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Combinatorial approach for the design of new, simplified chiral phase-transfer catalysts with high catalytic performance for practical asymmetric synthesis of α-alkyl-α-amino acids

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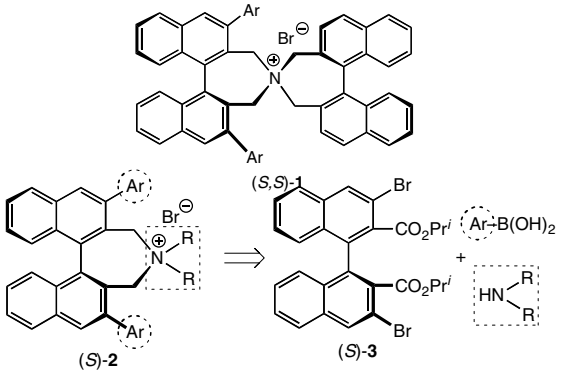
Abstract

A very efficient, chiral phase-transfer catalyst (*S*)-**2Db** was prepared by taking advantage of the combinatorial approach from the known, easily available (*S*)-1,1′-binaphthyl-2,2′-dicarboxylic acid. This catalyst exhibited the high catalytic performance (0.01–0.1 mol %) in the asymmetric alkylation of *N*-(diphenylmethylene)glycine *tert*-butyl ester compared to the existing chiral phase-transfer catalysts, thereby allowing to realize a general and useful procedure for highly practical enantioselective synthesis of structurally diverse natural and unnatural α-alkyl-α-amino acids.

Development of truly efficient methods in organic synthesis, especially in an enantiomerically pure form, has become of great importance. However, despite their numerous studies only a few catalytic systems have been reported in asymmetric phase-transfer chemistry with limited general applicability.[1] In this context, though we recently designed new, chiral spiro-type (*R,R*)- or (*S,S*)-3,4,5-trifluorophenyl-NAS bromide (*S,S*)-**1** (Ar = 3,4,5-F_3–C_6H_2)[2] for effecting asymmetric alkylation of α-amino acid derivatives,[3,4] the multi-step [5 steps for right-hand (*S*)-3,5-dihydro-4*H*-dinaphth[2,1-*c*:1′2′-*e*]azepine from (*S*)-binaphthol; 11 more steps from (*S*)-binaphthol] preparation of such spiro-type catalyst **1** constitutes severe drawback, and the simplification of catalyst **1** is crucially important to overcome the intrinsic problem in the chiral phase-transfer process chemistry.

To simplify the structure of the original catalyst (*S,S*)-**1**, we chose a basic structure of type **2** as a simplified chiral phase-transfer catalyst. Since the catalyst (*S*)-**2** can be readily prepared from three components, that is, a chiral binaphthyl part (*S*)-**3**, an arylboronic acid ($ArB(OH)_2$), and a secondary amine (R_2NH) as described previously,[5] the appropriate modification of $ArB(OH)_2$ and R_2NH parts should give a series of newly designed catalysts. Hence, we began to study the substituent effect of Ar and R moieties in detail by using combinatorial chemistry, since variation of the substituents Ar and R would allow the facile generation of large libraries of structures.



The requisite catalyst (*S*)-**2** can be easily prepared from the known, readily available (*S*)-1,1′-binaphthyl-2,2′-dicarb-

