Organic & Biomolecular Chemistry

Review

A new generation of chiral phase-transfer catalysts

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Phase-transfer catalysis has long been recognized as a versatile method for organic synthesis. In particular, during more than the past three decades, asymmetric phase-transfer catalysis based on the use of structurally well-defined chiral catalysts has become a topic of great scientific interest. Although various effective chiral catalysts have already been reported and these catalysts were utilized for practical asymmetric transformations, further design and development of new chiral phase-transfer catalysts are still attractive research subjects in organic chemistry due to the high utility and practicability of phase-transfer-catalyzed reactions. This review focuses on the recent examples of newly designed effective chiral phase-transfer catalysts.

1. Introduction

Phase-transfer catalysis has long been recognized as a versatile method for organic synthesis in both industry and academia, as it features simple experimental operations, mild reaction conditions, inexpensive and environmentally benign reagents and solvents, and the possibility to conduct large-scale preparations in process chemistry.[1] In particular, during more than the past three decades, asymmetric phase-transfer catalysis based on the use of structurally well-defined chiral, non-racemic catalysts has become a topic of great scientific interest (Fig. 1). Recent efforts have resulted in notable achievements, making it feasible to perform various bond formation reactions under mild phase-transfer-catalyzed conditions.[2] Cinchona alkaloid-derived tetraalkylammonium salts **1** and **2** are the pioneering, and still some of the most reliable, chiral phase-transfer catalysts.[3] More recently, cinchona alkaloid-derived quaternary ammonium salts **3** and **4** possessing an amide or a urea moiety as bifunctional phase-transfer catalysts have been reported.[4] These reports on the development of bifunctional catalysts clearly exhibited the possibility of new catalyst design with an amide and a urea group. Binaphthyl-modified tetraalkylammonium salts **5** and **6** developed by Maruoka are known as another reliable and widely applicable chiral phase-transfer catalysts.[5] Based on the design of catalysts **5** and **6**, phosphonium salt version **7**[6] and bifunctional-type catalysts **8**[7] have also been prepared by Maruoka. TADDOL-derived and/or multi-cyclic onium salts **9–14** have also behaved as effective chiral phase-transfer catalysts.[8] Crown ethers **15–17** are different types of representative chiral phase-transfer catalysts.[9] As a new concept of phase-transfer catalysis, Toste developed anion phase-transfer catalysis with chiral phosphoric acid catalysts,[10] such as catalysts

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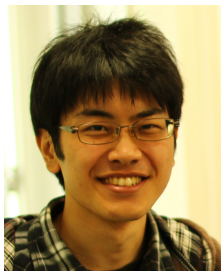

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18–20 (Fig. 2).[11] They used selectfluor as a versatile cationic fluorinating agent, which would normally be insoluble in nonpolar organic solvents. They hypothesized that lipophilic, bulky chiral phosphate anions, such as the conjugate base of **18**, could exchange with anions associated with selectfluor to bring the reagent into solution. The resulting chiral ion pair could then mediate asymmetric fluorinations in solution. Chiral carboxylic acid **21** also worked as an effective anionic phase-transfer catalyst.[12] Although these chiral phase-transfer catalysts have realized a wide variety of efficient and useful asymmetric transformations, further design and development of new chiral phase-transfer catalysts are still attractive research subjects in organic chemistry due to the high utility and practicability of phase-transfer-catalyzed reactions. In this context, new types of designed chiral phase-transfer catalysts have been appeared in the last few years. This review summarizes the recent examples of newly designed effective chiral phase-transfer catalysts.

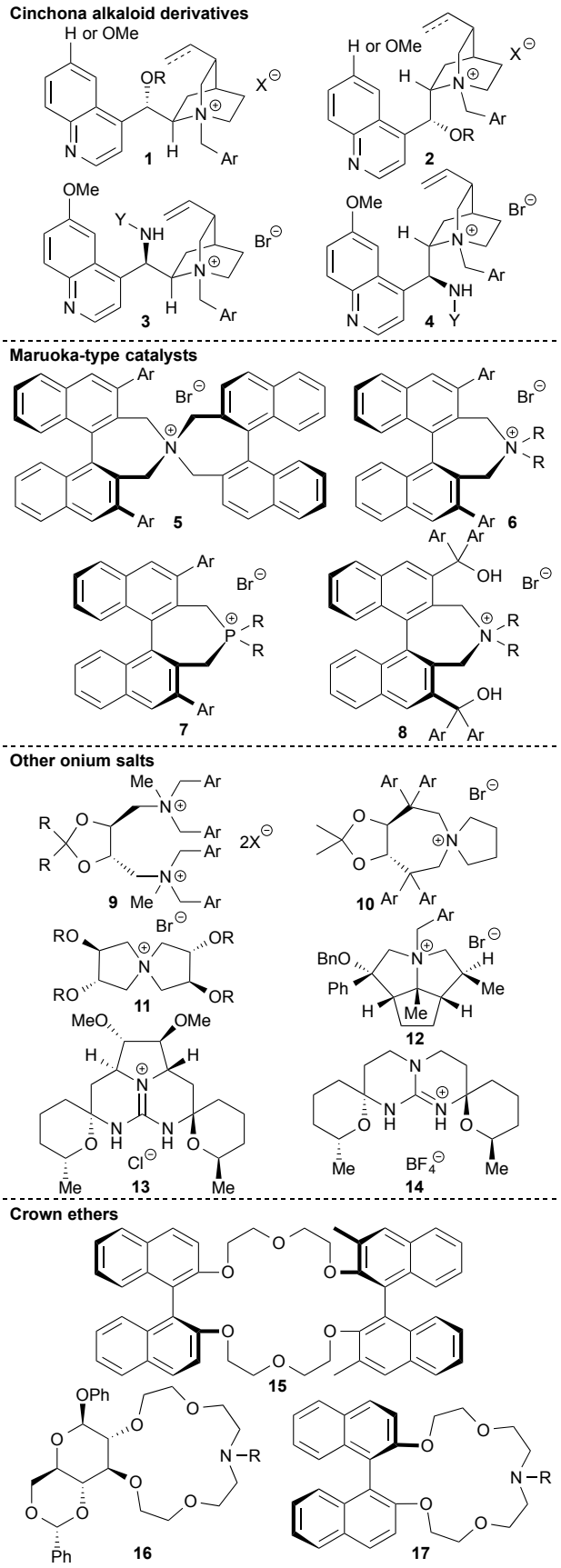


Fig. 1 Representative chiral phase-transfer catalysts.

