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Novel L-threonine-based ionic liquid supported organocatalyst for asymmetric *syn*-aldol reactions: activity and recyclability design

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Dedicated to Professor Oleg A. Rakitin on the occasion of his 65th anniversary

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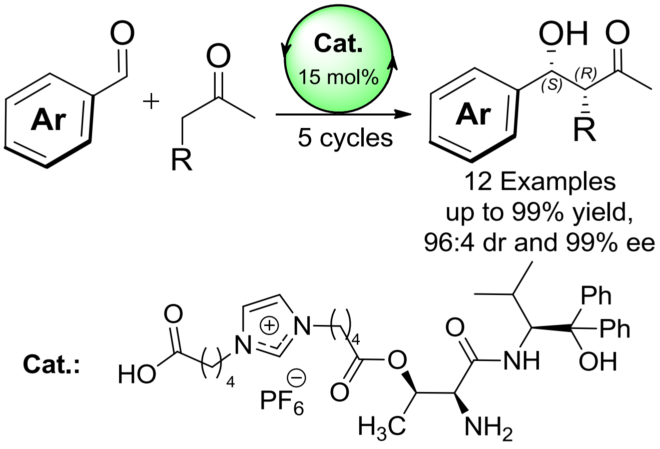
Abstract

A novel recyclable threonine-derived ionic-liquid-supported organocatalyst of asymmetric cross-aldol reactions has been developed. In its presence, aromatic aldehydes react with hydroxyacetone, methoxy-acetone and 2-butanone to afford the corresponding *syn*-aldol products in moderate to high yields with excellent diastereo- (*syn*/*anti* up to 96:4) and enantio-selectivity (up to 95 % *ee*), which was retained over five recycling experiments.



Keywords: Aldol reaction; asymmetric catalysis; organocatalysis; recyclable catalysts

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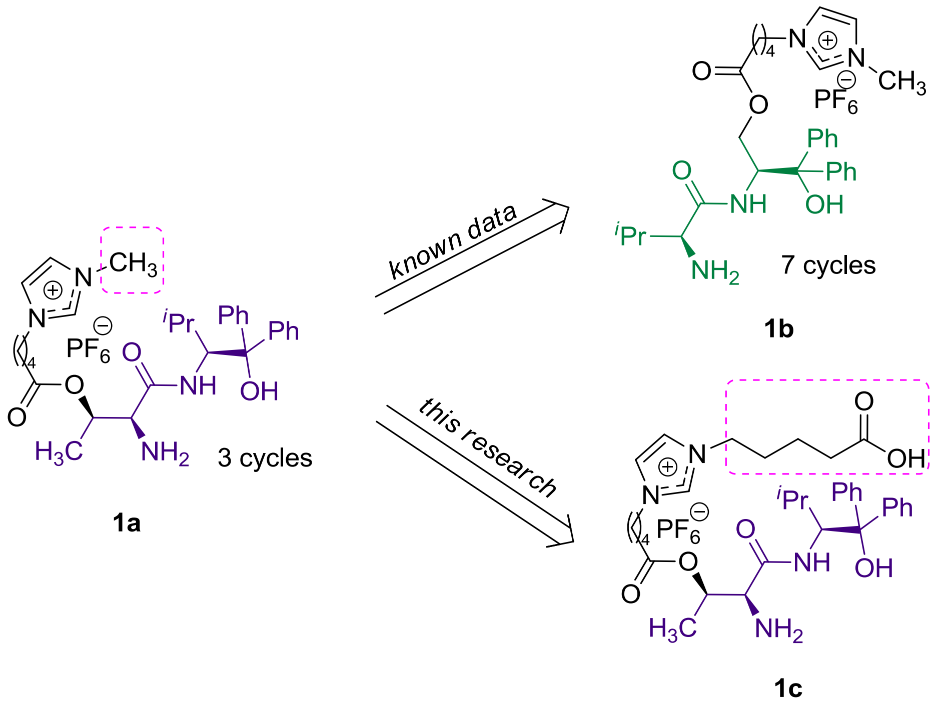
Introduction

