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Homogeneous silicone modified primary amine-Brønsted acid salt catalyzed aldol reaction: unexpected synergistic effect of polysiloxane with remarkable improvement of efficiency and stereoselectivity

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ABSTRACT

We have developed a new strategy to improve the stereoselectivity in enamine catalysis by the introduction of super-hydrophobic long-chain silicone/polysiloxane as support/functional group for a model aldol reaction. The homogeneous direct aldol reaction of cyclic ketones with different aromatic aldehydes catalyzed by polysiloxane-derived primary amines has been reported with high yields, good diastereoselectivity, and up to 99% ee.

The asymmetric aldol condensation, an ancient and fundamental organic reaction, is one of the most powerful methods for constructing carbon–carbon bonds in organic synthesis, creating the β-hydroxy carbonyl structural unit which is found in many natural products and drugs.[1] Since the pioneering work of List and Barbas in 2000,[2] the development of organocatalytic stereoselective methods for asymmetric direct aldol reactions has been an interesting subject of intense research. Among the numerous reports on organocatalysts, L-proline is arguably the most famous organocatalyst in a wide range of organic reactions.[3] The success of L-proline and its derivatives promoted the studies of other abundant chiral organic molecules as catalysts in organic transformation.[4] In fact, primary amino acid catalysis is effectively exploited by enzymes such as type I aldolases, decarboxylases, and dehydratases, each of which contain catalytically active lysine or threonine residues.[5] Although Hajos and Prrich[6], as well as Eder et al.[7] used phenylalanine in the first organocatalytic intramolecular aldol condition of achiral triones, and Buchschacher et al.[8] reported β-amino acids, such as β^3-homoproline, β^3-homophenylalanine, and also γ-amino acids are effective catalysts in intramolecular asymmetric aldol condensations (Hajo–Parrich–Eder–Sauer–Wiechert reactions or Robinson annulation), these findings have not been recognized either, until primary amino acids were reinvestigated from 2004/2005.[9] Interestingly, other amino acids with primary amine groups received considerable attention as organocatalyst,[10] and similarly, some progress has been made in the primary amine-based organocatalysis.[11] In this vein, several groups have reported recently the successful application of chiral diamine-derived primary amine thiourea catalysts in Michael addition,[12] and the primary–tertiary diamine catalyzed aldol and other reactions.[13]

Recent findings by Lu and co-worker showed that silicone group in *O*-TBS-threonine (TBS-protection of hydroxyl group in L-threonine) exhibited important functionality in aldol and Mannich reaction compared to unsubstituted threonine.[14] It is reasoned that TBS-protection of hydroxyl group resulted in hydrophobic catalyst and associated strongly with hydrophobic reactants. In this context, we demonstrated a new strategy that involves hydrophobic interactions by the introduction of super-hydrophobic long-chain polysiloxane as support/functional group to primary amine catalyst.

Polysiloxanes are hydrophobic, chemically resistant inorganic polymer, in which the chain is entirely inorganic, with alternating Si and O atoms, and organic side groups are attached to the silicon atoms. Most applications of polysiloxanes were derived from the extraordinary flexibility and super-hydrophobicity of the siloxane backbone. Although many applications of polysiloxanes include high-performance elastomers, membranes, electrical insulators, water repellent sealants, adhesives, protective coatings, and hydraulic, heat transfer, dielectric fluids, biomaterials, and catalyst supports have been reported in the past decades,[15] to the best of

