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Telaprevir Fragments as Organocatalysts in Asymmetric Direct Aldol Reactions of Aldehydes[1]

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Abstract—We have demonstrated that the fragments of Telaprevir can act as organocatalysts for asymmetric aldol reactions between aromatic aldehydes and acetone under mild conditions. The reaction conditions have been optimized in terms of the catalyst nature, choice of temperature, solvent, additive, and the catalyst loading. Under proper conditions, fairly good yield and enantioselectivity have been achieved.

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The aldol reaction is of great importance for the construction of C–C bonds in organic synthesis, including that of complex natural compounds. Therefore, a variety of synthetic approaches, catalysts, and reagents have been developed in order to achieve efficient addition with high stereo- and enantiomeric selectivity [1].

The first proline-catalyzed enantioselective intermolecular aldol reaction has been described [2]. Further on, proline has been used as efficient catalyst in other aldol reactions [3, 4].

The proposed mechanism of L-proline-catalyzed asymmetric aldol reaction is a typical example of enamine-based organocatalysis [5] proceeding via reversible condensation of the catalytic amine with a ketone to give nucleophilic enamine intermediate. In the reaction, the carboxylic group of proline plays an important part in activation and orientation of the aldehyde acceptor via hydrogen bonding [6]. Based on the mechanism, the activation energy of the addition stage should be similar to that of the enamine formation, indicating that the addition might be a rate-determining step. Indeed, this has been directly proved in the recent kinetic study [7].

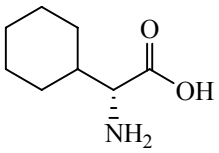
In spite of proline applicability as aldol reactions catalyst, it suffers from several drawbacks, such as slow reaction, high catalyst loadings and large excess of ketone needed, and poor results with certain substrates like unbranched aldehydes [4]; therefore, a great deal of effort was exerted to the development of the new catalysts. As proline is very common and cheap chemical, the new catalysts should reveal significant improvements, both in terms of selectivity and reac-tivity, to surpass proline. Many catalysts have been developed based on proline structure [4]. The structure modifications majorly aim to increase the hydro-phobicity and thus to improve solubility in organic solvents, or to introduce further polar groups in order to play with the hydrogen bonding properties [4, 8–16]. Other trends include adding bulky substituents or stereocenters to enhance the enantioselectivity [17–22]. The results reported so far are very promising [23–29].

In this work, we consider Telaprevir intermediates as possible organocatalysts of aldol reaction. Telaprevir has become a widely applied drug for hepatitis C treatment, thus the number of its intermediates available is also increasing. Moreover, the smaller fragments of Telaprevir may be formed in the human body as a result of the drug decay, and it is important to understand their activity in aldol reactions.

The structures of the catalysts **I–V** are listed below. Noteworthily, the catalysts included large chiral backbone along with the groups acting as hydrogen bonding donor, thus combining the both promising approaches of the proline modification mentioned

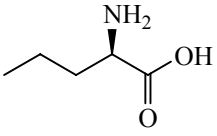
[1] The text was submitted by the authors in English.

above. The catalytic performance of the catalysts was evaluated in the model direct asymmetric aldol reaction of 4-nitrobenzaldehyde with acetone; the catalysts performance is compared in Table 1.



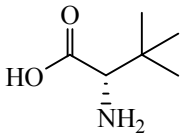
I

(*R*)-2-Amino-2-cyclohexylacetic acid



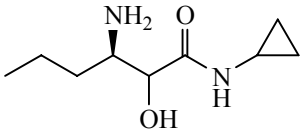
II

L-Norvaline



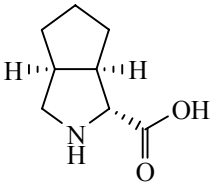
III

(*S*)-2-Amino-3,3-dimethylbutanoic acid



IV

(*S*)-2-Amino-*N*-cyclopropyl-2-hydroxypentanamide

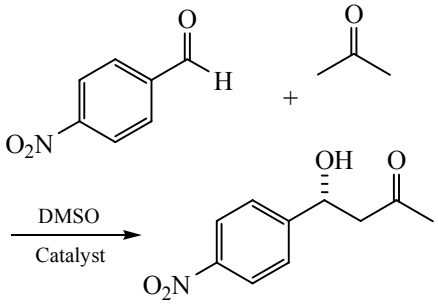


V

(1*R*,3a,6a*R*)-Octahydrocyclopenta[*c*]pyrrole-1-carboxylic acid

As seen from Table 1, **II** and **V** efficiently catalyzed the direct aldol reaction of 4-nitrobenzaldehyde with acetone, and the products revealed high enantiomeric excess; in the case of **V**, the enantioselectivity was higher as compared with L-proline (reference). Therefore, the catalyst **V** was chosen for further study.

