Green Chemistry

Critical Review

Chiral quaternary phosphonium salts as phase-transfer catalysts for environmentally benign asymmetric transformations

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Phase-transfer catalysis has been recognized as a powerful and green sustainable method for organic synthesis in both industry and academia. Since the pioneering studies on enantioselective phase-transfer reactions promoted by cinchona alkaloid-derived tetraalkylammonium salt catalysts, this research field has served as an attractive area for the pursuit of green sustainable chemistry. Although various types of chiral quaternary ammonium salts have been developed for highly selective asymmetric phase-transfer reactions in the last three decades, examples of chiral quaternary phosphonium salts as another onium salt catalysts were limited, and effective catalysts were appeared in relatively recent years. This review summarizes development of chiral quaternary phosphonium salts as phase-transfer and related catalysts for environmentally benign asymmetric transformations.

1. Introduction

Phase-transfer catalysis has been recognized as a powerful 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 preparation in process chemistry (Scheme 1).[1] Since the pioneering studies on enantioselective phase-transfer reactions promoted by cinchona alkaloid-derived tetraalkylammonium salts as chiral phase-transfer catalysts,[2] this research field has served as an attractive area for the pursuit of green sustainable chemistry.[3] A wide variety of highly enantioselective reactions have been achieved by the use of structurally well-defined chiral, nonracemic quaternary onium salt catalysts. Although various types of chiral quaternary ammonium salts have been developed for highly selective asymmetric phase-transfer reactions in the last three decades,[4] examples of chiral quaternary phosphonium salts as another onium salt catalysts were limited, probably due to the instability of chiral quaternary phosphonium salts under ordinary basic phase-transfer conditions. It is expected that corresponding phosphonium ylides are formed from alkyl quaternary phosphonium salts under basic conditions. To over come this problem, several groups tried to develop the chiral quaternary phosphonium salts, and effective catalysts were discovered in relatively recent years. In this context, further developments of effective chiral phosphonium salt catalysts were highly desired, and the research became a hot topic especially in the last few years.[5] This review focuses on development of chiral quaternary phosphonium salts as phase-transfer and related catalysts for environmentally benign asymmetric transformations.

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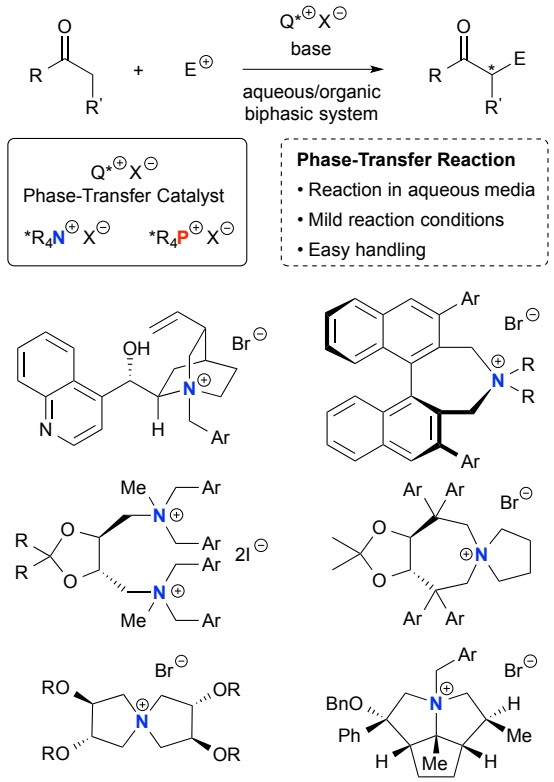
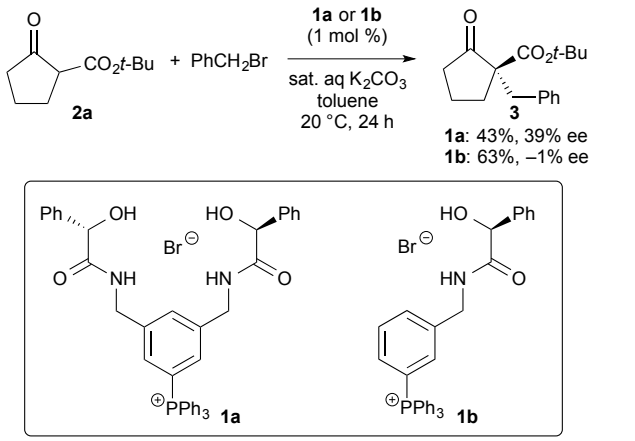


Scheme 1 Features of asymmetric phase-transfer reactions and representative chiral quaternary ammonium salt catalysts.