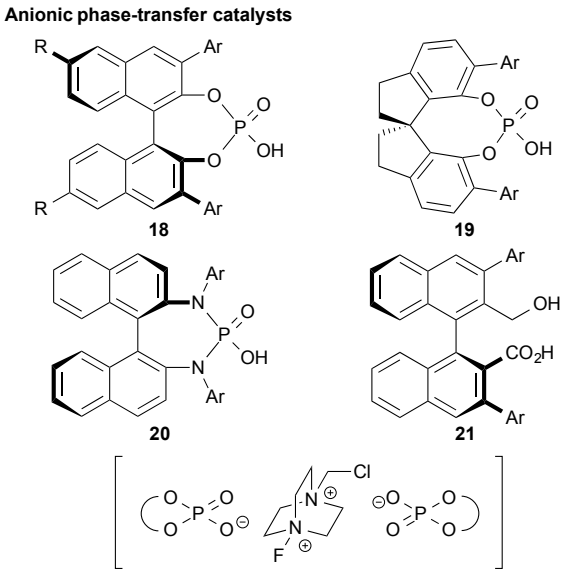
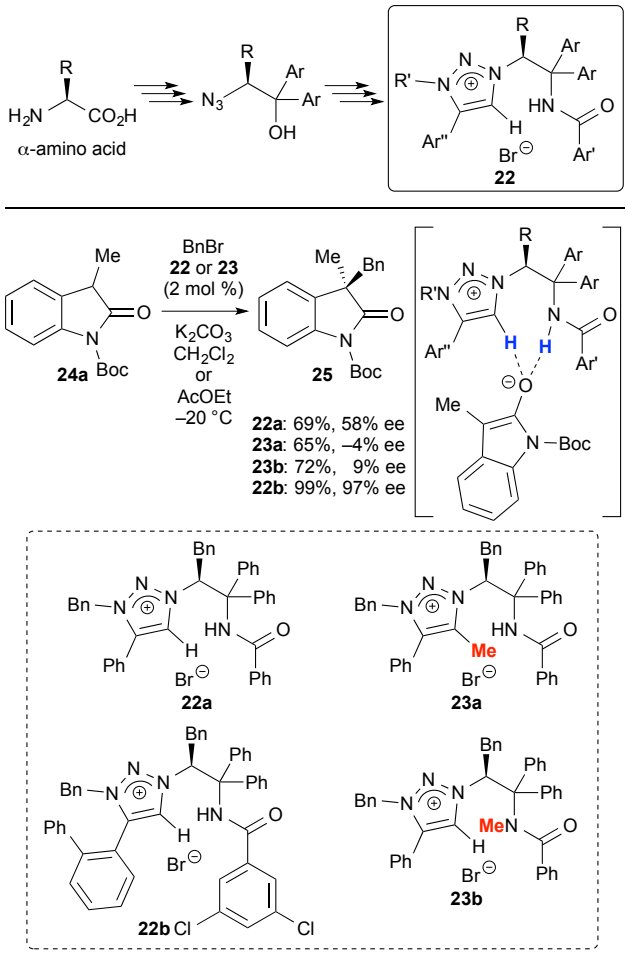


Fig. 2 New concept of anion phase-transfer catalysis.