Table 1. Model aldol reaction catalyzed with **I**–**V**[a]



Catalyst	Time, h	*ee*, %[b]
I	60	53
II	60	61
III	60	45
IV	60	0
V	24	73
L-Proline	24	58

[a] Reactions were carried out with 0.1 mmol of 4-nitrobenzaldehyde, 0.2 mL of acetone, 0.03 mmol of catalyst, and 0.8 mL dimethylsulfoxide at 10°C

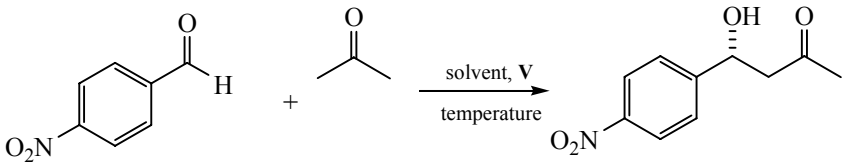
[b] Enantiomeric excess, as determined by chiral HPLC.

To investigate the effect of the solvent, we tested a variety of reaction media at different conditions (Table 2). The solvent affected both the product yield and the reaction enantioselectivity; a few products were obtained in alcoholic solutions (entries 5 and 6). All polar aprotic solvents, such as dimethylacetamide, dimethylsulfoxide, acetonitrile, dioxane, and tetrahydrofuran showed good results, but dimethylformamide was the best (entries 1−4, 8, 9). Without the solvent, the catalyst was not efficient.

The catalyst loading was varied to optimize the reaction conditions (Table 2, entries 1, 12, and 13). High enantioselectivity (65%) was still obtained even at relatively low catalyst loading (0.1 equiv., entry 12), however, the yield was poor (41%) due to low reaction rate. With the catalyst loading increased to 0.3 equiv., the yield was up to 78% at high enantioselectivity (76%). Therefore, the catalyst loading of 0.3 equiv. was used in further experiments.

The reaction proceeded with moderate to good enantioselectivity at 10°C. Decreasing the reaction temperature did not improve the enantioselectivity (data not shown). Increasing the reaction temperature to 30°C or 60°C accelerated the reaction, at the cost of more of side products formed, and thus decreased yield and enantioselectivity.

Table 2. The model aldol reaction catalyzed by **V** under different conditions[a]



Entry	Solvent	*T*, °C	Time, h	*ee*, %[b]	Yield, %[c]
1	Dimethylformamide	10	48	76	78
2	Dimethylsulfoxide	10	48	74	98
3	Dimethylacetamide	10	48	76	96
4	Acetonitrile	10	48	69	97
5	Ethanol	10	48	37	57
6	Methanol	10	48	35	71
7	Methylbenzene	10	48	53	64
8	Tetrahydrofuran	10	48	62	89
9	Dioxane	10	48	68	89
10	Dichloroethane	10	48	65	91
11	No solvent	10	48	47	96
12	Dimethylformamide[d]	10	48	65	41
13	Dimethylformamide[e]	10	48	76	60
14	Dimethylformamide	30	24	71	61
15	Dimethylformamide	60	24	69	51

[a] Reactions were carried out with 0.1 mmol of 4-nitrobenzaldehyde, 0.4 mL of acetone, 0.03 mmol of **V** and 1 mL of solvent.
[b] Enantiomeric excess, as determined by chiral HPLC.
[c] Yield in wt % after column chromatography purification.
[d] With 0.1 eq. of **V.**
[e] With 0.2 equin. of **V.**

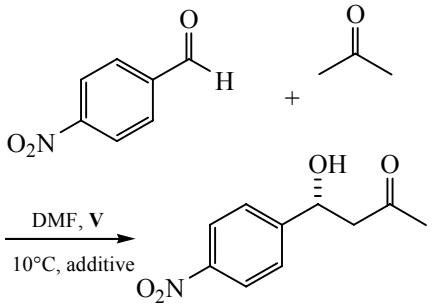
We further studied the effect of different additives on the reaction outcome, other conditions being the same (Table 3). It was found that with weak acids as additive, the desired product yield was of 67–91% (entries 2, 3, 8, and 9), and quartz sand showed similar effect (entry 1). On the contrary, addition of strong bases usually suppressed the reaction.

The reaction enantioselectivity was significantly improved with the preserved high yield when certain salts were introduced into the mixture (entries 11, 13, 15, 17, and 19); the rate of the reaction was increased as well. However, other salts led to very poor yield and the purity of the product (entries 12, 16, and 18).

