DOI: 10.1002/adsc.200600576

Effects of Aromatic Substituents on Binaphthyl-Based Chiral Spiro-Type Ammonium Salts in Asymmetric Phase-Transfer Reactions

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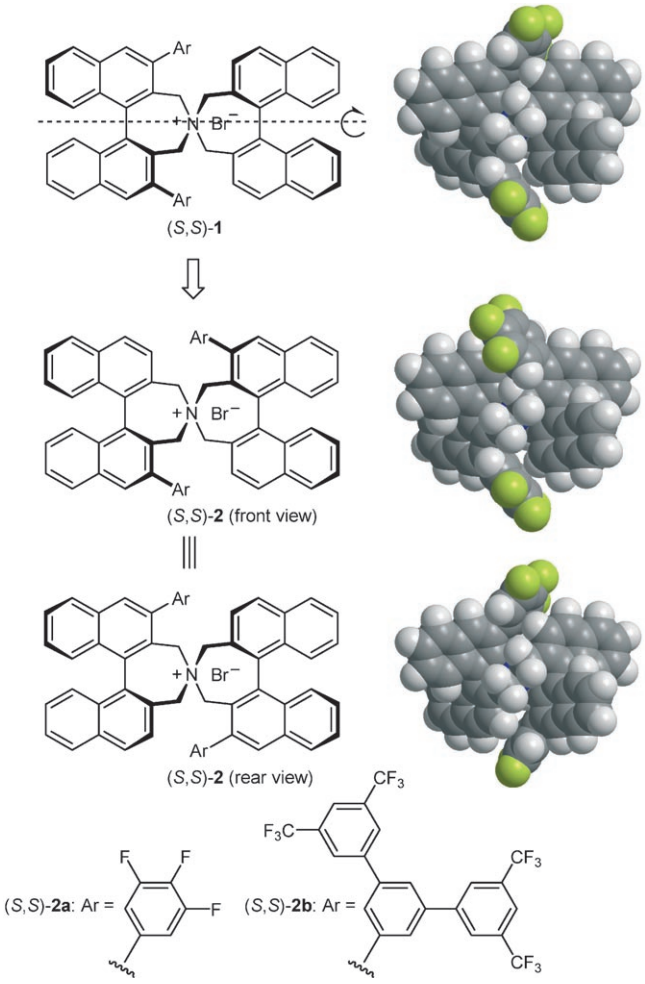
Received: November 5, 2006

Dedicated to Professor Masakatsu Shibasaki on the occasion of his 60th birthday

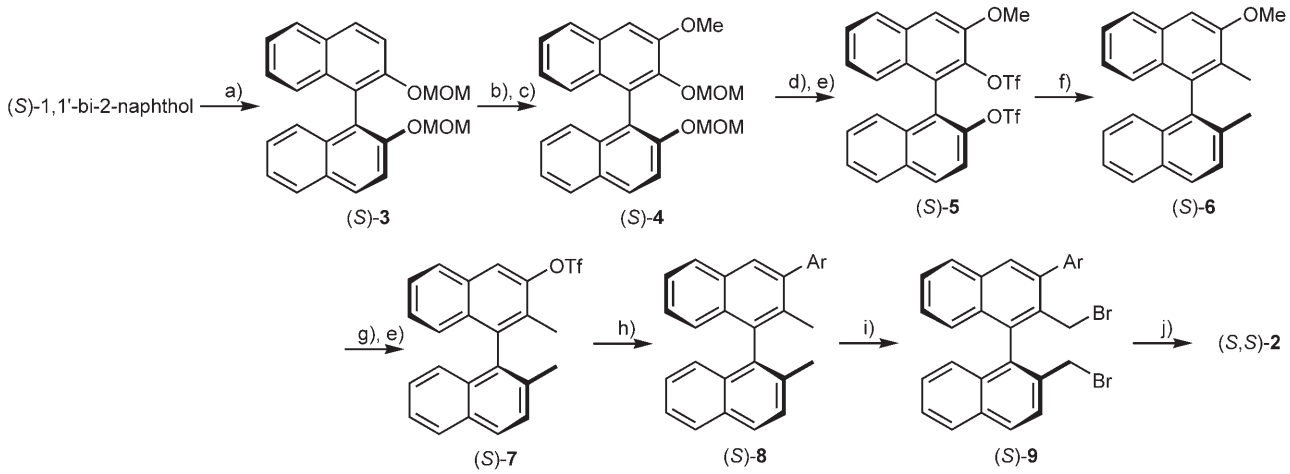
Abstract: Spiro-type phase-transfer catalysts prepared from two equivalents of a single binaphthyl subunit were designed and applied to the asymmetric alkylation and direct aldol reactions of a glycine derivative. The effects of the substitution pattern of the binaphthyl subunits on the enantioselectivity were also investigated.