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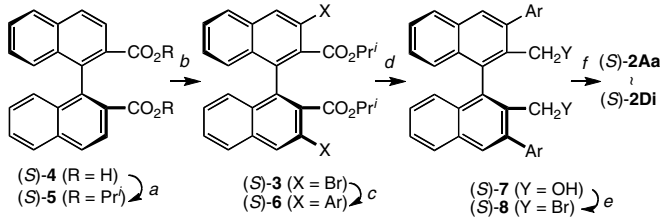
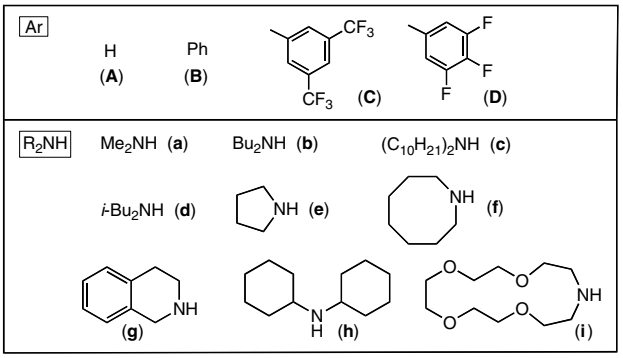
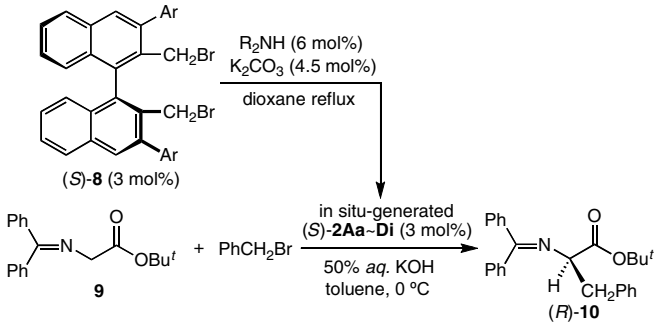
oxylic acid (*S*)-**4**[6] in 6-step sequence as outlined in Scheme 1.[7] Thus, (*S*)-dicarboxylic acid (*S*)-**4** was transformed with *i*-PrBr, catalytic $Bu_4N{\cdot}HSO_4$, and $KF{\cdot}2H_2O$ to the corresponding diisopropyl ester (*S*)-**5** in 95% yield. Treatment of (*S*)-**5** with freshly prepared $Mg(TMP)_2$ in THF and subsequent addition of Br_2 gave rise to (*S*)-3,3′-dibromo-1,1′-binaphthyl-2,2′-dicarboxylic ester (*S*)-**3** in 91% yield. Suzuki–Miyaura cross coupling of (*S*)-**3** with arylboronic acid, $ArB(OH)_2$ (Ar = Ph, 3,5-$(CF_3)_2$–C_6H_3, 3,4,5-F_3–C_6H_2) in the presence of catalytic $Pd(OAc)_2$, PPh_3, and K_2CO_3 in DMF afforded (*S*)-3,3′-diaryl-1,1′-binaphthyl-2,2′-dicarboxylic ester (*S*)-**6** in 57–68% yields. Reduction of (*S*)-**6** with $LiAlH_4$ in THF and subsequent treatment of the resulting crude alcohol (*S*)-**7** with PBr_3 in THF furnished (*S*)-dibromide (*S*)-**8** in moderate to high yields. Reaction of (*S*)-**8** with dialkylamine and K_2CO_3 in acetonitrile led to the formation of catalysts (*S*)-**2Aa**–**Di** in high yields.

To examine the substituent effect of catalyst (*S*)-**2** on the variation of the substituents Ar and R, we first prepared a library of quaternary ammonium salts (*S*)-**2Aa**–**Di** by combining use of 4 aryl substituents with 9 different dialkylamines. The chiral amplitude of these simplified phase-transfer catalysts (*S*)-**2Aa**–**Di** was screened efficiently by using an in situ-generated method from 3,3′-diarylated (*S*)-binaphthyl dibromide (*S*)-**8** (Ar = H, Ph, 3,5-$(CF_3)_2$–C_6H_3, 3,4,5-F_3–C_6H_2) in the asymmetric alkylation of *N*-(diphenylmethylene)glycine *tert*-butyl ester **9** (Scheme 2). Thus, reaction of **9** with benzyl bromide (1.2 equiv) and 50% aqueous KOH in toluene was carried out in the





Scheme 1. Reagents and conditions: (a) *i*-PrBr (10 equiv), $BuN{\cdot}HSO_4$ (20 mol %), $KF{\cdot}2H_2O$ (10 equiv), THF, reflux (95%); (b) (1) $Mg(TMP)_2$ (4 equiv), THF, rt, (2) Br_2 (8 equiv), −78 °C to rt (91%); (c) $ArB(OH)_2$ (2.4 equiv), $Pd(OAc)_2$ (5 mol %), PPh_3 (15 mol %), K_2CO_3 (3 equiv), DMF, 90 °C (57–68%); (d) $LiAlH_4$ (3 equiv), THF, 0 °C to rt (59–82%); (e) PBr_3 (1 equiv), THF, 0 °C (65–87%); (f) R_2NH (2 equiv), K_2CO_3 (1.5 equiv), CH_3CN, reflux (34–88%).