To demonstrate the potential of the catalytic system, the aldol reaction of acetone with differently substituted aromatic aldehydes was performed with **V** as catalyst and in the presence of EDTA (Table 4). The reaction appeared quite tolerant with respect to the steric effect of the benzaldehyde substituent, and the desired products could be obtained with good yields and excellent enantioselectivity (enantiomeric excess up to 84%, entries 1–8). However, the reaction of non-activated aldehydes, such as benzaldehyde and 4-methoxybenzaldehyde, led to moderate yield and enantioselectivity (entries 9 and 10). The absorption maximum of some products was shifted from 254 nm; that should have been taken into account in the course of HPLC detection.

To conclude, we have found that of the Telaprevir fragments, one is an efficient catalyst of direct asymmetric aldol reaction. The reaction procedure is simple and likely scalable, which should allow C–C bond formation with excellent yield and enantioselectivity. Various reaction conditions have been probed, and the best of them was selected, including proper choice of temperature, solvent, additive, and the catalyst loading. In future we plan to study the catalyst efficiency in other reactions.

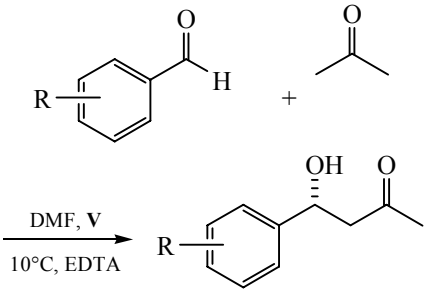
Table 3. The model aldol reaction catalyzed by **V** in the presence of different additives[a]



Run no.	Time, h	Additive	*ee*, %[b]	Yield, %[c]
1	10	Quartz sand	76	89
2	10	Diatomite	71	91
3	10	Silica gel	68	67
4	10	Triethylamine[d]	40	56
5	8	Imidazole[d]	76	85
6	10	Cyclodextrin[d]	69	68
7	8	EDTA[d]	77	82
8	8	Deoxycholic acid[d]	75	90
9	8	Ascorbic acid[d]	76	85
10	8	NaCl[e]	76	92
11	8	NaBr[e]	60	86
12	8	LiBr[e]	32	Trace
13	8	KI[e]	69	77
14	8	Al_2O_3[e]	65	93
15	8	NH_4Cl[e]	77	87
16	8	NH_4Br[e]	26	Trace
17	8	$(NH_4)_2C_2O_4$[e]	77	82
18	8	NH_4HCO_3[e]	31	Trace
19	8	EDTA[e]	78	89

[a] Reactions were carried out with 0.1 mmol of 4-nitrobenzaldehyde, 0.4 mL of acetone, 0.03 mmol of catalyst, and 1 mL of DMF at 10°C.
[b] Enantiomeric excess, as determined by chiral HPLC.
[c] Yield in wt% after column chromatography purification.
[d] 0.3 equiv. of the addictive.
[e] 4 equiv. of the addictive.

Table 4. The model aldol reaction of different substrates catalyzed by **V**, in the presence of EDTA



Run no.	R	Product	Time, h	*ee*, %[a]	Yield, %[b]
1	4-F-Ph	**VIa**	24	73	58
2	4-Br-Ph	**VIb**	24	75	70
3	4-Cl-Ph	**VIc**	24	73	50
4	3.4-Cl_2-Ph	**VId**	24	67	27
5	4-NO_2-Ph	**VIe**	8	78	78
6	3-NO_2-Ph	**VIf**	8	80	88
7	2-NO_2-Ph	**VIg**	8	84	93
8	4-OMe-Ph	**VIh**	32	72	54
9	H	**VIi**	32	68	53
10	2-F	**VIj**	24	58	74
11	4-CF_3	**VIk**	32	97	38

[a] Enantiomeric excess, as determined by chiral HPLC.
[b] Yield in wt % after column chromatography purification.

EXPERIMENTAL

The products were purified by chromatography using silica gel (200–300 mesh). ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker instrument (400 MHz and 100 MHz, respectively) and were internally referenced to residual protonated solvent signals ($CDCl_3$). Chiral High Performance Liquid Chromatography was performed with Chiralpak® AD or OJ-H column. The structures of aldol reaction products were elucidated by comparison with literature data.

