助剂对 L-脯氨酸催化直接不对称 Aldol 反应的影响

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摘要: 在 L-脯氨酸催化的芳香醛与丙酮直接不对称 aldol 反应体系中添加二醇或二酚类助剂可有效提高反应活性。助剂的使用降低了该反应体系中 L-脯氨酸的用量。特别是以邻苯二酚为助剂时, 最佳反应条件下, 仅用 5 mol% L-脯氨酸与 1 mol% 助剂催化 2-硝基苯甲醛与丙酮直接不对称 aldol 反应, aldol 产物产率高达 90%, 对映选择性为 80%。该反应产率比未加助剂条件下, L-脯氨酸用量为 30 mol% 时的反应产率高。采用量子化学计算研究了助剂对该反应的促进作用。结果表明, 助剂可与芳香醛的醛基形成氢键, 从而活化醛基, 提高反应效率。邻苯二酚结构中相邻的羟基能与底物芳香醛羰基的氧原子形成双氢键, 大大活化了底物芳香醛的羰基。因此, 该助剂可有效促进 L-脯氨酸催化剂的直接不对称 aldol 反应。

关键词: L-脯氨酸; 邻苯二酚; 芳香醛; 丙酮; 直接不对称 aldol 反应; 氢键作用

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Effect of Additives on L-Proline Catalyzed Direct Asymmetric Aldol Reactions

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Abstract: The direct asymmetric aldol reaction of aromatic aldehydes with acetone catalyzed by L-proline was accelerated by the addition of diols or diphenols. The use of additives decrease the amount of L-proline needed and allowed the use of solvent free conditions. Catechol with two adjacent hydroxy groups on aromatic ring was the most efficient additive. Under the optimized conditions, 5 mol% L-proline with 1 mol% catechol gave excellent chiral selectivity (80% ee value) with > 90% yield, which was higher than that obtained using 30 mol% L-proline without an additive. Computations indicated that the additive promoted the reaction by an intermolecular hydrogen bond between the hydrogen of the hydroxyl group and the oxygen of the carbonyl group, which activated the carbonyl group of the aldehyde. Catechol with two adjacent hydroxyl groups on the aromatic ring can form two hydrogen bonds with the oxygen of the carbonyl group on the corresponding aldehyde. Therefore, the combination of L-proline and catechol was very efficient in catalyzing the direct asymmetric aldol reaction and gave a high yield in a short time.

Key words: L-proline; catechol; aromatic aldehyde; acetone; direct asymmetric aldol reaction; hydrogen bond interaction

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The direct asymmetric aldol reaction is one of the most important carbon-carbon bond forming reaction to form either one or two vicinal stereo-centers in synthetic chemistry [1]. Yamada et al. [2] first reported the direct catalytic asymmetric aldol reactions of aldehydes with unmodified ketones, which brought about the revival of direct aldol reaction. More recently, new metal-free organocatalysts derived from L-proline were reported to be active in some cases [3–6]. Nevertheless, numerous drawbacks remain with using L-proline as the catalyst, including the use of a lot of the catalyst (30 mol%) and moderate activities [7–9]. Furthermore, high polarity solvents, e.g. *N,N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), are often necessary for the reaction. To solve these problems, attention was directed to the design of various proline derivatives [10–16] and novel potential catalysts based on the structure of proline [17,18]. Nevertheless, the use of such proline derivatives or *quasi*-proline as catalyst has been limited because their synthesis involves laborious routes.