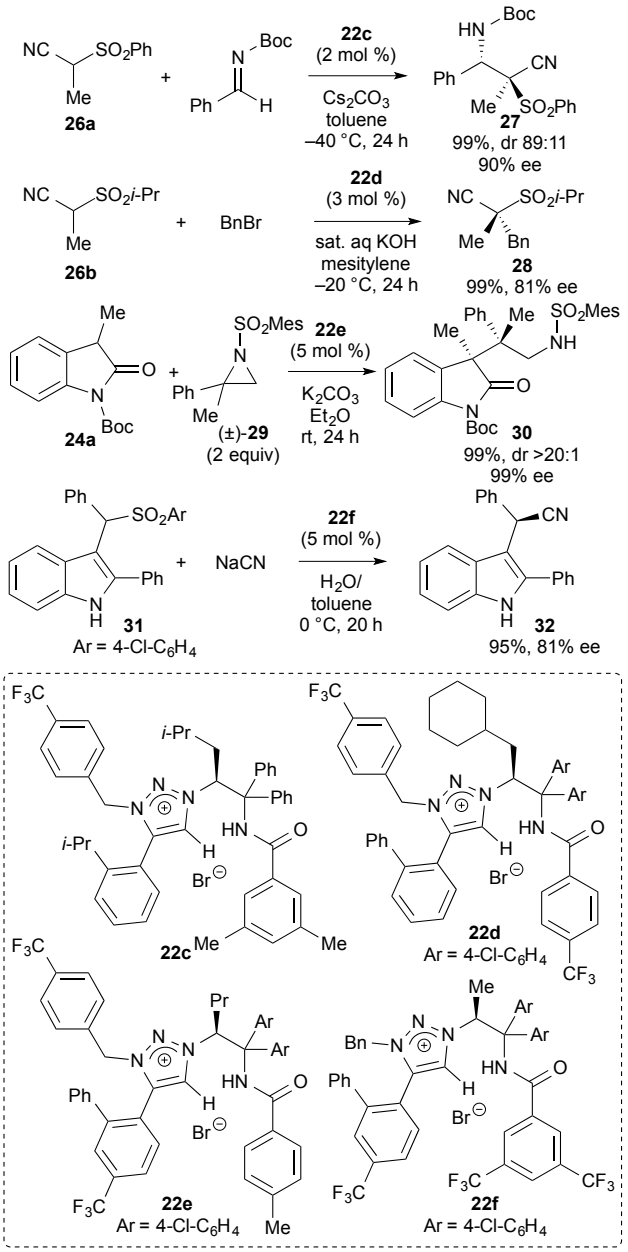
2. Amino acid-derived catalysts

Ooi and co-workers designed 1,2,3-triazolium catalysts of type **22** as new chiral phase-transfer catalysts (Scheme 1).[13–17] Chiral catalysts of type **22** were readily prepared from α-amino acids as a chiral source via copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of amino acid-derived azides with terminal alkynes, which is representative reaction in click chemistry.[18] The catalyst ability of **22** was initially examined in asymmetric phase-transfer alkylation of oxindole derivative **24a**.[13] Although newly-designed catalyst **22a** promoted the benzylation to give product **25** in good enantioselectivity, the reaction with either *C*(5)-methyltriazolium salt **23a** or *N*-methylbenzamide triazolium salt **23b** gave product **25** in very low enantioselectivities. These results indicate that the double hydrogen-bonding by the triazolium *C*(5)-H proton and the amide N-H proton of **22** to anion is essential to achieve highly enantioselective reactions. Further fine-tuning of the catalyst **22** improved the enantioselectivity, and the highly selective reaction was achieved by the use of optimized catalyst **22b**.



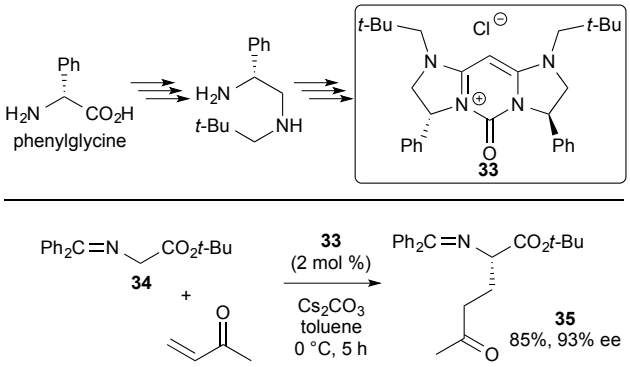
Scheme 1 Chiral 1,2,3-triazolium catalysts.

New chiral 1,2,3-triazolium catalysts **22** could also be applied to other asymmetric phase-transfer reactions (Scheme 2).[14–17] Highly enantioselective Mannich reaction of cyanosulfone **26a** to obtain product **27** was achieved with catalyst **22c**.[14] Asymmetric alkylation of cyanosulfone **26b** under the influence of catalyst **22d** was also reported, and benzylation product **28** was obtained in good enantioselectivity.[15] Ring-opening reaction of racemic 2,2-disubstituted aziridine **29** and 3-substituted oxindole **24a** with catalyst **22** under phase-transfer conditions was also examined to construct contiguous all-carbon quaternary stereocenters. Optimized catalyst **22e** could efficiently promote the reaction to give product **30** in high diastereo- and enantioselectivity.[16] After this reaction, unreacted aziridine **29** was recovered in an optically enriched form. Phase-transfer cyanation of alkylideneindolenine, generated in situ from sulfonylalkylindole **31**, under the influence of catalyst **22f** to obtain product **32** was also reported.[17] Notably, fine-tuning of catalysts **22** was key to achieve various efficient asymmetric transformations.



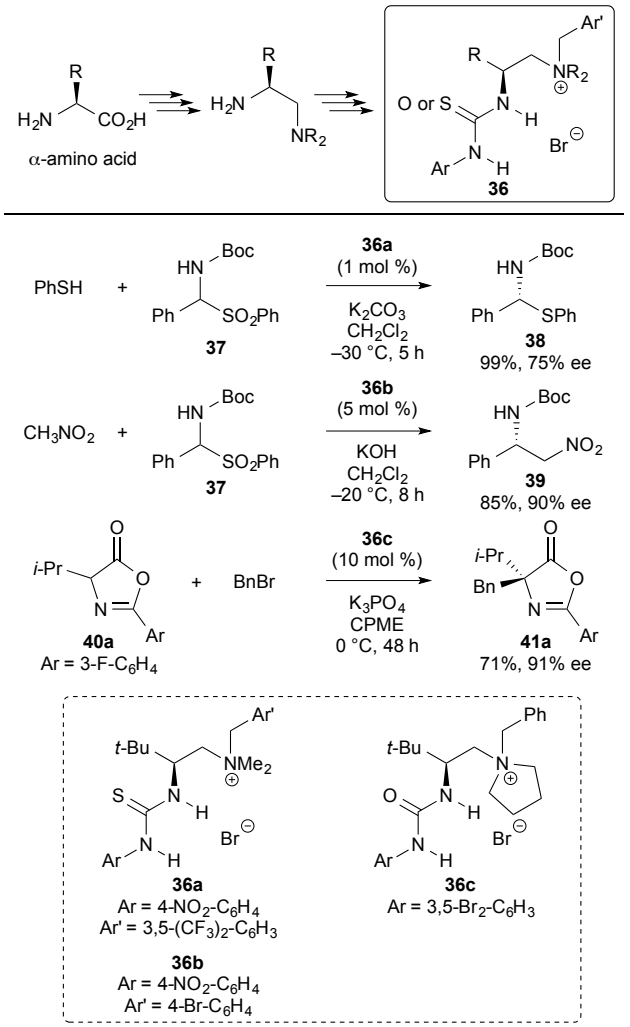
Scheme 2 Chiral 1,2,3-triazoliums-catalyzed asymmetric phase-transfer reactions.

Phenylglycine-derived chiral 2-oxopyrimidinium salt catalyst **33** was developed by Hii and co-workers (Scheme 3).[19] The ability of catalyst **33** was proved in the highly enantioselective conjugate addition of glycine derivative **34** with methyl vinyl ketone, as a one of the benchmark reaction in the phase-transfer chemistry, to obtain α-amino acid derivative **35**.



