

1-Naphthyl-TADDOL/Emim BF₄: A new catalytic system for the asymmetric addition of Chan's diene to aromatic aldehydes

Invited Paper

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Abstract: A new organocatalytic system was tested as a promoter for the asymmetric addition of Chan's diene to aldehydes under solvent-free conditions. This new organocatalyst generated in situ by mixing 1-naphthyl-TADDOL derivative and Emim BF₄ was able to give enantioenriched vinylogous aldols and hetero-Diels-Alder cycloadducts. A mechanistic investigation through the detection of nonlinear effects confirmed the involvement of the ionic liquid in the formation of a new catalytic supramolecular species.

Keywords: Organocatalysis • Hydrogen bonding • Chan's diene • Aldol reaction • Cycloaddition

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1. Introduction

In the last two decades, tetraaryl-1,3-dioxolane-4,5-dimethanols (TADDOLs) (Fig. 1) and their derivatives have proven to be very useful chiral auxiliaries in a wide variety of fundamental asymmetric metal-catalyzed processes [1,2].

Additional chemical properties of TADDOLs derive from their particular structural feature: in fact, the proximity of the –OH groups allows the formation of an intramolecular hydrogen bond and the free –OH group shows a strong tendency to associate with appropriate H-acceptors. This peculiarity has allowed their use in the resolution of racemic mixtures (through the formation of inclusion compounds) [2] and, more recently, in organocatalyzed reactions [3]. In particular, TADDOLs of type 1 have been conveniently employed in the vinylogous aldol condensation [4] of cyclic masked forms of acetoacetate esters 2 to give product 4, known precursor of δ -hydroxy- β -ketoesters 6, in good yields and enantiomeric excesses (ee.s) under metal-free

conditions, at low temperature and in the presence of organic solvents (Scheme 1) [5].

More recently, Chan's diene 5, a synthetic equivalent of acetoacetate dianion, demonstrated an unexpected reactivity towards electron-poor aldehydes: in the presence of TADDOL 1a, under solvent-free conditions at room temperature, starting materials 3 suffered a competing reaction mechanism, affording, in addition to the vinylogous aldols 6, the pyran-4-one derivatives 7 (Scheme 2) [3f]. Therefore, this organocatalytic approach promoted a different mechanistic pathway compared to organometallic catalysts [6].

Regarding the mechanistic aspects, both the occurrence of the vinylogous aldol condensation and the formation of the products 7 through a hetero-Diels-Alder reaction have been attributed to the organocatalytic properties of the used TADDOL. In fact, according to Rawal and Ding's model, the formation of an intermolecular hydrogen bond between the free –OH group of TADDOL and the aldehydic oxygen resulted in the carbonyl activation through the lowering of its LUMO energy [3a,c].

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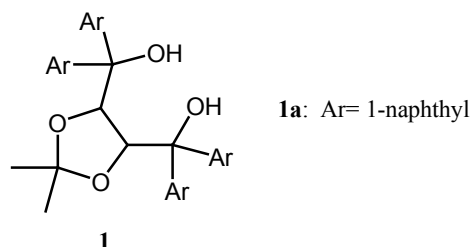
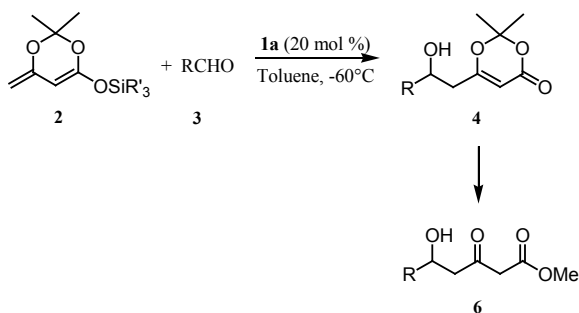
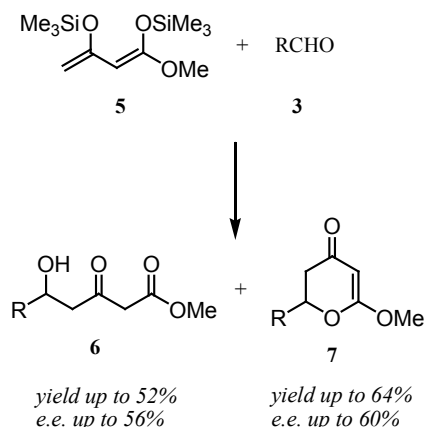