Scheme 2.

presence of 3 mol % of in situ-generated catalysts (*S*)-**2Aa**–**Di** under argon atmosphere at 0 °C to furnish benzylation product (*R*)-**10** and the results are shown in Table 1, which also includes the selected results by using isolated, optically pure catalyst (*S*)-**2** for comparison.

With bis(3,4,5-trifluorophenyl)-substituted catalyst (*S*)-**2D**, we examined the substituent effect of *R* by changing the number of straight alkyl chains as shown in Figure 1. In the asymmetric benzylation of *N*-(diphenylmethylene)glycine *tert*-butyl ester **9**, dimethylammonium salt, (*S*)-**2Da** exhibited very low enantioselectivity, and use of $(CH_3(CH_2)_{n-1})_2$ NH ($n \geqslant 4$) gave uniformly high asymmetric induction.

With this information at hand, we further screened the substituent effect of various Ar groups by preparing (*S*)-**2b** catalysts derived from dibutylamine and various 3,3′-diarylated (*S*)-binaphthyl dibromide (*S*)-**8** as shown in Figure 2. Among mono-substituted phenyl derivatives, *p*-substituted phenyl derivatives generally gave higher enantioselectivity than the corresponding *m*-substituted phenyl analogues in the asymmetric benzylation of **9**. In particular, *p*-(trifluoromethyl)phenyl and *p*-nitrophenyl derivatives exhibited high enantioselectivity (94% ee). These catalysts are more selective than various disubstituted

Table 1
Screening of in situ-generated catalyst (*S*)-**2Aa**–**Di** in the enantioselective phase-transfer benzylation of glycine derivative **9**[a]

Amine (R_2NH)	Ar = H (**A**)	Ar = Ph (**B**)	Ar = 3,5-$(CF_3)_2$–C_6H_3 (**C**)	Ar = 3,4,5-F_3–C_6H_2 (**D**)
(**a**)	12% ee	26% ee	1% ee	7% ee
(**b**)	–27% ee (–13% ee)	43% ee (60% ee)	93% ee (91% ee)	97% ee (99% ee)
(**c**)	–17% ee	58% ee	96% ee (93% ee)	97% ee (99% ee)
(**d**)	–9% ee	22% ee	44% ee	7% ee
(**e**)	–7% ee	5% ee	31% ee	43% ee
(**f**)	–23% ee	33% ee	41% ee	20% ee
(**g**)	–19% ee	26% ee (28% ee)	78% ee	81% ee
(**h**)	22% ee	3% ee	2% ee	6% ee
(**i**)	15% ee	41% ee	75% ee	83% ee (87% ee)

[a] The enantioselectivity in parentheses is obtained by using isolated, optically pure (*S*)-**2**.

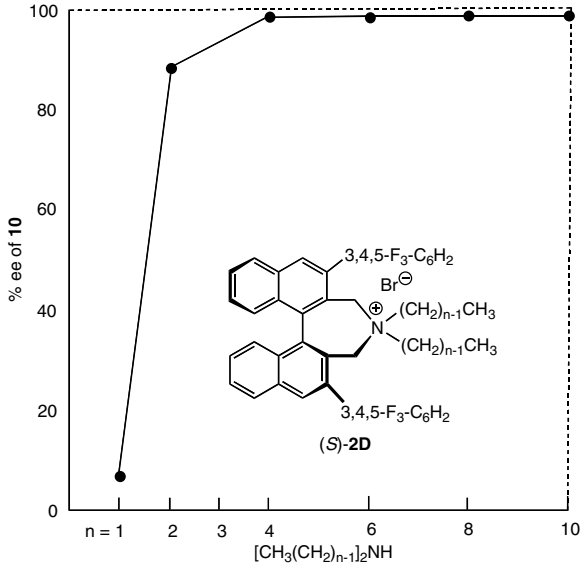


Fig. 1. Effect of the number of straight alkyl chain in (*S*)-**2D** on the enantioselectivity in the asymmetric benzylation of **9**.

phenyl derivatives. Among a variety of aryl substituents, catalyst (*S*)-**2Db** possessing 3,4,5-trifluorophenyl substituents was found to give the best result in terms of enantioselectivity (99% ee).