Asymmetric organocatalysis is an intensively developing area of modern organic chemistry.[1-3] One of the most important organocatalytic reactions is the asymmetric aldol reaction, which occur in Nature and is widely used in chemical research for enantioselective formation of the carbon-carbon bonds in organic compounds.[4] As a rule, major products of aldol reactions catalyzed by secondary amines have *anti*-configuration[5-7] whereas *syn*-aldols, which are key structural fragments of carbohydrates, are formed in aldolase-catalyzed enzymatic aldol reactions.[8-9] Some of these native catalysts (aldolases of type II) have a peptide structure with primary amino acid fragments as active sites.[10] Over the past decade, a number of similar *syn*-aldol reactions have been realized in laboratory (though, with a somewhat lower stereoselectivity) in the presence of properly designed primary aminocatalysts. Among them, *O*-protected serine or threonine amino acids,[11-16] their amides,[17] valine,[18] leucine,[19] *iso*-leucine[20] or *tert*-leucine derivatives[21] and some primary–tertiary 1,2-diamine organocatalysts[22-27] exhibited promising catalytic performance. However, unlike enzymes, these valuable catalysts could be used just once and until recently no information on their recovery and reuse in the catalytic process has been available.

A few years ago we presented the first "conditionally" recyclable catalyst **1a** of *syn*-aldol reactions, an ionic-liquid-supported (*S*)-threonine amide bearing an α,α-diphenylvalinol structural unit (Scheme 1).[28] Unfortunately, the catalytic activity of compound **1a** became lower after the first recovery and after the third one it became nearly inactive. Very recently, we discovered that main reason for this deactivation is the undesirable intramolecular *O-N* migration of the acyl fragment attached to ionic group which resulted in the amidation of the primary amino group which is key for the enamine catalysis.[29] To make the migration thermodynamically unfavorable, we designed catalyst **1b**, in which the acyl linker is located distantly from the amino group. Indeed, catalyst **1b** appeared much more sustainable and could be recycled 7 times with complete retention of stereoselectivity and only a slight conversion decrease.

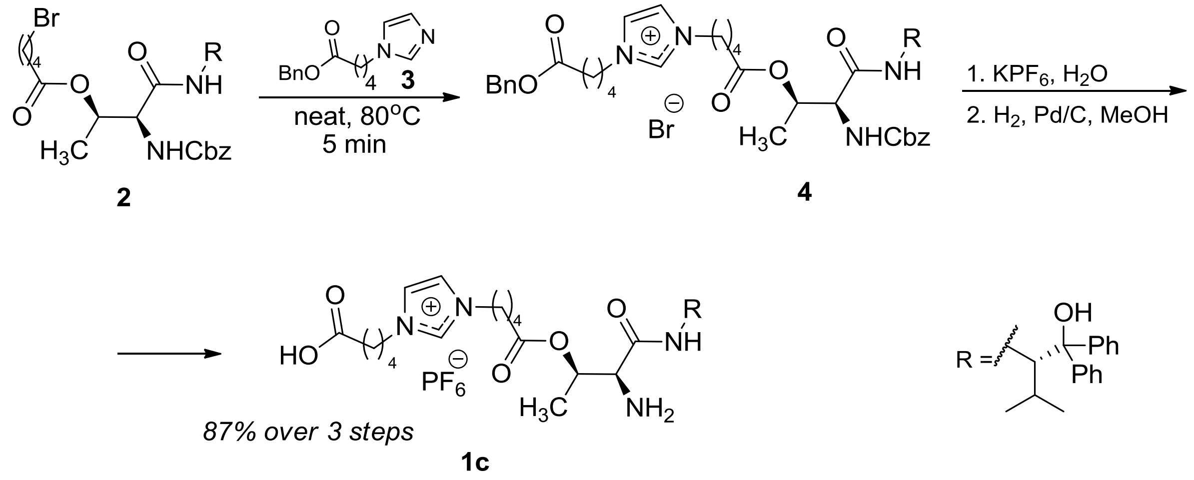


Scheme 1. Research strategy.