Figure 1. Structure of 1-naphthyl-TADDOL



Scheme 1. Vinyloligous aldol addition of diene **2** to aldehydes, according to Rawal's procedure



Scheme 2. Asymmetric addition of diene **5** to electron-poor aldehydes promoted by **1a** under solvent-free conditions

Furthermore, in these last years, the need to develop cleaner and more efficient organic processes is increased and so, the elaboration of solvent-free organocatalytic protocols has attracted particular interest. Although alternative and benign solvents (water, supercritical CO_2 , etc.) have been used, the realization of solvent-free methodologies is still the best option.

In this context an ever increasing interest was stimulated by the intrinsic properties of ionic liquids (ILs) [7] whose use as alternative solvents often resulted in an enhancement of reactivity and/or selectivity in a

variety of important chemical processes [8]. In fact, their solvation properties and their ability to interact with substrates, resulting in high degree of organisation in the transition state can dramatically influence the outcome of chemical reactions [9]. More recently, the possibility to use ILs as additives (in rather reduced amounts) in order to promote the formation of active species is emerging, above all in biocatalytic processes [10]. Particularly, as regards imidazolium-based ionic liquids, the reactivity of appropriate H-acceptors could be increased by hydrogen bond formation thanks to the acidic character of C(2)-H proton of the heterocyclic cation [11], as pointed out in procedures for Diels-Alder cycloaddition [12,13] and Baylis-Hillman reaction [14].

2. Experimental Procedure

2.1 General

All reactions were performed in oven-dried (140°C) vials. Thin-layer chromatography was performed on Merck Kiesegel 60 F254 plates eluting with the solvents indicated, visualized by a 254 nm UV lamp and aqueous ceric sulfate solution. Column chromatographic purification of products was carried out using silica gel 60 (70-230 mesh, Merck). All reagents (Aldrich, Fluka and Strem) were used without further purification. Infrared spectra were recorded on a Bruker 22 series FT-IR spectrometer. NMR spectra were recorded on a Bruker DRX 400 (400.135 MHz for ^1H and 100.03 MHz for ^{13}C) spectrometer. HPLC analysis were performed with Waters Associates equipment (Waters 2487 Dual λ absorbance Detector) using a CHIRALPAK AD or a CHIRALCEL OD column with mixtures and flow rates as indicated. Mass spectrometry analysis was carried out using an electrospray spectrometer Waters 4 micro quadrupole. MW-assisted reactions were carried out using a single mode CEM Discover apparatus in closed vessels under magnetic stirring with temperature measurement by IR detector and power control.

2.2 General procedure for the synthesis of **6** and **7** at room temperature (Procedure 1)

In a dry vial (**S,S**)-**1a** (0.025 mmol), **IL2** (100 μL), aldehyde **3** (0.25 mmol) and diene **5** (0.33 mmol) were added. The resulting mixture was stirred for 4.5 hours at room temperature, then dry THF (1 mL) was added. This solution was cooled at -78°C and TFA (0.1 mL) was added dropwise, then it was permitted to warm to room temperature and after completion of the desilylation reaction, it was neutralized by addition of saturated aq NaHCO_3 . The reaction mixture was extracted with AcOEt

and the combined organic phase was dried (MgSO₄) and concentrated. The residue was purified by non-flash chromatography (petroleum ether/ AcOEt from 8/2 to 1/1) to give the products **6** and **7**.

The spectroscopic (IR, ¹H NMR and ¹³C NMR) data of aldols **6** and HDA cycloadducts **7** matched the ones reported in the literature [15].