The chemical behavior of the simplified phase-transfer catalysts (*S*)-**2Cb**, (*S*)-**2Cc**, (*S*)-**2Db**, and (*S*)-**2Dc** was examined by carrying out asymmetric alkylation of *N*-(diphenylmethylene)glycine *tert*-butyl ester **9**, and quite surprisingly these types of catalysts are found to be by far the most active catalysts among existing chiral phase-transfer catalysts. Indeed, asymmetric reaction of **9** with benzyl bromide (1.2 equiv) and 50% aqueous KOH in toluene was effected in the presence of only 0.01–0.1 mol % of chiral catalyst (*S*)-**2Db** under argon atmosphere at 0 °C for 2–9 h to furnish benzylation product **10** almost quantitatively with excellent enantioselectivity (98–99% ee) (entries 1–3). However, use of 0.005 mol % of (*S*)-**2Db** resulted in lowering both the chemical yield and the enantioselectivity (entry 4). A similar tendency is also observed in the case of catalyst (*S*)-**2Dc** (entries 5 and 6).

Other selected examples are listed in Table 2. Several characteristic features of the present alkylations follow: (1) In contrast to the existing chiral phase-transfer catalysts, the chiral phase-transfer catalysts (*S*)-**2Cb**, (*S*)-**2Cc**, (*S*)-**2Db** or (*S*)-**2Dc** exhibited the high catalytic performance (0.05–0.1 mol %), demonstrating the remarkable efficiency and the practicability of the present approach for the enantioselective synthesis of α-alkyl-α-amino acids. (2) By using $CsOH{\cdot}H_2O$ in place of 50% KOH, asymmetric alkylation of **9** with simple alkyl halide such as ethyl iodide proceeded smoothly at −20 °C to furnish the corresponding α-alkyl-α-amino acids in good yield with high enantioselectivity (entry 21 vs 20).

A typical experimental procedure of catalytic enantioselective benzylation of *N*-(diphenylmethylene)glycine *tert*-butyl ester (**9**) is as follows (Table 2, entry 2): To a mixture of glycine derivative (**9**) (88.6 mg, 0.3 mmol) and chiral catalyst (*S*)-**2Db** (0.11 mg, 0.00015 mmol) in toluene (1.0 mL)–50% KOH aqueous solution (1.0 mL) was added benzyl bromide (43 μL, 0.36 mmol) dropwise at 0 °C. The reaction mixture was stirred vigorously at the same temperature for 2 h. The mixture was then poured into water

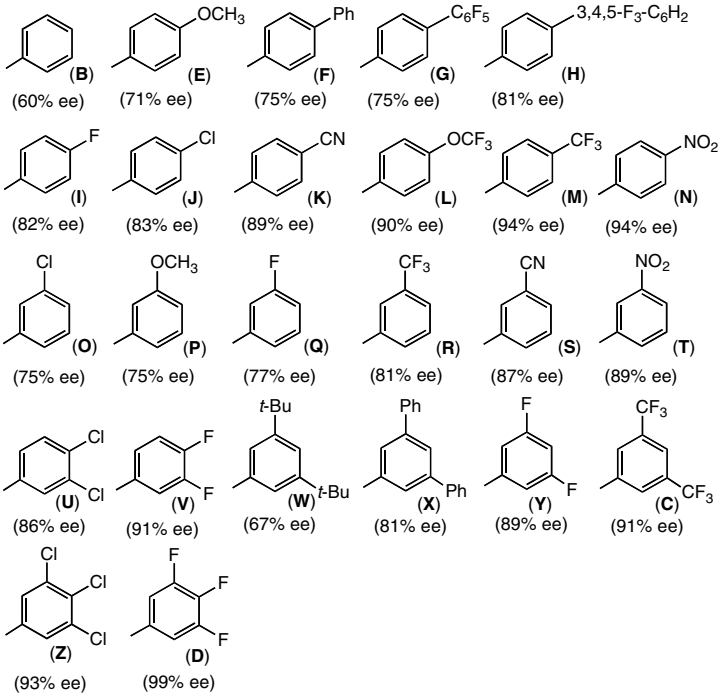


Fig. 2. Effect of aryl substituents of (*S*)-**2b** (R = Bu) on the enantioselectivity in the asymmetric benzylation of **9**.

