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Tetrahedron
Tetrahedron 62 (2006) 11425–11436

Asymmetric phase-transfer catalysis of homo- and heterochiral quaternary ammonium salts: development and application of conformationally flexible chiral phase-transfer catalysts

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Received 26 May 2006; revised 13 August 2006; accepted 14 August 2006
Available online 7 September 2006

Abstract—Inspired by the considerable difference of catalytic activity and stereocontrolling ability between the conformationally rigid, homo- and heterochiral quaternary ammonium bromides **1**, conformationally flexible, *N*-spiro chiral quaternary ammonium bromides of type **4** have been designed and synthesized. Reliable procedures for the preparation of the appropriately substituted biphenyl subunits have been established by the repeated use of *ortho* magnesiation–halogenation as a key synthetic tool. The relationship between the structure of achiral biphenyl moiety and the reactivity and selectivity of **4** has been evaluated in the asymmetric alkylation of glycinate Schiff base **2** under typical phase-transfer conditions, leading to the identification of **4l** as an optimal catalyst structure to exhibit an excellent enantiocontrol in the reactions with various alkyl halides. The molecular structure of **4l** was determined by X-ray crystallographic analysis and its unique behavior in solution was examined by a variable-temperature ^{1}H NMR study. These investigations uncovered that the observed high chiral efficiency originated from the efficient asymmetric phase-transfer catalysis of homochiral-**4l**, which rapidly equilibrated with heterochiral-**4l** of low catalytic activity and stereoselectivity.

1. Introduction

The use of chiral quaternary ammonium salts readily prepared from naturally occurring *cinchona* alkaloids, cinchonine and cinchonidine as chiral phase-transfer catalysts has provided a unique yet reliable tool for catalytic asymmetric synthesis, and its utility has been well documented in the number of valuable chemical transformations including stereoselective functionalization of protected glycine derivative **2**.[1] Recent attractive emergence of a series of appropriately modified *cinchona* alkaloid-based catalysts as well as the elaboration of purely synthetic chiral quaternary ammonium salts strongly suggest the significant importance and usefulness of rational molecular design of chiral catalysts.[1,2] Our own contribution to this rapidly growing area was the design of chiral C_2-symmetric quaternary ammonium bromides of type **1**, which efficiently catalyze the phase-transfer alkylation of **2** with excellent enantioselectivities, providing a practical method for the asymmetric synthesis of both natural and unnatural α-amino acids.[3] For example, the reaction of **2** with benzyl bromide (1.2 equiv) in the presence of 1 mol % of (*S*,*S*)-**1** in 50% aqueous KOH/toluene (volume ratio=1:3) at 0 °C for 3 h under argon atmosphere gave rise to the corresponding benzylation product **3a**, protected phenylalanine, in 91% yield with 94% ee (*R*). The characteristic feature of (*S*,*S*)-**1** is the conformationally rigid, *N*-spiro structure created by two chiral binaphthyl units. Since this structure seemed essential for attaining sufficient reactivity and enantioselectivity, we were intrigued by which binaphthyl moiety would be more critically associated with its chiral efficiency. This initial concern led us to prepare the diastereomeric, heterochiral quaternary ammonium bromide (*R*,*S*)-**1** and to evaluate its reactivity and selectivity as a chiral phase-transfer catalyst. Interestingly, the benzylation of **2** under similar conditions proceeded slowly, and, after 60 h, furnished **3a** in 47% yield with low enantiomeric excess (11% ee, *R*). We also observed that the enantiomeric (*S*,*R*)-**1** exerted comparable catalytic activity in the benzylation with the opposite sense of asymmetric induction (51%, 11% ee, *S*). The significant rate retardation apparently indicates that the parent homochiral ammonium bromide (*S*,*S*)- or (*R*,*R*)-**1** has substantially higher catalytic activity than the heterochiral (*R*,*S*)- or (*S*,*R*)-**1**.[4] Indeed, the benzylation of **2** with each 0.5 mol % of (*S*,*S*)-**1** and (*R*,*S*)-**1** under otherwise similar phase-transfer conditions at 0 °C for 13 h afforded **3a** in 88% yield with 94% ee, and the use of each 0.5 mol % of (*S*,*S*)-**1** and (*S*,*R*)-**1** as catalyst, though a mismatched combination in terms of the enantioselectivity, resulted in formation of **3a** in 92% yield with 93% ee after 8.5 h at 0 °C as shown in Scheme 1.

Keywords: Asymmetric phase-transfer alkylation; Atropinversion; Biphenyl unit; Conformational flexibility; Molecular design.
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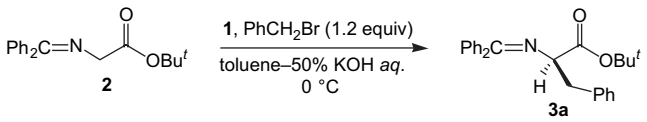
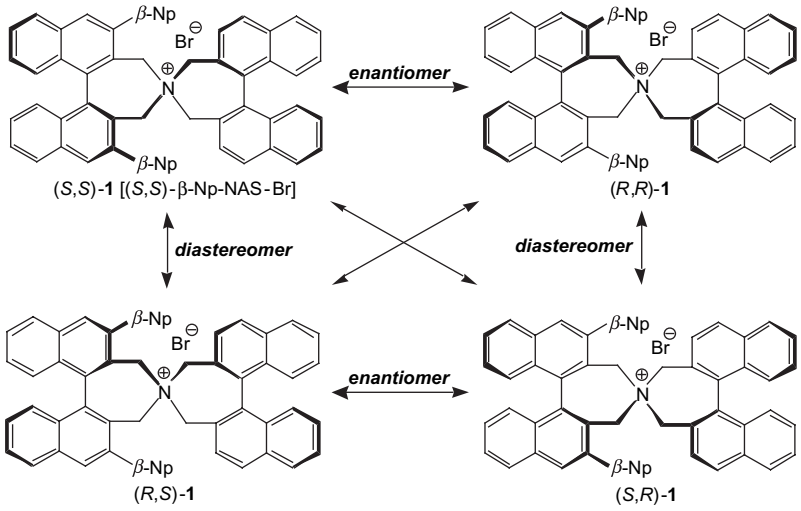
doi:10.1016/j.tet.2006.08.052

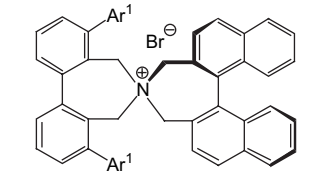


(*S*,*S*)-**1** (1 mol%), 3 h : 91%, 94% ee (*R*)
(*R*,*S*)-**1** (1 mol%), 60 h : 47%, 11% ee (*R*)
(*S*,*R*)-**1** (1 mol%), 60 h : 51%, 11% ee (*S*)
(*S*,*S*)-**1** (0.5 mol%), (*R*,*S*)-**1** (0,5 mol%), 13 h : 88%, 94% ee (*R*)
(*S*,*S*)-**1** (0.5 mol%), (*S*,*R*)-**1** (0,5 mol%), 8.5 h : 92%, 93% ee (*R*)

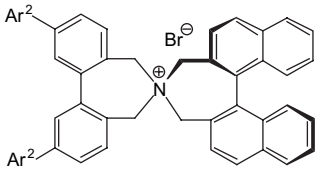


Scheme 1.

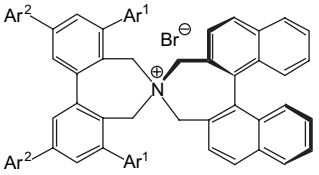
These results suggested that high levels of catalytic activity and stereoselectivity could be retained even if *one of the two chiral binaphthyl subunits of **1** was racemic*. On the basis of the interesting findings, we sought to develop a new *N*-spiro chiral C_2-symmetric quaternary ammonium bromide **4** by incorporating an achiral biphenyl structure. Our assumption was that the conformationally flexible biphenyl subunits could be atropisomerically biased by the simple chiral binaphthyl unit through the central nitrogen atom so that **4** could exert chiral efficiency as high as the conformationally rigid homochiral catalyst (*S*,*S*)-**1**. This approach, if successful, should lead to simplification of the molecular design and hence allows fruitful modification of the chiral catalysts. In this article, we wish to describe the detailed procedure for the facile synthesis of conformationally flexible **4**, and its reactivity and selectivity as chiral phase-transfer catalyst is explored in relation to the unique behavior in solution, revealing that **4** exhibits high chiral efficiency in the asymmetric alkylation of **2** by taking advantage of the considerable difference of activity between the two possible diastereomeric conformers through rapid interconversion.[5,6]



4a : Ar^1 = H
4b : Ar^1 = Ph
4c : Ar^1 = 3,5-Me_2-C_6H_3
4d : Ar^1 = 3,5-(*t*-Bu)$_2$-C_6H_3
4e : Ar^1 = 3,4,5-F_3-C_6H_2
4f : Ar^1 = 3,5-$(CF_3)_2$-C_6H_3
4g : Ar^1 = β-Np
4h : Ar^1= 3,5-Ph_2-C_6H_3



