

# Organocatalyzed enantioselective aldol and Henry reactions starting from benzylic alcohols

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**Abstract.** Pioneering aldol and Henry reactions starting from alcohols are described. The aldol reaction has been successfully performed following a one-pot strategy starting from alcohols, while the Henry reaction has been carried out following a sequential protocol for the first time. In both processes, enantiomerically enriched products were obtained with good yields and high enantioselectivities.

We have also demonstrated that in reactions sensitive to small amounts of acid the use of alcohols instead of aldehydes could be a good solution for improving the results of these reactions.

**Keywords:** alcohol; aldehyde; aldol; Henry; MnO<sub>2</sub>; organocatalysis; one-pot; oxidation.

## Introduction

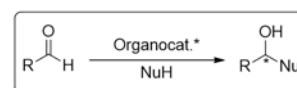
Many organic reactions that initially start from aldehydes lead to products of biological interest. Among the plethora of reactions that start from aldehydes, the aldol<sup>[1]</sup> and the Henry reactions<sup>[2]</sup> are important carbon-carbon bond-forming methods in organic synthesis.<sup>[3]</sup> These processes represent two potent strategies for the synthesis of valuable β-hydroxyketones and β-nitroalcohols providing, after further transformations, efficient access to interesting and highly functionalized intermediates. Both reactions have been developed under many different conditions and using diverse catalytic systems, providing from good-to-excellent enantioselectivities.<sup>[4-6]</sup>

During the development of our previous Henry protocol,<sup>[7]</sup> we realized that the presence of traces of acid in the aldehydes used could inactivate the small amount of catalyst employed (0.0044 mmol). It is well known that traces of acids are generated in aldehydes due to oxidation processes (see the supporting information for images of this process, Figure S1). This could be a serious problem that appears when using diverse aldehydes. In fact, many of these aldehydes that we used were purified before the reactions in order to avoid the inactivation of the catalyst. The influence of different amounts of acids on the reactivity and the enantioselectivity of diverse organocatalytic reactions (e.g., in aminocatalysis) has been also explored by other authors.

Hence, this problem encouraged us to explore the challenge of forming the aldehydes *in situ* by

oxidizing alcohols. In fact, there is a wider variety of alcohols available in comparison with aldehydes, and they are much easier to handle and work with. For this reason, it seems evident that the use of alcohols in organic processes instead of aldehydes would significantly increase the versatility of the reactions, especially when the aldehydes are unstable or difficult to handle.<sup>[8]</sup> Therefore, the exploration of new asymmetric catalytic methodologies of reactions where carbonyl compounds are used as starting materials is still important for an efficient construction of interesting building blocks. Consequently, the development of Henry and aldol reactions starting from alcohols would open a new area of research in the progress of these interesting reactions (Scheme 1).

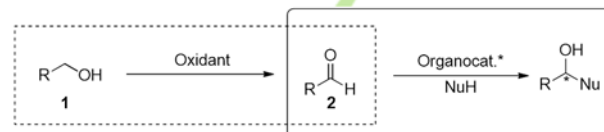
### Previous studies



### Advantages of replacing aldehydes with alcohols:

- ✓ No initial purification needed
- ✓ Much slower degradation
- ✓ Less intense smell

### This study



**Scheme 1.** The goal of this research: developing aldol and Henry reactions starting from alcohols.

The oxidation of alcohols to aldehydes or ketones is an important process in organic synthesis and several methods have been successfully developed to accomplish this transformation,<sup>[9]</sup> like for example, using organocatalytic procedures.<sup>[10]</sup> However, it is much rarer to find examples where the carbonyl group generated in the oxidation is involved in a subsequent asymmetric catalytic process. In fact, there are only a few studies on this and in all of them, the second reactions were carried out using proline-derived catalysts.<sup>[11]</sup> Therefore, the development of new oxidative processes of alcohols to generate aldehydes involved in subsequent organocatalytic protocols is highly desirable.