Keywords: aldol reactions; alkylation; amino acids; asymmetric catalysis; enantioselectivity; phase-transfer catalysis

Asymmetric organocatalysis is an important category of asymmetric synthesis, and hence a number of chiral organocatalysts have been designed and applied to a variety of asymmetric transformations in recent years.[1] Among them, asymmetric phase-transfer catalysis using optically pure quaternary ammonium salts has become a field of growing importance,[2] and currently, Cinchona-alkaloid derived chiral phase-transfer catalysts[3] and C_2-symmetric binaphthyl-based chiral spiro-type phase-transfer catalysts[4–6] are most well known in this area. In the latter case, chiral spiro-type ammonium salts of type (*S*,*S*)-**1** having two different binaphthyl-modified subunits were successfully applied to various asymmetric phase-transfer reactions.[4] The introduction of aromatic substituents into such binaphthyl-based phase-transfer catalysts is found to be crucial for obtaining excellent enantioselectivity in almost all reactions. Additionally, the chiral phase-transfer catalyst (*S*,*S*)-**1**, in which both aromatic substituents are introduced into one binaphthyl moiety, possesses a C_2-symmetry axis as indicated in Scheme 1, and hence both sides (front and rear) of (*S*,*S*)-**1** have an identical asymmetric environment. On the other hand, a newly designed spiro-type phase-transfer catalyst (*S*,*S*)-**2**, which is created by two equivalents of a single mono-aryl-substituted binaphthyl subunit, has two different asymmetric environments on both sides, which consequently might affect the enantioselectivity (Scheme 1). Accordingly, we were interested in the effects of the substitution pattern of binaphthyl subunits on the enantioselectivi-



Scheme 1. Chiral phase-transfer catalyst (*S*,*S*)-**1**.



Reagents and conditions: a) NaH, MOMCl, THF, 0 °C. b) BuLi, THF, –78 °C to r.t.; $B(OMe)_3$, –78 °C to r.t.; H_2O_2, benzene, 0 °C to r.t. c) MeI, K_2CO_3, acetone, reflux. d) HCl, THF, r.t. e) Tf_2O, Et_3N, CH_2Cl_2, –78 °C to r.t. f) MeMgI, $NiCl_2$(dppp), ether, reflux. g) BBr_3, CH_2Cl_2, 0 °C. h) $ArB(OH)_2$, $Pd(OAc)_2$, PPh_3, $K_3PO_4 \cdot n\,H_2O$, DMF, 110 °C. i) NBS, AIBN, benzene, reflux. j) NH_3, K_2CO_3, CH_3CN, reflux.