2.3 General procedure for the synthesis of **6** and **7** by MW-assisted protocol (Procedure 2)

TADDOL **1a** (0.025 mmol), **IL2** (100 μL), aldehyde (0.25 mmol) and Chan's diene (0.33 mmol) were introduced into a vessel for MW reactor. After cooling at -78°C for 30 min, the reaction mixture was submitted to MW irradiation at P = 10W for a period of time indicated in Table. Then, dry THF (1 mL) was added and the resulting solution was cooled at -78°C and TFA (0.1 mL) was added dropwise; after warming to room temperature and after completion of the desilylation reaction, it was neutralized by addition of saturated aq

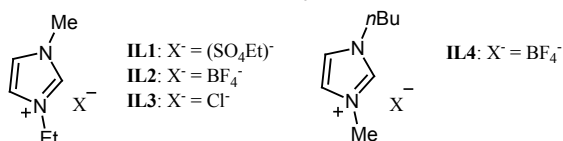


Figure 2. Ionic liquids evaluated in the reaction.

Table 1. ILs catalyzed vinylogous aldol reaction of **5** on *o*-nitro-benzaldehyde **3a**.

Entry	IL	Reac. Time / h	6a Yield / % ^a	7a Yield / % ^a
1	-	4.5	39	21
2	IL1	4.5	traces	-
3	IL1	24	22	-
4	IL2	4.5	34	24
5	IL3	4.5	27	-
6	IL4	4.5	31	-

^aYields refer to isolated chromatographically pure compounds, whose structures were confirmed by spectroscopic data (¹H-NMR, ¹³C-NMR, MS, IR).

Table 2. Solvent-free reaction of Chan's diene **5** with electron-poor aldehydes **3** promoted by organocatalytic systems (Procedure 1).

Entry	R-	Catalyst	Product	Yield% ^a	ee% ^b	Product	Yield% ^a	ee% ^b
1	<i>o</i> -NO ₂ C ₆ H ₄	IL2	6a	34	-	7a	24	-
2	<i>o</i> -NO ₂ C ₆ H ₄	1a	6a	37	19	7a	32	57
3	<i>o</i> -NO ₂ C ₆ H ₄	IL2 / 1a	6a	47	24	7a	46	62
4	<i>p</i> -CF ₃ C ₆ H ₄	IL2	6b	26	-	7b	17	-
5	<i>p</i> -CF ₃ C ₆ H ₄	1a	6b	45	29	7b	23	48
6	<i>p</i> -CF ₃ C ₆ H ₄	IL2 / 1a	6b	27	34	7b	56	51
7 ^c	<i>p</i> -CNC ₆ H ₄	1a	6c	35	29	7c	26	49
8	<i>p</i> -CNC ₆ H ₄	IL2 / 1a	6c	24	50	7c	32	52
9	<i>o</i> -CNC ₆ H ₄	IL2 / 1a	6d	17	ND	7d	45	63
10	<i>p</i> -NO ₂ C ₆ H ₄	IL2 / 1a	6e	32	40	7e	34	53
11 ^c	<i>p</i> -MeC ₆ H ₄	1a	6f	39	57	7f	-	-
12 ^c	<i>p</i> -MeC ₆ H ₄	IL2 / 1a	6f	18	42	7f	-	-

^aYields refer to isolated chromatographically pure compounds, whose structures were confirmed by spectroscopic data (¹H-NMR, ¹³C-NMR, MS, IR).

^bE.e.s were determined by HPLC analysis.

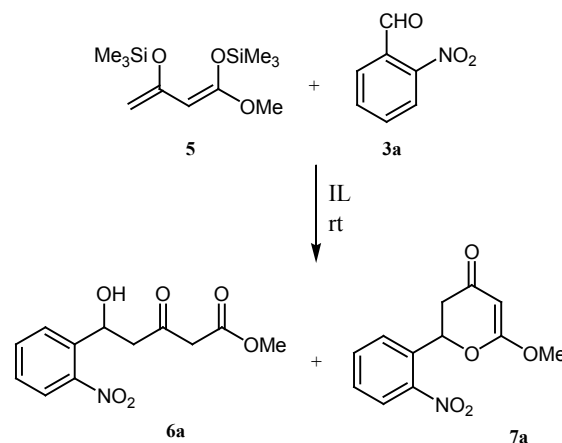
^cThe reaction was conducted for 24 h.