We hypothesized that the parasitic rearrangement may also be suppressed by a Brønsted-acidic group, which being incorporated into the catalyst would reduce nucleophilicity of the threonine amino group via the protonation. Furthermore, we expected that a remote carboxyl group in catalyst **1c** would simultaneously act as an acidic co-catalyst and reduce catalyst leaching during workup. A number of catalytic aldol reactions are known to proceed with a higher rate and better enantioselectivity in the presence of acidic additives.[5] A few examples of favorable impact of the incorporated carboxy group on the catalytic performance and recyclability of ionic-liquid-supported primary-amine-based chiral organocatalysts in asymmetric Michael[30] and *anti*-aldol reactions[31] have also been reported. However, to the best of our knowledge, this approach has never been used to improve the catalytic performance of primary amino acid-derived supported organocatalysts in asymmetric *syn*-aldol reactions.

Results and Discussion

To verify this hypothesis, we synthesized the carboxylated analog **1c**, in which the imidazolium cation is attached to a carboxylic group. The synthetic scheme included alkylation of *O*-protected 1-(4-benzyloxycarboxybutyl)-imidazole **3** with bromoester **2** followed by the conversion of the imidazolium bromide **4** into the carboxylated IL-supported catalyst **1c** via a sequence of anion exchange and catalytic hydrogenation (5% Pd/C) reactions (Scheme 2).

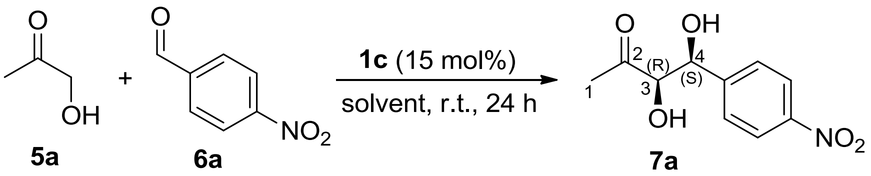


Scheme 2. Synthesis of carboxylated catalyst **1c**.

Having catalyst **1c** in hand, we at first optimized reaction conditions using hydroxyacetone **5a** and 4-nitrobenzaldehyde **6a** as model substrates (Table 1). It was found that in nonpolar aprotic solvent (e.g. toluene) product **7a** was generated with higher selectivity and conversion of **6a** than in other solvents.

