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# Ion-Tagged Prolinamide Organocatalysts for the Direct Aldol Reaction On-Water

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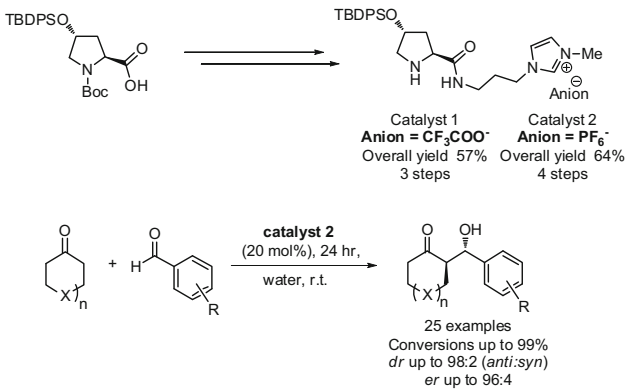
**Abstract** A concise synthesis of two imidazolium ion-tagged prolinamide organocatalysts 3 and 4, varying in anionic component ($CF_3COO^-$ and $PF_6^-$, respectively) is presented. The latter could be classified as an ionic liquid with a melting point of 66.3 °C, and glass transition temperature of 14.5 °C. The efficiency of each catalyst was compared via a direct aldol reaction revealing a large contrast in catalytic performance, with the catalyst bearing the $PF_6^-$ anion being superior. The optimal conditions were determined to be an on-water reaction system, and substrate scoping gave a range of desired aldol products in high conversion (up to >99 %), dr (up to 98:2), and er (up to 96:4). The application of these catalysts to beta-nitrostyrene conjugate addition is also presented.

*Graphical Abstract*




**Keywords** Organocatalyst · Imidazolium · Aldol · On-water

## 1 Introduction

Widely recognised as the third pillar of catalysis, organocatalysis has become a major field of research and a viable means of installing asymmetry within complex molecules [1–5]. While organic transformations carried out by organocatalysis have become increasingly complex, so too has the structure of the organocatalysts themselves [6–10]. Efforts in recycling organocatalysts have heavily centred on conjugation to a solid support, to remove the tethered catalysts by filtration [11–15]. Recently, the introduction of imidazolium salts into catalyst structures has been used as a means to control solubility properties of the catalyst allowing for separation of reaction products/reagents from the catalyst by selective solubilisation [14,

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16–33]. Of the published imidazolium supported catalysts, the majority are based on 4-hydroxyproline and incorporate the imidazolium group via the oxygen at the 4 position (Fig. 1 **1** and **2**). This approach leaves the amine and carboxylic acid of the proline scaffold unmodified and has shown to be a successful strategy to develop efficient catalysts of broad scope.

An exception to this trend was recently reported by Zlotin [16], who synthesised a $C_2$-symmetric *bis*-prolinamide organocatalyst, which displayed good catalytic activity and scope despite the absence of α-carboxylic acid. The focus of the current study was to explore the effect, if any, on installing the imidazolium salt via the C-terminus of *trans*-4-hydroxyproline scaffold. Given the hydrogen bonding capabilities of the imidazolium group, its presence in close proximity to the proline nitrogen may lead to enhanced catalytic performance or participation in hydrogen bonding within the transition state [34, 35].

We were also interested in how we may manipulate the physical behaviour of these catalysts by variations of anion (Fig. 1) in addition to their effectiveness as organocatalysts. The target imidazolium tagged prolinamides were to be decorated with a *tert*-butyldiphenyl silyl group at the 4-position, a widely reported modification that would allow for broad comparison of our catalysts to published examples [36–38]. In this manuscript we present the synthesis and evaluation of imidazolium supported organocatalysts which incorporate $PF_6^-$ and trifluoroacetate ($F_3CCOO^-$) anions. We compare the physical properties and catalytic performance of these compounds demonstrating their catalytic potential in both the direct aldol reaction and conjugate addition to β-nitrostyrenes.