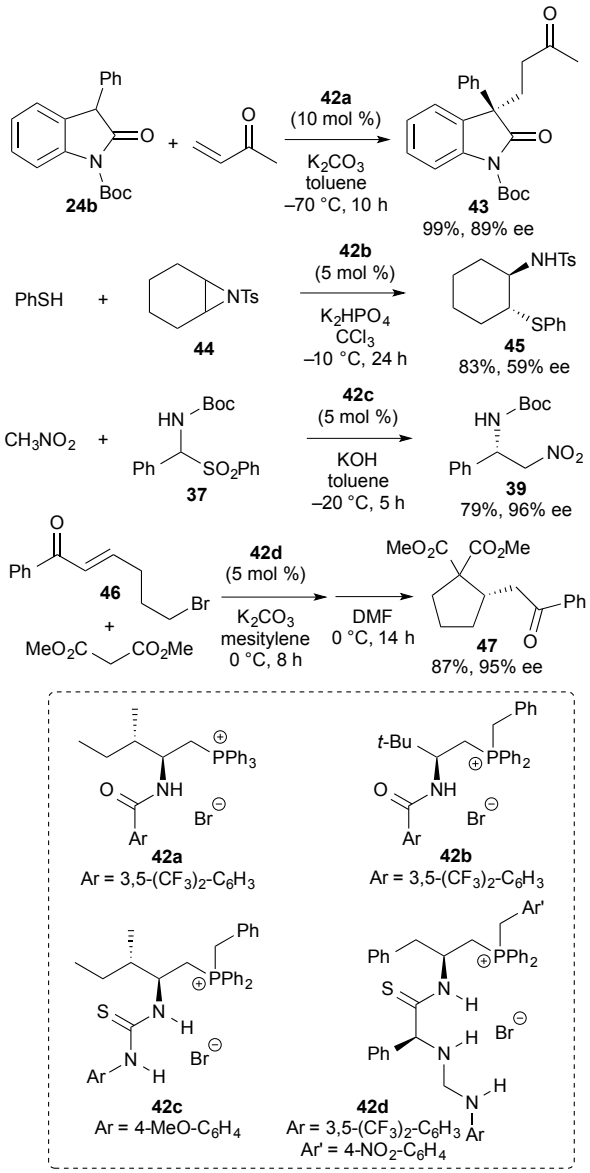
Scheme 3 Chiral 2-oxopyrimidinium salt catalyst.

Zhao and co-workers reported highly enantioselective phase-transfer reactions using α-amino acid-derived chiral bifunctional catalysts of type **36** possessing a thiourea moiety (Scheme 4). Bifunctional tetraalkylammonium bromide **36a** promoted the asymmetric addition reaction of thiophenol to imine precursor **37** to give a product **38** in good enantioselectivity.[20] Highly enantioselective aza-Henry reaction with **37** to obtain a product **39** was also achieved by the use of catalyst **36b**.[21] Related chiral bifunctional quaternary ammonium salt **36c** possessing a urea moiety was developed by Jiang and co-wokers.[22] The catalyst ability of **36c** was examined in asymmetric phase-transfer alkylation of azlactone **40a**. As a result of the benzylation of **40a**, α,α-dialkyl-α-amino acid derivative **41a** was obtained in high enantioselectivity.



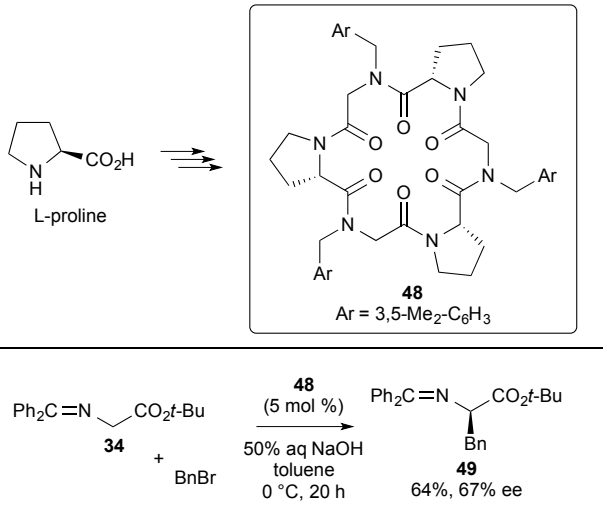
Scheme 4 Chiral bifunctional tetraalkylammonium salts possessing a thiourea or a urea moiety.

Based on the design of chiral bifunctional quaternary ammonium salts **36**, Zhao and co-workers also developed bifunctional quaternary phosphonium salts of type **42** (Scheme 5). Chiral quaternary phosphonium bromide **42a** possessing an amide moiety efficiently promoted asymmetric conjugate addition of 3-phenyloxindole **24b** under phase-transfer conditions to give conjugate adduct **43** in high yield and enantioselectivity.[23] The related catalyst **42b** could apply to asymmetric desymmetrization of *meso*-aziridine **44** with thiophenol, and product **45** was obtained with moderate enantioselectivity.[24] Bifunctional phosphonium bromide catalyst **42c** possessing a thiourea moiety was used for asymmetric aza-Henry reaction of imine precursor **37** with nitromethane to give product **39** with high enantioselectivity.[25] Dipeptide-derived multifunctional phosphonium bromide **42d** was effective catalyst for asymmetric cyclization via tandem Michael addition/intramolecular S_N2 reaction with substrate **46** and malonate.[26] As a result of the tandem reaction, cyclopentane derivative **47** was obtained in good yield with high enantioselectivity. In these cases, bifunctional design of the catalysts was essential to achieve highly enantioselective reactions.



Scheme 5 Chiral bifunctional quaternary phosphonium salts for asymmetric phase-transfer reactions.