The use of additives, such as bases, Lewis acids, and water, in the direct asymmetric aldol reaction provides an alternative approach to improve enantioselectivity and to accelerate the reaction [19–24]. Zhou et al. [25] recently employed (*R*)- and (*S*)-1,1'-bi-2-naphthol as promoter for the L-proline catalyzed aldol reaction. High catalyst loading (30 mol%) and long reaction time (48 h) were still required, although an enhanced enantioselectivity was obtained. The ability to use a lower catalyst loading and have higher reactivity is still needed for L-proline catalyzed asymmetric aldol reactions. Ji et al. [26] explored the influence of a multiple OH group phenol on the direct aldol reactions catalyzed by pyrrolidine and found that the multi-phenol (40 mol%) promoted the aldol reaction to proceed smoothly with 20 mol% loading of pyrrolidine. The positive effect of the multi-phenol encouraged us to employ cheap diols and diphenols as additives. We envisaged that the hydroxyl groups of diols and diphenols can interact with the carboxyl group of L-proline to activate the substrate, which would enhance catalytic efficiency. Here, a series of diols and diphenols were employed as additives in L-proline catalyzed asymmetric aldol reactions. The use of diols and diphenols, esp. diphenols with two adjacent hydroxyl groups on the aromatic ring, led to the expected higher conversion of 4-nitrobenzaldehyde under solvent-free conditions even when the L-proline loading was only 5 mol%. Quantum computation was used to study the role of the additive in the reaction. The result showed that hydrogen bond interactions between the aromatic aldehyde and the additive activated the carbonyl group of the aromatic aldehyde and enhanced its reactivity. The addition of a diphenol to the reaction medium provides a simple and efficient method to enhance the

catalytic efficiency of direct asymmetric aldol reactions catalyzed by L-proline.

1 Experimental

1.1 General procedure for the direct aldol reaction

2,3-Dihydroxynaphthalene and 2,2'-diphenol were purchased from TCI. The other commercially available chemicals were laboratory grade reagents from local suppliers. All solvents were purified by standard procedures before use.

L-Proline (0.006 g, 0.025 mmol) and the additive (0.005 mmol) were stirred in 2 ml acetone at 25 °C for 15 min. Then 4-nitrobenzaldehyde (0.0756 g, 0.5 mmol) was added into the mixture under stirring for 4 h. The mixture was treated with saturated aqueous ammonium chloride. The aqueous layer was extracted several times with ethyl acetate. The combined organic layers were dried with anhydrous Na₂SO₄ and evaporated, worked up and purified by flash column chromatography on silica gel (200–300 mesh; eluent: hexane/ethyl acetate = 5:1) to give the desired products. Enantioselectivity was expressed as ee (%) = 100 × (*R* – *S*)/(*R* + *S*). The resolution and separation factors for the separation of the products and further structure identification by ¹H NMR and ¹³C NMR were listed as follows.

(4*R*)-Hydroxy-4-(4'-nitrophenyl)-butan-2-one (**1a**). Isolated as oil by silica gel column chromatography (hexane/EtOAc = 5:1). ¹H NMR (CDCl₃, 500 MHz): δ 8.216–7.280 (m, 4H), 5.27 (s, 1H), 3.67 (s, 1H), 2.87 (d, *J* = 6.7 Hz, 2H), 2.231 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 208.6, 150.0, 147.3, 126.4, 123.8, 68.9, 51.5, 30.7. The enantioselectivity was determined by a Shimadzu LC-10A_{vp} HPLC using a Daicel CHIRALPAK OB-H column (hexane/*i*-propanol = 85:15; flow rate: 0.8 ml/min; λ = 254 nm). Major enantiomer: *t*_R = 14.0 min; minor enantiomer: *t*_R = 16.1 min. Resolution: 1.29. Separation factor: 1.15.

(4*R*)-Hydroxy-4-(2-nitrophenyl)-butan-2-one (**1b**). Isolated as oil by silica gel column chromatography (hexane/EtOAc = 5:1). ¹H NMR (CDCl₃, 500 MHz): δ 7.95–7.42 (m, 4H), 5.68 (d, *J* = 10.7 Hz, 1H), 3.73 (s, 1H), 3.15–2.72 (m, 2H), 2.24 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 208.8, 147.2, 138.4, 133.8, 128.3, 128.2, 124.4, 65.7, 51.0, 30.4. The enantioselectivity was determined by a Shimadzu LC-10A_{vp} HPLC using a Daicel CHIRALPAK OB-H column (hexane/*i*-propanol = 85:15; flow rate: 0.8 ml/min; λ = 254 nm). Major enantiomer: *t*_R = 8.4 min; minor enantiomer: *t*_R = 7.3 min. Resolution: 2.83. Separation factor: 1.15.