## Results and Discussion

Among the different oxidants analyzed in the literature (IBX, TEMPO, Swern oxidant, MnO<sub>2</sub>, etc.), we realized that the mildest and most efficient one for our aim was MnO<sub>2</sub>.<sup>[12]</sup> Moreover, the use of the other oxidants mentioned would lead to the generation of

acids during the oxidation reactions, which could inhibit the successive catalytic reactions in this investigation. In order to demonstrate our hypothesis, we first explored the aldol reaction depicted in Table 1.<sup>[13]</sup> This example represents the first one-pot aldol reaction starting from alcohols and catalyzed by a cinchona-derived primary amine.<sup>[14]</sup>

As reported in Table 1, it was possible to successfully oxidize alcohols in different solvents. Interestingly, the final product **5a** was produced with consistently better results when alcohol **1a** was used instead of aldehyde **2a**. In the original study starting from aldehydes, the authors noticed that when the amount of acid was higher than 15%, the yield of the reactions dropped.<sup>[13]</sup> Therefore, the decrease observed in the yield when **2a** is used could be mostly caused by the residual amounts of acid that this aldehyde generates through its oxidation over time. It is remarkable that, in all examples, the *in situ* generated aldehyde was used without having been purified, following a one-pot procedure.

**Table 1.** Screening of the one-pot cinchona-catalyzed aldol reaction starting from alcohol **1a** or aldehyde **2a** in different solvents.<sup>[a]</sup>

Entry	Solvent	Oxidation T (°C)	Time (min/h) oxidation of <b>1a</b>	Time (h) catalysis	Yield <b>5a</b> (%) <sup>[b,c]</sup> using <b>1a</b>	d.r. <b>5a</b> <sup>[b,d]</sup> <i>anti:syn</i> using <b>1a</b>	ee <b>5a</b> (%) <sup>[b,e]</sup> using <b>1a</b>	Yield <b>5a</b> (%) <sup>[f,c]</sup> using <b>2a</b>	d.r. <b>5a</b> <sup>[f,d]</sup> <i>anti:syn</i> using <b>2a</b>	ee <b>5a</b> (%) <sup>[f,e]</sup> using <b>2a</b>
1	THF	60	3 h	23	73	95:5	99	58	95:5	98
2	DMF	100	15 min	45	75	91:9	98	44	88:12	95
3	DMSO	100	15 min	45	77	86:14	98	70	84:16	97
4	Toluene	100	15 min	23	85	95:5	99	61	>95:5	99
5	CH <sub>2</sub> Cl <sub>2</sub>	30	15 h	12	39	94:6	96	32	94:6	99
6	CHCl <sub>3</sub>	55	3 h	22	32	90:10	94	30	89:11	93

<sup>[a]</sup> Experimental conditions: to a suspension of MnO<sub>2</sub> (2.5 mmol) in the solvent (0.5 mL) and at the temperature indicated in the table, alcohol **1a** (0.5 mmol) was added. After the oxidation time, the reaction was cooled down to room temperature and a mixture of catalyst **3** (0.05 mmol), TfOH (0.075 mmol) and **4** (1 mL) in 1.5 mL of the corresponding solvent was added in one portion. After the reaction time, the process was quenched with a saturated NH<sub>4</sub>Cl aqueous solution (20 mL) and extracted with AcOEt (3 x 30 mL). The organic phases were dried with MgSO<sub>4</sub> and the solvent was evaporated. Adduct **5a** was isolated by column chromatography. <sup>[b]</sup> Results starting from alcohol **1a**. <sup>[c]</sup> After isolation by column chromatography. <sup>[d]</sup> The diastereoisomeric ratio was determined by <sup>1</sup>H-NMR spectroscopy of the crude reaction mixture. <sup>[e]</sup> Determined by chiral HPLC analysis for the major diastereoisomer. <sup>[f]</sup> Results starting from commercially available aldehyde **2a**.

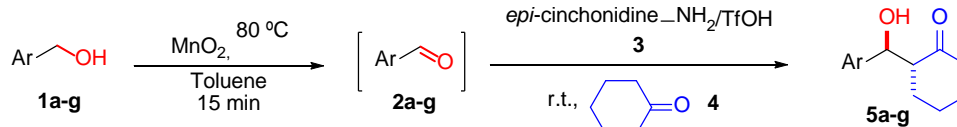
We then explored the efficiency of the one-pot protocol using a variety of alcohols (Table 2 and Scheme S1) under the best reaction conditions found during the screening (Table 1, entry 4). As depicted

in Table 2, the aldol reaction led to the desired β-hydroxyketones **5** in good yields and excellent enantioselectivities (up to 99% ee). The reactivity of

the process depends on the electronic effects of the aromatic rings, as better yields are obtained with electron-withdrawing substituents in shorter reaction

times. However, these electronic effects are not correlated with the enantioselectivity of the process.

