sc*CO₂ is denser, and hence has better solvent power. On lowering the pressure, *sc*CO₂ density and solvent power decrease, enhancing its selectivity. By changing system pressure it is therefore possible to decrease the solubility of a catalyst and selected solutes/by-products in CO₂, lowering (in case of organometallic catalysts, even to the limit of detection) their content in the condensed phase, and enhancing the product quality. The strategy should be to try and use *sc*CO₂ at the lowest possible density, where it can still dissolve reaction products, but does not carry any catalyst out of the ionic liquid solution.

Extraction experiments with 1-hexene proved that lowering CO₂ pressure has a dramatic effect on the osmium content of the extracts, and that it is necessary to work at as low pressure as possible [21] (for 1-hexene, 100 bar). The product **2** of methyl *trans*-cinnamate **1** is less soluble in CO₂ than 1,2-hexanediol, therefore higher extraction pressure should be needed.



Fig. 1. Apparatus used for supercritical CO₂ extraction: high pressure cell (1), water bath (2), mixing plate (3), cold traps (4).

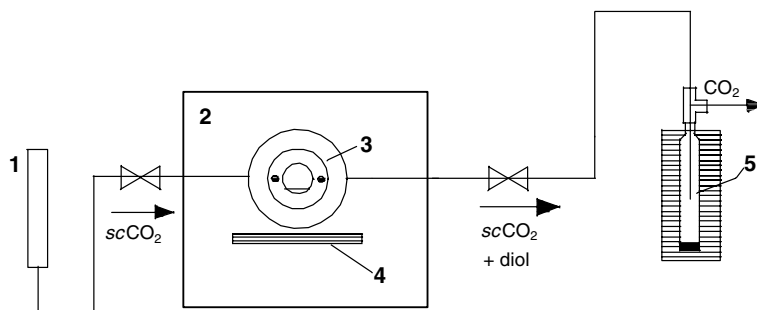


Fig. 2. Schematic diagram of the apparatus used in $scCO_2$ extraction experiments: (1) CO_2 screw injector pump; (2) constant temperature water bath; (3) high-pressure cell; (4) magnetic stirrer; (5) cold trap.

Table 3

Mass of extracted product **2**, yield and osmium content for extraction experiments with ionic liquids $[C_8mim]PF_6$ and $[bdmim]BF_4$, at two different pressures of $scCO_2$ ^a

| $scCO_2$ pressure | Extract (mg) ^b | Yield (%) ^b | Os content (%) ^c |
|-------------------|---------------------------|------------------------|-----------------------------|
| $[C_8mim][PF_6]$ | | | |
| 100 bar | 40 | 44 | <0.05 |
| 125 bar | 109 | 88 | <0.05 |
| $[bdmim][BF_4]$ | | | |
| 100 bar | 66 | 63 | 0.23 |
| 125 bar | 93 | 86 | 0.16 |

^a Reaction conditions: **1** (1.1 mmol), NMO (1.3 mol equiv.), $K_2OsO_2(OH)_4$ (0.5 mol%), $(DHQD)_2PYR$ (1 mol%), IL (2 mL), RT, 24 h, followed by extraction with $scCO_2$ at 40 °C.

^b Isolated mass and yield of the diol **2**.

^c Percentage of osmium relative to initial amount detected by ICP in the extracted $scCO_2$ phase (detection limit 0.05%).

This was confirmed in our experiments: higher yields of more than 80% were achieved only at 125 bar, while at 100 bar they were much lower, as presented in Table 3. On the other hand, osmium content in the extract was still low, even at 125 bar. In case of $[C_8mim]PF_6$ it was below the detection limit of the ICP method (0.05%) at both 100 and 125 bar of CO_2 pressure, while for $[bdmim]BF_4$, there was some, even though small, amount of osmium detected in the samples (Table 3). Supercritical CO_2 extraction from the ionic liquid $[C_8mim]PF_6$ proved therefore to be more selective. For this reason, $[C_8mim]PF_6$ was chosen for the study of the reuse of the ionic liquid + catalyst system.