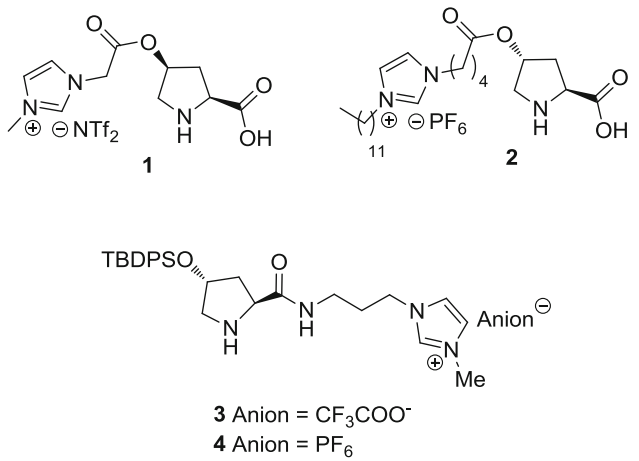



**Fig. 1** Known imidazolium salt supported organocatalysts **1** and **2**, with target organocatalysts for this study, **3** and **4**

## 2 Results and Discussion

### 2.1 Synthesis of Organocatalysts 3 and 4

Our strategy for accessing target catalysts was based on previous approaches used by Zlotin et al. and Maio et al. where the heterocyclic amine is liberated at the last step, typically by cleavage of Cbz, *N*-benzyl or Boc protecting group. We initially chose the latter, incorporating a Boc protecting group onto the proline nitrogen, in addition to a *tert*-butyldiphenyl silane on the alcohol moiety at the 4-position (**5**) as we have had extensive experience with this scaffold.

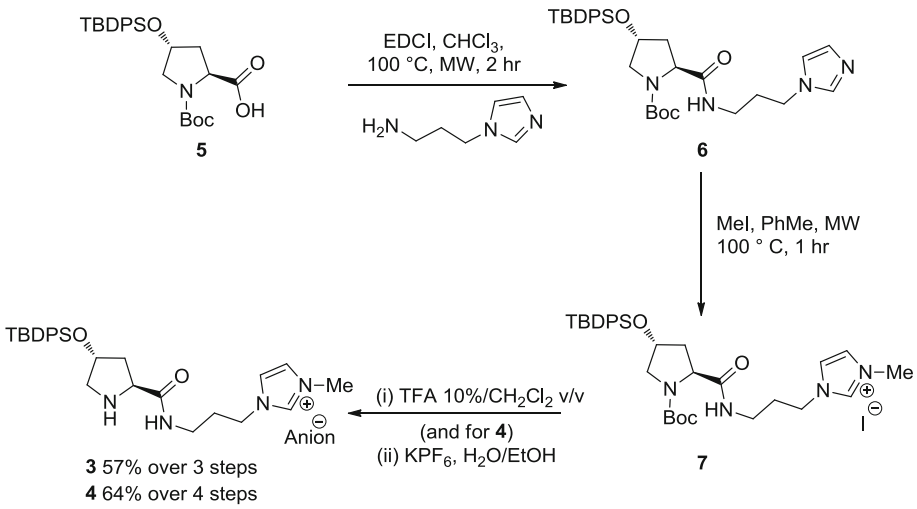
Amide formation using carboxylic acid **5** and 3-aminopropylimidazole gave **6** in excellent yield (99 %). This was followed by treatment of **6** with methyl iodide under microwave irradiation to generate the imidazolium **7** in good yield (79 %). Interestingly, the imidazolium salt **7** was able to be purified by column chromatography (Scheme 1).

From **7**, the removal of the Boc group was successfully carried out using 10 % TFA/$CH_2Cl_2$ overnight. This was accompanied by concomitant exchange of the anion from iodide to trifluoroacetate, indicated by the shift of the H2 proton observed by $^1$H NMR spectroscopy. Isolation of **3** was achieved by careful organic extraction and washing with $NaHCO_3$ which gave **3** in good yield (73 %). Alternatively, prior to aqueous work up, a solution of $KPF_6$ could be added to the solution, executing anion metathesis to give catalyst **4**, also in good yield (82 %). This gave excellent overall yields for both **3** and **4** (57 and 64 %, respectively), the slightly depressed yield for **3**, despite having one less step, was attributed to a slight solubility in water, thus a small amount being lost in work up.

### 2.2 Physical Characterization of 3 and 4

With imidazolium salts **3** and **4** in hand, our attention turned to determining if these materials could technically be classified as an ionic liquids. Ionic liquids are broadly defined as molten salts which possess a melting point under 100 °C, have negligable vapour pressure, and excellent thermal stability. We were pleased to see that the melting point of **4** was 66.3 °C, well below the generally accepted 100 °C cut-off, while **3** was 118 °C and thus not technically defined as an ionic liquid. This observation was attributed to the more charge diffuse nature of the $PF_6^-$ anion. Next we undertook isothermal thermogravimetric analysis (TGA) at 100 °C, with **4** only, to determine evaporation phenomena, if any. After 80 min at 100 °C no major loss in weight was observed for this material, consistent with the behaviour of ionic liquids.

