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Synthesis and evaluation of (*S*)-proline-containing dipeptidic organocatalysts bound to MBHA resin in asymmetric aldol reactions.

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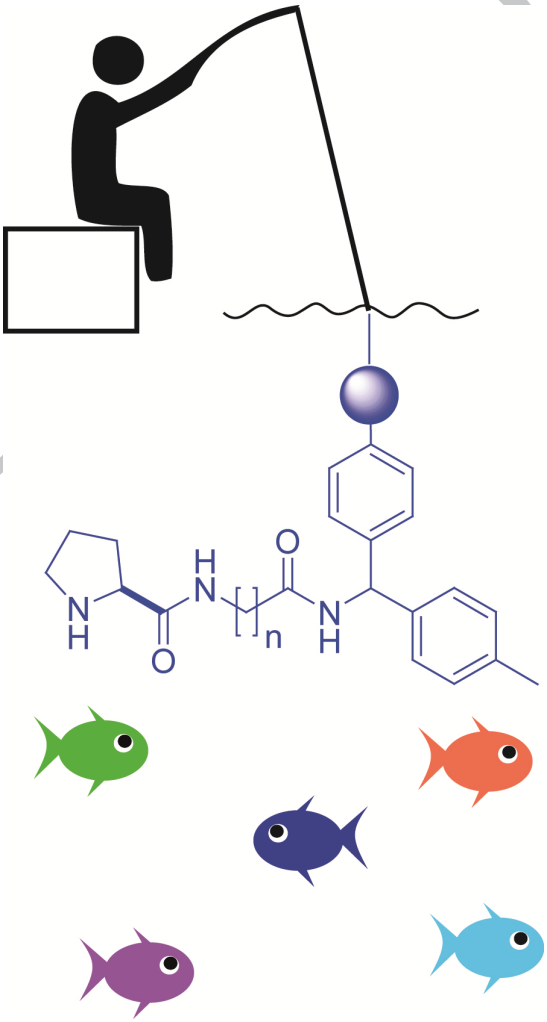

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ABSTRACT

The effectiveness of MBHA-bound dipeptidic organocatalysts **1a-d** in the asymmetric aldol reaction between cyclohexanone and several aldehydes was evaluated. Under the optimum reaction conditions, which involved the use of Brønsted acid and water as additives, it was found that the presence of one glycine or one β-alanine residue in **1b** and **1c** resulted in improved stereoselectivity relative to **1a**. Supported organocatalyst **1d** bound to the resin by a five methylene spacer was also effective as catalyst. Representative organocatalyst **1c** was re-used as catalyst in five consecutive cycles in the asymmetric aldol reaction maintaining its effectiveness, although some loss in yield and stereoselectivity was observed.

1. Introduction

In recent years, synthetic chemists have drawn inspiration from Nature when developing catalytic chemical reactions. A notable example is the enormous advancement that has been achieved in the area of asymmetric organocatalysis, inspired in large measure by the mechanism of action of type I and type II aldolases.[1,2] In this regard, (*S*)-proline and derivatives have proved to be particularly successful as a most simple enzymic mimics, and have become indeed privileged chiral organocatalysts.[3]

Recently, our research group has been involved in the design and evaluation of (*S*)-proline-containing dipeptides as potential organocatalysts.[4] In this context, we became interested in the preparation and use of derivatives that would be fixed to a resin in order to improve the reaction conditions, and to allow reuse of the catalyst, fulfilling one requirement of sustainable chemistry.[5,6]

The present study examined the catalytic activity of four (*S*)-proline-containing dipeptidic organocatalysts bound to MBHA resin in asymmetric aldol reactions. In particular, this study evaluated the effectiveness of the asymmetric catalyst when varying the length of the linking connector (spacer) to the resin. One goal of this analysis was to determine whether the spatial position of the catalysts in the resin plays a relevant role in their activity.

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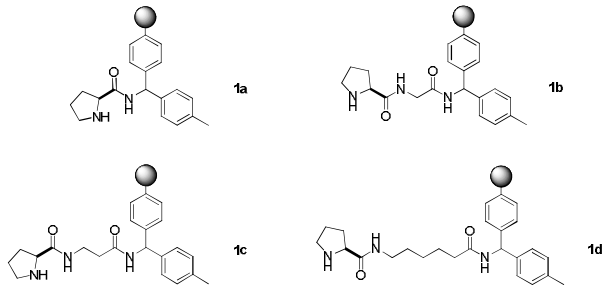
Results and discussion.