Aldol reaction *(general procedure)*. The typical aldol reaction procedure can be illustrated by the following example. Aromatic aldehyde (0.1 mmol) was added to a solution of the catalyst **V** (0.03 mmol) and EDTA (0.03 mmol) in DMF (1 mL). Then, acetone (0.4 mL) was added, and the reaction mixture was stirred at 10°C until the reaction was completed (TLC). The organic products were extracted three times with ethyl acetate and washed three times with water. The combined organic extracts were dried over anhydrous sodium sulfate. The solvent was evaporated, and the crude product was purified by flash column chro-matography with various petroleum ether (60–90°C)–EtOAc mixtures.

4-(4-Fluorophenyl)-4-hydroxybutan-2-one (VIa). ^{1}H NMR spectrum, δ, ppm: 7.33 d.d (*J* = 8.3, 5.6 Hz, 2H), 7.04 t (*J* = 8.6 Hz, 2H), 5.14 d.d (*J* = 8.7, 3.5 Hz, 1H), 2.83 m (2H), 2.21 s (3H). ^{13}C NMR spectrum, δ, ppm: 209.20, 163.40, 138.38, 127.36, 127.28, 115.48, 115.26, 69.17, 51.89, 30.78. HPLC (Daicel Chiralpak AD column, *n*-hexane–isopropanol 95 : 5, 1 mL/min, 245 nm) *ee* = 73%.

4-(4-Bromophenyl)-4-hydroxybutan-2-one (VIb). ^{1}H NMR spectrum, δ, ppm: 7.48 d (*J* = 8.0 Hz, 2H), 7.24 d (*J* = 8.0 Hz, 2H), 5.12 d.d (*J* = 7.7, 3.9 Hz, 1H), 2.83 m (2H), 2.20 s (3H). ^{13}C NMR spectrum, δ, ppm: 209.10, 141.66, 131.64, 127.40, 121.45, 69.19, 51.76, 30.82. HPLC (Daicel Chiralpak AD column, *n*-hexane–isopropanol 90 : 10, 1 mL/min, 205 nm) *ee* = 75%.

4-(4-Chlorophenyl)-4-hydroxybutan-2-one (VIc). ^{1}H NMR spectrum, δ, ppm: 7.31 (q, *J* = 8.7 Hz, 5H), 5.13 d.d (*J* = 8.1, 4.2 Hz, 1H), 2.83 m (2H), 2.21 s (3H). ^{13}C NMR spectrum, δ, ppm: 209.15, 141.11, 133.34, 128.70, 127.05, 69.16, 51.80, 30.82. HPLC (Daicel Chiralpak AD column, *n*-hexane–isopropanol 90 : 10, 1 mL/min, 215 nm) *ee* = 73% .

4-(3,4-Dichlorophenyl)-4-hydroxybutan-2-one (VId). ^{1}H NMR spectrum, δ, ppm: 7.45 d.d (*J* = 23.6, 4.9 Hz, 2H), 7.18 d.d (*J* = 8.3, 1.6 Hz, 1H), 5.12 t (*J* = 6.1 Hz, 1H), 2.82 d (*J* = 6.2 Hz, 2H), 2.22 s (3H). ^{13}C NMR spectrum, δ, ppm: 208.75, 142.94, 132.62, 131.44, 130.47, 127.73, 124.99, 68.59, 51.59, 30.74. HPLC (Daicel Chiralpak AD column, *n*-hexane–isopropanol 90 : 10, 1 mL/min, 205 nm) *ee* = 67%.

4-Hydroxy-4-(4-nitrophenyl)butan-2-one (VIe). ^{1}H NMR spectrum, δ, ppm: 8.21 d (*J* = 8.6 Hz, 2H), 7.54 d (*J* = 8.5Hz, 1H), 5.27 m (1H), 3.62 d (*J* = 2.8 Hz, 1H), 2.86 m (1H), 2.23 s (2H), 1.66 s (0H), 1.25 s (0H). ^{13}C NMR spectrum, δ, ppm: 208.64, 126.41, 123.79, 68.87, 65.88, 58.48, 51.50, 30.75, 18.42, 15.27. HPLC (Daicel Chiralpak OJ-H column, *n*-hexane–isopropanol 90 : 10, 1 mL/min, 245 nm) *ee* = 78%.

4-Hydroxy-4-(3-nitrophenyl)butan-2-one (VIf). ^{1}H NMR spectrum, δ, ppm: 7.48 d (*J* = 8.4 Hz, 2H), 7.24 d (*J* =8.3 Hz, 3H), 5.12 d.d (*J* = 7.8, 4.5 Hz, 1H), 3.39 s (1H), 2.83 m (2H), 2.21 s (3H). ^{13}C NMR spectrum, δ, ppm: 208.77, 148.33, 144.72, 131.83, 129.53, 122.61, 120.72, 68.75, 51.48, 30.74. HPLC (Daicel Chiralpak OJ-H column, *n*-hexane–isopropanol 90 : 10, 1 mL/min, 254 nm) *ee* = 80%.