4i : Ar^2 = Ph
4j : Ar^2 = β-Np
4k : Ar^2 = 3,4,5-F_3-C_6H_2

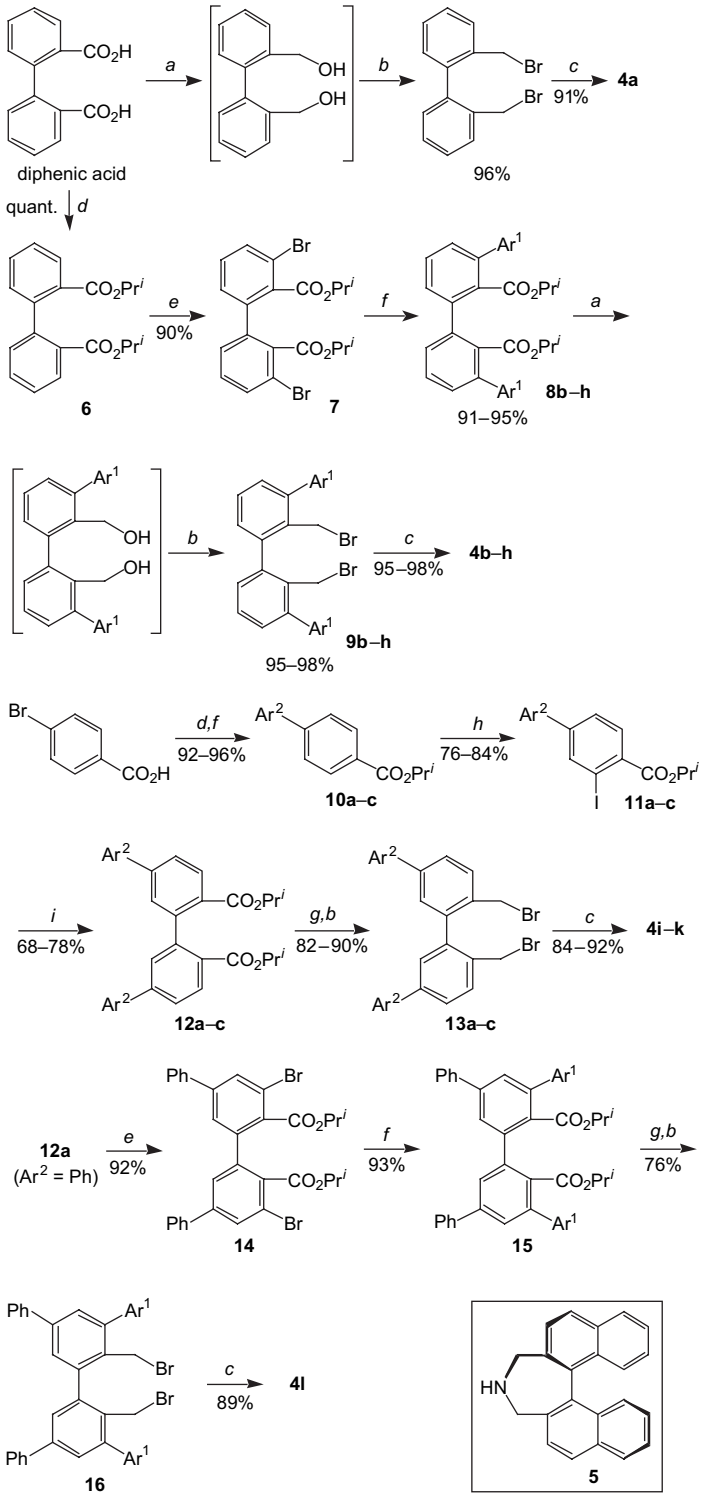


4l : Ar^1 = 3,5-Ph_2-C_6H_3, Ar^2 = Ph

2. Results and discussion

2.1. Synthesis of conformationally flexible C_2-symmetric chiral quaternary ammonium bromide 4

Because the simple chiral element of the new catalyst **4** can be served by previously known optically active *secondary* amine **5**,[3c,7] we focused on the synthesis of appropriately substituted achiral biphenyl moiety, which has been accomplished concisely in a five-step sequence starting from commercially available diphenic acid as illustrated in Scheme 2. Diphenic acid was first converted to the corresponding isopropyl ester **6** quantitatively. For the subsequent selective bromination of the 3,3′-position of **6**, we fortunately found that *ortho* magnesiation–bromination technique using magnesium 2,2,6,6-tetramethylpiperamide and bromine was quite effective, furnishing **7** in 90% yield.[8] This success allowed the preparation of **8** having a variety of 3,3′-aromatic substituents by Suzuki–Miyaura cross coupling reaction. Then, simple reduction of **8** by $LiAlH_4$ and, without any purification, subsequent treatment with PBr_3 afforded the requisite bis-bromide **9**. Finally, reaction of **9** with **5** under basic conditions as previously reported[3c] afforded conformationally flexible quaternary ammonium bromides **4b**–**h**.



Scheme 2. Reagents and conditions: (a) $LiAlH_4$, THF, reflux; (b) PBr_3, THF, 0 °C to rt; (c) **5**, K_2CO_3, CH_3CN, reflux; (d) $SOCl_2$, 0 °C to reflux, then *i*-PrOH, pyridine; (e) $(TMP)_2Mg$, THF, 0 °C to rt, then Br_2, −78 °C to rt; (f) $ArB(OH)_2$, $Pd(OAc)_2$, PPh_3, K_2CO_3, DMF, 90 °C; (g) $LiAlH_4$, THF, 0 °C to rt; (h) $(TMP)_2Mg$, THF, 0 °C to rt, then I_2, −78 °C to rt; (i) activated Cu, DMF, reflux.

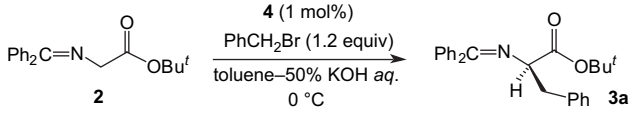
In addition, the synthesis of the catalyst **4** having an aromatic group at 5,5′-positions of the biphenyl subunit has also been executed by means of the *ortho* magnesiation–halogenation procedure[8] as included in Scheme 2. Commercially available 4-bromobenzoic acid was first transformed into its isopropyl ester and then coupled with an appropriate boronic acid using the palladium catalyst to prepare **10**. Treatment of the ester **10** with $(TMP)_2Mg$ in THF followed by the reaction with iodine resulted in the production of **11**, a requisite candidate for the next Ullmann coupling. Refluxing a mixture of **11** with activated copper in DMF facilitated the biphenyl formation to give **12**, which was further derivatized to **13** through the reduction and bromination sequences. The subsequent use of **13** for the quaternization of **5** led to the

formation of catalysts **4i**–**k**. In a meantime, installment of 3,3′-(3,5-diphenylphenyl) groups on **12** and the generation of bromomethyl functionality at 2,2′-position could be conducted in a manner as described. The final assembly of **16** thus obtained with **5** afforded **4l**.

2.2. Evaluation of the reactivity and selectivity of 4 in the asymmetric alkylation of glycinate Schiff base 2

We then pursued the systematic evaluation of the reactivity and selectivity of **4** in the phase-transfer-catalyzed benzylation of **2** starting from the use of **4a** consisted of (*S*)-binaphthyl and simple biphenyl subunits. Thus, treatment of **2** with benzyl bromide (1.2 equiv) in 50% aqueous KOH/toluene (volume ratio=1:3) in the presence of 1 mol % of **4a** at 0 °C for 36 h under argon atmosphere resulted in the formation of **3a** in 62% isolated yield. Its enantiomeric excess was revealed to be appreciable (64% ee) and the absolute configuration was assigned to be *R*, the same with that of the major enantiomer in the reaction with (*S*,*S*)-**1** (Table 1, entry 1). This observation could be rationalized by the preferred nature of homochiral conformer (*S*,*S*)-**4a** in solution on the basis of the elegant study of Lacour on the conformational preference of the simple spirobi[dibenzazepinium] cation.[9] It was of interest that introduction of phenyl substituent to 3,3′-position of the biphenyl subunit (**4b**) brought a substantial decrease of the enantioselectivity (53% ee, entry 2), while similar modification at 5,5′-position (**4i**) led to the enhancement of the selectivity (72% ee, entry 3). At this stage, we assumed that the erosion of enantiocontrol might stem from the intervention of heterochiral conformer (*R*,*S*)-**4b**. Meanwhile, the installment of aromatic substituents at 5,5′-position of the biphenyl moiety (Ar^2) would not deliver major influence on the stereodynamic of the chiral ammonium cation, and thus only the beneficial effect of the extended aromatic surface could be extracted. This interpretation prompted us to further examine the impact of steric and electronic properties of Ar^2 particularly on the stereoselectivity, which consequently turned out to be marginal as included in Table 1 (entries 4 and 5). In sharp contrast, however, manipulation of 3,3′-aromatic substituents dramatically altered both the reactivity and selectivity of the catalyst **4**. On one hand, the phase-transfer-catalyzed benzylation of **2** in the presence of 3,5-dimethylphenyl-substituted **4c** under otherwise similar conditions afforded **3a** in 90% yield with 80% ee (entry 6), though use of sterically more demanding **4d** as catalyst cancelled the improvement (entry 7). On the other, significant loss of the catalytic activity was observed when electron-withdrawing substituent such as 3,4,5-trifluorophenyl group was introduced and, to our surprise, no production of **3a** was detected under the influence of **4f** having 3,5-bis(trifluoromethyl)phenyl unit (entries 8 and 9). Eventually, highest level of enantioselectivity was obtained with **4g** possessing β-naphthyl group (entry 10), and more conjugated *meta*-terphenyl group was identified as an ideal 3,3′-substituent of this type of catalyst for attaining sufficient reactivity and selectivity (entry 11). These results clearly demonstrate that appropriate choice of the 3,3′-substituents allows the