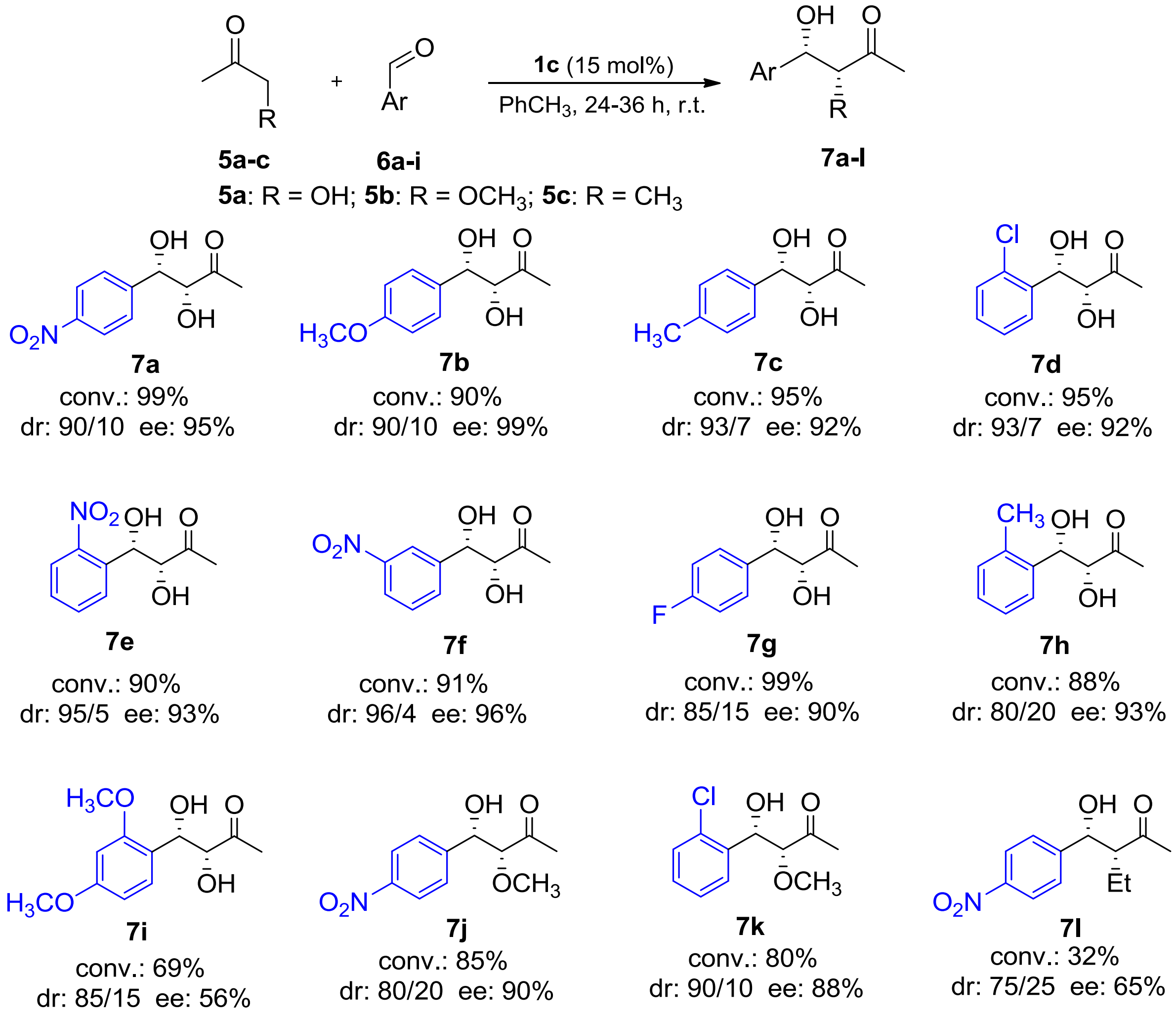
Under optimal conditions, hydroxyacetone (**5a**) reacted with benzaldehyde derivatives (**6a-i**) bearing acceptor or donor substituents in the aromatic ring to afford corresponding *syn*-aldols **7a-i** with high conversion and with good to excellent diastereo- and enantio-selectivity (for compounds **7a-h**, the *dr* and *ee* values were similar or even higher that reported with catalyst **1a**[28]) (Scheme 3). The methoxyacetone (**5b**) also appeared a suitable ketone-donor for the catalytic *syn*-aldol reactions with aldehydes **6a** and **6d** to give corresponding aldols **7j** and **7k** with reasonably high diastereo- and enantio-selectively. In case of 2-butanone (**5c**) the conversion and *dr* and *ee* values of generated aldol **7l** were significantly lower.

Table 1. Optimization of reaction conditions [a]



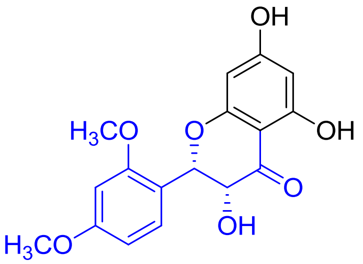
Solvent	Conv., % [b,d]	dr (*syn/anti*) [b,d]	ee (*syn*), % [c,d]
MeOH	88 (83)	70:30 (70:30)	79 (68)
NMP	14 (39)	90:10 (70:30)	90 (90)
CH_2Cl_2	53 (91)	94:6 (80:20)	92 (88)
Toluene	**99** (99)	**93:7** (92/8)	**95** (94)
o-Xylene	90	90/10	88

[a] Unless otherwise specified, all reactions were carried out with **5a** (15 mg, 14 μL, 0.2 mmol), **6a** (0.066 mmol), **1c** (6.5 mg, 0.01 mmol), and solvent (90 μL). [b] ^{1}H NMR spectroscopic data ($J^{3\text{-}4}_{syn}$ = 1.8–4.2 Hz, $J^{3\text{-}4}_{anti}$ = 6.1–8.8 Hz); [c] HPLC data (Daicel Chiralpak AD-H) for crude compound **7a**. [d] Corresponding data for catalyst **1a** are given in parentheses.