Organocatalysts **1a-d** (Scheme 1) were manually synthesized according to solid-phase peptide synthesis methodology, and using Fmoc as protecting group, and then supported on MBHA (4-methylbenzhydrylamine) resin.[7]

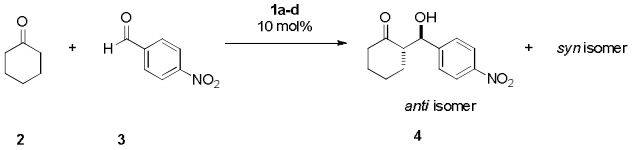


Scheme 1.Organocatalysts **1a-d** anchored to MBHA (4-methylbenzhydrylamine) resin studied in this work.

Organocatalysts **1a-d** were evaluated in the asymmetric aldol reaction between cyclohexanone and 4-nitrobenzaldehyde (Table 1). With **1a** and after 24 hours of reaction, the aldol product (2*S*,1'*R*)-**4** was obtained in 92% yield, an *anti:syn* diastereomeric ratio of 74:26, and enantiomer ratio of 77:23 for the major aldol product (2*S*,1'*R*)-**4** (Entry 1 in Table 1). By contrast, reaction with organocatalyst-**1b** afforded the aldol product in only 27%

yield, and low stereoselectivity (68:32 dr and 53:47 er. Entry 2 in Table 1). The low yield is probably the consequence of lack of homogeneity of the system during the reaction. Results with organocatalysts **1c** and **1d** are also included in Table 1. Both the diastereomeric ratio and enantiomeric ratio are slightly lower with **1c** and **1d**, relative to **1a**.

Table 1. Preliminary evaluation of the behavior of organocatalysts **1a-d** in the asymmetric aldol reaction between cyclohexanone and 4-nitrobenzaldehyde.



2 3 4

Entry	Cat.	Yield (%)[b]	dr (*anti:syn*)[c]	er[d]
1	**1a**	**92**	**74:26**	**77:23**
2	**1b**	27	68:32	53:47
3	**1c**	88	68:32	67:33
4	**1d**	99	68:32	67:33

[a]Reaction conditions: cyclohexanone **2** (0.5 mL), 4-nitrobenzaldehyde **3** (0.20 mmol), Catalyst **1a-d** (10mol %), 24 h. [b] Isolated yield. [c] Determined by ^{1}H NMR of the crude product. [d]Determined by chiral HPLC.

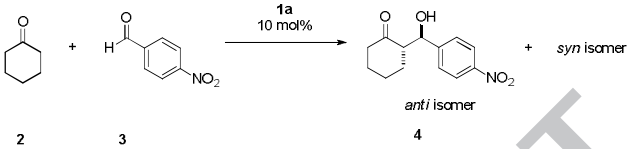
For reaction optimization, the aldol reaction that was catalyzed by dipeptide **1a** was used as model (Table 2).[8,9] In particular, seeking to improve the diastereomeric and enantiomeric ratios, we explored the effect of additives such as water and Brønsted acids. Indeed, with different amount of water present in the reaction system, both the reaction yield and diastereoselectivity increased significantly. The best ratio of cyclohexanone and H_2O turned out to be 1:1.5 (99% yield, 83:17 *anti*:*syn* dr, 85:15 er. Entry 4 in Table 2).

In addition, we evaluated several Brønsted acids as additives, a strategy that has proved useful to improve the enantioselectivity of organocatalyzed reactions.[10] When 10 mol% of benzoic acid under neat conditions in the absence of water was added, the reaction was substantially improved both in yield (the reaction was essentially quantitative) and in time, requiring only 6 h instead of 24 h (compare entries 1 and 5, Table 2).

To evaluate the potential synergistic effect of water and Brønsted acid additives, we examined the effect of including different amounts of benzoic acid in addition to a 1:1.5 mixture of cyclohexanone and water. As it turned out, with 20 mol% of benzoic acid in the presence of 1.5 mL of water, the degree of stereoselectivity was improved substantially, obtaining the adduct (2*S*,1'*R*)-**4** in 91:9 $dr_{anti:syn}$ and 83:17 enantiomeric ratio (Entry 8 in Table 2). These results could not be improved further with substituted benzoic acids (cf. entries 11 and 12 in Table 2) or even with chiral organic acids as additives (cf. entries 13 and 14 in Table 2).

Subsequently, we determined the optimum amount of **1a** necessary to catalyze the desired reaction, finding that10 mol% is the amount of organocatalyst that affords the best results (Entry 5 in Table 3).

Table 2. Optimization of the reaction conditions with organocatalyst **1a**, in the presence of water and Brønsted acid as additives.