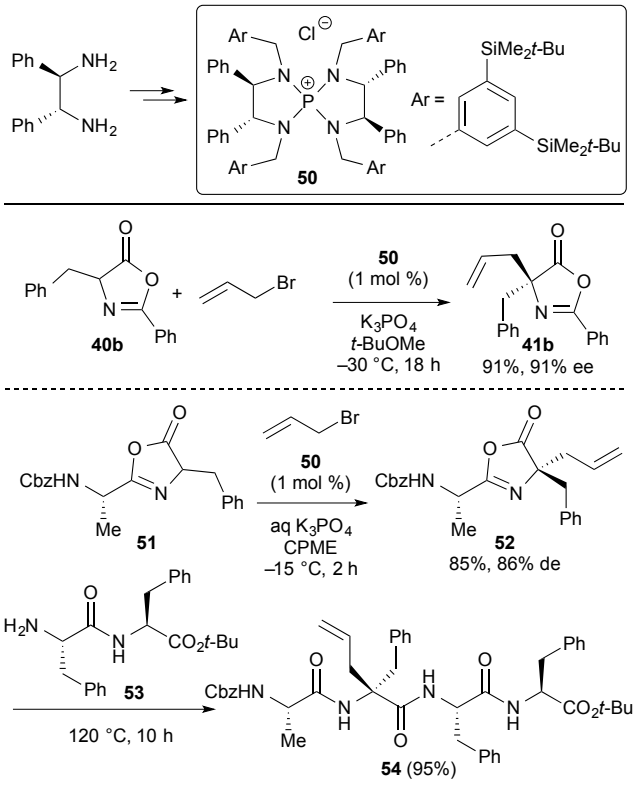
Della Sala and Izzo et al. reported the first application example of chiral cyclopeptoids as phase-transfer catalysts.[27] L-Proline-derived cyclopeptoid **48** was applied to asymmetric phase-transfer benzylation of glycine derivative **34** as a benchmark reaction. Although phenylalanine derivative **49** was obtained in only moderate enantioselectivity, this catalyst design was interesting approach to develop the new chiral phase-transfer catalysts.



Scheme 6 L-Proline-derived cyclopeptoid catalyst.

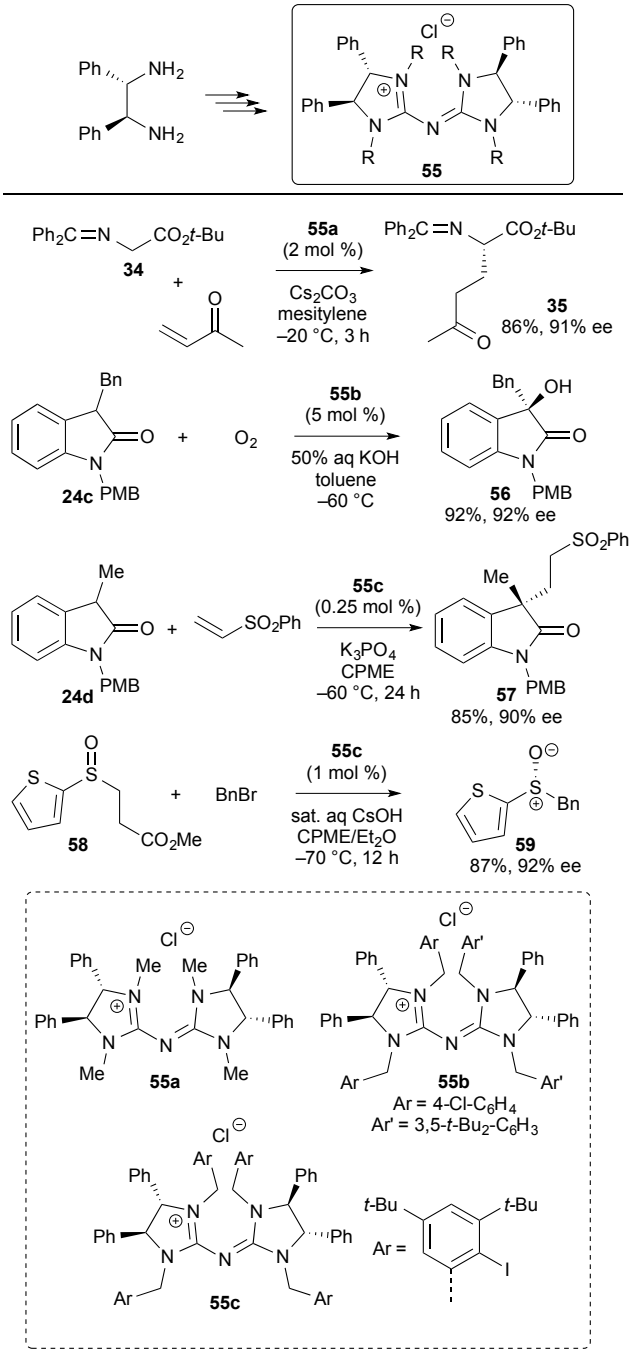
3. Chiral diamine-derived catalysts

Ooi and co-workers demonstrated that *P*-spiro chiral tetraaminophosphonium salt **50** derived from readily available chiral 1,2-diphenylethylenediamine can function as an effective chiral phase-transfer catalyst for the highly enantioselective alkylation of azlactone **40b** (Scheme 7).[28] The resulting alkylated azlactone **41b** can be readily converted into the corresponding α,α-dialkyl-α-amino acid through acidic hydrolysis. Based on the synthetic strategy for α,α-dialkyl-α-amino acids using azlactones, they also developed a novel elegant method for the synthesis of peptides containing quaternary stereogenic carbon centers. *C*-Terminal azlactone **51** derived from dipeptide underwent stereoselective alkylation with high efficiency by the use of a chiral tetraaminophosphonium salt **50** as a phase-transfer catalyst, and the alkylated azlactone product **52** could be employed directly for peptide ligation with dipeptide **53** to give growing peptides **54**.[29]



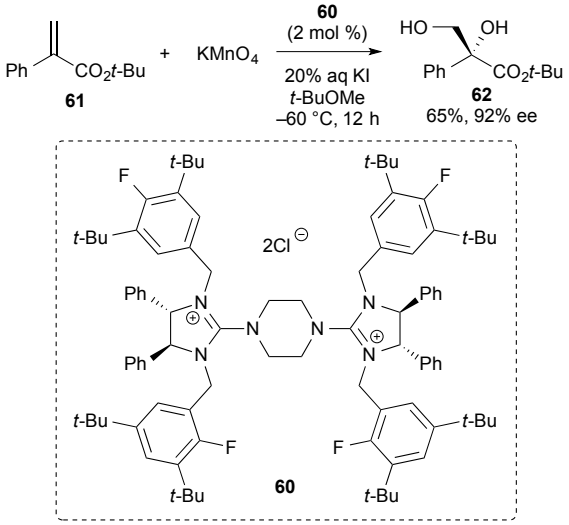
Scheme 7 *P*-Spiro tetraaminophosphonium salt catalyst.