**Scheme 1** Synthesis of target organocatalysts **3** and **4**




The initial loss in sample weight is presumably water being evaporated from the solid sample, as this occurrs after the temperature reaches 100 °C (red line, Fig. 2). The variation seen is typically <10 % of the sample weight and most likely due to evaporation of residual moisture. Additionally, differential scanning calorimetry (DSC) was conducted on **4**, giving a glass transition temperature ($T_g$) of 14.5 °C.

### 2.2.1 *Evaluation of Organocatalysts **3** and **4** as Organocatalysts*

Our attention now turned to evaluation of **3** and **4** as organocatalysts. We chose the direct asymmetric aldol reaction for catalyst evaluation as it is a benchmark reaction for catalyst evaluation in the literature and we have previous experience with this system. The optimisation began using catalyst **3** (bearing the trifluoroacetate anion) in neat reaction conditions (Table 1, Entry 2). We were pleased to see that full conversion to **9** had taken place, though the product showed no diastereoisomeric enrichment, an outcome that may have been due to the extended reaction times (72 h) in the presence of a basic counter ion ($F_3COO^-$).

Repeating the reaction on water at a reduced reaction time (Table 1, entry 3) gave only a slightly depressed conversion (93 %) and a *dr* of 71:29 (*anti:syn*). Unfortunately, the product was found to possess minimal enantioenrichment (5 %). When using the same reaction duration under neat reaction conditions (Table 1, Entry 4), a depressed conversion (88 %) and *dr* 68:32 (*anti:syn*) was observed. This is consistent with literature whereby neat reaction conditions result in a homogenous mixture while the addition of water creates an emulsion giving an 'on-water' effect that enhances reaction outcomes [36–49]. This phenomena was supported when reacting **3** in an organic solvent (Table 1, Entry 5) which gave very poor conversion to the desired product.

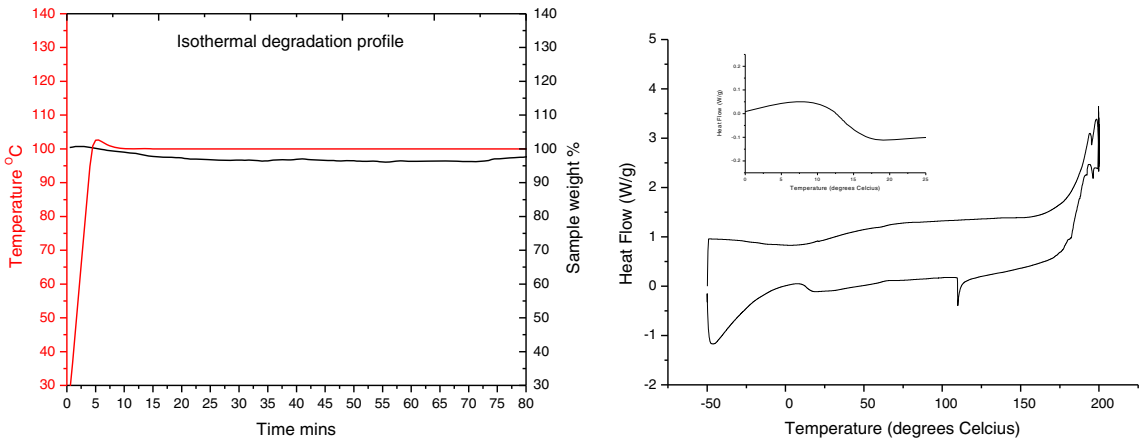
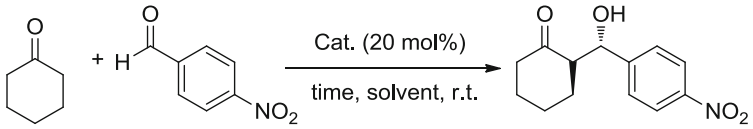



**Fig. 2** Isothermal TGA showing no evaporation of **4** when in the liquid state (*left*) and DSC showing *Tg* (*right*) with key curve (*inset*)