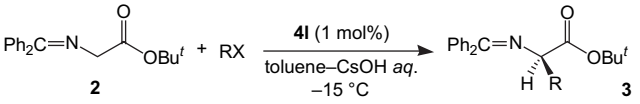
Table 1. Evaluation of the reactivity and selectivity of **4** in the phase-transfer-catalyzed asymmetric benzylation of **2**[a]

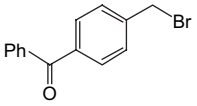
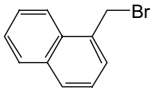
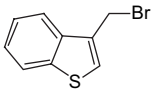


Entry	4	React. time (h)	% Yield[b]	% ee[c] (config)[d]
1	**4a** [Ar^1=H]	36	62	64 (*R*)
2	**4b** [Ar^1=Ph]	18	87	53 (*R*)
3	**4i** [Ar^2=Ph]	4	96	72 (*R*)
4	**4j** [Ar^2=β-Np]	32	73	67 (*R*)
5	**4k** [Ar^2=3,4,5-F_3-C_6H_2]	48	90	60 (*R*)
6	**4c** [Ar^1=3,5-Me_2-C_6H_3]	14	90	80 (*R*)
7	**4d** [Ar^1=3,5-(*t*-Bu)$_2$-C_6H_3]	2	70	60 (*R*)
8	**4e** [Ar^1=3,4,5-F_3-C_6H_2]	22	25	84 (*R*)
9	**4f** [Ar^1=3,5-$(CF_3)_2$-C_6H_3]	29	n.r.	n.d.
10	**4g** [Ar^1=β-Np]	18	85	87 (*R*)
11	**4h** [Ar^1=3,5-Ph_2-C_6H_3]	27	95	92 (*R*)
12	**4l** [Ar^1=3,5-Ph_2-C_6H_3, Ar^2=Ph]	48	81	95 (*R*)
13[e]	**4l** [Ar^1=3,5-Ph_2-C_6H_3, Ar^2=Ph]	16	87	94 (*R*)

[a] Unless otherwise noted, the reaction was carried out with **2** (0.5 mmol) and 1.2 equiv of benzyl bromide in the presence of 1 mol % of **4** in 50% aqueous KOH/toluene (volume ratio=1:3) at 0 °C for the given reaction time under argon atmosphere.
[b] Isolated yield.
[c] Enantiopurity of **3a** was determined by HPLC analysis using a chiral column with hexane/2-propanol as solvent.
[d] Absolute configuration of **3a** was determined by comparison of the HPLC retention time with the authentic sample independently synthesized by the reported procedure.[10]
[e] Use of $CsOH\cdot H_2O$ (3 equiv) in water (29.2 μL) as a base and the reaction was performed at −15 °C.

Table 2. Catalytic enantioselective phase-transfer alkylation of **2** with conformationally flexible catalyst **4l**[a]



Entry	RX	React. time (h)	% Yield[b]	% ee[c] (config)[d]
1	4-F-$C_6H_4CH_2Br$	36	83	95 (*R*)
2	4-Me-$C_6H_4CH_2Br$	29	83	96 (*R*)
3	2,6-Me_2-$C_6H_3CH_2Br$	64	90	90 (*R*)
4		18	91	94 (*R*)
5		18	92	92 (*R*)
6		19	91	93 (*R*)
7	CH_2=$CHCH_2Br$	16	85	93 (*R*)
8	CH_2=C(Me)CH_2Br	21	85	96 (*R*)
9[e]	EtI	15	61	93 (*R*)

[a] Unless otherwise specified, the reaction was conducted with **2** (0.5 mmol) and 1.2 equiv of RX in the presence of 1 mol % of **4l** in aqueous CsOH/toluene at −15 °C for the given reaction time under argon atmosphere.
[b] Isolated yield.
[c] Enantiopurity of **3** was determined by HPLC analysis using a chiral column with hexane/2-propanol as solvent.
[d] Absolute configuration of **3** was determined by comparison of the HPLC retention time with the literature value or the authentic sample independently synthesized by the reported procedure.[3c,10]
[e] With 5 equiv of alkyl halide.

homochiral (*S*,*S*)-**4** to exert high catalytic and chiral efficiency despite its conformational flexibility; this creates a solid basis for further fine-tuning of **4** by making use of the ample structural modularity of achiral biphenyl subunit. For instance, the catalyst **4l** having 3,3′-bis(3,5-diphenylphenyl)-5,5′-diphenyl-1,1′-biphenyl substructure can be readily assembled and was found to provide even more rigorous stereocontrol in the benzylation of **2** (entry 12). Although the reactivity was sacrificed to certain extent, it was recovered by the use of aqueous CsOH as a basic phase at a lower reaction temperature without detrimental effect on the enantioselectivity (entry 13).

As summarized in Table 2, the asymmetric phase-transfer catalysis of **4l** accommodates a variety of alkyl halides, and the corresponding alkylation products **3** were obtained in good to high chemical yields with excellent enantioselectivities using 1 mol % of the catalyst with stirring for 15–64 h at −15 °C. In detail, a series of benzylic bromides with substituents of different steric and electronic properties were employable, allowing the preparation of structurally diverse phenylalanine analogues (entries 1–4). The effectiveness of **4l** was further demonstrated by using 1-bromomethylnaphthalene and 3-bromomethylbenzothiophene as an electrophilic partner, respectively (entries 5 and 6). Enantiomerically enriched allylglycine derivatives are also accessible (entries 7 and 8), and the reaction with simple alkyl halide such as ethyl iodide appeared feasible (entry 9).

2.3. Elucidation of structure of 4 and its behavior in solution

To analyze the dynamic structural behavior of **4h** and **4l** in solution, a variable-temperature ^{1}H NMR study was conducted in dichloromethane-d_2. The temperature dependence of the ^{1}H NMR signals of benzylic protons of **4h** at low temperature range is shown in Figure 1. The peak broadening at 283–263 K and sharpening to two sets of four benzylic

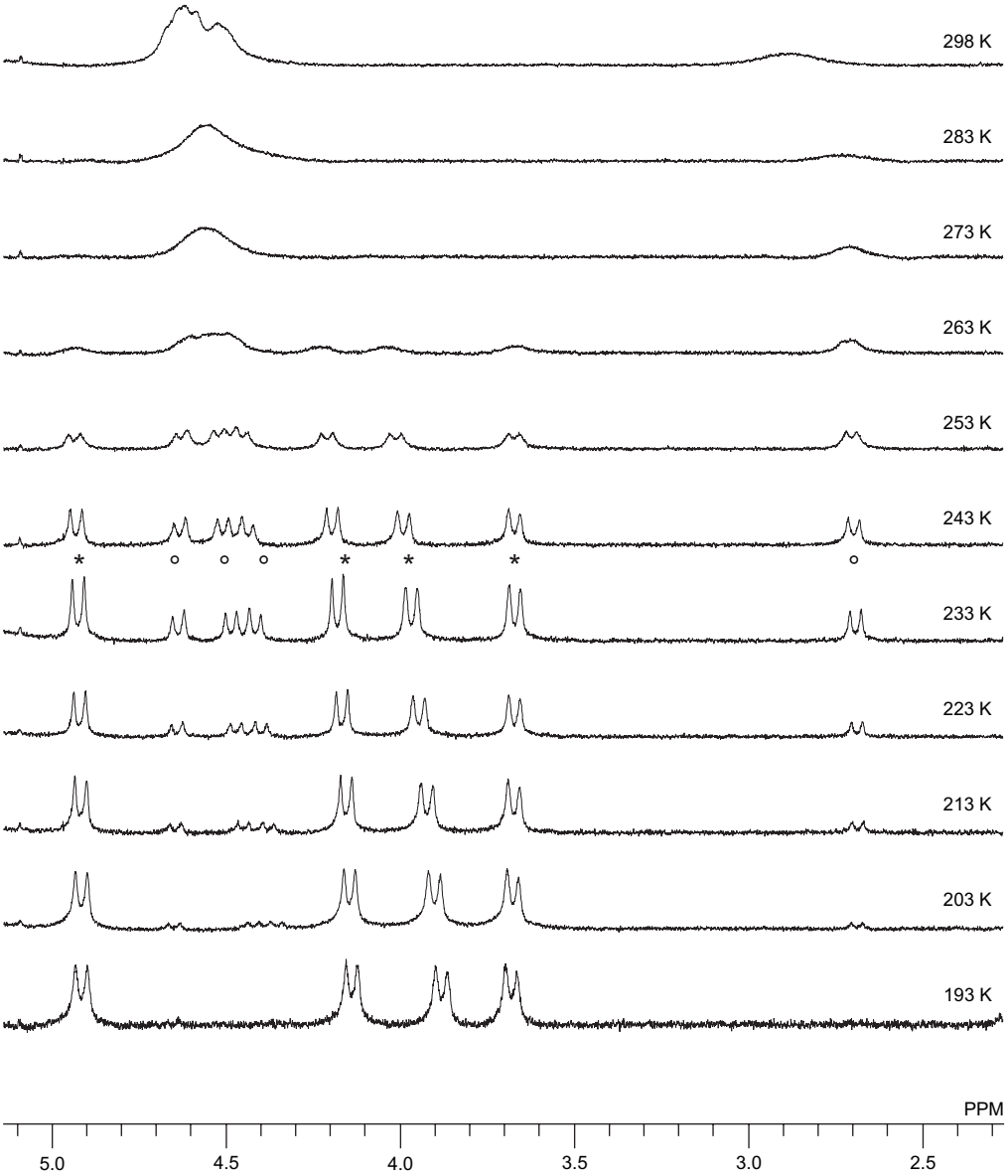


Figure 1. The temperature dependence of the ^{1}H NMR signals of the benzylic protons of homo- (★) and heterochiral (○) conformers of **4h**.[11]