(4*R*)-(2-Chlorophenyl)-4-hydroxy-2-butanone (**1c**). Isolated as oil by silica gel column chromatography (hexane/EtOAc = 5:1). ¹H NMR (500 MHz, CDCl₃): δ 7.61–7.18 (m, 4H), 5.52–5.49 (m, 1H), 3.63 (s, 1H),

3.00–2.65 (m, 2H), 2.21 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 209.3, 140.1, 131.1, 129.3, 128.6, 127.3, 127.1, 66.6, 50.0, 30.6. The enantioselectivity was determined by Shimadzu LC-10A_{vp} HPLC using Daicel CHIRALPAK AD column (hexane/*i*-propanol = 92.5:7.5; flow rate: 0.8 ml/min; λ = 254 nm). Major enantiomer: t_R = 10.9 min; minor enantiomer: t_R = 12.3 min. Resolution: 3.28. Separation factor: 1.13.

(4*R*)-(4-Bromophenyl)-4-hydroxy-2-butanone (**1d**). Isolated as oil by silica gel column chromatography (hexane/EtOAc = 5:1). ^1H NMR (500 MHz, CDCl_3): δ 7.47–7.21 (m, 4H), 5.10 (q, J = 8.7 Hz, 1H), 3.43 (s, 1H), 2.86–2.76 (m, 2H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 208.8, 141.7, 131.6, 127.3, 121.4, 69.2, 51.7, 30.7. The enantioselectivity was determined by a Shimadzu LC-10A_{vp} HPLC using a Daicel CHIRALPAK AD column (hexane/*i*-propanol = 92.5:7.5; flow rate: 0.8 ml/min; λ = 254 nm). Major enantiomer: t_R = 15.2 min; minor enantiomer: t_R = 16.1 min. Resolution: 2.71. Separation factor: 1.06.

(4*R*)-(4-Acetamidophenyl)-4-hydroxy-2-butanone (**1e**). Isolated as oil by silica gel column chromatography (hexane/EtOAc = 5:1). ^1H NMR (500 MHz, CDCl_3): δ 7.47–7.26 (m, 4H), 5.12–5.11 (m, 1H), 3.34 (s, 1H), 2.89–2.77 (m, 2H), 2.20 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 209.2, 168.4, 138.7, 137.3, 126.3, 120.0, 69.5, 51.8, 20.8, 24.6. The enantioselectivity was determined by a Shimadzu LC-10A_{vp} HPLC using a Daicel CHIRALPAK AD column (hexane/*i*-propanol = 90:10; flow rate: 0.8 ml/min, λ = 254 nm). Major enantiomer: t_R = 50.0 min; minor enantiomer: t_R = 55.7 min. Resolution: 3.11. Separation factor: 1.11.

(4*R*)-Hydroxy-4-(2-naphthyl)-2-butanone (**1f**). Isolated as oil by silica gel column chromatography (hexane/EtOAc = 5:1). ^1H NMR (500 MHz, CDCl_3): δ 7.80–7.43 (m, 7H), 5.31–5.29 (m, 1H), 3.50 (s, 1H), 2.96–2.84 (m, 2H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 209.1, 140.2, 133.3, 130.0, 128.4, 128.0, 127.7, 126.3, 126.0, 124.4, 123.8, 70.0, 51.9, 30.8. The enantioselectivity was determined by a Shimadzu LC-10A_{vp} HPLC using a Daicel CHIRALPAK AD column (hexane/*i*-propanol = 92.5:7.5; flow rate: 0.8 ml/min; λ = 254 nm). Major enantiomer: t_R = 22.6 min; minor enantiomer: t_R = 27.0 min. Resolution: 4.42. Separation factor: 1.19.

1.2 Quantum calculation

The quantum calculations were carried out with Gaussian 03. Geometries of 4-nitrobenzaldehyde and of the additive-4-nitrobenzaldehyde complexes were optimized using density functional theory (DFT) [27] with the B3LYP functional [28] and the standard 6-31+G(d,p) basis set [29]. The hydrogen bonding complexes were confirmed as true min-

ima on the potential energy surface by the presence of only real frequencies in the corresponding vibrational analysis. Natural bond orbital (NBO) analysis was used to investigate the intermolecular interactions of the O–H...O=C bond between the additive and 4-nitrobenzaldehyde.