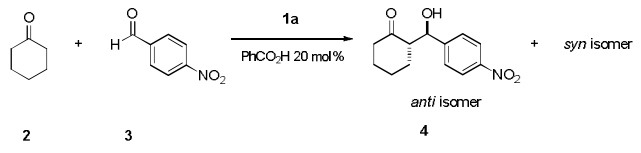


2 3 4

Entry	**2**:H_2O	Brønsted acid	Yield (%)[b]	dr (*anti:syn*)[c]	er[d]
1	**-----**	**------**	92	74:26	77:23
2	1.5:1	----	99	86:14	75:25
3	1:1	---	99	80:20	78:22
4	1:1.5	---	98	88:12	78:22
5	---	$PhCO_2H$ (10 mol%)	99	72:28	75:25
6	1:1.5	$PhCO_2H$ (5mol%)	99	85:15	81:19
7	1:1.5	$PhCO_2H$ (10 mol%)	99	89:11	81:19
8	**1:1.5**	**$PhCO_2H$ (20 mol%)**	**99**	**91:9**	**83:17**
9	1:1.5	$PhCO_2H$ (30mol%)	99	85:15	78:22
10	1:1.5	$PhCO_2H$ (40mol%)	99	86:14	80:20
11	1:1.5	4-NO_2-$PhCO_2H$ (20mol%)	99	87:13	78:22
12	1:1.5	2-HO-$PhCO_2H$ (20mol%)	99	85:15	78:22
13	1:1.5	(D)-mandelic acid(20mol%)	99	87:13	78:22
14	1:1.5	(L)-mandelic acid (20mol%)	99	90:10	77:23

[a]Reaction conditions: cyclohexanone **2** (0.5 mL), 4-nitrobenzaldehyde **3** (0.20 mmol), Catalyst **1a** (10mol %), H_2O (0.75 mL), $PhCO_2H$ (20 mol %), 6 h. [b] Isolated yield. [c] Determined by ^{1}H NMR of the crude product. [d]Determined by chiral HPLC.

Table 3.Evaluation of the amount of catalyst required for efficient catalysis.



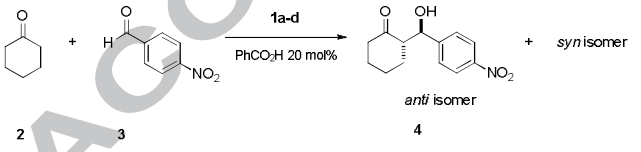
Entry	Amount	Yield (%)[b]	dr (*anti:syn*)[c]	er[d] (%)
1	resine	-----	-----	-----
2	1 %	53	92:8	72:28
3	3 %	91	90:10	78:22
4	5 %	98	92:8	72:28
5	**10 %**	**99**	**91:9**	**83:17**
6	20 %	99	84:16	75:25
7	30 %	99	87:13	80:20

[a]Reaction conditions: cyclohexanone **2** (0.5 mL), 4-nitrobenzaldehyde **3** (0.20 mmol), Catalyst **1a** (10mol %), H_2O (0.75 mL), $PhCO_2H$ (20 mol %), 6 h. [b] Isolated yield. [c] Determined by ^1H NMR of the crude product. [d]Determined by chiral HPLC.

Finally, we re-examined organocatalysts **1a-d** under the optimized reaction conditions, achieving the best results in the aldol reaction organocatalyzed by dipeptide **1c**. Thus, with 10 mol% of catalyst, 20 mol% of benzoic acid, and 1:1.5 cyclohexanone: water ratio, after 6 hours of reaction the desired product (2*S*,1′*R*)-**4a** was obtained in 99% yield, 94:6 dr, and 89:11 er (Entry 3 in Table 4).

Under the optimized reaction conditions, the observed stereoselectivity was rather similar with all four organocatalysts. Thus, the catalytic activity of the anchored organocatalysts is little influenced by the length of the connector to the resin. As the resin is a complex network of polymers, the different chains of the spacer are apparently not differentiated in the space occupied by the catalyst.

Table 4.Effect between the spacer in the resin organocatalysts **1a-d**.

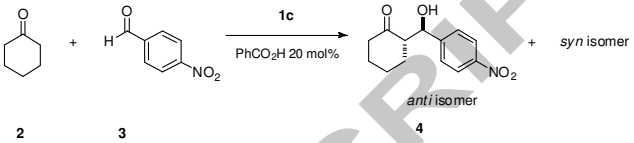


Entry	Cat.	Yield (%)[b]	dr (*anti:syn*)[c]	er[d] (%)
1	**1a**	99	91:9	83:17
2	**1b**	72	93:7	88:12
3	**1c**	**97**	**94:6**	**89:11**
4	**1d**	99	91:9	86:14

[a]Reaction conditions: cyclohexanone **2** (0.5 mL), 4-nitrobenzaldehyde **3** (0.20 mmol), Catalyst **1a-d** (10mol %), H_2O (0.75 mL), $PhCO_2H$ (20 mol %), 6 h. [b] Isolated yield. [c] Determined by ^1H NMR of the crude product. [d]Determined by chiral HPLC.