NaHCO₃. The reaction mixture was extracted with AcOEt and the combined organic phase was dried (MgSO₄) and concentrated. The residue was purified by non-flash chromatography (petroleum ether/ AcOEt from 8/2 to 1/1) to give the products **6** and **7**.

3. Results and Discussion

On the ground of these considerations, an investigation was devoted to examine the influence of commercially available ionic liquids (ILs) on the preparative (**6/7** ratios) and stereochemical aspects (level of enantioselectivity) on the reaction of electron-poor aldehydes of type **3** with Chan's diene in the presence of TADDOL **1a** as organocatalyst. Preliminarily, *o*-nitro-benzaldehyde was chosen as representative substrate and a set of imidazolium-based ionic liquids (Fig. 2) was used as solvent.

Unfortunately, Chan's diene **5** demonstrated a dramatic instability in all ionic liquids **IL1-IL4**, because of



Scheme 3. Addition of diene **5** to **3a** in the presence of ionic liquids

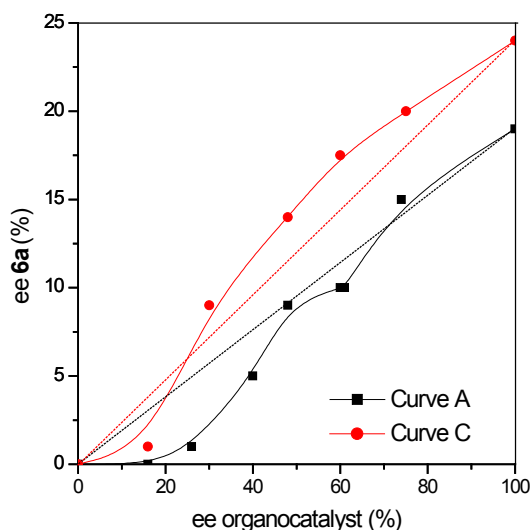


Figure 3. Experimental ee data for aldol **6a** produced by vinylogous aldol reaction catalyzed by a) enantioenriched organocatalyst **1a** (■; Curve A) [15] and b) enantioenriched **1a** / **IL2** system (●; Curve C).

a very fast decomposition leading to the parent methyl acetoacetate in almost quantitative yields. Conversely, no significant decomposition of **5** was observed when the reaction on **3a** was performed under solvent-free conditions in the presence of **ILs** used as additives (Scheme 3, Table 1). Furthermore the preparative outcome was found to depend on the anionic moiety of the ionic liquid.

Very interestingly, in entry 4, where the highest values of conversion could be observed, the vinylogous aldol **6a** and the cycloadduct **7a** were obtained in comparable yields with respect to the ones afforded by the background reaction (entry 1) performed in the absence of any catalyst. These results suggested that no particular influence was exerted by the presence of **IL2** as additive. Therefore, the experimental conditions of entry 4 seemed to be appropriate to point out different catalytic properties of 1-naphthyl-TADDOL **1a** and 1-naphthyl-TADDOL **1a** / **IL2** catalytic systems, through the detection of a different products distribution (**6a/7a** ratios) and /or different ee.s. In brief, a first indication of the possible formation of a supramolecular system **1a** / **IL2**, with different catalytic activity, could be taken simply by comparing the results of these two series of experiments.