2 Results and discussion

2.1 Effect of different additives on the direct asymmetric aldol reaction

4-Nitrobenzaldehyde was chosen as a typical aromatic aldehyde to investigate the influence of different additives on the direct asymmetric aldol reaction. The results are summarized in Table 1. 74% yield with 73% ee value of the aldol product **1a** was obtained with the use of 5 mol% L-proline without any additive (entry 1). Remarkable increases in the yield of the aldol product **1a** were observed when diols and diphenols were added into the reaction sys-

Table 1 Effect of different additives on the direct aldol reaction of acetone with 4-nitrobenzaldehyde

Entry	Additive	Additive amount (mol%)	Yield (%)	ee ^a (%)
1	—	—	74	73
2 ^b	—	—	84	72
3		1	80	71
4		1	84	72
5		0.5	86	75
6		1	92	75
7		5	92	75
8		10	91	75
9		1	92	74
10		1	90	71

Reaction conditions: L-proline 5 mol% of substrate, 4-nitrobenzaldehyde 0.5 mmol, acetone 2 ml, 4 h, 25 °C.

^aValues refer to the major enantiomer (*R*-isomer) and were determined by HPLC. The ee values were average values of at least duplicate experiments. The same below.

^bThe catalyst loading was 30 mol%.

tem (entries 3, 4, 6, 9, 10). In particular, when 1 mol% of a diphenol was used, 92% yield of the aldol product **1a** was obtained with only 5 mol% L-proline under solvent-free conditions. It can be noted that the yield of the aldol product **1a** was much higher than that with 30 mol% L-proline without any additive (entries 3, 4, 6, 9, 10 vs entry 2). The result showed a crucial role by the additives in the direct asymmetric aldol reaction. Also, diphenols were more effective than the other diols (entries 6, 9, 10 vs 3, 4). It is known that there are two steps in the aldol reaction catalyzed by L-proline: forming an enamine intermediate and nucleophilic addition. The forming of the enamine intermediate is the rate determining step. Subsequent nucleophilic addition of the carbonyl of aldehyde to the enamine affords the aldol adduct [30]. The employment of a diphenol accelerates the reaction by forming an intermolecular hydrogen bond between the hydroxyl groups of the diphenol and the carbonyl group of the aldehyde. This made the carbonyl carbon atom more electropositive and susceptible to nucleophilic addition. In particular, catechol and 2,3-dihydroxynaphthalene bearing two adjacent hydroxyl groups on the aromatic ring were the most effective additives (entries 6 and 9). But the additives had no effect on the enantioselectivity. From economic consideration, catechol was the appropriate additive for the reaction here. The effect of different amounts of catechol on the reaction is also summarized in Table 1 (entries 5–8). Only 1 mol% of catechol gave 92% yield with 75% ee value of the aldol product **1a**. With more catechol, the yield was constant.

Quantum calculations were carried out to compare the positive charge of the carbonyl carbon atom in the absence and presence of additives. The optimized geometries of 4-nitrobenzaldehyde and the additive-4-nitrobenzaldehyde complexes were obtained by DFT at the B3LYP/ 6-31+G (d,

p) level (see Fig. 1). The hydrogen bond length, hydrogen bond energy, and NBO charge of the carbonyl carbon atom are listed in Table 2. The NBO analysis revealed that all the additive-4-nitrobenzaldehyde complexes had a hydrogen bond interaction between the oxygen of the carbonyl and the hydrogen of the hydroxyl group, and the distance between them was about 0.2 nm (Table 2). Furthermore, two hydrogen bonds were formed between catechol/1,2-ethandiol and 4-nitrobenzaldehyde in their optimized geometries (models (c) and (d)). Clearly, in the presence of an additive, the NBO charge of the carbonyl carbon atom in the 4-nitrobenzaldehyde was more electropositive due to the formation of the intermolecular hydrogen bonds between the additive and the 4-nitrobenzaldehyde. On comparing the NBO charge of the carbonyl carbon atom of the five additive-4-nitrobenzaldehyde complexes, we noticed that the NBO charge of the carbonyl carbon atom decreased in the order: catechol/4-nitrobenzaldehyde > 2,2'-diphenol/4-nitrobenzaldehyde > 2,3-dihydroxynaphthalene/4-nitrobenzaldehyde > 1,2-ethandiol/4-nitrobenzaldehyde > 2,3-butanediol/4-nitrobenzaldehyde, which was the order of the