4-Hydroxy-4-(2-nitrophenyl)butan-2-one (VIg). ^{1}H NMR spectrum, δ, ppm: 7.96 d (*J* = 8.2 Hz, 1H), 7.93 d.d (*J* = 25.1, 8.1Hz, 2H), 7.90 d (*J* = 7.9 Hz, 1H), 7.67 t (*J* = 7.6 Hz, 1H), 7.44 t (*J* = 7.8 Hz, 1H), 5.68 d (*J* = 9.4 Hz, 1H), 3.74 d (*J* = 2.7 Hz, 1H), 3.13 d (*J* = 17.8 Hz, 1H), 2.73 d.d (*J* = 17.8, 9.4Hz, 1H), 2.24 s (3H). ^{13}C NMR spectrum, δ, ppm: 208.93, 147.11, 138.39, 133.88, 128.31, 128.20, 124.48, 65.63, 51.07, 30.48. HPLC (Daicel Chiralpak OJ-H column, *n*-hexane–isopropanol 90 : 10, 1 mL/min, 245 nm) *ee* = 84% .

4-Hydroxy-4-(4-methoxyphenyl)butan-2-one (VIh). ^{1}H NMR spectrum, δ, ppm: 7.27 d (*J* = 15.7 Hz, 1H), 6.92 d (*J*= 8.2 Hz, 2H), 6.82 m (1H), 5.14 d.d (*J* = 8.9, 3.3 Hz, 1H), 3.82 s (3H), 2.85 q.d (*J* = 17.7, 6.2 Hz, 2H), 2.20 s (3H). ^{13}C NMR spectrum, δ, ppm: 209.29, 159.80, 144.37, 129.63, 117.86, 113.22, 111.05, 69.76, 55.26, 51.97, 30.83. HPLC (Daicel Chiralpak AD column, *n*-hexane–isopropanol 90 : 10, 1 mL/min, 205 nm) *ee* = 72%.

4-Hydroxy-4-phenylbutan-2-one (VIi). ^{1}H NMR spectrum, δ, ppm: 7.31 m (6H), 5.16 d.d (*J* = 9.0, 3.3 Hz, 1H), 2.90 d.d (*J* = 17.7, 9.0 Hz, 2H), 2.83 d.d (*J* = 17.7, 3.3 Hz, 1H), 2.21 s (3H). ^{13}C NMR spectrum, δ, ppm: 209.29, 142.59, 125.61, 127.70, 128.56, 69.80, 51.92, 30.79. HPLC (Daicel Chiralpak AD column, *n*-hexane–isopropanol 95 : 5, 1 mL/min, 245 nm) *ee* = 68%.

4-(2-Fluorophenyl)-4-hydroxybutan-2-one (VIj). ^{1}H NMR spectrum, δ, ppm: 7.54 d.d (*J* = 8.1, 7.0 Hz, 1H), 7.25 m (1H),7.17 t (*J* = 7.5 Hz, 1H), 7.02 d.d (*J* = 10.0, 8.8 Hz, 1H), 5.44 d.d (*J* = 9.2, 2.5Hz, 1H), 2.95 m (2H), 2.83 d.d (*J* = 17.9, 9.2 Hz, 1H), 2.21 s (3H). ^{13}C spectrum, δ, ppm: 209.35, 160.50, 158.06, 129.01, 128.93, 127.24, 127.20, 124.42, 124.39, 115.28, 115.07, 64.07, 64.05, 50.39, 30.64. HPLC (Daicel Chiralpak AD column, *n*-hexane–isopropanol 95 : 5, 1 mL/min, 245 nm) *ee* = 58%.

4-Hydroxy-4-[4-(trifluoromethyl)phenyl]butan-2-one (VIk). ^{1}H NMR spectrum, δ, ppm: 7.61 d (*J* = 8.1 Hz, 2H),7.48 d (*J* = 8.1 Hz, 2H), 5.21 t (*J* = 7.4 Hz, 1H), 3.54(d, *J* = 3.2 Hz, 1H), 2.85 m (2H), 2.21 s (3H).^{13}C NMR spectrum, δ, ppm: 208.77, 146.70, 130.00, 125.94, 125.50, 122.76, 69.22, 51.74, 30.73. HPLC (Daicel Chiralpak AD column, *n*-hexane–isopropanol 90 : 10, 1 mL/min, 215 nm) *ee* = 97%

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