**Table 1** Optimisation of organocatalyst **3** and **4**




**7** **8** **9**

| Entry | Cat. | Solvent | Time (h) | Conversion[a] (%) | *dr*[a] (*anti:syn*) | *er*[b] |
|---|---|---|---|---|---|---|
| 1 | – | Neat | 24 | 0 | 0 | 0 |
| 2 | **3** | Neat | 72 | 97 | 1:1 | – |
| 3 | **3** | $H_2O$ | 24 | 93 | 71:29 | 60:40 |
| 4 | **3** | Neat | 24 | 88 | 68:32 | 53:47 |
| 5 | **3** | $CHCl_3$ | 24 | 15 | 72:28 | – |
| 6 | **4** | Neat | 24 | 99 | 80:20 | 76:24 |
| 7 | **4** | $H_2O$ | 24 | 71 | 85:15 | 76:24 |
| 8 | **4** | Neat[c] | 24 | 96 | 96:4 | 92:8 |
| 9 | **4** | $CHCl_3$ | 24 | 18 | 82:18 | – |

[a] Determined by $^1$H NMR spectroscopy

[b] Determined by chiral HPLC (Diacel AD-H, *i*PA/*n*-Heptane, 5:95)

[c] Reaction carried out in 0.25 mL (12.5 eqivalents) of **7**. Reaction conditions: Aldehyde (0.1 mmol), ketone (0.5 mmol), and catalyst (20 µmol), in water (250 µL) were stirred for 24 h at room temperature, followed by aqueous work-up Note: no HPLC was conducted when conversion was <20 %

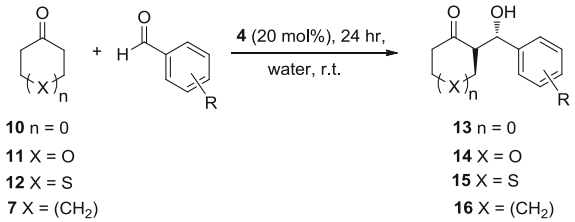
Our focus then moved to the use of catalyst **4** under the same reaction conditions to determine the effect, if any, of the IL counter ion. Employing **4** in the direct aldol reaction using neat reaction conditions (Table 1, Entry 6) gave improved *dr* 80:20 (*anti:syn*) and *er* of 77:23 compared to those furnished by **3**. The addition of water to the reaction system (Table 1, Entry 7) gave a slightly depressed yield, though an improved *dr*, 85:15 (*anti:syn*), and good *er* (76:24). It is worth noting that the 'on-water' reactions were much easier from a practical standpoint as the small amount of cyclohexanone **7** used in the neat reactions (100 µL) made solvation of all reaction components difficult. To ensuring total solvation of reagents, the neat asymmetric aldol reaction (Table 1, Entry 8) was carried out a vast excess of **7,** affording excellent outcomes in yield (96 %), very high *dr* 96:4 (*anti:syn*) and *er* 92:8. Finally, assessing **4** in an organic solvent (Table 1, Entry 9), gave poor conversion (18 %) and moderate *dr* 82:18 (*anti:syn*), similar to that provided by catalyst **3**.

This preliminary evaluation of catalysts **3** and **4** highlights the variability in reaction outcome and catalyst performance by simply changing the anionic component of the catalyst. The influence of counter ions on catalyst performance has been observed in other work, though in this instance the performance of the catalyst is extremely pronounced [33, 50, 51].

The optimal conditions were determined to be the on water process using catalyst **4** (Table 1, Entry 7). Though, the best stereochemical outcome for catalyst **4** employed a vast excess of cyclohexanone **7** (Table 1, Entry 8), the use of the ketone **7** as the reaction solvent on such a scale was considered impractical and thus was not considered. The scope of catalyst **4** was investigated with a range of ketones and aldehydes, the latter of which possess a cross-section of substituents on the aromatic portion, representing a variety of electronic effects on the aldehyde.

Using cyclopentanone **10** with the chosen aldehydes showed excellent conversions in all cases (Table 2, Entries 1–4) which is consistent with our previous work [36–38]. Also consistent when employing **10** predominant formation of the *syn*-diastereomer in preference to the *anti*-diastereomer. The *dr* and *er* values observed for these reactions varied from poor to moderate (Table 2, Entries 1 and 3, respectively). This has again been observed in our work published by this group where cyclopentanone typically gives excellent yields, but poor stereo-discrimination of the ultimate aldol product. We believe that the low *ee* values obtained when employing cyclopentanone **10** are a result of epimerisation of the products due to the presence of the catalyst reforming then substituted enamine and thus scrambling the enantiomeric centre, a more detailed discussion of this point has been provided below. Moving on to tetrahydropyranone **11** gave much better reaction outcomes across all parameters (Table 2, Entries 5–8). Though conversions varied from 55–99 %, good to high *dr* and *er* values were observed, especially when using