For this reason, a number of experiments was performed on electron-poor aldehydes (Table 2, entries 1-10). The comparison of entries 2 and 3, 5 and 6, 7 and 8 pointed out significant modifications on **6/7** ratios and, usually, an increase of the level of enantioselectivity suggesting the involvement of **IL2** in

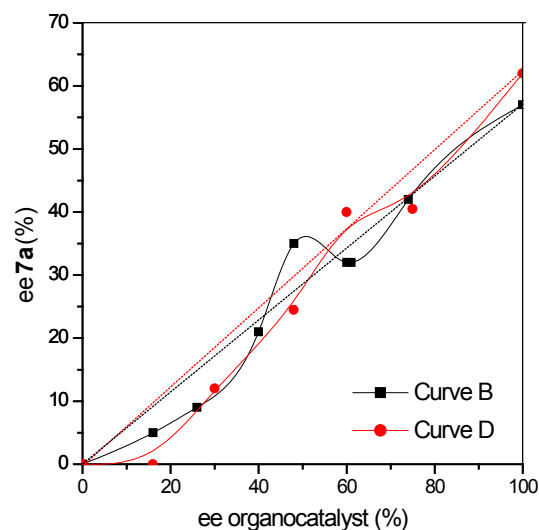


Figure 4. Experimental ee data for cycloadduct **7a** produced by reaction catalyzed by a) enantioenriched organocatalyst **1a** (■; Curve B) [15] and b) enantioenriched **1a** / **IL2** system (●; Curve D).

a new catalytic system. Similar results were obtained in entries 9 and 10. Of course, the results obtained by using **1a** / **IL2** (Scheme 4, *path c*) could not derive by the simple outcome of two independent catalytic activities (Scheme 4, *path a + path b*), that is by **1a** and by **IL2** catalysis: in fact, in this case, by using **1a** / **IL2** as catalyst we would had to observe a product with reduced optical purity, compared to that produced by using only **1a**, because the reaction in the presence of only **IL2** produces a racemic product and this is in disagreement with the experimental results.

Conversely, in the case of a non-activated aldehyde (entries 11-12), aldol **6f** proved to be the only reaction product and the presence of the additive caused a notable drop both of the yield and the ee, suggesting also in this case the formation of a new catalytic species with a different activity. The control of the formation of a new catalytic system by classical analytic methods (for example *via* NMR) appeared particularly difficult because this supramolecular aggregate was generated in solvent-free conditions and the introduction of a solvent could introduce a perturbation in the studied system. In recent years the detection of nonlinear effects (NLE) has proven to be a powerful tool in investigations in situ on the mechanistic aspects of an asymmetric process [16] and, in many reactions, these studies were used to identify a higher order molecularity of the catalyst (dimeric or oligomeric species) [16a,17].

In a previous paper [15], *o*-nitro-benzaldehyde, chosen as representative substrate, was reacted with Chan's diene in the presence of enantioenriched

Table 3. MW-assisted vinylogous aldol reaction of Chan's diene **5** on electron-poor aldehydes **3** realized via Scheme 5 (Procedure 2).