Regarding the ability to reuse the anchored organocatalysts, it was confirmed that **1c** can be reused at least 5 times, although some loss in yield and stereoselectivity was observed (Table 5). In this context, the organocatalyst can be recovered by simply washing the resin with DCM before its reuse.

Table 5.Recycling organocatalyst **1c** in the asymmetric aldol reaction.



Entry	Cycle	Yield (%)[b]	dr (*anti:syn*)[c]	er[d] (%)
1	1	97	94:6	89:11
2	2	93	76:24	84:16
3	3	60	86:14	80:20
4	4	63	84:16	83:17
5	5	75	84:16	96:4

[a]Reaction conditions: cyclohexanone **2** (0.5 mL), 4-nitrobenzaldehyde **3** (0.20 mmol), Catalyst **1c** (10mol %), H_2O (0.75 mL), $PhCO_2H$ (20 mol %), 6 h. [b] Isolated yield. [c] Determined by ^1H NMR of the crude product. [d]Determined by chiral HPLC.

By contrast, organocatalysts **1a-d** were not effective with less electrophilic aldehydes. This behavior apparently has been observed previously with other peptidic organocatalysts.[11]

2. Conclusion

We carried out the synthesis of various (*S*)-containing dipeptidic organocatalysts bound to MBHA resin and evaluated their efficiency in the asymmetric aldol reactions between cyclohexanone and 4-nitrobenzaldehyde. Spacers with different chain size; i. e., with varying number of methylene units linking the organocatalyst to the resin, were employed. Best results were obtained with supported dipeptide **1c**.

The supported organocatalysts can be reused, representing a promising strategy for implementing the principles of green chemistry.

Acknowledgments

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7. The dipeptides were manually synthesized on MBHA resin (for **1a** 0.43 mmoles, for **1b** 0.29 mmoles, for **1c** 0.27 mmoles, and for **1d** 0.22 mmoles) with 0.63 mmol/gloading on T-bags reactors and using Fmoc chemistry. In parallel, a second series was synthesized on Rink-MBHA resin (0.74 mmol/g) using the same reaction conditions. Syntheses were carried out only with (*S*)-amino acids protected with *N*-α-fluorenylmetoxycarbonyl group (Fmoc). The resins were solvated by successive washing steps with DCM (3 x 1min), 1% DIEA in (3x 1min), DCM (3x 1min) and DMF (3x 1min). Fmoc protected (*S*)-amino acids were incorporated using standard procedures and DIC/HOBt (1:1) in DMF (0.3M of Fmoc-aminoacid) as coupling agents. The Fmoc group was removed by treatment with 37 % piperidine and 0.07% Triton® X-100 in DMF. After each deprotection, peptidyl resins were washed with DMF (7 x 1min) and DCM (2 x 1 min). The ninhydrin test was used to monitor amino acid couplings and deprotections along the dipeptide synthesis. Finally, the reference peptides on Rink-MBHA resin were cleaved by treatment with 5 mL of a mixture of TFA/H_2O (95:5 v/v) at 0ºC for 15 minutes and at room temperature for 1.5 hours. TFA was removed by evaporation and the crude peptide was precipitated with *tert*-butyl methyl ether/cyclohexane mixture (1:1). The final peptidyl-resins substitution degree obtained by the Fmoc-group spectrophotometric method using DBU wasin line with anticipation.
8. **General information**. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol ECA-500 (500 MHz) spectrometer. Chemical shifts (δ) are given in parts per million downfield from tetramethylsilane as an internal reference. Coupling constants *J* are given in Hertz (Hz). Molecular weights were determined by means of high-resolution mass spectrometry on an Agilent LC/MSD-TOF model 1069A. Infrared spectra (IR) are reported in reciprocal centimeters and were recorded on a spectrophotometer Varian 640-IR FT-IR. Enantiomeric ratios were measured byUV detector at 210 or 254 nm with Chiralpak AD-H column. Reactions carried out under neat and solution conditions. The products were characterized by HPLC-MS and ESI-TOF mass spectrometry on an HPLC Dionex model Ultimate 3000. UV detection was performed at 220nm to identify the dipeptides.
9. **General procedure for the intermolecular aldol reaction catalyzed by dipeptides 1a-d.** A mixture of cyclohexanone**2** (0.5 mL),*p*-nitrobenzaldehyde**3** (0.20 mmol) and catalyst **1a-d** (10 mol%) was milled for 6 or 24 hours at room temperature. Following reaction, the resulting mixture was extracted with EtOAc. The organic phase was dried over anh. Na_2SO_4 and concentrated to give the crude product, that was purified by flash chromatography (silicagel, hexane/EtOAc, 10:1 to 3:1) to afford the aldol product as*anti:syn*diastereomeric mixture. Er values in the major diastereomeric product were determined by HPLC on Chiralpak AD-H column.
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