Tan and co-workers developed 1,2-diphenylethylenediamine-derived chiral pentanidium salt catalysts of type **55** (Scheme 8).[30–33] The catalyst ability of pentanidium salts **55** was first examined in the conjugate addition of glycine derivative **34** with methyl vinyl ketone as a benchmark reaction. The reaction was efficiently promoted by catalyst **55a** to give α-amino acid derivative **35** in high yield and enantioselectivity.[30] Pentanidium **55b** could apply to asymmetric oxidation of 3-substituted oxindole derivative **24c** using molecular oxygen under phase-transfer conditions. The oxidation reaction gave a product **56** in high yield and enantioselectivity.[31] Highly enantioselective conjugate addition of oxindole derivative **24d** to give product **57** was also achieved by the use of catalyst **55c**.[32] Furthermore, this catalyst system achieved highly enantioselective synthesis of chiral sulfoxides.[33] As a result of the benzylation of sulfenate anion generated from sulfoxide **58** under the influence of catalyst **55c**, chiral sulfoxide **59** was obtained in high yield and enantioselectivity. It should be noted that fine-tuning of R groups on nitrogen in pentanidium salt **55** was essential to achieve these highly enantioselective phase-transfer reactions.



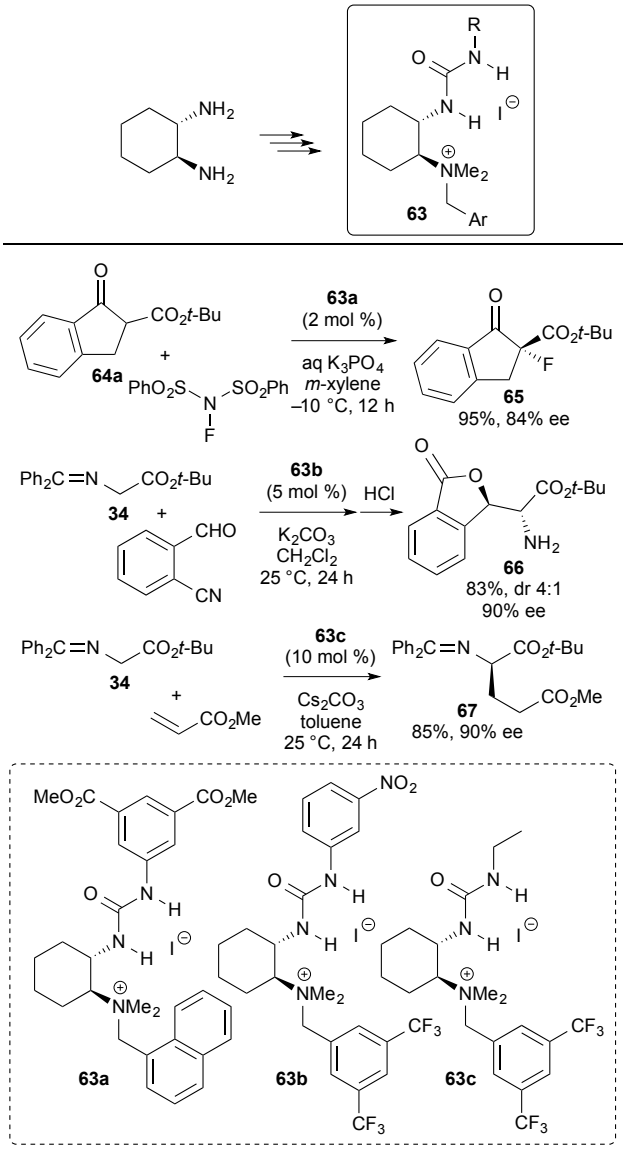
Scheme 8 Chiral pentanidium salts-catalyzed asymmetric phase-transfer reactions.

Based on the design of pentanidium salt catalysts **55**, Tan and co-workers also developed chiral bis-guanidinium salt **60** (Scheme 9).[34] The catalyst **60** worked as an effective catalyst for asymmetric oxidation reaction of alkene **61** with potassium permanganate to obtain diol **62** in moderate yield with high enantioselectivity.



Scheme 9 Chiral bis-guanidinium salt catalyst.

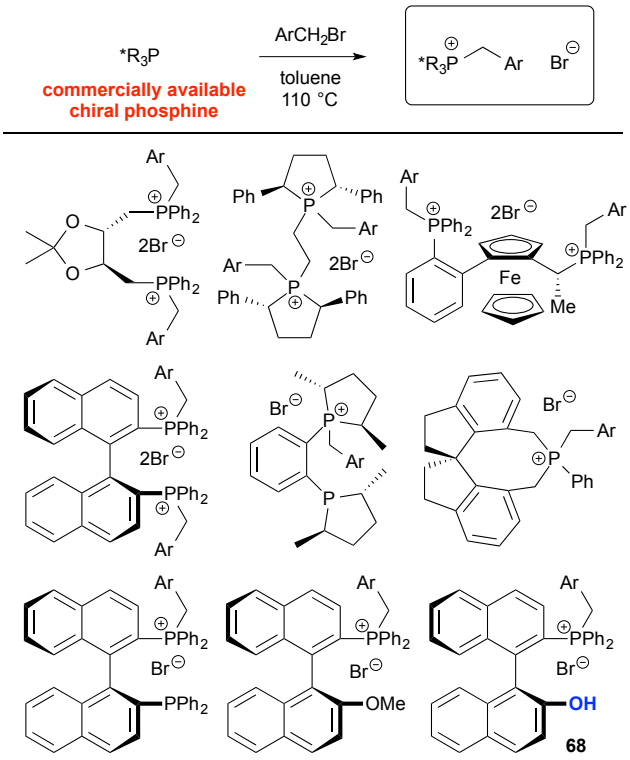
Waser and Massa et al. reported 1,2-cyclohexanediamine-derived chiral bifunctional tetraalkylammonium salt catalysts of type **63** (Scheme 10).[35–38] The ability of chiral bifunctional tetraalkylammonium salts, such as catalyst **63**, was examined in asymmetric fluorination of 1-oxo-2-indanecarboxylate **64a** to obtain product **65**.[35] Various chiral diamine-derived bifunctional quaternary ammonium salts were submitted to the fluorination, and the best catalyst for this reaction was 1,2-cyclohexanediamine-derived ammonium salt **63a**. The catalyst of type **63** could further apply to asymmetric phase-transfer reactions with glycine derivative **34**. The optimized catalyst **63b** realized highly enantioselective aldol-initiated cascade reaction of glycine derivative **34** with 2-cyanobenzaldehyde to obtain lactone **66** in good selectivity.[36,37] Highly enantioselective conjugate addition of **34** to produce glutamic acid derivative **67** was also achieved with catalyst **63c**.[37] The bifunctional catalysts of type **63** could also apply to other important asymmetric transformations.[38]