Table 2
Catalytic enantioselective phase-transfer alkylation of glycine derivative **9** catalyzed by (*S*)-**2Cb**, (*S*)-**2Cc**, (*S*)-**2Db**, and (*S*)-**2Dc**[a]

Entry	Catalyst (mol %)	R–X	Cond. (°C, h)	Yield[b] (%)	% ee[c] (config)[d]
1	(*S*)-**2Db** (0.1)	$PhCH_2Br$	0, 2	99	99 (*R*)
2	(*S*)-**2Db** (0.05)		0, 2	98	99 (*R*)
3	(*S*)-**2Db** (0.01)		0, 9	92	98 (*R*)
4	(*S*)-**2Db** (0.005)		0, 48	51	57 (*R*)
5	(*S*)-**2Dc** (0.05)		0, 4	94	99 (*R*)
6	(*S*)-**2Dc** (0.01)		0, 24	79	98 (*R*)
7	(*S*)-**2Cb** (0.1)		0, 4	89	91 (*R*)
8	(*S*)-**2Cb** (0.05)		0, 5	87	91 (*R*)
9	(*S*)-**2Cb** (0.01)		0, 48	9	90 (*R*)
10	(*S*)-**2Cc** (0.05)		0, 48	85	93 (*R*)
11	(*S*)-**2Cc** (0.01)		0, 48	51	77 (*R*)
12	(*S*)-**2Db** (0.05)	$CH_2{=}CHCH_2Br$	0, 3	87	98 (*R*)
13	(*S*)-**2Db** (0.01)		0, 48	62	82 (*R*)
14	(*S*)-**2Dc** (0.05)		0, 5	99	97 (*R*)
15	(*S*)-**2Cb** (0.01)		0, 48	60	83 (*R*)
16	(*S*)-**2Cc** (0.05)		0, 48	59	91 (*R*)
17	(*S*)-**2Db** (0.05)	$HC{\equiv}CCH_2Br$	0, 4	88	98 (*R*)
18	(*S*)-**2Db** (0.01)		0, 48	28	88 (*R*)
19	(*S*)-**2Cb** (0.05)		0, 46	80	88 (*R*)
20	(*S*)-**2Db** (0.1)	CH_3CH_2I[e]	0, 72	12	91 (*R*)
21	(*S*)-**2Db** (0.1)	CH_3CH_2I[e,f]	–20, 1	67	99 (*R*)

[a] Unless otherwise specified, the reaction was carried out with 1.2 equiv of RX in the presence of cat. (*S*)-**2** in 50% aqueous KOH/toluene (volume ratio = 1:1) under the given reaction conditions.
[b] Isolated yield.
[c] Enantiopurity of (*R*)-**10** was determined by HPLC analysis of the alkylated imine using a chiral column [DAICEL Chiralcel OD] with hexane–isopropanol as solvent.
[d] Absolute configuration was determined by comparison of the HPLC retention time with the authentic sample independently synthesized by the reported procedure.[2]
[e] Use of 5 equiv of alkyl halide.
[f] Use of $CsOH{\cdot}H_2O$ as base.

and extracted with ether. The organic extracts were washed with brine and dried over Na_2SO_4. Evaporation of solvents and purification of the residual oil by column chromatography on silica gel (ether/hexane = 1:10 as eluant) gave the benzylation product (*R*)-**10** (113 mg, 0.294 mmol, 98% yield) as a colorless oil. The enantiomeric excess was determined by chiral HPLC analysis (DAICEL CHIRALCEL OD, hexane/isopropanol = 100:1, flow rate = 0.5 mL/min, retention time; 14.8 min (*R*) and 28.2 min (*S*)).

Acknowledgments

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