**Table 2** Substrate scoping for catalyst **3**




| Entry | R | X | Prod | Conversion[a] (%) | *dr*[a] (*anti:syn*) | *er*[b] |
|---|---|---|---|---|---|---|
| 1 | 4-$NO_2$ | – | **13a** | 99 | 27:73 | 54:46 |
| 2 | H | – | **13b** | 99 | 30:70 | 66:34 |
| 3 | 4-Me | – | **13c** | 83 | 34:66 | 76:24 |
| 4 | 4-Br | – | **13d** | 99 | 35:65 | 74:26 |
| 5 | 4-$NO_2$ | O | **14a** | 99 | 69:31 | 85:15 |
| 6 | H | O | **14b** | 55 | 84:16 | 96:4 |
| 7 | 4-Me | O | **14c** | 65 | 89:11 | 80:20 |
| 8 | 4-Br | O | **14d** | 84 | 71:29 | 81:19 |
| 9 | 4-$NO_2$ | S | **15a** | 99 | 97:3 | 85:15 |
| 10 | H | ($CH_2$) | **16b** | 54 | 89:11 | 77:23 |
| 11 | 4-Me | ($CH_2$) | **16c** | 29 | 86:14 | 90:10 |
| 12 | 4-Br | ($CH_2$) | **16d** | 87 | 88:12 | 92:8 |
| 13 | 3-$NO_2$ | ($CH_2$) | **16e** | 91 | 96:4 | 85:15 |
| 14 | 2-$NO_2$ | ($CH_2$) | **16f** | 83 | 98:2 | 85:15 |

[a] Determined by $^1$H NMR spectroscopy, dr reported for major distereomer only

[b] Determined by chiral HPLC (Diacel AD-H, *i*PA/*n*-Heptane, 5:95. Reaction conditions: Aldehyde (0.1 mmol), ketone (0.5 mmol), and catalyst (20 μmol), in water (250 μL) were stirred for 24 h at room temperature, followed by aqueous work-up Note: no HPLC was conducted when conversion was <20 %

4-nitrobenzaldehyde (Table 2, Entry 5), giving *er* value of 85:15, and benzaldehyde (Table 2, Entry 7), with an *er* of 96:4. Replacement of the oxygen heteroatom of **11** for sulphur (**12**) (Table 2, Entry 9) gave excellent conversion (99 %) and diastereoselectivity (97:3), and an excellent *er* of 85:15. Similarly, employing cyclohexanone **7** for the remaining aldehydes (Table 2, Entries 9–11) gave excellent stereochemical outcomes. We also examined substitution on the aryl ring and the effects on stereochemical outcome by employing 3- and 2-nitrobenzaldehyde to give **16e** and **16f**, respectively. In both cases (Table 2, Entries 13 and 14) excellent conversion and *dr* were observed. This was complemented in the *er* with very high enantiomeric ratios of 85:15 in each case.

We were interested in determining if **4** could be recycled for multiple uses in the same reaction system. This was undertaken by repeating the on-water reaction of cyclohexanone **7** and 4-bromobenzaldehyde, giving product **14d**. The full aqueous work-up was replaced by simple addition of a diethyl ether:hexane (1:1) solution to extract the aldol products only, which we had previously determined that catalyst **4** was not soluble in. It was therefore surprising to see catalyst **4** had leeched into the extraction solvent, albeit in small quantity. This may be due to the solubility of catalyst **4** in the ketone reaction partner of this aldol reaction. In the interest of thoroughness, we continued the recycling study by re-addition of fresh cyclohexanone **7** and 4-bromobenzaldehyde to the aqueous phase containing the majority of catalyst **4**. The extraction of products and addition of fresh reagents was repeated again, and it was seen that after each extraction catalyst **4** was lost in this process and the subsequent reaction gave progressively lower yields. For this data please refer to the supplementary information.

Finally, we were curious the effects observed in the aldol reaction were similar for other reaction systems. Therefore we employed catalysts **3** and **4** in the conjugate addition of cyclohexanone **7** with *trans*-β-nitrostyrene **17**, another commonly used reaction to evaluate organocatalysts [52–55].