Scheme 2. Synthesis of catalysts (*S*,*S*)-**2**.

ty and the possibility of utilizing (*S*,*S*)-**2** in the asymmetric phase-transfer reactions. Herein, we wish to report the synthesis of (*S*,*S*)-**2** and its application to asymmetric alkylation[5] and direct aldol reactions of a glycine derivative.[6]

The requisite chiral spiro-type ammonium salts (*S*,*S*)-**2** were prepared in an 11-step sequence from (*S*)-1,1′-bi-2-naphthol, as shown in Scheme 2. First, the hydroxy groups of (*S*)-1,1′-bi-2-naphthol were protected as the methoxymethyl ethers (99%). A methoxy group was then introduced on the 3-position of binaphthyl core by *ortho*-hydroxylation through lithiation of bis(methoxymethyl) ether (*S*)-**3** with BuLi, trapping with $B(OMe)_3$, and oxidation by H_2O_2 in one pot, and the subsequent protection of the resulting hydroxy group with MeI (82% for two steps). Selective deprotection of the methoxymethyl groups of (*S*)-**4** was conducted under acidic conditions followed by treatment with Tf_2O and Et_3N, giving triflates (*S*)-**5** (90% for two steps). The subsequent Ni-catalyzed cross-coupling reaction of (*S*)-**5** with methylmagnesium iodide afforded (*S*)-**6** in 91% yield, and then the methoxy group at the 3-position was converted to the triflate in two steps (98% for two steps). A 3,4,5-trifluorophenyl group was successfully introduced by Suzuki–Miyaura coupling of triflate (*S*)-**7** with 3,4,5-trifluorophenylboronic acid in 88% yield. Exposure of the resulting (*S*)-**8** (Ar = 3,4,5-trifluorophenyl) to the radical bromination conditions furnished the requisite (*S*)-**9** almost quantitatively. Treatment of (*S*)-**9** (Ar = 3,4,5-trifluorophenyl) with ammonia afforded chiral spiro-type ammonium bromide (*S*,*S*)-**2a** in 65% yield.

Another chiral ammonium bromide (*S*,*S*)-**2b** possessing the sterically more hindered 3,5-bis[3,5-bis(trifluoromethyl)phenyl]phenyl group[7] as the Ar moiety was also prepared in a similar manner. The structure of (*S*,*S*)-**2a** determined by X-ray crystallographic analysis is shown in Figure 1.

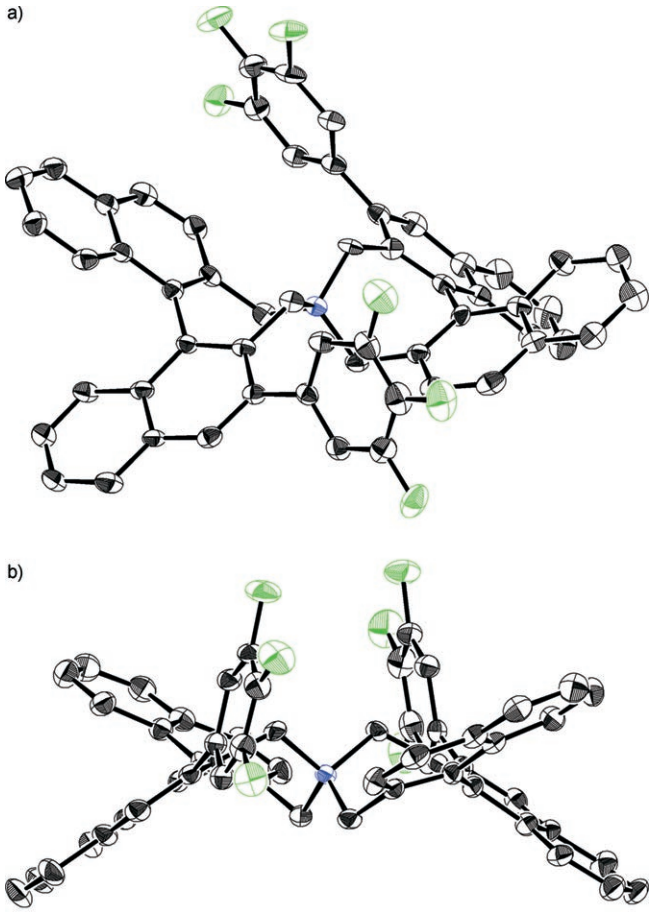
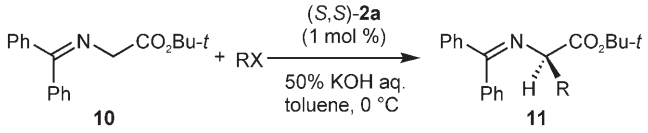
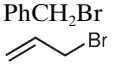
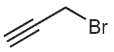