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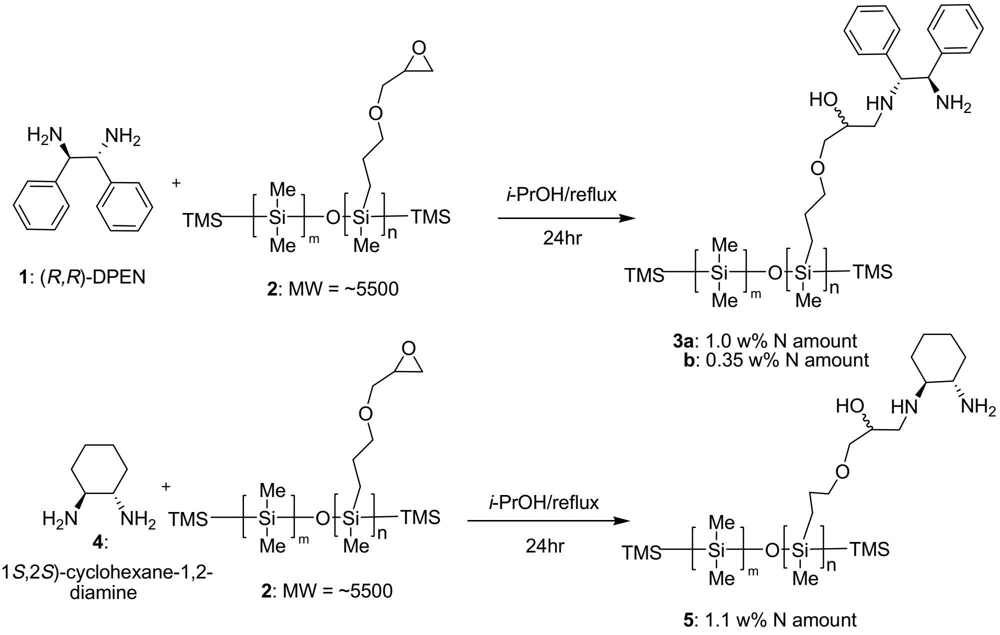
our knowledge, very few examples are known where the polysiloxanes were used as a linker or as a group or even as a supporter in organocatalyst. Only Siegel[16] and Bergbreiter[17] reported recently used polysiloxanes as soluble inorganic polymer supports for a Lewis base organocatalyst, Cinchona alkaloid, in the Michael addition of thiol and α,β-unsaturated ketones and esters, which gave low ee value (~20% ee).

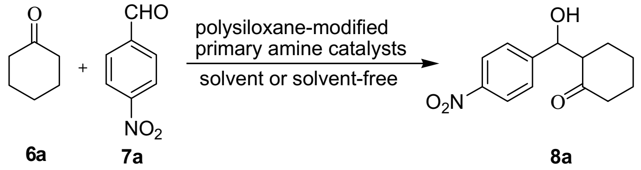
To explore the potential of using hydrophobic polysiloxane in organocatalysis, we prepared different nitrogen amounts of polysiloxane with chiral primary amine backbone (Scheme 1).[18] The



Scheme 1. The preparation of polysiloxane-modified primary amine catalysts.

Table 1

Screening results of polysiloxane containing primary amine-brønsted acid catalyzed aldol reaction[a]



Entry	Cat.	Sol.	Acid	*T* (h)	Y (%)/dr[b]	Ee% (*anti*/*syn*)[c]
1	**3a**	DCM	TfOH	96	34 (5.7/1)	97/91
2	**3a**	Hex.	TfOH	24	58 (3.8/1)	82/40
3	**3a**	THF	TfOH	96	46 (5.7/1)	99/89
4	**3a**	DMF	TfOH	24	66 (6.1/1)	99/80
5	**3a**	H_2O	TfOH	24	73 (5.7/1)	98/72
6	**3a**	Brine	TfOH	24	64 (5.7/1)	98/79
7	**3a**	–	TfOH	16	84 (6.1/1)	98/80
8	**3b**	–	TfOH	24	46 (4.6/1)	87/30
9	**5**	–	TfOH	12	95 (4.0/1)	96/82[d]
10[e]	**3a**	–	TfOH	24	53 (5.7/1)	97/70
11	**3a**	–	TFA	24	84 (6.1/1)	97/50
12	**3a**	–	TsOH	24	36 (5.7/1)	95/76
13	**3a**	–	4-Nitrobenzoic acid	24	53 (1/1.2)	8/64
14[f]	**3a**	–	TfOH	24	92 (6.7/1)	99/86
15[g]	**3a**	–	TfOH	24	83 (4.6/1)	99/91
16[f]	**3a**	–	4-Nitrobenzoic acid:TfOH(1:1)	12	97 (6.7/1)	99/86
17[h]	**3a**	–	4-Nitrobenzoic acid:TfOH(1:1)	38	78 (6.7/1)	99/87

[a] The reaction were performed with 1.0 mmol of *p*-nitrobenzaldehyde, 10 equiv of cyclohexanone, primary amine-based catalyst (20 mol %), Brønsted acid (40 mol %), solvent or neat, at room temperature.