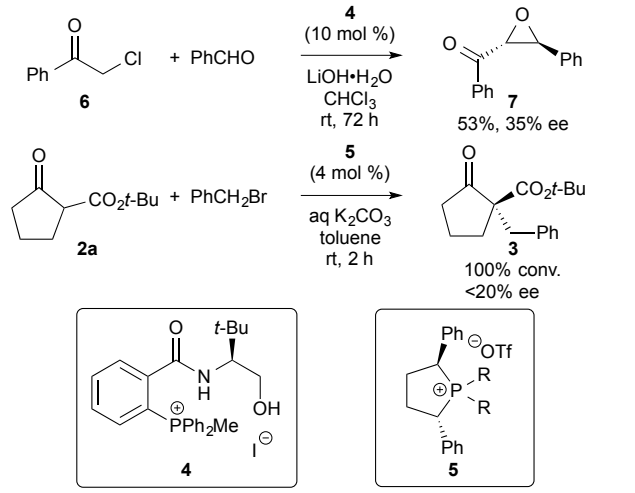
2. Early examples

As a pioneering example of chiral quaternary phosphonium salt as a phase-transfer catalyst, Manabe developed tetraarylphosphonium salt **1a** possessing multiple hydrogen-bonding sites (Scheme 2).[6] The tetraarylphosphonium salts do not form phosphonium ylides under basic phase-transfer conditions, and then the catalysts may work as effective chiral phase-transfer catalysts. The catalyst **1a** was applied to asymmetric benzylation of 2-oxocyclopentanecarboxylate **2a** under aqueous-organic biphasic phase-transfer conditions. As a result of the phase-transfer reaction, benzylation product **3** was obtained in moderate yield and enantioselectivity. The importance of the multiple hydrogen-bonding sites of catalyst **1a** was proved in the comparison with reactions using catalyst **1b** and hydroxy group-protected catalyst. Although the reaction with catalyst **1a** gave product **3** with only moderate selectivity, this is a valuable example of chiral quaternary phosphonium salt as phase-transfer catalyst.



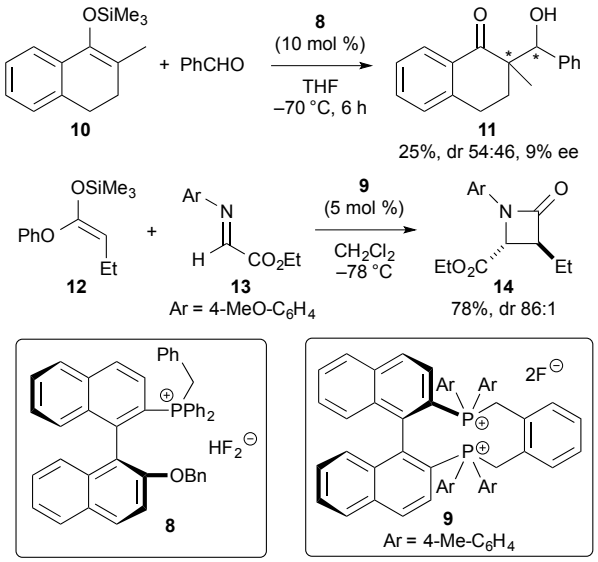
Scheme 2 Pioneering example of chiral quaternary phosphonium salt catalyst.

After the report by Manabe, other groups also developed the new chiral phosphonium salts **4** and **5** (Scheme 3). Multifunctional phosphonium salt **4** was applied to asymmetric Darzens reaction with 2-chloroacetophenone **6** and benzaldehyde to give product **7** in moderate enantioselectivity.[7] Chiral tetraalkylphosphonium salts **5** possessing phospholane backbone were developed by Toffano and co-workers.[8] Although benzylation of 2-oxocyclopentanecarboxylate **2a** was efficiently promoted by catalyst **5** under phase-transfer conditions, product **3** was obtained with low enantioselectivity.



Scheme 3 Chiral quaternary phosphonium salts for asymmetric phase-transfer reactions.