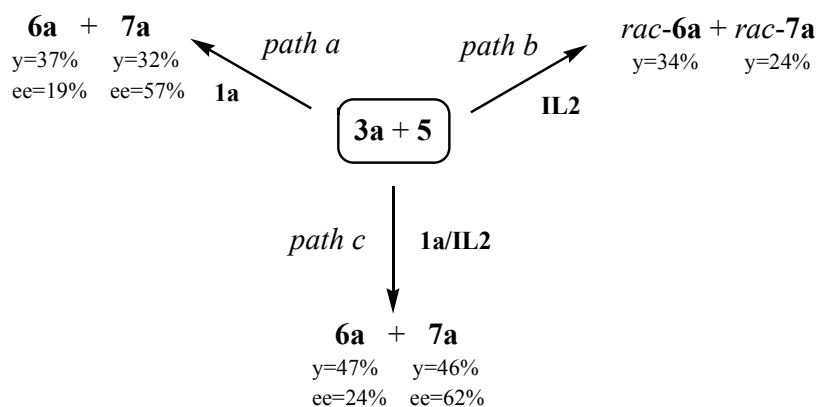
Entry	R-	Catalyst	Product	Yield% ^a	ee% ^b	Product	Yield% ^a	ee% ^b
1 ^c	<i>o</i> -NO ₂ C ₆ H ₄	-	6a	26	-	7a	23	-
2 ^d	<i>o</i> -NO ₂ C ₆ H ₄	-	6a	43	-	7a	27	-
3 ^c	<i>o</i> -NO ₂ C ₆ H ₄	1a	6a	29	18	7a	49	54
4 ^d	<i>o</i> -NO ₂ C ₆ H ₄	1a	6a	40	28	7a	54	61
5 ^d	<i>o</i> -NO ₂ C ₆ H ₄	IL2 / 1a	6a	29	44	7a	23	71
6 ^d	<i>p</i> -NO ₂ C ₆ H ₄	1a	6e	13	32	7e	13	42
7 ^d	<i>p</i> -NO ₂ C ₆ H ₄	IL2 / 1a	6e	21	41	7e	27	50
8 ^c	<i>p</i> -CN C ₆ H ₄	1a	6c	29	36	7c	34	47
9 ^d	<i>p</i> -CF ₃ C ₆ H ₄	1a	6b	23	28	7b	24	45
10 ^d	<i>p</i> -CF ₃ C ₆ H ₄	IL2 / 1a	6b	10	41	7b	11	57

^aYields refer to isolated chromatographically pure compounds, whose structures were confirmed by spectroscopic data (¹H-NMR, ¹³C-NMR, MS, IR).

^bE.e.s were determined by HPLC analysis.

^cThe reaction was conducted by submitting the pre-cooled reaction mixture to MW irradiation (15 min, P = 10 W).

^dThe reaction was conducted by submitting the pre-cooled reaction mixture to cycles of MW irradiation (6 cycles, 5 min each cycle, P = 10 W).

**Scheme 4.** Summary scheme of the reaction of Chan's diene **5** with **3a**, promoted by different catalytic systems

TADDOL derivative **1a** under solvent-free conditions.

The resulting multishaped curves A and B (respectively Figs. 3 and 4) suggested the involvement of an oligomeric catalytic species both in the vinylogous aldol addition and the cycloaddition reaction. Probably, in the absence of any solvent, the involvement of structures with more than one TADDOL molecule ("autoassociation") in the catalytic cycle is favoured differently from Rawal and Ding's model (*vide supra*), proposed for reactions taking place in solution, and involving one only TADDOL molecule in the transition state.

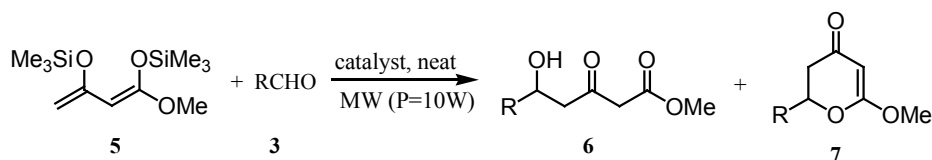
In a similar way, **3a** was reacted with Chan's diene **5** in the presence of **IL2** / enantioenriched **1a** system. The attainment of multishaped curves C and D (Figs. 3 and 4 respectively) notably differing from A and B represented a further confirmation of the participation of the ionic liquid to the formation of new oligomeric supramolecular species, resulting, in most reported cases, in an increased enantioselectivity. To the best of our knowledge, this is the first study of NLEs on organocatalytic reactions based on the hydrogen-bonding activation of a carbonyl compound.

In the recent years an important contribution for the achievement or the improvement of expeditious and selective synthetic procedures has been afforded

by micro-wave (MW) irradiation [18]. In this area, the possibility to apply this alternative energy source to solvent-free organocatalyzed reactions in order to realize procedure at low environmental impact is particularly intriguing and so, a variety of reactions under solvent-free conditions has been widely explored, without any significant loss of efficiency and selectivity. Generally it is very difficult to realize vinylogous aldol additions under MW irradiation, due to the thermal instability of the employed silyloxydienes. Therefore, it seemed interesting to evaluate the catalytic properties of TADDOL derivative **1a**, under MW-irradiation [19], in the reaction of Chan's diene **5** with aldehydic substrates (Scheme 5).