[b] Isolated yield; dr number is *anti*/*syn* in parenthesis, and determined by ^{1}H NMR analysis.

[c] The ee values were determined by HPLC.

[d] The absolute configuration of adduct product is opposite in comparison with that of catalyst **3**.

[e] In entry 10, 10 mol % of primary amine catalyst, 20 mol % of acid.

[f] In entries 14 and 16 and 20 mol % of primary amine catalyst, 20 mol % of acid.

[g] In entry 15, 20 mol % of catalyst and 10 mol % of acid.

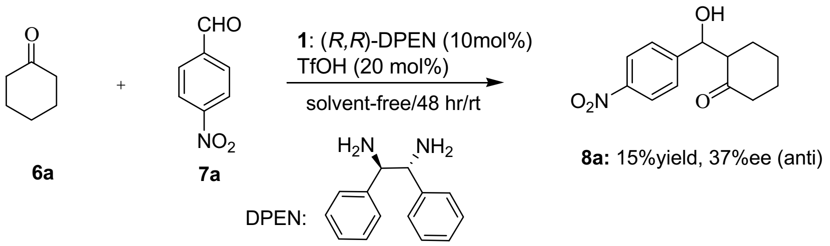
[h] In entry 17, 10 mol % of catalyst, 10 mol % of acid.

primary amine (1,2-diphenylethylenediamine and cyclohexane-1,2-diamine)-substituted polysiloxane was prepared from the one-pot ring-opening of polysiloxane containing side group of epoxide with chiral diamine in *i*-PrOH under reflux for 24 h. The functional polysiloxane was completely soluble in acetone, toluene, chloroform, etc. we focused on undertaking a systematic investigation of this polysiloxane-modified primary amine salt as potential catalysts for the model reaction of cyclohexanone (**6**) with 4-nitrobenzaldehyde (**7a**). As shown in Table 1, among the standard reaction parameters, solvent choice and Brønsted acid proved particularly important. While reactions carried out in non-polar or low-polar solvents, such as THF, DCM, and hexane, were slow or only with moderate enantioselectivity (Table 1, entries 1–3), those run in highly polar and/or protic solvents, such as DMF, water, and brine, proceeded with useful rates along with excellent enantioselectivity (entries 4–6). And we were then pleased to find that polysiloxane-modified primary amine (silicone-DPEN) **3a** exhibited high catalytic activity under solvent-free conditions. It is on problem that neat cyclohexanone was suitable as both reactant and solvent in terms of enantioselectivity and catalyst reactivity. In this case, the corresponding adduct was cleanly isolated in 84% yield with a promising 98% ee after 16 h, and the *anti*-isomer was favorably formed with 6.1:1 dr (entry 7). Under the same conditions, polysiloxane derivative (silicone-DPEN) **3b** with low loading of chiral active primary amine salt catalyst showed decreased enantioselectivity with lower yield (entry 8, 46% yield, 87% ee of *anti*-isomer). Similarly, polysiloxane-modified primary amine **5** almost exhibited the same enantioselectivity and catalytic activity to **3a** (entry 9). Even with 10 mol % of **3a**, the corresponding *anti*-adduct was obtained with 97% ee in acceptable yield (entry 10). To our surprise, Brønsted acid had a significant impact on both reactivity and diastereoselectivity. The enantioselectivity could be obtained above 95% ee when the aldol reaction was conducted in the presence of TFA and TsOH (entries 11, 12), however, the employment of 4-nitrobenzoic acid decreased the enantioselectivity of *anti*-isomer to only **8** with poor dr (entry 13). Interestingly, the amount of triflic acid (TfOH) used considerably affected the reactivity of the catalyst. 20 mol % or 10 mol % of acid in combination with 20 mol % of catalyst was suitable for the reaction in terms of enantioselectivity, diastereoselectivity, and reactivity (Table 1, entries 14 and 15: 99% ee of *anti*-isomer and 91% ee of *syn*-iomer). The employment of two different Brønsted acid, triflic acid with 4-nitrobenzoic acid, further enhanced the enantioselectivity and reactivity (entries 16, 17).