Scheme 3. The reaction scope.

It is worthy of note that the previously unknown compound **7i** is a close structural analog of flavanonol – an inhibitor of nitric oxide (NO) production in inflammatory cells (Figure 1).[32]

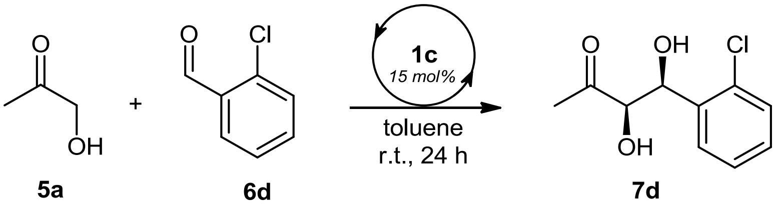


Inhibitor against nitric oxide (NO) production in inflammatory cells

Figure 1. Biologically active flavanonol – a structural analog of **7i**.

Finally, we examined the recyclability of catalyst **1c** in the asymmetric *syn*-aldol reaction between compounds **5a** and **6d** (Table 2). After completion of the reaction, the solvent was evaporated under reduced pressure, aldol product **7d** was extracted with Et_2O, and a fresh solution of the starting compounds in toluene was added to the remaining catalyst. In this manner, catalyst **1c** was successfully recycled five times without any reduction of the *dr* and *ee* values, though, with a slight conversion decrease. These data are in agreement with a favorable impact of the carboxy group in catalyst **1c** on its sustainability and recyclability under proposed conditions as compared with catalyst **1a**.

Table 2. Recyclability of catalyst **1c** in the model reaction between **5a** and **6d**



Cycle	Conv., %	dr, syn/anti, %	ee, %
1	95	95/5	95
2	94	95/5	95
3	89	95/5	95
4	83	95/5	95
5	79	95/5	95

Conclusions

The obtained results show that simple modification with the carboxylic group may be considered as a promising approach to improve sustainability of IL-supported primary amino acid derived organocatalysts in asymmetric *syn*-aldol reactions. Based on this approach, a novel carboxylated threonine amide derived IL-tagged catalyst of asymmetric aldol reactions between aromatic aldehydes and linear ketones has been developed which exhibited improved catalytic activity and good diastereo- (*syn/anti* up to 96/4) and enantio-selectivity (up to 95% *ee*) over five recycling experiments.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM 300 spectrometer in $CDCl_3$ and DMSO-d_6. The chemical shifts of ^{1}H and ^{13}C signals were measured relative to Me_4Si or $CDCl_3$, respectively. The high-resolution mass spectra (HRMS) were measured with a Bruker microTOF II spectrometer using electrospray ionization (ESI). The measurements were taken either in the positive ion mode (interface capillary voltage 4500 V) or in the negative ion mode (3200 V) in a mass range m/z = 50–3000 Da; external or internal calibration was done with electrospray calibrant solution (Fluka). Syringe injection was used for solution in MeCN/H_2O (1:1, v/v) (flow rate 3 µL/min). Nitrogen was applied as a dry gas, and the interface temperature was set at 180 °C. Silica gel 0.060–0.200 µm (Acros) was used for column chromatography. Threonineamide (**2**) and benzyl 5-(1*H*-imidazol-1-yl)pentanoate (**3**) were synthesized according to known methods. Compounds **5** and **6** were purchased from Aldrich and used without purification. The solvents were purified by standard procedures. For experimental details and spectral or HPLC data see Supporting Information.