In the second round of extraction experiments, successive reaction-extraction cycles were performed with the same ionic liquid + osmium-chiral ligand catalyst solution. In each new cycle, the substrate and co-oxidant were added to the IL phase that remains in the cell after $scCO_2$ extraction. After the reaction time has passed, a new $scCO_2$ extraction would be performed. The results of recycling experiments of osmium catalyst immobilized in $[C_8im]PF_6$ are presented in Table 4.

The results show that most of the product (180 mg out of 188 mg extracted in run 2, the whole amount in

Table 4

Mass of extracted product, yield, enantiomeric excess and osmium content for recycling experiments of osmium catalyst, immobilized in ionic liquid $[C_8im]PF_6$ extracted with $scCO_2$ ^a

| Run | Extract (mg) ^b | Yield (%) ^b | e.e. (%) ^b | Os content (%) ^c |
|-----|---------------------------|------------------------|-----------------------|-----------------------------|
| 1 | 198 | 91 | 77 | <0.05 |
| 2 | 188 (180) | 87 | 83 | <0.05 |
| 3 | 193 (193) ^d | 89 | 85 | <0.05 |
| 4 | 191 (170) ^d | 88 | 84 | <0.03 |
| 5 | 196 (177) ^d | 90 | 80 | <0.03(0.06) ^d |
| 6 | 185 (168) ^d | 85 | 84 | <0.03 |

^a Reaction conditions: **1** (1.1 mmol), NMO (1.3 mol equiv.), $K_2OsO_2(OH)_4$ (0.5 mol%), $(DHQD)_2PYR$ (1 mol%), IL (2 mL), RT, 24 h, followed by extraction $scCO_2$ at 125 bar, 40 °C, and reload of substrate **1** and NMO.

^b Isolated mass, yield and observed e.e. of the diol **2**.

^c Percentage of osmium relative to initial amount detected by ICP in the extracted $scCO_2$ phase. The detection limits of 0.05% and 0.03% were achieved, respectively, for runs 1–3 and 4–6.

^d The results in brackets represent the mass of product after 60 cm³ of CO_2 at 125 bar and 40 °C was introduced.

run 3) is extracted when 60 cm³ of CO_2 at 40 °C and 125 bar are passed through the system. Since the density of $scCO_2$ at these conditions is around 730 kgm⁻³, the quantity used for extraction corresponds to 1 mol of CO_2 , and the CO_2 /product molar ratio of around 900. This high value is a necessary consequence of the high selectivity towards the product. This is obtained for all cycles in high yield (around 90%) and enantiomeric excess (above 80%), and remarkably without contamination with osmium (lower than the ICP detection limit, 0.03% and 0.05%). For the production of the diol **2** by the AD reaction in IL, it is clearly more advantageous to perform the product extraction by $scCO_2$ than by common organic solvents, because the extraction is more efficient and no contamination of osmium in the product is still achieved.

3. Conclusions

Performing asymmetric dihydroxylation of methyl *trans*-cinnamate **1** in ILs has proved to be a very efficient,

simple and robust method for the immobilisation of the catalyst system in the AD reaction. When combined with *sc*CO₂ extraction system, it allows a cleaner process with high product quality, as well as easy product recovery.

4. Experimental

4.1. General

The following chemicals were purchased from Aldrich or Fluka and used as supplied: methyl *trans*-cinnamate **1**, K₂CO₃, K₂OsO₂(OH)₄, K₃[Fe(CN)₆], (DHQD)₂PHAL, (DHQD)₂PYR, *t*-butanol and osmium ICP standard. All aqueous solutions were prepared using distilled water. The ILs 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim]PF₆), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim]BF₄), 1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₄mim][NTf₂]), 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([C₈mim]PF₆) and 1-*n*-butyl-2,3-methylimidazolium tetrafluoroborate ([bdmim]BF₄) were prepared according to reported procedures [34]. ¹H, and ¹³C NMR spectra were recorded on a Bruker AMX 400 spectrometer. Chemical shifts are reported downfield in parts per million (ppm) from a tetramethylsilane reference for ¹H and ¹³C NMR. IR spectra were recorded on a Mattson Instruments model Satellite FTIR as thinly dispersed films. HPLC analyses were performed using Merck & Hitachi components L-600A, L-4250, T-6300, D-6000 and Dionex components P680 and UVD340S using Daicel Chiralcel OD column at room temperature. Inductively Coupled Plasma spectroscopy (ICP) analysis were performed by the Analytical services laboratory of REQUIMTE using JOBIN YVON-HORIBA, ULTIMA model, a free-running 27.0 MHz generator operating 1250 W.