Figure 1. ORTEP drawings of (*S*,*S*)-**2a**. Br^-, solvent, and hydrogen atoms have been omitted for clarity.

Table 1. Catalytic asymmetric alkylation of **10** with alkyl halides.[a]



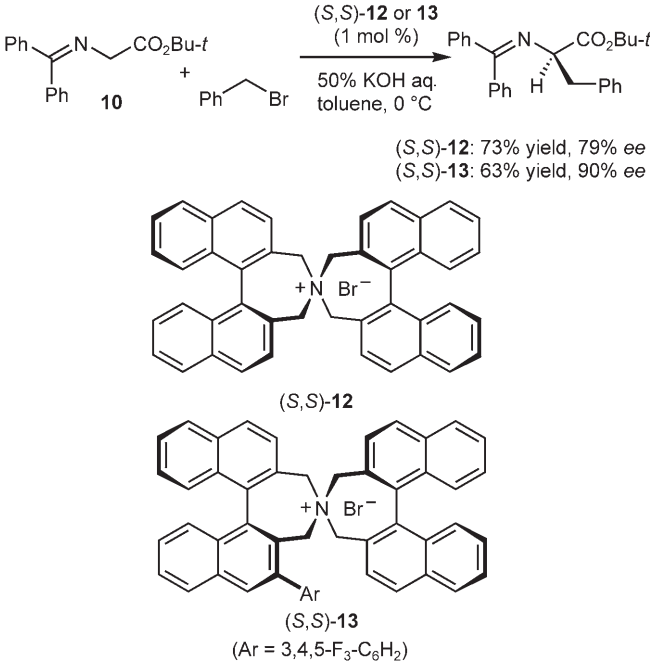
Entry	RX	Time [h]	Yield [%][b]	% *ee*[c]	Configuration[d]
1	$PhCH_2Br$	2.5	95	95	(*R*)
2		4	84	94	(*R*)
3[e]		12	79	92	(*R*)
4[e]	CH_3CH_2I	12	55	91	(*R*)

[a] Unless otherwise specified, the reaction was carried out with 1.2 equivs. of RX in the presence of 1 mol% of (*S*,*S*)-**2a** in 50% aqueous KOH/toluene (volume ratio = 1:3) under the given reaction conditions.
[b] Isolated yield.
[c] Enantiopurity of **11** was determined by HPLC analysis using a chiral column (DAICEL Chiralcel OD) with hexane/2-propanol as solvent.
[d] Absolute configuration of **11** was determined by comparison of the HPLC retention time with the authentic sample independently synthesized by the reported procedure.[5f]
[e] The reaction was carried out at −15 °C using saturated CsOH (5 equivs.) as base.

The chiral efficiency of (*S*,*S*)-**2a** was examined by asymmetric alkylation of the glycine Schiff base **10** and the results are summarized in Table 1. When **10** was treated with benzyl bromide in the presence of 1 mol% of (*S*,*S*)-**2a** in toluene/50% aqueous KOH (v/v, 3:1) at 0 °C under an argon atmosphere, a phenylalanine derivative **11** (R = $PhCH_2$) was obtained in excellent yield and enantiomeric excess (entry 1). It was also found that the reaction with other alkyl halides gave the corresponding products **11** with good to excellent enantioselectivity (entries 2–4).