Scheme 10 Chiral cyclohexanediamine-derived bifunctional tetraalkylammonium salts possessing a urea moiety.

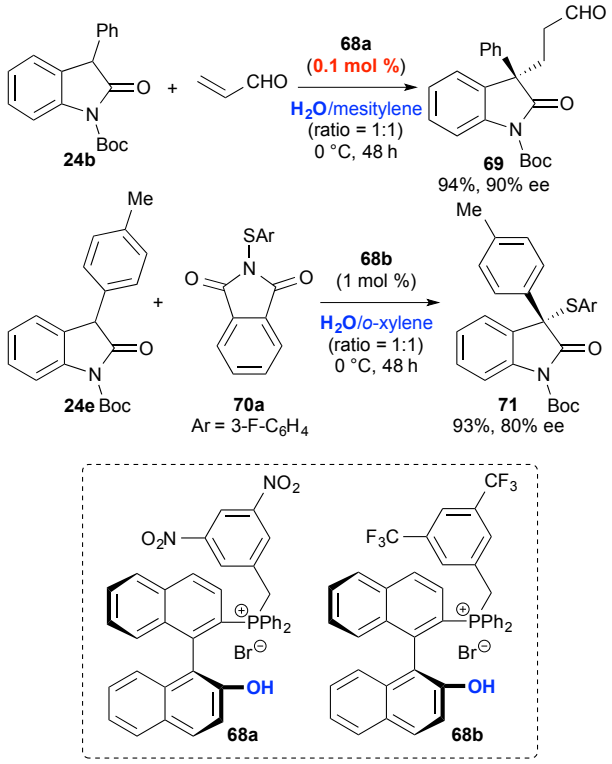
4. Chiral phosphine-derived catalysts

We examined development of effective chiral quaternary phosphonium bromides as phase-transfer catalysts. In the history of catalytic asymmetric synthesis, the research and development of chiral phosphine compounds as ligands for metal catalysts was most extensively studied to establish the practical asymmetric reactions. Hence, numerous kinds of chiral phosphines have been synthesized so far, and a lot of privileged chiral phosphine ligands have now been commercially available. Our approach for the discovery of effective chiral quaternary phosphonium salts relies on the use of commercially available chiral phosphine compounds as catalyst precursors. This approach allows facile construction of a catalyst library of chiral quaternary phosphonium salts with various structures. A catalyst library of chiral quaternary phosphonium salts with various structures was readily constructed by benzylation of corresponding commercially available phosphines (Scheme 11).[39]



Scheme 11 Library of chiral quaternary phosphonium salt catalysts.

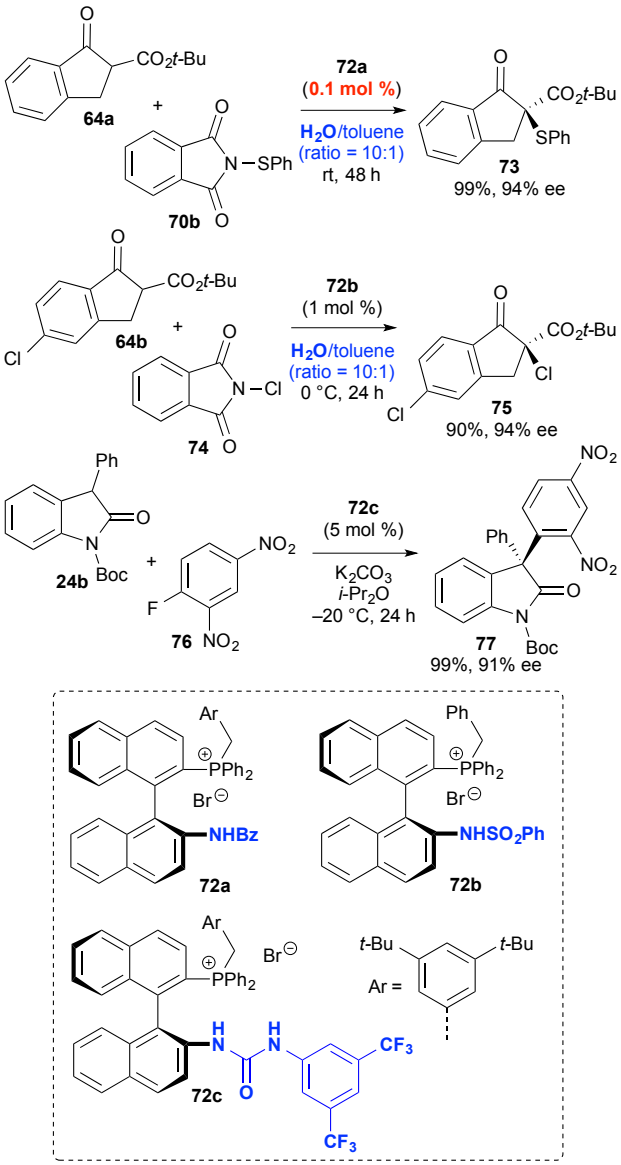
After careful optimization of the catalyst library as shown in Scheme 11, we found that bifunctional catalyst of type **68** possessing a hydroxy group at 2'-position of binaphthyl moiety was effective for asymmetric conjugate addition of 3-phenyloxindole **24b** (Scheme 12).[39] The reaction was efficiently promoted by phosphonium bromide **68a** with low catalyst loading under base-free neutral phase-transfer conditions[40] to give product **69** in high yield and enantioselectivity. Highly enantioselective base-free sulfenylation reaction of oxindole derivative **24e** with *N*-(arylthio)phthalimide **70a** was also achieved by the use of catalyst **68b**.[39]



Scheme 12 Bifunctional phosphonium salt-catalyzed asymmetric conjugate addition and sulfenylation of 3-aryloxindoles.