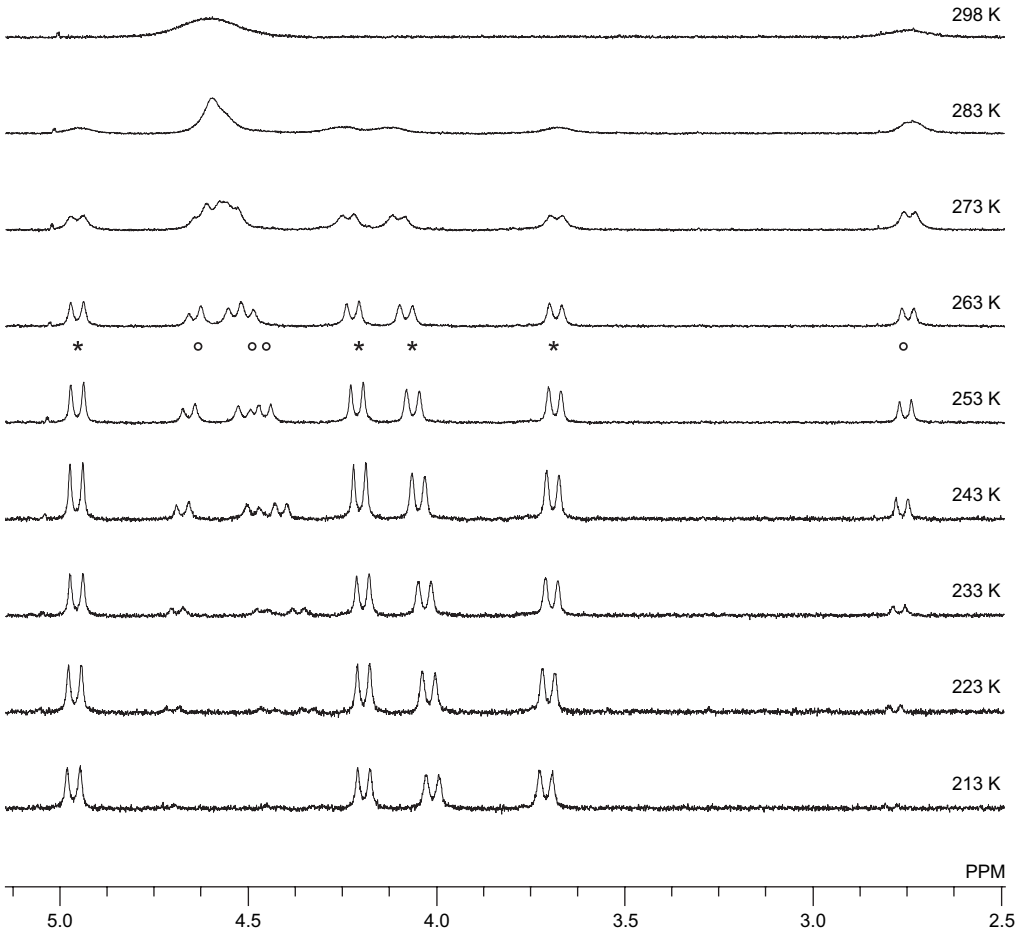
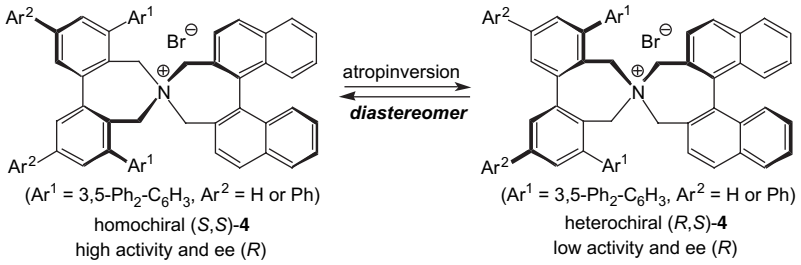


Figure 2. The temperature dependence of the ^{1}H NMR signals of the benzylic protons of homo- (★) and heterochiral (○) conformers of **4l**.[11]

signals (nearly 1:1 ratio) at 243 K clearly indicates that there is a rapid equilibrium between two diastereomeric, homochiral (*S*,*S*)-**4h** and heterochiral (*R*,*S*)-**4h**, and the composition of conformational structures depends on temperature. On the basis of the initial studies with conformationally rigid catalyst of type **1**, the homochiral isomer is assumed to be catalytically more active and, interestingly, the existence ratio of (*S*,*S*)-**4h** was found to decrease as the temperature was increased, being approximately 1:2.8 of (*S*,*S*)-**4h**/(*R*,*S*)-**4h** at 0 °C.[12] Similar tendency was observed in the case of **4l** (Fig. 2), and the stereochemical preference toward the heterochiral isomer at higher temperature (above 25 °C) was also supported by the single crystal X-ray diffraction analysis of **4l** after recrystallization from CH_2Cl_2/hexane at room temperature, uncovering its heterochiral molecular structure (Fig. 3).[13] However, the ratio of (*S*,*S*)-**4l**/(*R*,*S*)-**4l** was revealed to be 1:1.2 at 0 °C and 1:0.68 at −15 °C.[12] The increased existence ratio of homochiral (*S*,*S*)-**4l** around the reaction temperature suggested that the introduction of 5,5′-diphenyl substituents not only extended the attractive aromatic surface but also affected the stereodynamic of **4l**, consequently imparting it with higher enantiocontrolling ability than **4h**.



3. Summary

We have designed and prepared conformationally flexible, *N*-spiro chiral quaternary ammonium bromides **4** incorporating a modular achiral biphenyl structure as a conceptually new chiral phase-transfer catalyst. The concise synthetic route to the appropriately substituted biphenyl subunit has

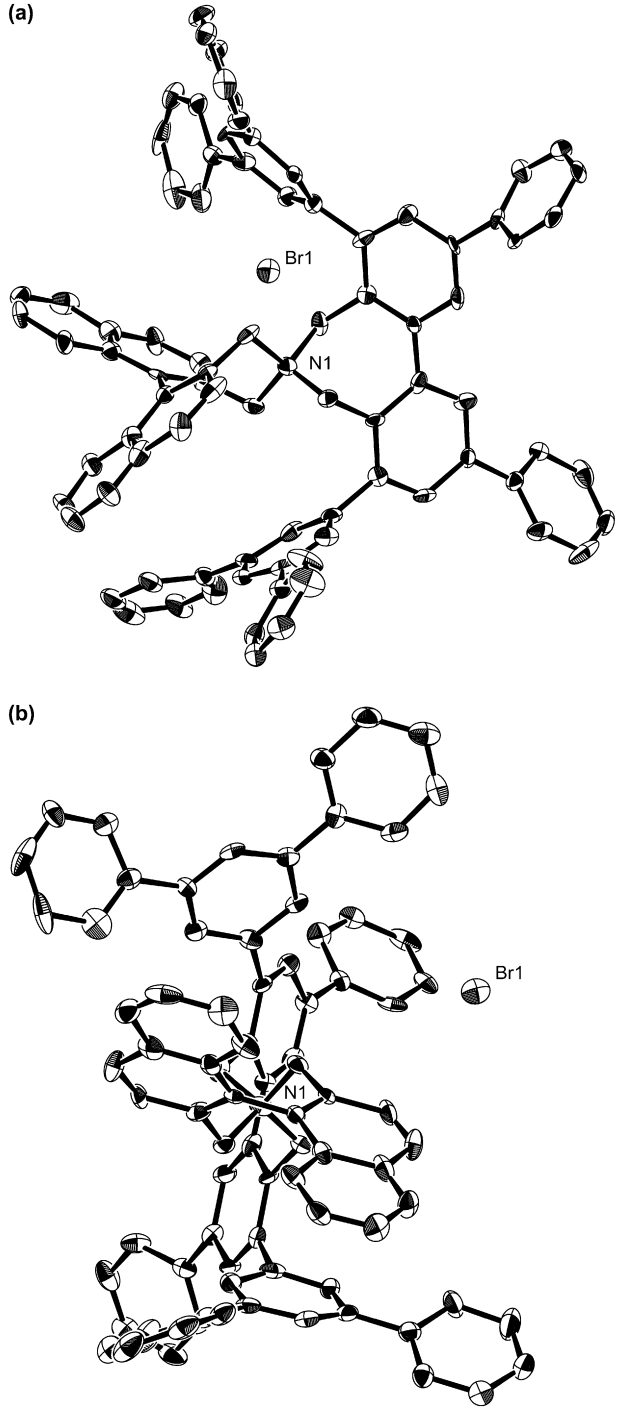


Figure 3. ORTEP diagram of (*S*)-**4l** [(a) top view; (b) side view].

been established by employing the selective *ortho* magnesiation–halogenation as an essential technique. Systematic evaluation of the structure–activity relationship of **4** in the phase-transfer-catalyzed asymmetric benzylation of glycinate Schiff base **2** revealed that **4l** possessing 3,3′-bis(3,5-diphenylphenyl)-5,5′-diphenyl-1,1′-biphenyl substructure displayed a prominent enantiocontrolling ability. Further, the general applicability of the **4l**-catalyzed enantioselective alkylation was demonstrated with representative alkyl halides. The three-dimensional molecular structure of **4l** was unequivocally determined by X-ray crystallographic analysis, and its behavior in solution was investigated by a variable-temperature ^{1}H NMR study, together with the similar stereodynamic of structurally more simple **4h**. This provided a compelling evidence to support that the origin of the high chiral efficiency laid on the considerable difference of catalytic activity between the rapidly equilibrated homo- and heterochiral isomers, and homochiral-**4l** is primarily responsible for the efficient asymmetric phase-transfer catalysis to produce the corresponding alkylation product **3** with high enantiomeric excess, while heterochiral-**4l** showed low reactivity and stereoselectivity. Our approach parallels the successful utilization of flexible ligand to magnify the effect of other chiral ligand through coordinative interaction with metal center,[6] and should offer a new yet simple strategy for the molecular design of chiral phase-transfer catalysts.