Despite the slightly lower enantioselectivity observed with (*S*,*S*)-**2a** (95% *ee*) compared to (*S*,*S*)-**1** (99% *ee*) in the benzylation of **10**,[5f] the substitution pattern of binaphthyl subunits of catalysts was found not to have a strong influence on the enantioselectivity,[5g,h] and both catalysts showed much higher enantioselectivity than a non-aryl substituted catalyst (*S*,*S*)-**12**.[5a] Furthermore, somewhat lower but still satisfactory enantioselectivity was observed in the reaction even with a mono-aryl substituted catalyst (*S*,*S*)-**13**, which was prepared from (*S*)-**9** in a similar manner to (*S*,*S*)-**1** (Scheme 3).[5f] These results might indicate the existence of secondary interaction between the aryl group on the catalyst and **10** in the ammonium enolate intermediate.

With the catalyst (*S*,*S*)-**2b** in hand, some selected examples of direct asymmetric aldol reaction of **10**

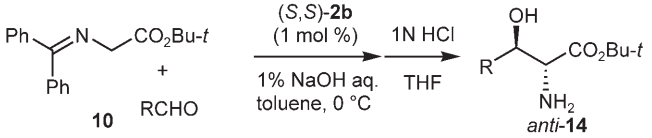


Scheme 3.

with aldehydes are summarized in Table 2. High levels of enantioselectivity and moderate *anti*-selectivity were obtained when 3-phenylpropanal and 4-pentenal were used (entries 1 and 2).

In summary, a spiro-type phase-transfer catalyst prepared from two equivalents of a single binaphthyl subunit was found to exhibit high enantioselectivity in asymmetric alkylation and direct aldol reactions.

Table 2. Direct asymmetric aldol reactions of **10** with aldehydes.[a]



Entry	R	Time [h]	Yield [%][b]	*anti*/*syn*[c]	% *ee*[d]
1	$PhCH_2CH_2$	6	90	72:28	90
2	CH_2=$CHCH_2CH_2$	6	70	82:18	86

[a] The reaction was carried out with 2 equivs. of aldehyde in the presence of (*S*,*S*)-**2b** (1 mol%) in toluene/aqueous NaOH (1%) at 0 °C.
[b] Isolated yield.
[c] Determined by ^{1}H NMR analysis.
[d] Enantiomeric excess of *anti*-**14**, which was determined, after conversion to the corresponding oxazolidine-2-thione, by HPLC analysis using a chiral column (DAICEL Chiralcel AD-H) with hexane/2-propanol as solvent.

Experimental Section

General Procedure for the Synthesis of 2

Dibromide (*S*)-**9** was prepared from (*S*)-1,1′-bi-2-naphthol in a similar manner to that described for the precursors of (*S*,*S*)-**1**[5f] except for the amount of each reagent used for transformation at the 3-position of binaphthyl group. A mixture of (*S*)-**9** (Ar = 3,4,5-F_3-C_6H_2) (114 mg, 0.2 mmol) and aqueous ammonia (55 μL, 0.8 mmol) in CH_3CN (10 mL) was stirred at 80 °C overnight. After standard work-up procedure, the crude product was purified by column chromatography on silica gel to give the desired chiral spiro-type ammonium bromide (*S*,*S*)-**2a**; yield: 118 mg (0.13 mmol, 65 %); $[\alpha]_D^{30}$: 22.9° (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (2H, s, Ar-H), 8.04 (2H, d, *J* = 8.0 Hz, Ar-H), 7.97 (2H, d, *J* = 8.0 Hz, Ar-H), 7.8–7.0 (4H, br, Ar-H), 7.62–7.55 (6H, m, Ar-H), 7.31–7.26 (4H, m, Ar-H), 7.13 (2H, d, *J* = 8.5 Hz, Ar-H), 7.05 (2H, d, *J* = 8.5 Hz, Ar-H), 6.62 (2H, d, *J* = 8.2 Hz, Ar-H), 4.84 (2H, d, *J* = 13.3 Hz, Ar-CH_2), 4.54 (2H, d, *J* = 13.9 Hz, Ar-CH_2), 4.51 (2H, d, *J* = 13.9 Hz, Ar-CH_2), 3.91 (2H, d, *J* = 13.5 Hz, Ar-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8 (d, $J_{C,F}$ = 247 Hz), 140.1 (dt, $J_{C,F}$ = 257, 14.8 Hz), 139.5, 136.4, 136.3, 135.8 (dt, $J_{C,F}$ = 7.5, 4.9 Hz), 133.9, 133.6, 133.0, 131.5, 131.1, 128.7, 128.6, 128.5, 128.4, 128.0, 127.64, 127.56, 127.21, 127.16, 126.0, 124.8, 121.5, 115.2 (d, $J_{C,F}$ = 18.1 Hz), 61.7, 57.8; IR (neat): ν = 3354, 3055, 2924, 2357, 1614, 1525, 1447, 1358, 1047, 854, 754 cm^{-1}; HR-MS (ESI-TOF): *m*/*z* = 834.2610, calcd. for $C_{56}H_{34}F_6N$ $[M-Br]^+$: 834.2590.