Based on the design of chiral bifunctional phosphonium bromides **68** possessing a hydroxy group, we also prepared new chiral bifunctional phosphonium bromides **72** with amide or urea moiety (Scheme 13). As a model reaction to examine the ability of new bifunctional phosphonium salts possessing an amide moiety, the asymmetric sulfenylation of β-keto ester was selected. The reaction between *tert*-butyl 1-oxo-2-indanecarboxylate **64a** and *N*-(phenylthio)phthalimide **70b** in H_2O/toluene (ratio = 10:1) took place in the presence of catalyst **72a** (0.1 mol %) possessing a benzamide group at 25 °C over 48 h, affording the sulfenylation product **73** in excellent yield with high enantioselectivity.[41] To further expand the synthetic utility of our bifunctional quaternary phosphonium bromides with an amide moiety, we also examined the asymmetric chlorination of β-keto esters under base-free neutral phase-transfer conditions. Although the reaction of β-keto ester **64b** and *N*-chlorophthalimide **74** with benzamide-substituted catalyst **72a** gave a product **75** in moderate enantioselectivity, benzenesulfonamide-substituted catalyst **72b** improved the enantioselectivity to give the chlorination product **75** in high yield and enantioselectivity.[41] These results suggest that the tunable acidity of an amide moiety of the catalyst could open up further possibility for realizing other types of asymmetric transformation using these bifunctional catalysts.

Although asymmetric nucleophilic aromatic substitution (S_NAr) reaction of carbonyl compounds provides an efficient means to realize enantioselective α-arylations to produce biologically interesting α-aryl carbonyl compounds, the successful examples were quite limited.[42] In this context, we have been interested in the development of chiral quaternary phosphonium salts-catalyzed asymmetric S_NAr reaction under phase-transfer conditions. We examined asymmetric S_NAr reaction of 3-phenyloxindole **24b** and electron deficient aryl fluoride **76** under the influence of chiral bifunctional phosphonium bromides as phase-transfer catalysts (Scheme 13).[43] Although catalysts **68**, **72a**, and **72b** possessing a hydroxy group or an amide group gave arylation product **77** in low to moderate enantioselectivities, the reaction with newly-designed chiral bifunctional quaternary phosphonium bromide **72c** possessing a urea moiety gave a product **77** in high yield and enantioselectivity. It is expected that the urea moiety of catalyst **72c** interacts with nitroarene **76** through double hydrogen-bonding, giving rise to a well organized transition states that provides high stereocontrol.



Scheme 13 Asymmetric phase-transfer reactions with bifunctional quaternary phosphonium salts possessing an amide or a urea group.

5. Conclusions

Recent examples of new chiral phase-transfer catalysts were summarized in this review. As new types of cationic heterocyclic catalysts, chiral 1,2,3-triazolium, 2-oxopylimidinium, and pentanidium salt catalysts were developed for asymmetric phase-transfer reactions. Careful optimization of the catalyst structure for each reaction was required to achieve highly enantioselective reactions. Hence, tunable design of the catalyst was important direction to develop the widely applicable catalysts. Another trend of the catalyst design was bifunctional design of phase-transfer catalysts. Even in the relatively simple design of catalysts with an amide or a urea moiety, highly enantioselective phase-transfer reactions were achieved. Although ordinary approach for construction of a catalyst library was limited to related structure of the initial catalyst design, our approach solved this problem. That is to say, we have employed the commercially available chiral phosphine compounds with various structures as catalyst precursors. In our approach, a catalyst library of chiral quaternary phosphonium salts with a wide variety of structures was readily constructed by benzylation of corresponding commercially available phosphines. We have successfully discovered the effective chiral phosphonium salt catalysts from the library for base-free neutral phase-transfer reactions.

Before close of this review, we should mention the current problem on the development of asymmetric phase-transfer reactions. Although a wide variety of effective asymmetric phase-transfer reactions have already been achieved by the use of well-designed chiral phase-transfer catalysts, a troublesome catalyst screening for each reaction was required to achieve a highly enantioselective reaction. It is difficult to expect the best catalyst for the phase-transfer reaction before the trial, and we must take a time to find the effective catalyst. Several computational studies for asymmetric phase-transfer reactions have recently appeared in the literature.[44] These studies will aid in further understanding of the catalyst-substrate interactions in phase-transfer chemistry, and the understanding will help the selection and design of appropriate chiral phase-transfer catalyst for target transformations.

The design of recently developed chiral phase-transfer catalysts shown in this review may inspire new ideas for design of effective chiral catalysts. Further new-type chiral phase-transfer catalysts for practical organic synthesis will appear in the near future.

Acknowledgements

Part of the research by our group on this topic was partially supported by a Grant-in-Aid for Scientific Research on Innovative Areas “Advanced Molecular Transformations by Organocatalysts” from MEXT (Japan) and The Naito Foundation.

Notes and references

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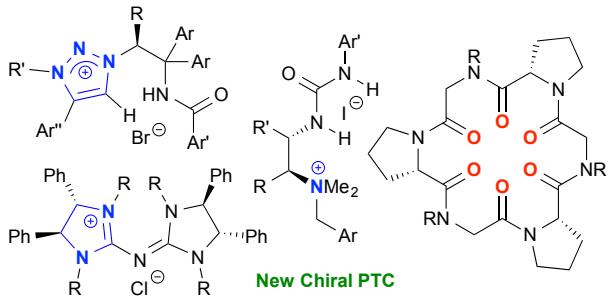
Graphical Abstract



A new generation of chiral phase-transfer catalysts was summarized.