We were pleased to see that catalyst **3** was able to effectively catalyse the formation of **18**, though the yield was excellent the *dr* was very low (53:47, *anti*:*syn*), and as such an *er* was not determined for this material (Table 3,

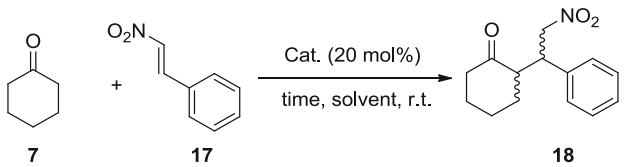
Entry 2). Repeating the reactions in organic solvents, toluene and THF, gave promising results as conversions and *dr*s were high (Table 3, Entries 3 and 4). Of these two reactions the one performed in THF gave a superior enantioenrichment (*er* (67:33) versus toluene (52:48)).

Interestingly, and in contrast to previous results presented in this manuscript, inferior stereochemical outcomes resulted when the reaction was carried out on-water or neat (Table 3, Entries 6 and 7) when compared to THF. This same preference for THF for organocatalyzed nitro-conjugate addition was also observed by Lin *et al.* [55]. Nevertheless, *dr* could be improved under neat reaction conditions by extended reaction times (Table 3, Entry 7), at the expense of *er*. Nevertheless, decreasing the catalyst loading to 5 mol% showed minimal effect on reaction outcome giving similar conversion, diastereo- and enantioenrichment when 20 mol % was employed (Table 3, Entries 8 and 9). In an effort to bolster the reaction outcomes in THF, we repeated the reactions in this solvent with additives present in the reaction mixture, which is common for this class of reaction. Unfortunately, in each case (Table 3, Entries 8–10) the conversions were depressed, and no gain in *er* was observed in any case, though improvements in *dr* were observed for benzoic acid derived additives. Despite these moderate results we are encouraged that with further examination of this system and investigation into a broader range of anions, may improve these preliminary values.

### 2.3 Regarding the Effect of the Trifluoroacetate anion on Reaction Outcome

Within this study we have attributed the poor stereoselectivities observed when employing catalyst **3**, to the effect of the trifluoroacetate anion. This is especially evident when using cyclopenanone **10** as the ketone donor in the aldol reaction (compounds **13a–13d**). In our hands, it is common to observe lower diastereo- and enantioenrichment when using cyclopentanone [36–38], which we have previously attributed to epimerisation at the α-carbon due to reformation of the enamine in the presence of the organocatalyst. The propensity of cyclopentanone to undergo epimerisation may be due to the $K_{eq}$ of the ketone-enamine equilibrium being markedly higher ($K_{eq}$ 2.3) than that of the cyclohexanone-enamine pair ($K_{eq} = 0.8$), as reported by Vilarrasa et al. (Scheme 2) [56].

**Table 3** Application of catalysts **3** and **4** to the conjugate addition of cyclohexanone **7** with *trans*-β-nitrostyrene **17**




**7** **17** **18**

| Entry | Cat. | Solvent | Time (h) | Conversion[a] (%) | *dr*[a] (*anti:syn*) | *er*[b] |
|---|---|---|---|---|---|---|
| 1 | – | Neat | 24 | 0 | 0 | 0 |
| 2 | **3** | Neat | 72 | 99 | 53:47 | – |
| 3 | **4** | PhMe | 24 | 87 | 83:17 | 52:48 |
| 4 | **4** | THF | 24 | 88 | 88:12 | 67:33 |
| 5 | **4** | Water | 24 | 83 | 75:25 | 63:37 |
| 6 | **4** | Neat | 24 | 95 | 81:19 | 63:37 |
| 7 | **4** | Neat | 96 | 90 | 91:9 | 66:34 |
| 8[f] | **4** | Water | 24 | 90 | 93:7 | 67:33 |
| 9[f] | **4** | Neat | 24 | 95 | 91:9 | 65:35 |
| 10 | **4** | THF[c] | 24 | 75 | 95:5 | 57:43 |
| 11 | **4** | THF[d] | 24 | 83 | 97:3 | 56:44 |
| 12 | **4** | THF[e] | 24 | 76 | 84:16 | 60:40 |

[a] Determined by $^1$H NMR spectroscopy

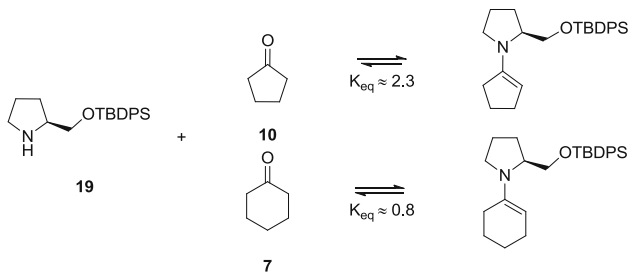
[b] Determined by chiral HPLC (Diacel AD-H, *i*PA/*n*-Heptane, 5:95) for major diastereoisomer only