Flash chromatography was carried out using an MN-Kiesel-gel 60 M gel (230–400 mesh ASTM, Art. 815381). All eluents were distilled prior to use. Preparative and analytical thin layer chromatography (TLC) was carried out using, respectively, MN Kieselgel G/UV₂₅₄ (Art. 816320) glass-backed plates and MN Alugram[®] SIL G/UV₂₅₄ (Art. 818133). The plates were visualised using ultraviolet light (254 nm) or using phosphomolybdic acid.

4.1.1. General procedure used for the AD reaction presented in Table 1 using K₃Fe(CN)₆ as co-oxidant

A 5 mL flask was charged with K₃[Fe(CN)₆] (495 mg; 1.5 mmol); K₂CO₃ (210 mg; 1.5 mmol); using a biphasic system ionic liquid/water (0.5:1.0 mL; 1:2), or a monophasic system: ionic liquid/water/*t*-butanol (0.5:0.5: 1.0 mL; 1:1:2) or ionic liquid (1.0 mL) under stirring the ligand (DHQD)₂PHAL or (DHQD)₂PYR

(1.0 mol%) and the catalyst K₂OsO₂(OH)₄ (0.5 mol%) were added. The olefin methyl *trans*-cinnamate **1**, (90 mg, 0.55 mmol) was then added at once, and the reaction mixture stirred at room temperature during 24 h. The obtained mixture was extracted with dichloromethane (3 × 25 mL) and the resulting solution was dried (MgSO₄), evaporated in vacuo and purified by TLC or flash chromatography. In the case of monophasic system using only ionic liquid, the reaction mixture was dissolved in a small amount of dichloromethane (2 mL) and purified by flash chromatography (eluent: ethyl acetate/1-hexane (1:3)) to give the corresponding diol **2** as a white solid. The enantiomeric excess (e.e.) was determined by HPLC analysis [eluent: hexane/ⁱPrOH 90:10; flow rate: 1.0 mL/min]; *t*_R = 17.0 min (minor); *t*_R = 23.0 min (major); spectral data are identical to authentic sample and to those previously reported [12a].

4.1.2. General procedure used for the AD reaction presented in Table 1 using NMO as a co-oxidant

A 5 mL flask was charged with NMO (100 mg; 1.3 mol equiv.); using a biphasic system ionic liquid/water (0.5:1.0 mL; 1:2), or a monophasic system: ionic liquid/water/*t*-butanol (0.5:0.5:1.0 mL; 1:1:2) or ionic liquid (1.0 mL) under stirring were added the ligand (DHQD)₂PHAL or (DHQD)₂PYR (1.0 mol%) and the catalyst K₂OsO₂(OH)₄ (0.5 mol%). The olefin methyl *trans*-cinnamate **1** (90 mg, 0.55 mmol) was then added at once, and the reaction mixture stirred at room temperature during 24 h. The obtained mixture was extracted with dichloromethane (3 × 25 mL) and the resulting solution was dried (MgSO₄), evaporated in vacuo and purified by TLC or flash chromatography. In the case of monophasic system using only ionic liquid, the reaction mixture was dissolved in a small amount of dichloromethane (2 mL) and purified by flash chromatography (eluent: ethyl acetate/1-hexane (1:3)) to give the corresponding diol **1** as a white solid. The enantiomeric excess (e.e.) was determined by HPLC as described above.

4.1.3. General procedure for the reuse of the K₂OsO₂(OH)₄/(DHQD)₂PYR/IL system and NMO as co-oxidant and extraction with Et₂O or hexane (Table 2)

A 5 mL flask was charged with NMO (100 mg; 1.3 mol equiv.); [C₈mim]PF₆ (2 mL), and under stirring the ligand [(DHQD)₂PYR] (4.5 mg; 1 mol%) and the catalyst K₂OsO₂(OH)₄ (1.0 ± 0.1 mg; 0.5 mol%) were added. Methyl *trans*-cinnamate **1** (90 mg, 0.55 mmol) was then added at once, and the resulting mixture stirred for 24 h at room temperature. The ionic liquid was extracted with diethyl ether (2 × 5 mL) or hexane (2 × 5 mL) and the combined organic phase was divided in two equal parts. One part was dried (MgSO₄), evaporated in vacuo and purified by flash chromatography

