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Facile preparation of optically pure diamines and their applications in asymmetric aldol reactions

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ABSTRACT

A family of optically pure diamines with tertiary–primary amine motif has been synthesized from optically pure binaphthol and amino acids. The catalysts are highly tunable in structure and has demonstrated high efficiency in direct aldol reactions. Thus, a variety of aldehydes or methyl 2-oxoacetates reacted with acetone in the presence of 10 mol % of catalyst and 20 mol % TFA, furnishing the desired alcohols in up to 99% yield with excellent enantioselectivities (up to 96% ee).

The advantages of organocatalysis have been demonstrated in asymmetric transformations by the facile preparation of the catalysts, the mild reaction conditions, and by their environmentally benign aspects as compared to metal catalysis.[1] Chiral amines such as cinchona, and 1,2-cyclohexane-1,2-diamine or their derivatives have received great attention for their unique activation modes and high efficiencies.[2] Reactions catalyzed by nucleophilic chiral amines such as ketene acylation, β-lactam formation, Baylis–Hillman reactions and other transformations were developed over the past few years.[3] Recently, chiral amines featured with a primary–tertiary amine structure have been widely employed in asymmetric reactions. In these asymmetric transformations, the chiral amines act as bifunctional catalysts, deprotonating the α-H of carbonyl compounds to form enamines or condensing with carbonyl functionalities of α,β-unsaturated compounds to form α,β-unsaturated imines in the presence of an achiral Brønsted acid. Recently, 9-amino(9-deoxy)epi-quinine in combination with achiral acids was reported to be an effective catalyst for the asymmetric conjugate addition of carbon-centered nucleophiles to simple enones, and aldol reactions between aldehydes and enones via iminium-ion catalysis.[4] In 2007, Chen reported a highly efficient aldol reaction catalyzed by chiral diamines derived from optically pure cyclohexane–diamine.[5] All these aforementioned amines feature a tertiary–primary amine structure in the catalysts. We also disclosed an enantioselective aldol reaction catalyzed by a cinchonine-derived amine.[6] However, the amines used in the asymmetric aldol reactions were mostly derived from proline, cinchona and 1,2-cyclohexanediamine. They were either difficult to synthesize or modulate the reactivity through structure modifications. These shortcomings restricted their further applications. Herein, we wish to describe a facile synthesis of novel chiral diamines (Fig. 1) using optically pure binaphthol and chiral amino acids, and their application in enantioselective aldol reactions based on the following considerations: (1) both enantiomers of binaphthol and amino acids are commercially available, and optically pure binaphthol has shown excellent performance in a series of asymmetric transformations;[7] (2) high enantioselectivities can be obtained, when the two stereocenters in the synthesized diamines are matched; and, especially, (3) the amines are highly tunable with respect to structural modification, simplifying the introduction of substituents at different positions of binaphthol. Furthermore, chiral amino acids are readily available.

The syntheses of catalysts **1a–d** are shown in Scheme 1. The readily prepared chiral amine **2**[8] was condensed with *N*-Boc protected (*S*)-phenyl glycine in the presence of stoichiometric EDCI affording the corresponding amides in 93% yield. After Boc deprotection with TFA in CH_2Cl_2 and subsequent reduction of amide carbonyl group using borane (BH_3–Me_2S) in THF afforded the desired diamines in 70–89% yield in two steps.[9] Attempts to obtain the product using other reduction methods such as $LiAlH_4$, DIBAL-H, and $NaBH_4$–I_2 were unsuccessful.

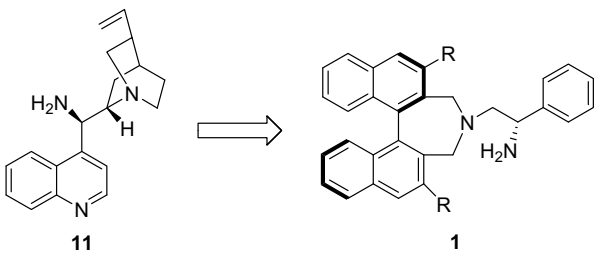

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Figure 1. Structure of amines derived from Cinchona and new amines.