4. Experimental

4.1. General information

Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million from tetramethylsilane as an internal standard. Data were reported as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, quint=quintet, hept=heptet, sept=septet, m=multiplet, br=broad), coupling constants (hertz), and assignment. ^{13}C NMR spectra were recorded on a JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million from the residual solvent as an internal standard. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using 4.6 mm×25 cm Daicel Chiralcel OD or OD-H. The high-resolution mass spectra (HRMS) were performed on Applied Biosystems Mariner 8295 API-TOF workstation, Bruker microTOF, and JMS-HX100. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. Melting points were determined on a BÜCHI Melting Point B-545 and are uncorrected. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck 1.09386.9025, 230–400 mesh). In experiments requiring dry solvents, ether, and tetrahydrofuran (THF) were purchased from Kanto Chemical Co. Inc. as 'dehydrated'. Toluene was dried over sodium metal. Other simple chemicals were purchased and used as such.

4.2. Representative procedure for catalytic asymmetric alkylation of glycine *tert*-butyl ester benzophenone Shiff base (2) under phase-transfer conditions (Table 1, entry 13)

To a 10 mL two-neck flask containing a Teflon-coated magnetic stirring bar and $CsOH\cdot H_2O$ (265 mg, 1.5 mmol) was introduced water (29.2 μL) with stirring under argon atmosphere. Then, (*S*)-**4l** (5.0 mg, 0.005 mmol) and a solution of glycine *tert*-butyl ester benzophenone Schiff base (**2**; 148 mg, 0.5 mmol) in toluene (3 mL) were added and the mixture was cooled to −15 °C. After 10 min of gentle

stirring, benzyl bromide (73.6 μL, 0.6 mmol) was added dropwise and the reaction mixture was stirred vigorously for 16 h. The resulting mixture was poured into brine and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated. The residual oil was purified by column chromatography on silica gel (EtOAc/hexane=1:12 to 1:6 as eluent) to give **3a**[10] (168 mg, 0.436 mmol; 87% yield, 94% ee) as a colorless oil. The catalyst (*S*)-**4l** can be recovered by further eluting with MeOH/CH_2Cl_2.[14] The enantiomeric excess of **3a** was determined by chiral HPLC analysis (Daicel Chiralcel OD, hexane/2-propanol=100:1, flow rate=0.5 mL min^{-1}, retention time=13.7 min (*R*) and 24.6 min (*S*)).

4.3. Characterization of chiral quaternary ammonium salt (*R*,*S*)-1 (Ar^1=2-naphthyl)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (2H, s, ArH), 8.09 (2H, d, *J*=8.3 Hz, ArH), 7.85 (2H, br, ArH), 7.79–7.75 (4H, m, ArH), 7.70–7.64 (6H, m, ArH), 7.59 (2H, d, *J*=8.7 Hz, ArH), 7.47–7.44 (6H, m, ArH), 7.36–7.30 (6H, m, ArH), 7.26–7.21 (4H, m, ArH), 7.06–7.02 (2H, m, ArH), 6.90 (2H, d, *J*=8.7 Hz, ArH), 4.66 (4H, s, $ArCH_2$), 4.40 (2H, d, *J*=12.7 Hz, $ArCH_2$), 2.60 (2H, d, *J*=12.3 Hz, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.4, 136.0, 135.8, 134.2, 133.7, 131.9, 131.1, 130.2, 129.5, 129.1, 128.8, 128.2, 128.0, 127.7, 127.6, 127.5, 127.2, 127.2, 126.9, 126.8, 126.6, 126.5, 126.4, 126.2, 125.9, 124.4, 63.6, 59.5 ppm; IR (KBr) 3647, 3400, 3047, 3008, 2989, 1624, 1589, 1506, 1456, 1351, 1028, 895, 877, 821, 777, 746 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{64}H_{44}N$ (M^+): 826.3476, found: 826.3474; $[\alpha]_D^{28}$ 146.6 (*c* 0.25, $CHCl_3$).

4.4. Representative procedure for the preparation of (*S*)-4a–h and their characterizations

4.4.1. 2,2′-Bis(isopropoxycarbonyl)-1,1′-biphenyl (6). Diphenic acid (1.26 g, 5.0 mmol) was placed in a dry two-neck flask with a stirring bar under argon atmosphere and $SOCl_2$ (5 mL) was introduced at 0 °C. The mixture was refluxed for 4 h and excess $SOCl_2$ was removed under reduced pressure. Then, *i*-PrOH (5 mL) and pyridine (1 mL) were added and the mixture was heated to reflux for 1 h. The resulting solution was washed with H_2O and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (short-pass, EtOAc/hexane=1:4 as eluent) to give **6** (1.63 g, quant.) as a white powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (2H, dd, *J*=1.2, 7.5 Hz, ArH), 7.49 (2H, dt, *J*=1.2, 7.5 Hz, ArH), 7.42 (2H, dt, *J*=1.2, 7.5 Hz, ArH), 7.18 (2H, dd, *J*=1.2, 7.5 Hz, ArH), 4.92 (2H, sept, *J*=6.3 Hz, $CH(CH_3)_2$), 0.99 (6H, d, *J*=6.3 Hz, CH_3), 0.89 (6H, d, *J*=6.3 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 143.1, 130.7, 130.1, 129.9, 129.6, 126.7, 67.8, 21.3, 21.2 ppm; IR (KBr) 2974, 1699, 1599, 1439, 1373, 1350, 1288, 1105, 1049, 916, 770, 710 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{22}O_4Na$ ([M+Na]$^+$): 349.1411, found: 349.1410.

4.4.2. 3,3′-Dibromo-2,2′-bis(isopropoxycarbonyl)-1,1′-biphenyl (7). To a THF solution of $(TMP)_2Mg$ (0.31 M, 2.25 mmol)[8] was added **6** (126 mg, 0.5 mmol) in THF (2 mL) dropwise at 0 °C under argon atmosphere and the mixture was stirred for 3 h at room temperature. After being cooled to −78 °C, Br_2 (264 μL, 5.0 mmol) was added and stirring was continued for 1 h at room temperature. This mixture was then poured into cooled 1 N HCl, washed with saturated Na_2SO_3, and extracted with Et_2O. The organic layer was dried over Na_2SO_4 and concentrated. Purification of the residue by column chromatography on silica gel (EtOAc/hexane=1:20 to 1:10 as eluent) furnished **7** (218 mg, 0.450 mmol, 90%) as a white powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (2H, dd, *J*=2.4, 6.7 Hz, ArH), 7.26–7.21 (4H, m, ArH), 4.97 (2H, sept, *J*=6.3 Hz, $CH(CH_3)_2$), 1.18 (6H, s, CH_3), 0.89 (6H, s, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 138.1, 135.9, 132.1, 129.4, 128.7, 119.1, 69.2, 21.5, 20.9 ppm; IR (KBr) 2980, 1724, 1583, 1551, 1439, 1375, 1286, 1101, 1059, 912, 858, 795, 766 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{20}Br_2O_4Na$ ([M+Na]$^+$): 504.9623, found: 504.9621.

4.4.3. 2,2′-Bis(isopropoxycarbonyl)-3,3′-bis(3,5-diphenylphenyl)-1,1′-biphenyl (8h). A mixture of **7** (484 mg, 1.0 mmol), 3,5-diphenylphenylboronic acid (658 mg, 2.4 mmol), $Pd(OAc)_2$ (11.6 mg, 0.05 mmol), PPh_3 (40.1 mg, 0.15 mmol), and K_2CO_3 (419 mg, 3.0 mmol) in DMF (5 mL) was degassed and backfilled with argon. This mixture was heated at 90 °C for 8 h. After cooling to room temperature, the resulting mixture was poured into 1 N HCl and extracted with Et_2O. The organic extracts were dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography on silica gel (EtOAc/hexane=1:20 to 1:10 as eluent) afforded **8h** (744 mg, 0.95 mmol, 95%) as a white powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (2H, t, *J*=2.0 Hz, ArH), 7.68–7.64 (12H, m, ArH), 7.51–7.34 (18H, m, ArH), 4.75 (2H, sept, *J*=6.3 Hz, $CH(CH_3)_2$), 0.86 (6H, d, *J*=5.9 Hz, CH_3), 0.67 (6H, d, *J*=5.9 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 141.7, 141.5, 140.7, 139.9, 138.3, 133.9, 129.1, 129.0, 128.9, 128.4, 127.4, 127.2, 126.3, 125.0, 68.4, 21.4, 21.0 ppm; IR (KBr) 2976, 1722, 1595, 1574, 1499, 1450, 1412, 1373, 1265, 1103, 1065, 883, 760, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{56}H_{46}O_4Na$ ([M+Na]$^+$): 805.3273, found: 805.3288.