Chiral Spiro-Type Ammonium Bromide (*S*,*S*)-2b

(*S*,*S*)-**2b** was prepared in a similar manner as described above; yield: 60 %; $[\alpha]_D^{30}$: −26.6° (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (2H, s, Ar-H), 8.50 (4H, s, Ar-H), 8.34 (2H, s, Ar-H), 8.12 (2H, s, Ar-H), 8.11 (2H, s, Ar-H), 8.07 (2H, d, *J* = 8.3 Hz, Ar-H), 7.89 (2H, d, *J* = 8.3 Hz, Ar-H), 7.83 (4H, s, Ar-H), 7.78 (2H, s, Ar-H), 7.63–7.54 (4H, m, Ar-H), 7.35 (2H, d, *J* = 8.5 Hz, Ar-H), 7.32–7.28 (4H, m, Ar-H), 7.18 (2H, d, *J* = 8.8 Hz, Ar-H), 7.12 (2H, s, Ar-H), 7.06 (2H, d, *J* = 9.0 Hz, Ar-H), 6.65 (2H, d, *J* = 8.6 Hz, Ar-H), 4.85 (2H, d, *J* = 13.7 Hz, Ar-CH_2), 4.72 (2H, d, *J* = 14.2 Hz, Ar-CH_2), 4.67 (2H, d, *J* = 14.8 Hz, Ar-CH_2), 3.75 (2H, d, *J* = 13.2 Hz, Ar-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 142.3, 141.82, 141.78, 140.7, 139.5, 137.5, 136.8, 133.9, 133.7, 133.6, 133.2, 133.0, 132.8, 132.7, 132.5, 132.3, 132.0, 131.5, 131.1, 130.9, 130.7, 129.6, 128.8, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.2, 127.1, 127.0, 126.6, 126.5, 126.3, 125.5, 124.6, 124.2, 122.4, 121.8, 121.5, 121.3, 119.1, 118.8, 61.9, 57.7; IR (neat): ν = 3332, 3055, 1618, 1368, 1278, 1177, 1134, 771 cm^{-1}; HR-MS (ESI-TOF): *m*/*z* = 1574.3415, calcd. for $C_{88}H_{48}F_{24}N$ $[M-Br]^+$: 1574.3398.