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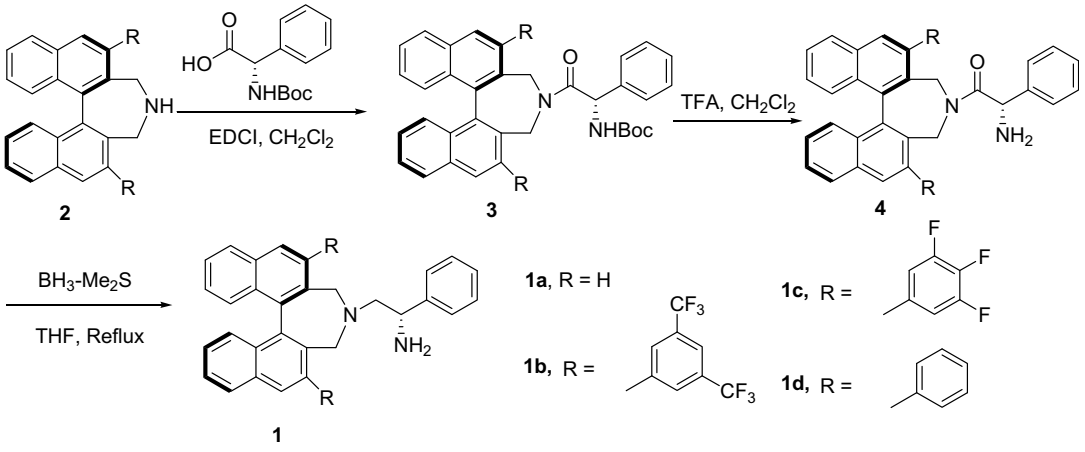
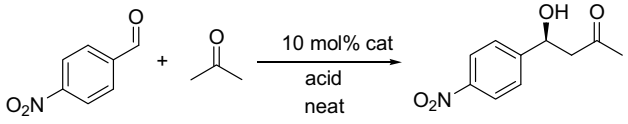


Scheme 1. Synthesis of novel diamines.

To develop the potential applications of the synthesized diamines in organocatalysis, the chiral diamines were then surveyed in the direct enantioselective aldol reactions between ketones and aromatic aldehydes. The aldol reaction between 4-nitrobenzaldehyde and acetone was chosen as the model reaction (Table 1). 4-Nitrobenzaldehyde reacted with acetone smoothly, affording the product in 50% yield with 91% ee (in the presence of 10 mol % **1a** and 15 mol % TFA (entry 6)). (*S*)-BINOL-derived catalyst (*S*′,*R*)-**1a** afforded 81% ee (55% yield) with the same configuration (*R*). Introduction of substituents such as phenyl, 3,5-trifluoromethylphenyl, and 3,4,5-trifluorophenyl (**1b**, **1c**, and **1d**) led to very low enantioselectivities (18–25% ee, entries 8–10). It seems that both binaphthyl and amino motif have significant impacts on the reaction.

Table 1
Optimization of aldol reactions between aromatic aldehydes and ketones[a]



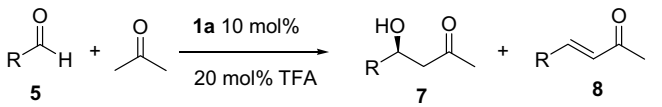
Entry	Cat.	Solvent	Temperature	Acid (mol %)	Yield (%)	ee (%)
1	**1a**	Neat	25	TfOH (15%)	87	64
2	**1a**	Neat	25	TsOH (15%)	6	50
3	**1a**	Neat	25	$ClCH_2COOH$ (15%)	94	43
4	**1a**	Neat	25	TFA (5%)	98	62
5	**1a**	Neat	25	TFA (10%)	76	86
6	**1a**	Neat	25	TFA (15%)	50	91
7	S′,*S*-**1a**	Neat	25	TFA (15%)	55	81
8	**1b**	Neat	25	TFA (15%)	52	18
9	**1c**	Neat	25	TFA (15%)	68	25
10	**1d**	Neat	25	TFA (15%)	58	28
11	**1a**	Neat	25	TFA (20%)	43	94
12	**1a**	Neat	25	TFA (25%)	38	90
13	**1a**	THF	25	TFA (20%)	42	93
14	**1a**	DMSO	25	TFA (20%)	52	54
15	**1a**	Hexane	25	TFA (20%)	29	89
16	**1a**	H_2O	25	TFA (20%)	35	27
17	**1a**	CH_2Cl_2	25	TFA (20%)	44	95
18	**1a**	Et_2O	25	TFA (20%)	38	93
19	**1a**	EtOH	25	TFA (20%)	35	68
20	**1a**	DMF	25	TFA (20%)	63	61
21	**1a**	Neat	40	TFA (20%)	44	89
22	**1a**	Neat	0	TFA (20%)	67	73
23	**1a**	Neat	−18	TFA (20%)	38	72

[a] All reactions were carried out with 0.1 mmol of aldehydes and 0.5 mL (4.8 mmol) of acetone at 0 °C. The enantioselectivity was measured using chiral AD–H.