Taking in mind the well-known thermal instability of **5** [20], the experimental conditions had to be carefully chosen in order to avoid overheating of the reaction mixture. Therefore, MW-assisted reactions were carried out using a single mode cavity dedicated reactor (CEM Discover). A preliminary experiment was performed on *o*-nitro-benzaldehyde, chosen as representative substrate, in the absence of organocatalyst (entry 1, Table 3) and the reaction mixture, previously pre-cooled at -78°C [21], was submitted to MW irradiation for 15 min.

Power-controlled conditions (P = 10W) ensured



Scheme 5. Asymmetric addition of diene **5** to aldehydes under MW irradiation

values of temperature lower than 35°C and the attainment of vinylogous aldol **6a** and cycloadduct **7a** (respectively 26% and 23% yield) confirmed an acceptable compatibility of MW treatment with the thermal lability of Chan's diene **5**. Although no significant improvement was observed after more prolonged reaction time, the mode of irradiation had a deep influence on the preparative outcome. In fact, when entry 1 was repeated by submitting the pre-cooled reaction mixture to cycles of MW irradiation (6 cycles, 5 min each cycle, P = 10W) a different efficiency and products distribution was observed as supported by the attainment of **6a** and **7a** respectively in 43% and 27% yield (entry 2). In entries 3 and 4 both the modes of MW irradiation were used to examine the influence of the organocatalyst **1a**. We were pleased to observe significant enhancement of the efficiency of the process and, most interestingly, the achievement of comparable levels of enantioselectivity for products **6a** and **7a** with respect to the conventional procedure (cfr entry 2 of Table 2 with entries 3 and 4 of Table 3).

As predictable, when **1a** / **IL2** catalytic system was used, overheating was rather difficult to avoid because of the increased polarity of the reaction mixture, so that the thermal decomposition of Chan's diene showed to be the predominant process. In fact in entry 5, the temperature enhancement up to 55°C resulted in a notable decrease of both the yields of **6a** and **7a**. Conversely, most interestingly, the employment of the new catalytic species **1a** / **IL2** allowed to attain products **6a** and **7a** in higher ee.s (respectively 44% and 71% ee).

The scope of the procedure was evaluated by submitting to the usual treatments other electron-poor aldehydes: satisfactory results were obtained in entries 8 and 9, while, rather surprisingly, *p*-nitro-benzaldehyde pointed out a rather modest reactivity resulting in a significant drop of efficiency (entry 6). Conversely, improved yields and ee.s both for products **6** and **7** were afforded by the new **1a** / **IL2** catalytic system.

4. Conclusions

In conclusion, naphthyl TADDOL derivative **1a** has confirmed its synthetic versatility since, in combination with suitable imidazolium-based ionic liquids has been conveniently used in a solvent-free procedure for the reaction of Chan's diene with activated aromatic aldehydes. A mechanistic investigation, based on the detection of nonlinear effects, has pointed out the participation of several TADDOL molecules in the catalytic cycle and then the involvement of the used ionic liquid in the formation of a new supramolecular catalytic species; the extension of this activation strategy to other hydrogen-bonding organocatalysts reasonably discloses interesting perspectives in asymmetric synthesis, especially by considering that in solvent-free conditions the intermolecular interactions are enhanced. Furthermore, through an accurate control of temperature, the reaction of **5** with electron-poor aldehydes was performed under MW irradiation affording the corresponding aldols **6** and cycloadducts **7** in satisfactory yields and ee.s at very low power values (only 10 W) and in rather reduced reaction times compared to the conventional thermal treatment. Finally, in some cases, the use of naphthyl TADDOL derivative/ ionic liquid catalytic system under MW irradiation resulted in an enhancement of enantioselectivity.

Acknowledgments

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