Table 2 Hydrogen bond length, hydrogen bond energy (ΔE), and NBO charge of the carbonyl carbon atom of the hydrogen bond complexes

Mode	H-bond length (nm)	ΔE /(kJ/mol)	NBO charge (a.u.)
(a)	—	—	0.393 (C11)
(b)	H4...O18	0.2008	4.27
(c)	H4...O18	0.2131	4.69
	H6...O18	0.2148	2.01
(d)	H12...O26	0.2016	4.94
	H14...O26	0.1871	5.27
(e)	H34...O12	0.1830	4.31
(f)	H38...O12	0.1827	4.31

Fig. 1. Optimized geometries of 4-nitrobenzaldehyde (a), 2,3-butanediol/4-nitrobenzaldehyde (b), 1,2-ethandiol/4-nitrobenzaldehyde (c), catechol/4-nitrobenzaldehyde (d), 2,3-dihydroxynaphthalene/4-nitrobenzaldehyde (e), and 2,2'-diphenol/4-nitrobenzaldehyde (f).

Table 3 Direct aldol reaction of acetone with different aromatic aldehydes accelerated by catechol

Entry	Ar	Product	No additive		Addition of 1% catechol	
			Yield (%)	ee (%)	Yield (%)	ee (%)
1	4-NO ₂ C ₆ H ₄	1a	74	73	92	75
2	2-NO ₂ C ₆ H ₄	1b	70	79	90	80
3	2-ClC ₆ H ₄	1c	80	57	90	61
4	4-BrC ₆ H ₄	1d	45	63	62	62
5	4-AcNHC ₆ H ₄	1e	40	56	60	60
6	2-Naphthyl	1f	27	62	44	61

Reaction conditions: L-proline 5 mol% of substrate, catechol 1 mol% of substrate, aromatic aldehydes 0.5 mmol, acetone 2 ml, 25 °C, 4 h.

catalysis shown in Table 1. Furthermore, no imaginary frequency was observed for their geometries in the vibrational frequency analyses performed at the same level as the optimization calculations.

2.2 Effect of catechol on the aldol reaction of acetone with different aromatic aldehydes

To widen the scope of the application of the additives, different aromatic aldehydes were evaluated. The results are listed in Table 3. The yield of the corresponding aldol product was significantly improved with the addition of 1 mol% of catechol, and the acceleration obtained with catechol was independent of whether the aromatic aldehyde had an electron-withdrawing or electron-donating group. When nitrobenzaldehydes were used as aldol acceptors, *Para*-nitrobenzaldehyde showed a lower enantioselectivity and slightly higher activity than *ortho*-nitrobenzaldehyde (entry 1 vs 2). This may be due to that the nitro group located at the *ortho* position was more favourable for the formation of the hydrogen bond, which would retard the rotation leading to the enantiomer. However, on comparing with *para*-nitrobenzaldehyde, the nitro group located at the *ortho* position was unfavourable for nucleophilic attack due to steric hindrance, and it therefore gave a slightly lower yield of the corresponding aldol product. *ortho*-Chlorobenzaldehyde showed a similar activity to nitrobenzaldehyde, but with much lower enantioselectivity (entry 3 vs entries 1 and 2). When *para*-bromobenzaldehyde was used as the aldol acceptor, the yield was much lower than that with *ortho*-chlorobenzaldehyde, but there was no obvious difference in enantioselectivity (entry 4 vs 3). *Para*-Acetamidobenzaldehyde showed moderate reactivity and enantioselectivity with the addition of 1 mol% of catechol (entry 5). 2-Naphthaldehyde was less active under identical conditions due to the steric hindrance of bulky 2-naphthyl group (entry 6).

3 Conclusions

The employment of catechol accelerated the direct asymmetric aldol reactions catalyzed by L-proline, such that 5 mol% loading of L-proline was sufficient for the aldol reaction under solvent-free conditions. The formation of two hydrogen bonds between catechol and the aldehyde activated the aromatic aldehyde, which accounted for the improved yield of the aldol product.

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