However, the configuration of amino motif determined the configuration of the product. A comparison of the effects of acid revealed that TFA was the best choice (entries 1–3 vs 6). The amount of TFA used considerably affected the reactivity of the catalyst. Lowering the amount of TFA was beneficial for the yield of reaction, but was deleterious for the enantioselectivity (entries 4–6 and 11–12). The reaction was dependent on the solvents used, less polar solvents such as THF, ether, and DCM afforded high ee values, albeit in lower yields (entries 13, 15, 17, 18). Polar solvents were deleterious for the enantioselectivities (entries 14, 16, 19, 20).

Based on this study, the optimal reaction condition was 10 mol % of **1a** in combination with 20 mol % TFA as catalyst and neat acetone as the solvent (see Supplementary data).[10] Various aromatic aldehydes reacted with acetone, and the results are summarized in Table 2. These trials indicated that the reaction was dramatically dependent on the electron effect of the substituents. For example, 4- or 3-nitrobenzaldehydes and 4-cyanobenzaldehyde underwent aldol reactions in moderate yields (43–56%) and excellent enantioselectivities (91–94% ee, entries 1–3, Table 2). Less electron-deficient aldehydes such as 4-trifluoromethyl and 2-chlorobezaldehydes afforded products in lower enantioselectivities (entries 4 and 6). 2-Nitrobenzaldehyde gave only 86% ee (entry 5) compared to that of 4-nitrobenzaldehyde, perhaps due to the

Table 2
Reactions between aldehydes and ketones[a]



Entry	R	Yield (%) 7 (**8**)	ee (%)	Configuration[b]
1	4-$NO_2C_6H_4$	43 (55)	94	*R*
2	3-$NO_2C_6H_4$	56 (41)	91	*R*
3[a]	4-CNC_6H_4	50 (43)	94	*R*
4	2-ClC_6H_4	58 (40)	90	*R*
5	2-$NO_2C_6H_4$	62 (30)	86	*R*
6	4-$CF_3C_6H_4$	41 (40)	85	*R*
7	4-$CH_3C_6H_4$	11 (9)	66	*R*
8[c]	4-$NO_2C_6H_4$	95	82	—

[a] Unless otherwise stated, the reaction was carried out at 25 °C with 0.25 mmol of methyl 2-oxoacetates and 1.0 mL (9.6 mmol) of acetone in the presence of 10 mol % of catalyst **1a** in combination with 20 mol % TFA. The enantioselectivities were determined by chiral AD–H.

[b] The configuration was determined by the comparison of retention time reported in the literature.[5]

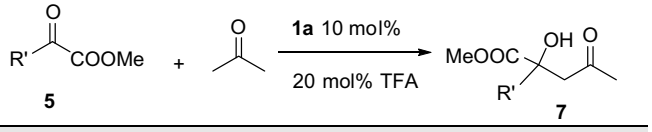
[c] Cyclohexanone was used.

steric hindrance. The substrates with electron-donating groups at the aromatic ring were less satisfactory. For example, 4-methylbenzaldehyde afforded the product in only 11% yield after long reaction time with moderate enantioselectivity (66% ee, entry 7). When cyclohexanone was used to replace acetone in the system, the *anti*-isomer was favorably formed (95% yield, 82% ee, dr 94:6, entry 8). A careful investigation found that the low yield of aldol reactions between aldehydes and acetone resulted from dehydration of the aldol product to form the corresponding α,β-unsaturated ketone **8**.