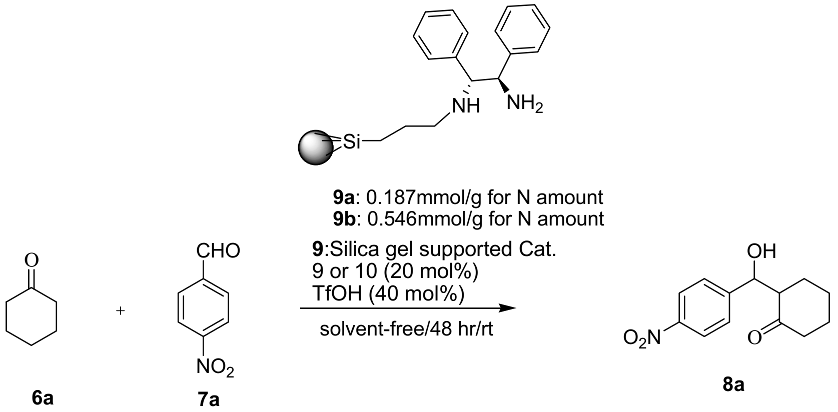
For comparison, other similar silica gel-supported primary amine catalyst and the (*R*,*R*)-1,2-diphenylethylenediamine (DPEN) were also investigated. We found that the primary diamine **1** (DPEN) reacted very slowly in the presence of TfOH under solvent-free conditions to give a poor yield and enantioselectivity of **8a** (Scheme 2, 15% yield, 37% ee for major *anti*-isomer).

Silica gel-supported primary amines (silica-DPEN) were also prepared according to the reported method[19] and were used in the present aldol reaction. As shown in Scheme 3, all the silica gel-supported DPEN (silica-DPEN) with different amounts of nitrogen gave good yield and excellent enantioselectivities (up to 75% yield, 95% ee). However, these results were not better than those of polysiloxane-modified primary amine catalysts **3** and **5**. All the above mentioned experimental results showed that polysiloxane-modified primary amine gave privileged reactivity and enantioselectivity in this aldol reaction.

With optimized conditions established for the model reaction of 4-nitrobenzaldehyde with cyclohexanone, we explored the scope



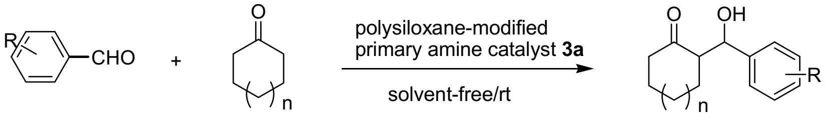
Scheme 2. DPEN-catalyzed aldol reaction under solvent-free condition.



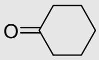
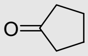
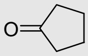
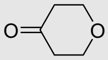
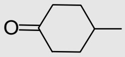
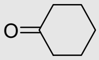
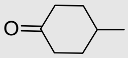
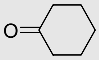
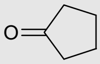
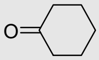
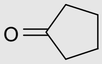
Cat. **9a**: solvent-free, 24 h,yield = 75%, dr (*anti/syn*) = 2.4/1, ee% = 95 (*anti*)/70(*syn*)
reused data, for the second time: yield = 71% , ee% = 87/64
reused data, for the third time: yield = 56% , ee% = 89/63
Cat. **9b**: solvent-free, 48 h, 45% yield, dr (*anti/syn*) = 3/1, ee% = 80 (*anti*)/61(*syn*)

Scheme 3. Silica gel-supported primary amine-catalyzed aldol reaction under solvent-free condition.