3-[5-(Benzyloxy)-5-oxopentyl]-1-(5-[((2*R*,3*S*)-3-{[(benzyloxycarbonyl)amino]-4-[((*S*)-1-hydroxy-3-methyl-1,1-diphenylbutan-2-yl)amino]-4-oxobutan-2-yl}oxy)-5-oxopentyl]-1*H*-imidazol-3-ium hexafluorophosphate (**4**). Benzyl 5-(1*H*-imidazol-1-yl)pentanoate (**3**) (0.22 g, 0.83 mmol) was gradually added to a solution of (2R,3S)-3-[(benzyloxycarbonyl)amino]-4-[((*S*)-1-hydroxy-3-methyl-1,1-diphenylbutan-2-yl)amino]-4-oxobutan-2-yl 5-bromopentanoate (**2**) (0.45 g, 0.69 mmol) in CH_3OH (2 mL). The reaction mixture was kept at ambient temperature for 10 min and evaporated under reduced pressure (20 Torr) at 40 ^{o}C. The residue was heated at the same pressure (rotary evaporator, 80 ^{o}C) for 5 min, cooled to ambient temperature and diluted with distilled water (3.0 mL). A solution of KPF_6 (128 mg, 0.69 mmol) in distilled water (1.5 mL) was added to the resulting aqueous solution and the reaction mixture was stirred for 1 h at ambient temperature. The precipitate was filtered, washed successively with distilled water (3 x 3 mL) and Et_2O (2 x 1 mL), and dried in air to afford **4** (0.612 g, 90%). White powder, mp 97-100 ^{o}C. ^{1}H NMR (600 MHz, DMSO-d_6): 0.65 (d, *J* 6.5 Hz, 3H, CH_3); 0.70 (d, *J* 6.5 Hz, 3H, CH_3); 0.87 (d, *J* 6.5 Hz, 3H, CH_3); 1.38-1.45 (m, 2H, CH_2); 1.48-1.55 (m, 2H, CH_2); 1.69-1.78 (m, 3H, CH_2 + C*H*$(CH_3)_2$); 1.78-1.85 (m, 2H, CH_2); 2.13-2.24 (m, 2H, CH_2); 2.40 (t, *J* 7.3 Hz, 2H, CH_2); 3.99 (t, *J* 8.2 Hz, 1H, CH); 4.11 (t, *J* 6.9 Hz, 2H, CH_2); 4.18 (t, *J* 6.9 Hz, 2H, CH_2); 4.84 (m, 1H, CH); 4.89 (d, *J* 9.5 Hz, 1H, CH); 5.04 (2H, CH_2 AB system, J_{HH} 12.66 Hz); 5.10 (s, 2H, CH_2); 5.64 (s, 1H, OH); 7.08 (t, *J* 7.2 Hz, 1H, CH); 7.13-7.21 (m, 3H, CH); 7.26-7.41 (m, 12H, CH); 7.46-7.55 (m, 4H, CH); 7.60 (d, *J* 10.0 Hz, 1H, NH); 7.71 (d, *J* 8.9 Hz, 1H, NH); 7.79 (d, *J* 5.0 Hz, 2H, NCHCHN); 9.15-9.24 (m, 1H, NCHN); ^{13}C NMR (125.76 MHz, DMSO-d_6): 16.6, 18.2, 21.3, 21.4, 23.2, 29.05, 29.15, 33.1, 33.2, 48.9, 58.2, 59.2, 65.9, 69.8, 81.3, 122.9, 125.7, 125.8, 126.6, 128.0, 128.1, 128.3, 128.4, 128.5, 128.8, 128.9, 136.4, 136.6, 137.5, 146.5, 147.7, 156.5, 169.3, 172.1, 172.9. Elemental analysis: calcd for $C_{49}H_{59}F_6N_4O_8P$: C, 60.24; H, 6.09; N, 5.73; found: C, 60.06; H, 6.14, N, 5.79%.