[c] Benzoic acid additive at 20 mol%

[d] *p*-nitrobenzoic acid additive at 20 mol%

[e] Trifluoroacetic acid additive at 20 mol%

[f] 5 mol% of catalyst was used in this reaction. Reaction conditions: Nitrostyrene (0.1 mmol), ketone (0.5 mmol), and catalyst (20 μmol), in water (250 μL) were stirred for 24 h at room temperature, followed by aqueous work-up




**Scheme 2** Work by Vilarrasa et al. [56] regarding the $K_{eq}$ of enamine formation for cyclic ketones

Nevertheless, the stereochemical outcomes for any aldol product, regardless of donor ketone, from this study seem unusually low when catalyst **3** was employed. We propose that the deleterious role of the trifluoroacetate anion is via encouraging epimerization at the α-position of the aldol products. The poor basicity and high dilution of a trifluoroacetate anionic additive would normally prevent this effect from occurring to a substantial degree, but in this case the anion is held in close proximity to the organocatalyst. Thus when imine formation occurs, causing the subsequent decrease in pKa of the α-protons, enamine (and thus epimerisation) is promoted by the trifluoroacetate counterion associated to the organocatalyst.

## 3 Conclusion

Presented herein is a concise and high yielding synthesis of two ionic liquid supported organocatalysts **3** and **4**, accessed in three synthetic steps. Variation of the anionic component of the cationic imidazolium partner, $CF_3CCO^-$ (catalyst **3**) and $PF_6^-$ (catalyst **4**) had a pronounced effect on both the physical properties and catalytic behaviour of these compounds. The latter catalyst (**4**) being technically classified as a chiral ionic liquid, possessing a melting point below 100 °C and exhibiting no evaporation phenomena by isothermal TGA and a $T_g$ of 14.5 °C. Evaluation of these catalysts in the direct asymmetric aldol reaction revealed a significant contrast in catalytic performance between **3** and **4**, with the former giving good reaction conversion but very poor stereochemical outcome for both *dr* and *er*, attributed to the presence of the trifluoroacetate anion in solution. We have proposed that the unsuitability of the trifluoroacetate anion is a result of encouraging epimerisation of the aldol products. Conversely, catalyst **4** performed well in the direct aldol reaction and showed excellent application across a range of ketones and aldehydes.

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## References

1. Dondoni A, Massi A (2008) Angew Chem Int Ed 47:4638–4660
2. Gaunt MJ, Johansson CC, McNally A, Vo NT (2007) Drug Discov Today 12:8–27
3. Pellissier H (2007) Tetrahedron 63:9267–9331
4. List B, Lerner RA, Barbas CF III (2000) J Am Chem Soc 122:2395–2396
5. Mukherjee S, Yang JW, Hoffmann S, List B (2007) Chem Rev 107:5471–5569
6. Chen XH, Yu J, Gong LZ (2010) Chem Commun 46:6437–6448
7. Lo CM, Chow HF (2009) J Org Chem 74:5181–5191
8. Moorthy JN, Saha S (2010) Eur J Org Chem 2010:6359–6365
9. Tian H, Gao J-L, Xu H, Zheng L-Y, Huang W-B, Liu Q-W, Zhang S-Q (2011) Tetrahedron Asymmetry 22:1074–1080
10. Guizzetti S, Benaglia M, Pignataro L, Puglisi A (2006) Tetrahedron Asymmetry 17:2754–2760
11. Akagawa K, Sakamoto S, Kudo K (2005) Tetrahedron Lett 46:8185–8187
12. Alza E, Sayalero S, Kasaplar P, Almasi D, Pericas MA (2011) Chem Eur J 17:11585–11595
13. Goren K, Portnoy M (2010) Chem Commun 46:1965–1967
14. Li P, Wang L, Zhang Y, Wang G (2008) Tetrahedron 64:7633–7638
15. Miranda PO, Lizandara-Pueyo C, Pericàs MA (2013) J Catal 305:169–178
16. Kochetkov SV, Kucherenko AS, Kryshtal GV, Zhdankina GM, Zlotin SG (2012) Eur J Org Chem 2012:7129–7134
17. Kucherenko AS, Siyutkin DE, Nigmatov AG, Chizhov AO, Zlotin SG (2012) Adv Synth Catal 354:3078–3086
18. Larionova NA, Kucherenko AS, Siyutkin DE, Zlotin SG (2011) Tetrahedron 67:1948–1954
19. Maltsev OV, Chizhov AO, Zlotin SG (2011) Chem Eur J 17:6109–6117
20. Maltsev OV, Kucherenko AS, Zlotin SG (2011) Mendeleev Commun 21:146–148
21. Siyutkin DE, Kucherenko AS, Frolova LL, Kuchin AV, Zlotin SG (2011) Tetrahedron Asymmetry 22:1320–1324
22. Siyutkin DE, Kucherenko AS, Frolova LL, Kuchin AV, Zlotin SG (2013) Tetrahedron Asymmetry 24:776–779
23. Siyutkin DE, Kucherenko AS, Struchkova MI, Zlotin SG (2008) Tetrahedron Lett 49:1212–1216
24. Siyutkin DE, Kucherenko AS, Zlotin SG (2009) Tetrahedron 65:1366–1372
25. Siyutkin DE, Kucherenko AS, Zlotin SG (2010) Tetrahedron 66:513–518
26. Lombardo M, Easwar S, Pasi F, Trombini C (2009) Adv Synth Catal 351:276–282
27. Miao W, Chan TH (2006) Adv Synth Catal 348:1711–1718
28. Khan SS, Shah J, Liebscher J (2011) Tetrahedron 67:1812–1820
29. Liebscher J, Shah J, Khan S, Blumenthal H (2009) Synthesis 2009:3975–3982
30. Brozinski HL, Delaney JP, Henderson LC (2013) Aust J Chem 66:844
31. Li J, Liu L (2013) Synth Commun 43:476–485
32. Luo S, Mi X, Zhang L, Liu S, Xu H, Cheng JP (2006) Angew Chem Int Ed 45:3093–3097
33. Ni B, Zhang Q, Headley AD (2008) Tetrahedron Lett 49:1249–1252
34. Hunt PA, Kirchner B, Welton T (2006) Chem Eur J 12:6762–6775