Crystal Structure Analysis

Single crystals of (*S*,*S*)-**2a** for X-ray diffractioni experiments were grown by slow evaporation of a solution of (*S*,*S*)-**2a** in CH_2Cl_2/hexane at room temperature. The data were collected at −130 °C on a Rigaku R-AXIS RAPID IP diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5419 Å). The crystal structure was solved by direct methods using SIR97[8] and refined in SHELXL-97[9] by full matrix least-squares using anisotropic thermal displacement parameters for all non-hydrogen atoms. The bromine atom was disordered and was refined in two positions with occupancy factors of 0.82 and 0.18. Crystallographic data for (*S*,*S*)-**2a**: $4(C_{56}H_{34}BrF_6N)\cdot 4CH_2Cl_2$, colorless prisms, 0.6 × 0.25 × 0.1 mm^3, tetragonal, $P4_3$, *a* = 10.29(4), *b* = 10.29(4), *c* = 43.01(2) Å, *V* = 4557(4) $Å^3$, ρ_{calcd} = 1.457 g cm^{-3}, *Z* = 4, $2\theta_{max}$ = 68.21°, μ = 2.860 mm^{-1}. A total of 46016 reflections were measured. *R* = 0.082, and *Rw* = 0.200 for 7884 observed reflections with $I > 2.0\sigma(I)$. CCDC-625781 [(*S*,*S*)-**2a**] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Representative Procedure for Catalytic Enantioselective Alkylation Reaction

To a mixture of **10** (88.5 mg, 0.3 mmol) and chiral catalyst (*S*,*S*)-**2a** (2.74 mg, 0.003 mmol) in toluene (2.1 mL)-50 % KOH aqueous solution (0.7 mL) was added benzyl bromide (43 μL, 0.36 mmol) dropwise at 0 °C under an argon atmosphere. The reaction mixture was stirred vigorously at the same temperature for 2.5 h. The mixture was then poured into water 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 (ethyl acetate/hexane = 1:30 as eluent) gave the alkylation product **11** (R = $PhCH_2$) as a colorless oil; yield: 110 mg (0.285 mmol, 95 %). The enantiomeric excess was determined by chiral HPLC analysis [DAICEL Chiralcel OD, hexane/2-propanol = 100:1, flow rate 0.5 mL min^{-1}, retention time; 12.5 min (*R*) and 17.0 min (*S*)].

Representative Procedure for Catalytic Enantioselective Direct Aldol Reaction

Aqueous NaOH (1 %, 0.8 mL) was added at 0 °C under an argon atmosphere to a solution of **10** (59.1 mg, 0.2 mmol) and (*S*,*S*)-**2b** (3.31 mg, 0.002 mmol) in toluene (2.0 mL), and 3-phenylpropanal (53.3 μL, 0.4 mmol) was introduced dropwise. The whole mixture was stirred for 6 h at 0 °C, and water and diethyl ether were then added. The ether phase was separated and washed with brine. The organic phase was dried over Na_2SO_4 and concentrated. The crude product was dissolved in THF (8.0 mL) and treated with HCl (1.0 N, 2.0 mL) at 0 °C for 1 h. After removal of THF under vacuum, the aqueous solution was washed with diethyl ether three times and neutralized with $NaHCO_3$. The mixture was then extracted with CH_2Cl_2 three times. The combined extracts were dried over Na_2SO_4 and concentrated. Purification of the residue by column chromatography on silica gel (MeOH/CH_2Cl_2 = 1:30 as eluent) afforded the corresponding β-hydroxy-α-amino ester **14** (R = $PhCH_2CH_2$); yield: 48 mg (0.118 mmol, 90 %); *anti*/*syn* 72:28. The enantiomeric excess of the major *anti* isomer was determined to be 90 % by HPLC analysis after conversion to the corresponding oxazolidine-2-thione [DAICEL Chiralcel AD-H, hexane/2-propanol = 10:1, flow rate 0.5 mL min^{-1}, retention time; 19.9 min (minor) and 22.9 min (major)].[6b]

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas "Advanced Molecular Transformation of Carbon Resources" from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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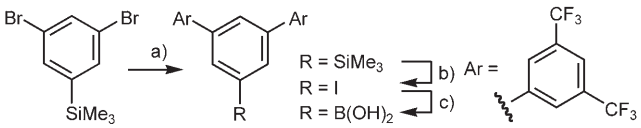

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