4.4.4. 2,2′-Bis(bromomethyl)-3,3′-bis(3,5-diphenylphenyl)-1,1′-biphenyl (9h). To a suspension of $LiAlH_4$ (142 mg, 3.0 mmol) in THF (3 mL) was added **8h** (783 mg, 1.0 mmol) portionwise at 0 °C and the reaction mixture was stirred for 4 h at room temperature. Then, ether (3 mL) was added and the reaction was quenched by the sequential treatment with H_2O (142 μL), 15% NaOH (142 μL), and H_2O (284 μL). After 1 h of additional stirring, this mixture was filtered through a pad of Celite and the filtrate was concentrated. This crude 3,3′-bis(3,5-diphenylphenyl)-2,2′-bis(hydroxymethyl)-1,1′-biphenyl was used for the subsequent bromination without further purification. A THF (ca. 3 mL) solution of 3,3′-bis(3,5-diphenylphenyl)-2,2′-bis(hydroxymethyl)-1,1′-biphenyl (1.0 mmol) was cooled to 0 °C and PBr_3 (52.8 μL, 0.5 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 1 h and poured into H_2O. Extractive workup was performed with EtOAc and the combined extracts were dried over Na_2SO_4. Removal of volatiles and purification of the residue by column chromatography on silica gel (CH_2Cl_2/hexane=1:10 as eluent) gave **9h** (605 mg, 0.76 mmol, 76%

in two steps) as a white powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (2H, t, J=1.6 Hz, ArH), 7.75–7.73 (12H, m, ArH), 7.50–7.43 (14H, m, ArH), 7.40–7.36 (4H, m, ArH), 4.43 (2H, d, J=9.7 Hz, $ArCH_2$), 4.30 (2H, d, J=9.7 Hz, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 141.5, 141.3, 140.9, 140.6, 133.2, 130.4, 129.8, 128.8, 128.0, 127.5, 127.2, 126.8, 125.0, 31.3 ppm; IR (KBr) 3038, 1593, 1580, 1497, 1410, 1217, 1030, 885, 758, 700, 615, 538 cm^{-1}. Fragment peaks could be detected; MS (APCI) *m/z* 867.787 (M^+).

4.4.5. Chiral quaternary ammonium salt (*S*)-4h (Ar^1= 3,5-diphenylphenyl). A mixture of **9h** (398 mg, 0.5 mmol), chiral *secondary* amine **5** (147 mg, 0.5 mmol), K_2CO_3 (139 mg, 1.0 mmol) in CH_3CN (3 mL) was refluxed for 6 h. This mixture was poured into H_2O and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (MeOH/CH_2Cl_2=1:30 to 1:10 as eluent) to give **4h** (440 mg, 0.435 mmol, 87%) as a white powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.08 (44H, br m, ArH), 4.83 (4H, d, J=13.1 Hz, $ArCH_2$), 4.57 (2H, d, J=13.5 Hz, $ArCH_2$), 2.78 (2H, br, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 142.6, 139.8, 139.6, 136.2, 133.7, 131.0, 130.7, 130.5, 130.0, 129.7, 129.2, 128.6, 128.4, 127.6, 127.0, 127.0, 126.9, 126.8, 126.6, 126.2, 124.8, 124.6, 63.3, 58.1 ppm; IR (KBr) 3399, 3055, 2959, 1593, 1574, 1499, 1454, 1414, 1358, 883, 825, 760, 696 cm^{-1}; HRMS (FAB) calcd for $C_{72}H_{62}N$ (M^+): 930.4103, found: 930.4101; $[\alpha]_D^{24}$ 55.0 (*c* 0.25, $CHCl_3$); mp 243–245 °C (dec).

4.4.6. Chiral quaternary ammonium salt (*S*)-4a (Ar^1=H). White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (2H, d, J=8.3 Hz, ArH), 8.08–8.04 (4H, m, ArH), 7.88 (2H, br d, J=6.3 Hz, ArH), 7.74–7.68 (6H, m, ArH), 7.64–7.60 (2H, m, ArH), 7.44 (2H, d, J=8.7 Hz, ArH), 7.39–7.36 (2H, m, ArH), 4.75 (2H, d, J=13.1 Hz, $ArCH_2$), 4.32 (2H, d, J=13.1 Hz, $ArCH_2$), 3.99 (2H, d, J=13.5 Hz, $ArCH_2$), 3.93 (2H, d, J=13.1 Hz, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.7, 134.4, 132.0, 131.8, 131.3, 130.8, 129.7, 129.3, 128.6, 127.7, 127.6, 127.5, 127.3, 126.3, 125.5, 61.4, 60.9 ppm; IR (KBr) 3638, 3385, 3053, 2359, 1622, 1456, 1354, 1200, 1028, 878, 854, 818, 758 cm^{-1}; HRMS (FAB) calcd for $C_{36}H_{28}N$ (M^+): 474.2223, found: 474.2238; $[\alpha]_D^{28}$ −110.2 (*c* 0.25, $CHCl_3$).

4.4.7. Chiral quaternary ammonium salt (*S*)-4b (Ar^1= Ph). White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.04 (28H, br, ArH), 4.61 (4H, br, $ArCH_2$), 4.41 (2H, d, J=13.3 Hz, $ArCH_2$), 2.71 (2H, br, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.5, 138.8, 136.2, 133.9, 130.9, 130.6, 129.5, 129.1, 128.3, 127.5, 127.1, 127.0, 126.7, 126.0, 124.1, 63.1, 57.7 ppm; IR (thin film) 3356, 3055, 2955, 2891, 2178, 1595, 1508, 1464, 1360, 1250, 1196, 1030, 922, 870, 839, 826, 797, 760, 727, 706 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{48}H_{36}N$ (M^+): 626.2842, found: 626.2842; $[\alpha]_D^{24}$ 213.9 (*c* 0.25, $CHCl_3$); mp 298–299 °C (dec).

4.4.8. Chiral quaternary ammonium salt (*S*)-4c (Ar^1= 3,5-dimethylphenyl). White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–6.49 (24H, br, ArH), 4.56–4.45 (6H, m, $ArCH_2$), 2.82 (2H, br, $ArCH_2$), 2.04 (12H, br, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.6, 138.8, 138.3, 136.4, 134.1, 131.0, 130.8, 129.5, 129.2, 128.9, 128.4, 127.4, 127.3, 127.2, 126.9, 126.2, 124.1, 63.2, 57.8 ppm; IR (thin film) 3335, 3053, 3007, 2949, 2916, 2176, 1599, 1578, 1508, 1456, 1379, 1360, 1304, 1250, 1225, 1200, 1030, 922, 908, 854, 837, 822, 793, 748, 727 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{52}H_{44}N$ (M^+): 682.3464, found: 682.3468; $[\alpha]_D^{24}$ 190.0 (*c* 0.25, $CHCl_3$); mp 280–283 °C (dec).

4.4.9. Chiral quaternary ammonium salt (*S*)-4d (Ar^1= 3,5-di-*tert*-butylphenyl). White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–6.79 (24H, m, ArH), 4.68 (2H, d, J=12.8 Hz, $ArCH_2$), 4.53 (2H, d, J=13.2 Hz, $ArCH_2$), 4.15 (2H, d, J=12.4 Hz, $ArCH_2$), 2.58 (2H, d, J=12.8 Hz, $ArCH_2$), 0.98 (18H, s, CH_3), 0.86 (18H, s, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 144.3, 142.0, 137.8, 135.8, 133.6, 130.5, 130.3, 129.8, 128.3, 128.1, 127.0, 126.5, 126.3, 125.7, 124.6, 122.2, 120.6, 63.5, 58.5 ppm; IR (thin film) 3337, 3055, 2961, 2903, 2868, 2174, 1707, 1593, 1578, 1464, 1427, 1395, 1362, 1250, 1223, 1200, 1032, 924, 907, 880, 839, 826, 787, 750, 723 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{64}H_{68}N$ (M^+): 850.5345, found: 850.5346; $[\alpha]_D^{22}$ 101.5 (*c* 0.25, $CHCl_3$); mp 354–356 °C (dec).

4.4.10. Chiral quaternary ammonium salt (*S*)-4e (Ar^1= 3,4,5-trifluorophenyl). White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.99 (6H, m, ArH), 7.74–7.73 (4H, m, ArH), 7.60 (2H, t, J=7.4 Hz, ArH), 7.41–7.29 (6H, m, ArH), 7.26 (2H, s, ArH), 7.01 (2H, br, ArH), 5.04 (2H, d, J=11.8 Hz, $ArCH_2$), 4.85 (2H, d, J=13.3 Hz, $ArCH_2$), 4.32 (2H, d, J=13.3 Hz, $ArCH_2$), 2.89 (2H, d, J=12.6 Hz, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6 (d, J_{C-F}=257 Hz), 142.4, 140.5, 137.9, 136.7, 134.8 (m), 134.2, 131.4, 131.1, 130.7, 130.2, 129.9, 128.7, 127.8, 127.4, 127.0, 126.1, 124.3, 114.0, 63.7, 58.3 ppm; IR (thin film) 3055, 3011, 2955, 2926, 2893, 1614, 1526, 1422, 1362, 1281, 1246, 1209, 1146, 1043, 922, 908, 891, 866, 837, 822, 795, 764, 748, 731 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{48}H_{30}NF_6$ (M^+): 734.2269, found: 734.2277; $[\alpha]_D^{24}$ 147.3 (*c* 0.25, $CHCl_3$); mp 293–295 °C (dec).