**Table 2** Scope of the one-pot cinchona-catalyzed aldol reaction starting from alcohols **1a-g**.<sup>[a]</sup>



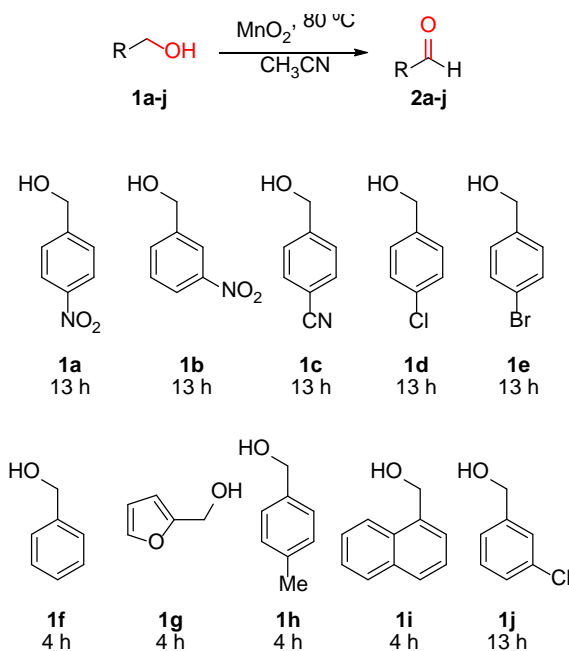
Entry	Ar ( <b>1a-h</b> )	Time (h) catalysis	Yield <b>5</b> (%) <sup>[b]</sup>	d.r. <b>5</b> <sup>[c]</sup> <i>anti:syn</i>	ee <b>5</b> (%) <sup>[d]</sup>
1	4-NO <sub>2</sub> Ph ( <b>1a</b> )	17	83	93:7	99
2	3-NO <sub>2</sub> Ph ( <b>1b</b> )	17	71	92:8	99
3	4-CNPh ( <b>1c</b> )	18	75	91:9	98
4	4-ClPh ( <b>1d</b> )	63	76	92:8	97
5	4-BrPh ( <b>1e</b> )	64	70	90:10	97
6	Ph ( <b>1f</b> )	100	53	90:10	>99
7	2-furyl ( <b>1g</b> )	101	71	75:25	93

<sup>[a]</sup> Experimental conditions: to a suspension of MnO<sub>2</sub> (2.5 mmol) in toluene (0.5 mL) at 80 °C, alcohol **1** (0.5 mmol) was added. After the oxidation time, the reaction was cooled down to room temperature and a mixture of catalyst **3** (0.05 mmol), TfOH (0.075 mmol) and **4** (1.5 mL) was added in one portion. After the reaction time, the process was quenched with a saturated NH<sub>4</sub>Cl aqueous solution (20 mL) and extracted with AcOEt (3 x 30 mL). The organic phases were dried with MgSO<sub>4</sub> and the solvent was evaporated. Adduct **5** was isolated by column chromatography. <sup>[b]</sup> After isolation by column chromatography. <sup>[c]</sup> The diastereoisomeric ratio was determined by <sup>1</sup>H-NMR spectroscopy of the crude reaction mixture. <sup>[d]</sup> Determined by chiral HPLC analysis for the *anti* diastereoisomer.

Recently, we have developed a trifunctional squaramide catalyst that promotes the Henry reaction through a multidentate activation.<sup>[7]</sup> Encouraged by the results obtained for the aldol reaction, we envisioned to apply this idea (Scheme 1) also to that reaction.

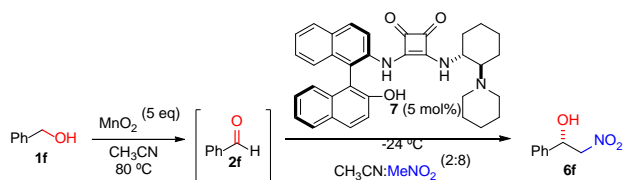
Initially, the screening of the oxidation reaction using alcohol **1f** (reported in Table S1) was conducted in CH<sub>3</sub>CN, since the following catalytic Henry step was successfully performed in mixtures of this solvent with MeNO<sub>2</sub>. Compound **1f** reacted completely in the oxidative process using 5 equivalents of MnO<sub>2</sub> at 80 °C (Table S1, entry 6). Interestingly, traces of acid or other by-products from alcohol **1f** were not detected by <sup>1</sup>H-NMR during the process even after long reaction times, supporting our initial aim.

Then, the time necessary for the total conversion of each alcohol **1** in its corresponding aldehyde **2** was analyzed (Scheme 2). We observed that alcohols with aromatic rings that bear electron-withdrawing groups (alcohols **1a-e,j**) required longer oxidation times in comparison with alcohols **1f-i**.