(eluent: ethyl acetate/hexane (1:3)). The other part was evaporated in vacuo, diluted with water (5 mL) and the osmium content was analysed by inductively coupled plasma spectroscopy (ICP) ($\lambda = 228.226$ nm) using a calibration curve based on standard solutions prepared from Os standard for ICP (Fluka, 1000 ppm). Then, more methyl *trans*-cinnamate **1** (90 mg, 0.55 mmol), NMO (100 mg; 1.3 mol equiv.) was added to the recycled ionic liquid and the cycle was repeated. After cycle 6, the ionic reaction mixture was purified by flash chromatography using the same procedure described above (4.1.2), giving, respectively, 61 mg (52%) and 168 mg (142%) of diol **2** for the AD reaction resulted of extraction with Et₂O and hexane.

4.1.4. AD reaction in ionic liquids [C₈mim]PF₆ or [bdmim]BF₄, using K₂OsO₂(OH)₄/(DHQD)₂PYR or (DHQD)₂PHAL system and NMO as a co-oxidant, followed by scCO₂ extraction at two different pressures

Ionic liquids [C₈mim]PF₆ or [bdmim]BF₄ (2 mL), with (DHQD)₂PYR or (DHQD)₂PHAL ligand, respectively, (1 mol%), K₂OsO₂(OH)₄ (2.0 ± 0.1 mg; 0.5 mol%), NMO (200 mg; 1.3 mol equiv.) and substrate methyl *trans*-cinnamate **1** (180 mg, 1.1 mmol) were added into the high pressure cell. The reaction was carried out for 24 h at atmospheric pressure and room temperature. After the reaction was finished, the high pressure cell was connected to the scCO₂ extraction apparatus that consists of screw injector pump, water bath and two cold traps for collecting samples (Fig. 1). The water bath was heated to 40 °C, and supercritical CO₂ at either 100 or 125 bar was added. When the system equilibrated, scCO₂ extraction at constant pressure was performed. The cold traps were cooled with (liquid nitrogen + ethanol) mixture, and ethanol samples collected at different points of extraction. This was done in order to determine the amount of CO₂ needed to extract most of the product. Samples were then divided in two equal parts. One was used for the determination of the osmium content by ICP, and the other for the isolation of the product and for the determination of the enantiomeric excess as described before.

4.1.5. General procedure for reuse of the K₂OsO₂(OH)₄/(DHQD)₂PYR/IL system using NMO as a co-oxidant, followed by scCO₂ extraction at 125 bar (Table 4)

Ionic liquid [C₈mim]PF₆ (2 mL), with (DHQD)₂PYR ligand (9 mg; 1 mol%), K₂OsO₂(OH)₄ (2.0 ± 0.1 mg; 0.5 mol%), NMO (200 mg; 1.3 mol equiv.) and substrate methyl *trans*-cinnamate **1** (180 mg, 1.1 mmol) was added into the high pressure cell. The reaction was carried out for 24 h at atmospheric pressure and room temperature. After the reaction was finished, the high pressure cell was connected to the scCO₂ extraction apparatus (Fig. 1), and placed in the temperature controlled bath at 40 °C. Supercritical CO₂ at 125 bar was added, and

when the system equilibrated, scCO₂ extraction at constant pressure was performed. The samples were collected as described above. Fresh quantity of NMO co-oxidant (200 mg, 1.3 mol equiv.) and substrate **1** (180 mg, 1.1 mmol) were added to the ionic liquid phase that remains in the high pressure cell after the extraction. After the reaction time of 24 h, the new scCO₂ extraction at 125 bar was carried out.

Acknowledgements

This work was funded by Fundação para a Ciência e a Tecnologia (Lisbon, Portugal) and FEDER (Projects Refs. POCTI/EQU/35437/1999 and POCTI/QUI/38269/2001, and Doctoral Grants SFRH/BD/6792/2001 and SFRH/BD/10623/2002). We gratefully acknowledge Solchemar company (<http://www.solchemar.com>) for providing some of the ionic liquids.

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