1-(5-{(2*R*,3*S*)-3-Amino-4-[((*S*)-1-hydroxy-3-methyl-1,1-diphenylbutan-2-yl)amino]-4-oxobutan-2-yl}oxy)-5-oxopentyl}-3-(4-carboxybutyl)-1*H*-imidazol-3-ium hexafluorophosphate (**1c**). 5% Pd/C (50 mg) was added to a solution of **4** (120 mg, 0.12 mmol) in freshly distilled methanol (3 mL) and the reaction mixture was vigorously stirred under H_2 atmosphere (~1 bar) for 5 h at ambient temperature. The reaction mixture was filtered and evaporated under reduced pressure (20 Torr). The residue was dried in *vacuo* (2 Torr) at 40 ^{o}C for 1 h to afford **1c** (89 mg, 96%). A yellow powder, mp 89-91 ^{o}C. ^{1}H NMR (600 MHz, DMSO-d_6): 0.58 (d, *J* 3.2 Hz, 3H, CH_3); 0.68-0.73 (m, 3H, CH_3); 0.80-0.90 (m, 3H, CH_3); 1.40-1.53 (m, 4H, $2xCH_2$); 1.62-1.74 (m, 1H, CH *i*-Pr); 1.71-1.87 (m, 4H, $2xCH_2$); 2.18 (t, *J* 7.1 Hz, 2H, CH_2); 2.28 (t, *J* 7.2 Hz, 2H, CH_2); 3.64-3.72 (m, 1H, CH_3C*H*OH); 3.98 (t, *J* 7.4 Hz, 1H, C*H*(NH)CONH); 4.13-4.24 (m, 4H, $2xCH_2$); 4.50-4.62 (m, 1H, C*H*(*i*-Pr)NH); 4.87 (d, *J* 9.5 Hz, 1H, OH); 5.67 (s, 1H, OH); 7.06-7.23 (m, 4H, CH); 7.29 (t, *J* 7.7 Hz, 2H, CH); 7.42 (d, *J* 10.1 Hz, 1H, NH); 7.49 (t, *J* 6.7 Hz, 4H, CH); 7.81 (d, *J* 11.7 Hz, 2H, NCHCHN); 7.94 (d, *J* 8.4 Hz, 1H, NH); 9.24 (s, 1H, NCHN); 12.08 (s, 1H, COOH); ^{13}C NMR (125.76 MHz, DMSO-*d*$_6$): 18.2, 19.9, 21.5, 22.2, 23.3, 28.9, 29.1, 29.3, 29.6, 33.3, 34.6, 49.0, 49.1, 57.9, 59.4, 66.1, 81.3, 122.9, 125.6, 126.0, 126.6, 128.1, 128.5, 136.4, 146.7, 170.8, 172.1, 174.5; HRMS (ESI): *m/z* calcd. for $C_{34}H_{47}N_4O_6^+$: 607.3490, found: 607.3493.

General procedure for *syn*-aldol reactions. Aldehyde **6a-i** (0.066 mmol) and catalyst **1c** (7.5 mg, 0.01 mmol) were dissolved in dry toluene (90 µL). Then, ketone **5a-c** (0.2 mmol) was added to the resulting solution. The reaction mixture was stirred at ambient temperature for 24-48 h (TLC-monitoring), filtered through a silica gel pad and evaporated (40 °C, 8 mbar). Conversions and *dr* values of aldol products **7a-l** were measured by ^1H NMR spectroscopy. The *ee* values of aldol products **7a-l** were determined by chiral HPLC column (Daicel Chiralpak AD-H).

(3*R*,4*S*)-4-(2,4-Dimethoxyphenyl)-3,4-dihydroxybutan-2-one (**7i**). Pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$): 2.27 (s, 3H, CH_3), 3.82 (d, 6H, $(OCH_3)_2$), 4.41 (s, 1H), 5.31 (s, 1H), 6.42-6.60 (m, 2H, Ar), 7.31 (m, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$): 26.4, 55.8, 56.0, 69.5, 71.5, 80.2, 80.4, 99.0, 104.8, 104.9, 121.5, 128.1, 129.0, 157.3, 161.13, 208.86; HRMS (ESI) *m/z* calcd. for $[C_{12}H_{16}O_5+Na]$: 263.0890; found: 263.0890.

General procedure for catalyst 1c recycling. After 24 h, the mixture of hydroxyacetone (5a) (74 mg, 70µl, 1 mmol), 2-chlorobenzaldehyde (6d) (46.8 mg, 0.33 mmol), catalyst 1c (37.5 mg, 0.05 mmol) and toluene (0.45 mL) was gently evaporated (40 °C, 8 mbar). Product 7d and unchanged starting compounds were carefully extracted from the residue by Et_2O (3 x 0.7mL). Fresh portions of reagents and toluene were added to the remaining catalyst 1c and the catalytic procedure was performed again as described.

Acknowledgements

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Supplementary Material

^1H, ^{13}C, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC and ESI-MS spectra for compounds **4** and **1c**. HPLC traces for compounds **7**.

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