4.4.11. Chiral quaternary ammonium salt (*S*)-4f [Ar^1= 3,5-bis(trifluoromethyl)phenyl]. White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–7.23 (24H, m, ArH), 5.27 (2H, d, J=12.3 Hz, $ArCH_2$), 4.96 (2H, d, J=13.5 Hz, $ArCH_2$), 4.07 (2H, d, J=13.5 Hz, $ArCH_2$), 2.52 (2H, d, J=12.3 Hz, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 141.4, 140.3, 136.7, 134.1, 131.5, 131.0, 130.6, 130.6, 129.7, 128.4, 127.4, 127.0, 126.9, 126.7, 126.0, 124.5, 122.5 (q, $^1J_{C-F}$=273 Hz), 121.1 (m), 63.1, 58.0 ppm; IR (thin film) 3057, 3011, 2986, 2953, 2891, 1618, 1508, 1458, 1377, 1277, 1173, 1132, 1051, 1030, 922, 903, 870, 847, 835, 820, 791, 731, 714 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{52}H_{32}NF_{12}$ (M^+): 898.2303, found: 898.2338; $[\alpha]_D^{24}$ 116.4 (*c* 0.25, $CHCl_3$); mp 316–318 °C (dec).

4.4.12. Chiral quaternary ammonium salt (*S*)-4g (Ar^1= 2-naphthyl). White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–7.20 (18H, br m, ArH), 7.79 (4H, t, J=7.9 Hz, ArH), 7.34 (4H, t, J=7.1 Hz, ArH), 7.05 (2H, t, J=7.5 Hz,

ArH), 6.90 (2H, d, J=8.7 Hz, ArH), 4.83 (2H, br, $ArCH_2$), 4.56–7.52 (4H, br, $ArCH_2$), 2.98 (2H, br, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.7, 136.2, 135.8, 133.5, 132.8, 132.2, 131.7, 130.9, 130.3, 129.3, 129.0, 128.8, 128.6, 127.9, 127.5, 127.2, 126.8, 126.8, 126.7, 126.5, 126.4, 126.3, 125.5, 124.0, 63.0, 57.6 ppm; IR (thin film) 3383, 3051, 1622, 1595, 1504, 1456, 1357, 1197, 864, 821, 797, 752 cm^{-1}; HRMS (FAB) calcd for $C_{56}H_{40}N$ (M^+): 726.3163, found: 726.3167; $[\alpha]_D^{22}$ 174.2 (c 0.25, $CHCl_3$); mp 202–203 °C (dec).

4.5. Typical procedure for the synthesis of (*S*)-4i–k and their characterizations

4.5.1. 4-Phenylbenzoic acid isopropyl ester (10a). The title compound was prepared from 4-phenylbenzoic acid, and the esterification was conducted as described for the synthesis of **6** [chromatography on silica gel (short-pass, EtOAc/hexane=1:4 as eluent), colorless oil, quant.]; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (2H, d, J=8.3 Hz, ArH), 7.64 (2H, d, J=7.9 Hz, ArH), 7.60 (2H, d, J=7.5 Hz, ArH), 7.46–7.43 (2H, m, ArH), 7.39–7.35 (1H, m, ArH), 5.28 (1H, sept, J=6.3 Hz, CH(CH_3)$_2$), 1.38 (6H, d, J=6.3 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 145.2, 139.9, 129.9, 129.5, 128.7, 127.9, 127.1, 126.8, 68.3, 22.0 ppm; IR (neat) 2980, 1713, 1611, 1478, 1404, 1279, 1178, 1101, 1009, 920, 858, 748, 698 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{16}O_2Na$ ([M+Na]$^+$): 263.1041, found: 263.1043.

4.5.2. 2-Iodo-4-phenylbenzoic acid isopropyl ester (11a). To a THF solution of $(TMP)_2Mg$ (0.31 M, 12.5 mmol)[8] was added **10a** (1.20 g, 5.0 mmol) in THF (20 mL) dropwise at 0 °C under argon atmosphere and the mixture was stirred for 3 h at room temperature. After being cooled to −78 °C, a THF (5 mL) solution of I_2 (7.63 g, 30.0 mmol) was added and stirring was continued for 1 h at room temperature. This mixture was then poured into cooled 1 N HCl, washed with saturated Na_2SO_3, and extracted with Et_2O. The organic layer was dried over Na_2SO_4 and concentrated. Purification of the residue by column chromatography on silica gel (EtOAc/hexane=1:20 to 1:10 as eluent) afforded **11a** (1.54 g, 4.20 mmol, 84%) as an yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (1H, d, J=2.0 Hz, ArH), 7.85 (1H, d, J=7.9 Hz, ArH), 7.60 (1H, dd, J=2.0, 7.9 Hz, ArH), 7.58–7.55 (2H, m, ArH), 7.48–7.44 (2H, m, ArH), 7.42–7.38 (1H, m, ArH), 5.29 (1H, sept, J=6.3 Hz, CH(CH_3)$_2$), 1.42 (6H, d, J=6.3 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 145.1, 139.6, 138.2, 133.8, 130.9, 128.8, 128.3, 127.0, 126.3, 94.5, 69.4, 21.9 ppm; IR (neat) 2980, 1720, 1593, 1468, 1373, 1285, 1250, 1103, 1015, 756, 693 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{15}O_2INa$ ([M+Na]$^+$): 389.0006, found: 389.0009.

4.5.3. 2,2′-Bis(isopropoxycarbonyl)-5,5′-diphenyl-1,1′-biphenyl (12a). The solution of **11a** (1.46 g, 4.0 mmol) in dry DMF (4 mL) was added activated Cu (2.0 g) and the mixture was refluxed for 3 days. After cooling to room temperature, the resulting mixture was filtered through a pad of Celite to remove Cu. This filtrate was washed with 1 N HCl and brine, and concentrated. Purification of the crude product by column chromatography on silica gel (EtOAc/hexane=1:20 as eluent) furnished **12a** (746 mg, 1.56 mmol, 78%) as a white powder; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (2H, d, J=7.9 Hz, ArH), 7.67 (2H, dd, J=1.6, 7.9 Hz, ArH), 7.64–7.61 (4H, m, ArH), 7.48 (2H, d, J=1.6 Hz, ArH), 7.45–7.42 (4H, m, ArH), 7.38–7.34 (2H, m, ArH), 4.95 (2H, sept, J=6.3 Hz, CH(CH_3)$_2$), 1.00 (6H, d, J=2.4 Hz, CH_3), 0.89 (6H, d, J=2.4 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 143.9, 143.7, 139.7, 130.6, 129.0, 128.8, 128.7, 127.9, 127.1, 125.4, 68.0, 21.5, 21.4 ppm; IR (KBr) 2982, 1695, 1604, 1452, 1383, 1288, 1148, 1105, 916, 851, 760, 698 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{32}H_{30}O_4Na$ ([M+Na]$^+$): 501.2037, found: 501.2036.

4.5.4. 2,2′-Bis(bromomethyl)-5,5′-diphenyl-1,1′-biphenyl (13a). The title compound was obtained as described for the synthesis of **9h**; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69–7.63 (8H, m, ArH), 7.59 (2H, d, J=1.7 Hz, ArH), 7.44 (4H, t, J=7.5 Hz, ArH), 7.36 (2H, t, J=7.5 Hz, ArH), 4.46 (2H, d, J=10.2 Hz, CH_2), 4.30 (2H, d, J=9.9 Hz, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 139.9, 139.8, 131.2, 128.9, 128.8, 127.8, 127.3, 127.2, 31.9 ppm; IR (thin film) 3057, 3028, 2972, 2924, 2853, 1601, 1564, 1477, 1437, 1379, 1223, 1204, 903, 864, 837, 820, 756, 733 cm^{-1}. Fragment peaks could only be detected; MS (APCI) m/z 411.331 (M^+).

4.5.5. Chiral quaternary ammonium salt (*S*)-4i (Ar^2= phenyl). White powder; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (2H, d, J=8.5 Hz, ArH), 8.10 (2H, d, J=8.5 Hz, ArH), 8.09 (2H, d, J=8.2 Hz, ArH), 8.03–7.92 (4H, m, ArH), 7.94 (2H, s, ArH), 7.71–7.69 (4H, m, ArH), 7.65–7.61 (2H, m, ArH), 7.52–7.37 (10H, m, ArH), 4.77 (2H, d, J=13.3 Hz, $ArCH_2$), 4.43 (2H, d, J=13.3 Hz, $ArCH_2$), 4.04 (4H, t, d, J=13.9 Hz, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 141.4, 139.4, 136.9, 134.6, 132.8, 131.5, 131.0, 129.1, 128.8, 128.5, 128.4, 128.1, 127.9, 127.7, 127.5, 127.4, 125.7, 125.4, 61.4, 60.6 ppm; IR (thin film) 3055, 3030, 2955, 2924, 2853, 2158, 1730, 1597, 1558, 1508, 1485, 1454, 1356, 1261, 1157, 1028, 1016, 923, 889, 864, 824, 799, 760, 725 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{48}H_{36}N$ (M^+): 626.2855, found: 626.2842; $[\alpha]_D^{26}$ −208.0 (c 0.25, $CHCl_3$); mp 323–326 °C (dec).