Table 2
Enantioselective aldol reactions of cyclic ketones to aromatic aldehydes



7a-d **6a-d** **8a-k**

Entry[a]	R-	Ketone	Product	Time (h)	Yield[b] (%)	dr (*anti*/*syn*)[c]	Ee% (*anti*/*syn*)[d]
1	*p*-NO_2		**8a**	12	97	6.7/1	99/86
2	*p*-NO_2		**8b**	24	70	4.0/1	65/45
3	*o*-NO_2		**8c**	24	53	2.7/1	82/61
4	*p*-NO_2		**8d**	96	22	>19/1	98/–
5	*p*-NO_2		**8e**	16	94	>19/1	98/–
6	*o*-NO_2		**8f**	40	71	>99/1	97/–
7	*o*-NO_2		**8g**	60	65	>19/1	94/–
8	*m*-NO_2		**8h**	22	96	13.3/1	99/81
9	*m*-NO_2		**8i**	30	53	3.2/1	95/68
10	*p*-CN		**8j**	24	95	5.7/1	99/80
11	*p*-CN		**8k**	60	65	2.1/1	96/64

[a] The reactions were performed with 1.0 mmol of aldehydes, 10 equiv of ketones, 20 mol % of primary amine-based catalyst **3a**, 10 mol % of triflic acid, and 10 mol % of 4-nitrobenzoic acid, neat (solvent-free), stirred at room temperature.

[b] Isolated yield.

[c] Determined by ^1H NMR analysis.

[d] The ee values were determined by HPLC.

of useful cyclic ketones and aldehydes substrates using homogeneous polysiloxane-modified primary amine as a more practical reacting partner. As expected, under these conditions, a wide range of aromatic benzaldehydes underwent reaction with cyclic ketones in high yields and enantioselectivities in most cases (Table 2). The results of these trials indicated that the reaction is dramatically dependent on the electronic effect of the substituent. Unsubstituted aromatic aldehydes or with electron donating groups at aromatic ring were less reactive, because benzaldehyde, *p*-fluorobenzaldehyde, *p*-methyl benzaldehyde, and 1-naphthylaldehyde afforded only low to moderate yields but with excellent enantioselectivity (below 20% yield, up to 99% ee). However, *o*-, *m*-, and *p*-nitrobenzaldehyde as well as *p*-cyanobenzaldehyde underwent smoothly with cyclic ketones in good yields and excellent enantiselectivities except few examples.

Although the functional polysiloxane was not soluble in hexane, the simple separation of catalyst except column chromatography and ultrafiltration was not easy.[16] However, polysiloxane is a viable functional group for the modification of primary amine-based organocatalyst, and also is a useful material for mediating aldol reactions.

In conclusion, an enantioselective direct aldol reaction of cyclic ketones with different aromatic aldehydes catalyzed by polysiloxane-derived primary amines has been reported with high yields, good diastereoselectivity, and up to 99% ee. The aromatic aldehydes with electron-withdrawing groups are suitable substrates for this reaction. Although the reaction scope of substrates seems to be limited, this work provides a new strategy to improve the stereoselectivity in enamine catalysis by the introduction of superhydrophobic long-chain silicone/polysiloxane as support/functional group for a model aldol reaction, also provide a practical and convenient method for the synthesis of optically enriched hydroxyl ketones.

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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.2008.09.145.

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18. *General procedure of preparation of polysiloxane-modified primary amine*: Under a nitrogen flow, a Schlenk tube was charged with 1 mmol of diamine (excess, such as DPEN), 1 g of polysiloxane containing epoxide (obtained from Hangzhou Bald Silicone Co., Ltd, 0.5 mmol epoxide/g polysiloxane, $M_w \sim 5500$), and 10 mL of *i*-PrOH. And then the solution was refluxed for 24 h. After completion of the reaction, the solvent was removed under reduced pressure, the resulting crude product was washed several times with H_2O, ethanol, and hexane. The pure product was confirmed by NMR (see Supplementary data) and elementary analysis (the N% amount was shown in Scheme 1).
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