**Scheme 2.** Oxidation of alcohols **1**. Reaction conditions: 1 mmol of **1** and 5 mmol of MnO<sub>2</sub> in 1 mL of CH<sub>3</sub>CN at 80 °C.

With the optimal reaction conditions in hand for the oxidation step (Scheme 2), we firstly analyzed the catalytic Henry system following a one-pot protocol as shown in Scheme 3.



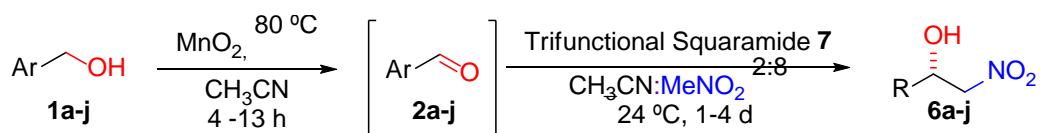
**Scheme 3.** One-pot Henry reaction.

Unfortunately, product **6f** was not observed after 4 days of reaction. This fact made us think that some of the reagents or by-products that come from the oxidation step were inactivating the subsequent Henry process. To avoid these impurities, the solid generated during this step was filtered and the

catalytic reaction was performed in a sequential manner. Then, 100  $\mu\text{L}$  of the filtered solution, without purification of the *in situ* generated aldehyde, were added over a mixture of catalyst **7** and  $\text{MeNO}_2$ . The process worked well in terms of enantioselectivity (83% ee) and reactivity (53% yield) (Table 3, entry 6) and, again, better yields were found when alcohol **1f** was employed in comparison with the outcomes observed when using aldehyde **2f** (35% yield).

The efficiency of this protocol was further studied for a range of different alcohols (**1a–j**) and the results were compared to those obtained when the initial reagents were the corresponding commercially available aldehydes (**2a–j**) (Table 3).

**Table 3.** Scope of the squaramide-catalyzed Henry reaction starting from alcohols **1a–j** and from aldehydes **2a–j** under the same reaction conditions.<sup>[a]</sup>



Entry	R	Time (h)	Yield <b>6</b> (%)		ee <b>6</b> (%)	
			using <b>1</b> <sup>[b,c]</sup>	using <b>2</b> <sup>[c,e]</sup>	using <b>1</b> <sup>[b,d]</sup>	using <b>2</b> <sup>[d,e]</sup>
1	4-NO <sub>2</sub> Ph ( <b>1a</b> )	23	>95	>95	79	80
2	3-NO <sub>2</sub> Ph ( <b>1b</b> )	23	>95	>95	93	93
3	4-CNPh ( <b>1c</b> )	23	76	>95	81	80
4	4-ClPh ( <b>1d</b> )	96	89	73	83	85
5	4-BrPh ( <b>1e</b> )	96	86	33	84	85
6	Ph ( <b>1f</b> )	69	53	35	83	85
7	2-furyl ( <b>1g</b> )	93	69	26	92	90
8	4-MePh ( <b>1h</b> )	93	37	n.r. <sup>f</sup>	86	n.d. <sup>g</sup>
9	1-Naphthyl ( <b>1i</b> )	93	66	n.r. <sup>f</sup>	80	n.d. <sup>g</sup>
10	3-ClPh ( <b>1j</b> )	96	87	n.r. <sup>f</sup>	83	n.d. <sup>g</sup>

<sup>[a]</sup> Experimental conditions: to a suspension of  $\text{MnO}_2$  (5 mmol) in  $\text{CH}_3\text{CN}$  (1 mL) at 80 °C, alcohol **1** (1 mmol) was added. After the oxidation time (Scheme 2), the reaction was cooled down to room temperature and the suspension was filtered using a HPLC filter of 0.22  $\mu\text{m}$ . Then, 0.1 mL of the solution filtrated were collected and added to a solution of catalyst **7** (0.005 mmol) in  $\text{MeNO}_2$  (0.4 mL) at -24 °C. After the reaction time, adduct **6** was isolated by column chromatography. <sup>[b]</sup> Results starting from alcohols **1**. <sup>[c]</sup> After isolation by column chromatography. <sup>[d]</sup> Determined by chiral HPLC analysis. <sup>[e]</sup> Results starting from commercially available aldehydes **2**. <sup>[f]</sup> No reaction observed after 3 days. <sup>[g]</sup> Not determined.