4.5.6. Chiral quaternary ammonium salt (*S*)-4j (Ar^2= 2-naphthyl). White powder; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (2H, d, J=8.2 Hz, ArH), 8.19 (2H, s, ArH), 8.14–8.07 (10H, m, ArH), 7.98 (2H, d, J=8.7 Hz, ArH), 7.96–7.93 (2H, m, ArH), 7.91–7.88 (2H, m, ArH), 7.84 (2H, dd, J=1.7, 8.5 Hz, ArH), 7.64 (2H, t, J=7.0 Hz, ArH), 7.56–7.52 (4H, m, ArH), 7.48 (2H, d, J=8.5 Hz, ArH), 7.40 (2H, t, J=7.6 Hz, ArH), 4.83 (2H, d, J=13.1 Hz, $ArCH_2$), 4.47 (2H, d, J=13.5 Hz, $ArCH_2$), 4.16 (2H, d, J=13.1 Hz, $ArCH_2$), 4.05 (2H, d, J=12.1 Hz, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 141.6, 136.9, 136.7, 134.6, 133.6, 133.1, 132.9, 131.5, 131.0, 128.9, 128.8, 128.8, 128.4, 127.9, 127.7, 127.7, 127.5, 126.7, 126.6, 126.6, 125.7, 125.4, 125.3, 61.5, 60.6 ppm; IR (thin film) 3313, 3196, 3053, 2172, 1609, 1597, 1558, 1506, 1497, 1456, 1395, 1348, 1192, 1028, 1018, 924, 908, 872, 816, 750, 727 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{56}H_{40}N$ (M^+): 726.3155, found: 726.3155; $[\alpha]_D^{26}$ −127.9 (c 0.25, $CHCl_3$); mp 329–330 °C (dec).

4.5.7. Chiral quaternary ammonium salt (*S*)-4k (Ar^2= 3,4,5-trifluorophenyl). White powder; ^1H NMR (400 MHz,

$CDCl_3$) δ 8.29 (2H, d, J=8.0 Hz, ArH), 8.10–8.06 (4H, m, ArH), 8.00 (2H, br, ArH), 7.87–7.82 (4H, m, ArH), 7.64 (2H, t, J=7.3 Hz, ArH), 7.47–7.38 (4H, m, ArH), 7.33 (3H, t, J=7.1 Hz, ArH), 7.23 (1H, d, J=6.5 Hz, ArH), 4.92–4.85 (2H, m, $ArCH_2$), 4.42 (2H, br, $ArCH_2$), 4.32–4.16 (2H, m, $ArCH_2$), 4.00 (2H, br, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 152.8, 152.8, 152.7, 151.5 (ddd, J_{C-F}=4.1, 9.8, 51.6 Hz), 150.3, 150.3, 150.2, 150.2, 142.0, 141.4, 139.9 (dt, J_{C-F}=15.5, 15.5, 254 Hz), 136.9, 135.6 (dd, J_{C-F}=7.4, 12.3 Hz), 134.6, 133.2, 131.5, 131.0, 128.8, 128.6, 128.0, 127.9, 127.7, 127.7, 127.6, 126.6, 125.5, 111.7 (m), 61.4, 60.1 ppm; IR (thin film) 3352, 3049, 2986, 2932, 2178, 1618, 1595, 1568, 1499, 1443, 1393, 1360, 1296, 1242, 1119, 989, 908, 874, 822, 764, 752, 727 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{48}H_{30}NF_6$: 734.2274 (M^+), found: 734.2277 (M^+); $[\alpha]_D^{22}$ −210.3 (*c* 0.25, $CHCl_3$); mp 308–310 °C (dec).

4.6. Synthesis of (*S*)-4l

Chiral quaternary ammonium salt (*S*)-**4l** was prepared from **12a** in a manner similar to the preparation of (*S*)-**4b–h** from **6**. Characterizations of each intermediate and (*S*)-**4l** are as follows.

4.6.1. 3,3′-Dibromo-2,2′-bis(isopropoxycarbonyl)-5,5′-diphenyl-1,1′-biphenyl (14). ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (2H, d, J=1.6 Hz, ArH), 7.58–7.54 (6H, m, ArH), 7.46–7.44 (4H, m, ArH), 7.41–7.37 (2H, m, ArH), 5.00 (2H, sept, J=6.3 Hz, $CH(CH_3)_2$), 1.12 (6H, d, J=1.6 Hz, CH_3), 0.89 (6H, d, J=1.6 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 142.7, 138.7, 138.0, 134.3, 130.4, 128.8, 128.3, 127.4, 126.9, 119.7, 69.3, 21.5, 21.0 ppm; IR (KBr) 2980, 1722, 1595, 1537, 1499, 1373, 1281, 1177, 1141, 1101, 1043, 916, 883, 758, 696 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{32}H_{28}O_4Br_2Na$ ($[M+Na]^+$): 657.0264, found: 657.0247.

4.6.2. 2,2′-Bis(isopropoxycarbonyl)-3,3′-bis(3,5-diphenylphenyl)-5,5′-diphenyl-1,1′-biphenyl (15). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (2H, s, ArH), 7.75 (2H, s, ArH), 7.71–7.65 (18H, m, ArH), 7.48–7.33 (18H, m, ArH), 4.76 (2H, sept, J=6.3 Hz, $CH(CH_3)_2$), 0.82 (6H, d, J=6.3 Hz, CH_3), 0.68 (6H, d, J=6.3 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 141.6, 141.4, 141.3, 140.6, 140.6, 139.4, 138.9, 132.5, 128.7, 128.6, 127.7, 127.7, 127.6, 127.5, 127.3, 127.1, 127.0, 126.2, 125.1, 68.4, 21.2, 20.9 ppm; IR (KBr) 2983, 1720, 1593, 1497, 1450, 1387, 1277, 1101, 1078, 881, 760, 698 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{68}H_{54}O_4Na$ ($[M+Na]^+$): 957.3948, found: 957.3914.

4.6.3. 2,2′-Bis(bromomethyl)-3,3′-bis(3,5-diphenylphenyl)-5,5′-diphenyl-1,1′-biphenyl (16). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (2H, s, ArH), 7.83 (4H, s, ArH), 7.79–7.71 (16H, m, ArH), 7.50–7.34 (18H, m, ArH), 4.54 (2H, d, J=9.7 Hz, $ArCH_2$), 4.40 (2H, d, J=9.7 Hz, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.6, 141.4, 141.3, 140.6, 139.5, 132.1, 129.0, 128.8, 128.8, 128.4, 127.8, 127.5, 127.3, 127.1, 126.8, 125.2, 31.3 ppm; IR (KBr) 3058, 3032, 1592, 1496, 1448, 1411, 1389, 1217, 1075, 1028, 881, 759, 696 cm^{-1}. Fragment peaks could only be detected; MS (APCI) *m/z* 867.787 (M^+).

4.6.4. Chiral quaternary ammonium salt (*S*)-4l (Ar^1=3,5-diphenylphenyl, Ar^2=Ph). White powder; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02–7.10 (52H, br m, ArH), 4.96 (2H, d, J=13.5 Hz, $ArCH_2$), 4.85 (2H, br, $ArCH_2$), 4.65 (2H, d, J=13.1 Hz, $ArCH_2$), 2.77 (2H, br, $ArCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.6, 139.5, 136.1, 133.6, 130.4, 129.6, 128.8, 128.5, 128.2, 128.1, 127.8, 127.6, 127.4, 126.9, 126.7, 126.5, 63.3, 58.0 ppm; IR (KBr) 3370, 3057, 3033, 1593, 1497, 1456, 1383, 1354, 1028, 881, 819, 760, 698 cm^{-1}; HRMS (FAB) calcd for $C_{84}H_{60}N$: 1082.4729 (M^+), found: 1082.4713 (M^+); $[\alpha]_D^{25}$ 41.2 (*c* 0.25, $CHCl_3$); mp 303–306 °C (dec).

4.7. X-ray structure determination of chiral quaternary ammonium salt (*S*)-4l

The single crystal of (*S*)-**4l** (colorless needle) was obtained by recrystallization from CH_2Cl_2/hexane solvent system and was mounted on a CryoLoop (Hampton Research Co. Ltd). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated Mo Kα radiation (λ= 0.71069 Å) to a maximum 2θ value of 55°. All of the crystallographic calculations were performed using teXsan software package of the Molecular Structure Corp. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using SIR-97. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The crystallographic data were summarized in the following table.

Experimental details			
Empirical formula	$C_{87}H_{66}BrNCl_6$	T, °C	−150.0
Formula weight	1418.11	μ (Mo Kα), cm^{-1}	8.75
Crystal system	Monoclinic	No. of reflns measrd	30,354
Space group	$P2_1$ (#4)	No. of reflns obsd	8194
a, Å	12.8560 (6)	No. of variable	856
b, Å	18.0233 (8)	$R1$	0.048
c, Å	15.0569 (9)	wR	0.123
V, Å^3	3463.9 (3)	Goodness of fit	1.20
Z	2	Max shift/error in final cycle	0.002
D_{calcd}, g cm^{-3}	1.360		

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. M.K. is grateful to the Japan Society for the Promotion of Science for Young Scientists for a research fellowship.

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