35. Izgorodina EI, MacFarlane DR (2011) J Phys Chem B 115:14659–14667
36. Delaney JP, Brozinski HL, Henderson LC (2013) Org Biomol Chem 11:2951–2960
37. Delaney JP, Henderson LC (2011) Int J Mol Sci 12:9083–9094
38. Delaney JP, Henderson LC (2012) Adv Synth Catal 354:197–204
39. Aratake S, Itoh T, Okano T, Usui T, Shoji M, Hayashi Y (2007) Chem Commun 24:2524–2526
40. Giorgi G, López-Alvarado P, Miranda S, Rodriguez J, Menéndez JC (2013) Eur J Org Chem 2013:1327–1336
41. Gruttadauria M, Giacalone F, Noto R (2009) Adv Synth Catal 351:33–57
42. Hayashi Y (2006) Angew Chem Int Ed 45:8103–8104
43. Jung Y, Marcus RA (2007) J Am Chem Soc 129:5492–5502
44. Mase N, Barbas CF III (2010) Org Biomol Chem 8:4043–4050
45. Tzeng Z-H, Chen H-Y, Huang C-T, Chen K (2008) Tetrahedron Lett 49:4134–4137
46. Beattie JK, McErlean CS, Phippen CB (2010) Chem Eur J 16:8972–8974
47. Mlynarski J, Paradowska J (2008) Chem Soc Rev 37:1502–1511
48. Raj M, Singh VK (2009) Chem Commun 44:6687–6703
49. Simon MO, Li CJ (2012) Chem Soc Rev 41:1415–1427
50. Li P, Wang L, Wang M, Zhang Y (2008) Eur J Org Chem 2008:1157–1160
51. Luo S, Mi X, Zhang L, Liu S, Xu H, Cheng J-P (2006) Angew Chem Int Ed 45:3093–3097
52. Lin J, Tian H, Jiang Y-J, Huang W-B, Zheng L-Y, Zhang S-Q (2011) Tetrahedron Asymmetry 22:1434–1440
53. Lu A, Liu T, Wu R, Wang Y, Zhou Z, Wu G, Fang J, Tang C (2010) Eur J Org Chem 2010(30):5777–5781
54. Zhong J, Guan Z, He Y-H (2013) Catal Commun 32:18–22
55. Lin J, Tian H, Jiang Y-J, Huang W-B, Zheng L-Y, Zhang S-Q (2011) Tetrahedron Asymmetry 22:1434–1440
56. Sanchez D, Bastida D, Bures J, Isart C, Pineda O, Vilarrasa J (2012) Org Lett 14(2):536–539