The use of catalyst **1a** can be extended to the direct aldol reaction of methyl 2-oxo-2-phenylacetate and ketones. This reaction was investigated by Feng's group using cyclohexanone-1,2-diamine-derived prolinamide as catalyst.[11] Although chiral tertiary alcohols are important intermediates in pharmaceutical industry,[12] their syntheses are rarely reported. The same reaction was also reported by other groups.[13] In the presence of 10 mol % of catalyst **1a** in combination with 20 mol % of trifluoroacetic acid, the reaction proceeded smoothly at 0 °C, affording the desired chiral tertiary alcohol in 99% yield with excellent enantioselectivity (96% ee, entry 1, Table 3). Lowering the temperature resulted in the slight enhancement of enantio selectivity, but prolonged the reaction time (see Supplementray data). To our knowledge, this was the best result attained. Various substituted methyl 2-oxo-2-acetates reacted with acetone smoothly at 0 °C, and the results are listed in Table 3. Both electron enriched and deficient substrates can be tolerated in the system affording excellent yields and enantioselectivities. For example, 4-methoxyphenyl-, 4-methylphenyl-, and phenyl-substituted esters all gave almost quantitative yields and 96% ee. The pattern of substituents on the aromatic ring seems to have a slight effect on the enantioselectivities of the reaction. For example, the 4-methyl phenyl-substituted ester provided higher enantioselectivity than did the 3-methyl variant (entries 3 and 4). Similarly, methyl 2-oxo-2,4′-flurophenyl acetate was reacted in comparable yield with 94% ee, a much better result than that of methyl 2-oxo-2,3′-flurophenyl acetate (entries 6 and 7). It is noteworthy that methyl 1-naphthylacetate afforded the product with 92% ee, a significant increase compared to the literature procedure[11] (entry 8).

In conclusion, a family of novel chiral amines which featured a tertiary–primary amine structure was synthesized. Their catalytic performance was demonstrated in asymmetric aldol reactions between aldehydes or activated ketones and acetone. A variety of aldehydes and methyl 2-oxo-acetates reacted with acetone affording the corresponding β-hydroxy ketones in high yields with excellent stereoselectivities. The studies on mechanism of direct aldol reactions and further application of the catalysts and their derivatives in asymmetric transformations are under way, and will be reported in due course.

Table 3
Reactions between α-keto esters and ketones



Entry	R′	R	Yield (%) 7	ee (%)
1	C_6H_5	COOMe	99	96 (*R*)[a]
2	4-$MeOC_6H_5$	COOMe	98	96
3	4-MeC_6H_5	COOMe	99	96
4	3-MeC_6H_5	COOMe	99	90
5	2-Naphth	COOMe	99	92
6	3-FC_6H_5	COOMe	99	90
7	4-FC_6H_5	COOMe	99	94
8	1-Naphthyl	COOMe	71	92

Unless otherwise stated, the reaction was carried out with 0.25 mmol of methyl 2-oxoacetates and 1.0 mL (9.6 mmol) of acetone in the presence of 10 mol % of catalyst **1a** in combination with 20 mol % TFA at 0 °C. The enantioselectivities were determined by chiral AD–H. The absolute configuration of the product is not determined.

[a] See Refs. 11 and 13c.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.10.085.