As shown in Table 3, the Henry reaction took place rendering the desired  $\beta$ -nitroalcohols **6** in good to excellent yields (up to >95%) and high enantioselectivities (up to 93% ee) with very clean reaction crudes. The enantioselectivity did not depend on the electronic effects of the alcohols. However, the reactivity is probably correlated with the electronic effects of the aromatic rings since the reagents with an electron-withdrawing group in the aromatic ring exhibited more reactivity (Table 3, entries 1–5 and 10). Although the enantiomeric excesses observed when using alcohols are practically identical compared with those obtained when aldehydes are employed, the reactivity is better in almost all the cases (see **1d–j**). It is remarkable that in the reactions using commercially available aldehydes **2h–j** without previous purification no products were formed. This

occurs because the presence of traces of acid in these aldehydes inactivates the small amount of catalyst used in the process. In fact, in our previous research,<sup>[7a]</sup> many of the aldehydes required a preliminary treatment in order to remove the acids and avoid such inactivation. In some cases, a few minutes after purifying the aldehydes, the generation of acid was observed in the aldehydes.

## Conclusion

In summary, we have successfully developed the first asymmetric catalytic aldol and Henry reactions starting from alcohols **1**. The combination of an oxidation and a successive aldol or Henry protocol produced  $\beta$ -hydroxyketones **5** and  $\beta$ -nitroalcohols **6**,

respectively, with very good results. It was found that, in some cases, the same Henry reactions using commercially available aldehydes **2** did not work after four days. Moreover, we have proven that the oxidation step can be carried out for diverse substituted aromatic alcohols using different solvents without impairing in the results of the reaction. Our protocol demonstrates that using alcohols leads in general, to better results than using aldehydes, especially in cases where aldehydes oxidized easily or are difficult to handle. The procedure described herein could open new opportunities and could be applied to other reactions which start from aldehydes. Further research on the efficacy of this organocatalytic approach in other asymmetric reactions is ongoing in our lab in order to extend this idea.

## Experimental Section

**General experimental methods.** Purification of reaction products was carried out by column chromatography using silical-gel (0.063-0.200 mm). Analytical thin layer chromatography was performed on 0.25 mm silical gel 60-F plates. <sup>1</sup>H-NMR spectra were recorded at 300 MHz; <sup>13</sup>C-APT-NMR spectra were recorded at 75 MHz; CDCl<sub>3</sub> was used as the deuterated solvents. Chemical shifts were reported in the  $\delta$  scale relative to residual CHCl<sub>3</sub> (7.28 ppm) for <sup>1</sup>H-NMR and to the central line of CDCl<sub>3</sub> (77 ppm) for <sup>13</sup>C-APT-NMR.

**Materials.** Spectral data for **5a-g**,<sup>[13]</sup> **6a**,<sup>[15]</sup> **6b**,<sup>[16]</sup> **6c**,<sup>[17]</sup> **6d**,<sup>[15]</sup> **6e**,<sup>[17]</sup> **6f**,<sup>[17]</sup> **6g**,<sup>[17]</sup> **6h**,<sup>[18]</sup> **6i**,<sup>[18]</sup> and **6j**<sup>[18]</sup> are consistent with values previously reported in the literature. See supporting information for all spectra and HPLC chromatograms.

### Representative procedure for the organocatalyzed aldol reaction starting from alcohols.

To a suspension of MnO<sub>2</sub> (2.5 mmol) in toluene (0.5 mL) at 80 °C, alcohol **1a-g** (0.5 mmol) was added. After the oxidation time, the reaction was cooled down to room temperature and a mixture of catalyst **3** (0.05 mmol), TfOH (0.075 mmol) and **4** (1.5 mL) was added in one portion. After the reaction time (Table 2), the process was quenched with a saturated NH<sub>4</sub>Cl aqueous solution (20 mL) and extracted with AcOEt (3 x 30 mL). The organic phases were dried with MgSO<sub>4</sub> and the solvent was evaporated. Adduct **5** was isolated by column chromatography.

### Representative procedure for the organocatalyzed Henry reaction starting from alcohols.

To a suspension of MnO<sub>2</sub> (5 mmol) in CH<sub>3</sub>CN (1 mL) at 80 °C, alcohol **1a-j** (1 mmol) was added. After the oxidation time (Scheme 2), the reaction was cooled down to room temperature and the suspension was filtered using a HPLC filter of 0.22  $\mu$ m. Then, 0.1 mL of the solution filtrated were collected and added to a solution of catalyst **7** (0.005 mmol) in MeNO<sub>2</sub> (0.4 mL) at -24 °C. After the reaction time (Table 3), adduct **6** was isolated by flash chromatography.

## Acknowledgements

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