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9. *The characterization of catalyst* **1a**: 84%, mp 92–93 °C, $[\alpha]_D^{20}$ −203.3 (*c* 0.06 in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) 7.93–7.97 (m, 4H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.43–7.48 (m, 6H), 7.35–7.39 (m, 2H), 7.24–7.29 (m, 3H), 4.36 (dd, *J* = 10.4, 3.3 Hz, 1H), 3.76 (d, *J* = 12.2 Hz, 2H), 3.24 (d, *J* = 12.2 Hz, 2H), 2.76 (dd, *J* = 12.9, 3.3 Hz, 1H), 2.36 (dd, *J* = 12.9, 10.8 Hz, 1H), 1.89 (br, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 143.8, 134.9, 133.2, 133.1, 131.3, 128.5, 128.4, 128.2, 127.7, 127.4, 127.3, 126.7, 125.7, 125.4, 62.1, 54.9, 53.6 ppm; IR (film, *v* cm^{-1}): 3431, 2924, 2859, 1628, 1474, 1188, 1039, 837, 746. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2$ ([M+H$^+$]) = 415.2174, found 415.2176.
Compound **1b**: >99% yield, mp 124–125 °C, $[\alpha]_D^{20}$ −103.25 (*c* 0.4 in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) 8.12 (s, 3H), 7.98–8.02 (m, 7H), 7.56 (t, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.34–7.39 (m, 2H), 7.16–7.18 (m, 3H), 6.75–6.78 (m, 2H), 3.92 (d, *J* = 12.9 Hz, 2H), 3.23–3.32 (m, 3H), 2.25 (dd, *J* = 12.9, 3.3 Hz, 1H), 2.03 (dd, *J* = 12.9, 11.0 Hz, 1H), 1.67 (br, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 143.5, 143.4, 137.1, 136.808, 132.5, 132.1, 131.7, 131.3, 130.3, 130.1, 130.0, 128.5, 128.3, 127.4, 127.2, 126.9, 126.7, 126.1, 121.31, 121.26, 121.21, 61.6, 53.5, 50.3. IR (film, *v* cm^{-1}): 3390, 2974, 2925, 1597, 1450, 1087, 1050, 758, 702. HRMS (ESI-TOF) calcd for $C_{46}H_{31}F_{12}N_2$ ([M+H$^+$]) = 839.2296, found 839.2301.
Compound **1c**: 94% yield, mp 120–121.5 °C, $[\alpha]_D^{20}$ −52.5 (*c* 0.4 in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) 7.95 (m, *J* = 8.2 Hz, 2H), 7.89 (s, 2H), 7.49–7.55 (m, 2H), 7.40–7.42 (m, 2H), 7.31–7.34 (m, 2H), 7.19–7.29 (m, 7H), 6.92–6.95 (m, 2H), 3.93 (d, *J* = 12.7 Hz, 2H), 3.55 (dd, *J* = 10.3, 3.1 Hz, 1H), 3.16 (d, *J* = 12.8 Hz, 2H),

2.50–3.20 (br, 2H), 2.32 (dd, J = 13.2, 3.1 Hz, 1H), 2.19 (dd, J = 13.2, 10.3 Hz, 1H). ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 152.7, 152.6, 149.4, 149.33, 149.25, 149.2, 137.3, 137.22, 137.16, 136.6, 132.4, 131.0, 130.4, 129.6, 128.41, 128.39, 127.6, 127.4, 126.7, 126.6, 126.5, 114.3, 114.0, 60.6, 53.9, 50.4 ppm; IR (film, v cm^{-1}): 3429, 2923, 1614, 1527, 1447, 1241, 1045, 750, 703. HRMS (ESI-TOF) calcd for $C_{42}H_{29}F_6N_2$ ([M+H$^+$]) = 675.2234, found 675.2207.

Compound **1d**: 82% yield, mp 112.5–113 °C, $[\alpha]_D^{20}$ −18.75 (c 0.4 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) 7.94–7.97 (m, 4H), 7.62 (d, J = 6.4 Hz, 4H), 7.43–7.53 (m, 10H), 7.26–7.31 (m, 2H), 7.16–7.22 (m, 3H), 6.83–6.86 (m, 2H), 4.04 (d, J = 12.5 Hz, 2H), 3.33 (dd, J = 10.5, 3.0 Hz, 1H), 3.21 (d, J = 12.5 Hz, 2H), 2.34 (dd, J = 12.8, 3.0 Hz, 1H), 2.06 (br, 2H), 1.95 (dd, J = 12.8, 10.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 141.4, 140.2, 136.4, 132.5, 131.2, 130.7, 130.0, 129.4, 128.7, 128.4, 128.2, 128.1, 127.5, 127.2, 127.1, 125.9, 125.8, 60.6, 53.2, 50.1 ppm; IR (film, v cm^{-1}): 3390, 2973, 2925, 1489, 1449, 1087, 1050, 885, 758, 702. HRMS (ESI-TOF) calcd for $C_{42}H_{35}N_2$ ([M+H$^+$]) = 567.2800, found 567.2802.

10. *General procedure for the direct aldol reactions*: A mixture of anhydrous acetone (1.0 mL), aromatic aldehydes or α-keto esters (0.25 mmol), catalyst **1a** (10.4 mg, 0.025 mmol, 10 mol%) TFA (3.7 μL, 0.05 mmol, 20 mol%) was stirred at ambient temperature for 32–41 h (aldehydes) or at 0 °C for 34–168 h (α-keto esters). The mixture was directly purified through flash column chromatography on a silica gel (n-hexane/ethyl acetate = 8/1–2/1) to give the pure adduct affording the desired adducts.
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