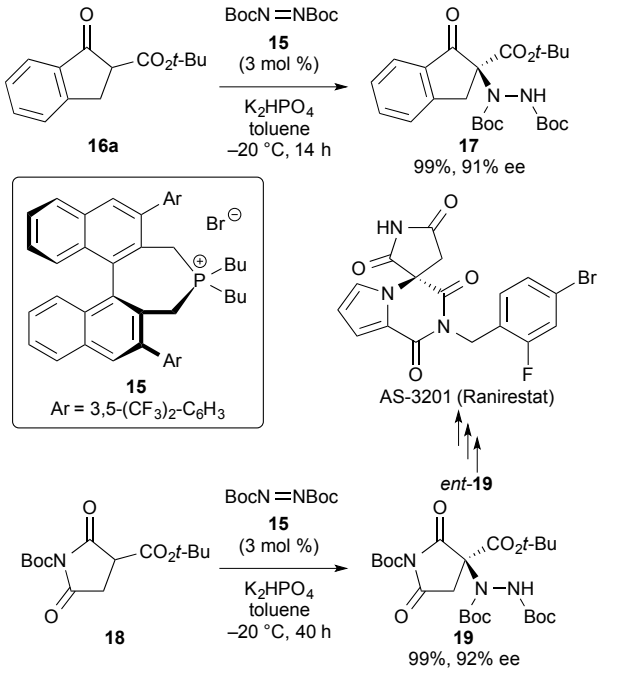
Chiral quaternary phosphonium fluorides **8** and **9** with binaphthyl backbone were also developed, and these catalysts were utilized as Lewis base catalysts (Scheme 4). Shioiri and co-workers reported asymmetric Mukaiyama aldol reaction of silyl enol ether **10** and benzaldehyde catalyzed by catalyst **8**. The reaction gave aldol product **11** in low yield and stereoselectivity.[9] Lectka and co-workers applied the tol-BINAP-derived bis-phosphonium fluoride catalyst **9** to highly diastereoselective synthesis of β-lactam **14** via cycloaddition with ketene silyl acetal **12** and imine **13**.[10] Although high diastereoselectivity was reported in this reaction, the enantioselectivity of product **14** was not mentioned in this report.



Scheme 4 Chiral quaternary phosphonium fluorides with binaphthyl backbone.

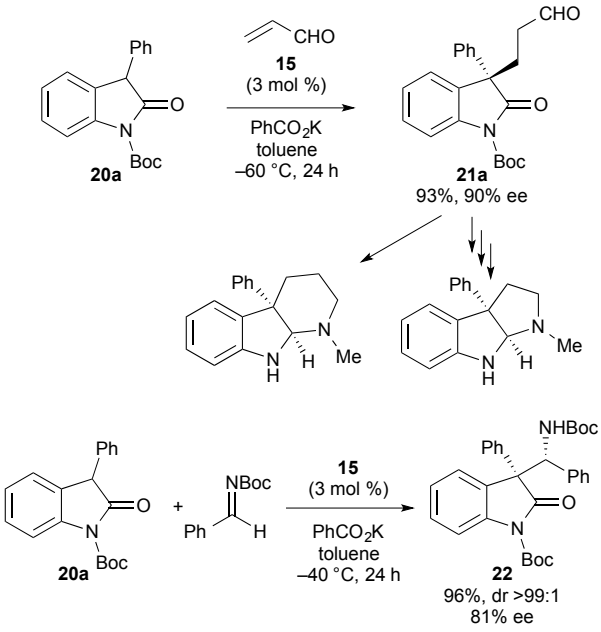
3. Binaphthyl-modified tetraalkylphosphonium bromides

Based on the design of very powerful binaphthyl-modified tetraalkylammonium bromide catalyst developed by Maruoka,[4b] they also prepared phosphonium salt version of the catalyst, such as **15** (Scheme 5).[11] Catalyst **15** was successfully applied to highly enantioselective amination of 1-oxo-2-indanecarboxylate **16a** to give product **17** in high yield and selectivity. Furthermore, this reaction system could be applied to the synthesis of key intermediate **19** of AS-3201 (Ranirestat), as an important drug,[12] by the phase-transfer amination of **18**. It should be noted that this report is the first successful example of highly enantioselective phase-transfer reactions catalyzed by quaternary phosphonium salt. The same amination reactions were also performed by the use of related binaphthyl-modified chiral quaternary ammonium salt catalysts, and the amination products were also obtained with high enantioselectivities.[13]



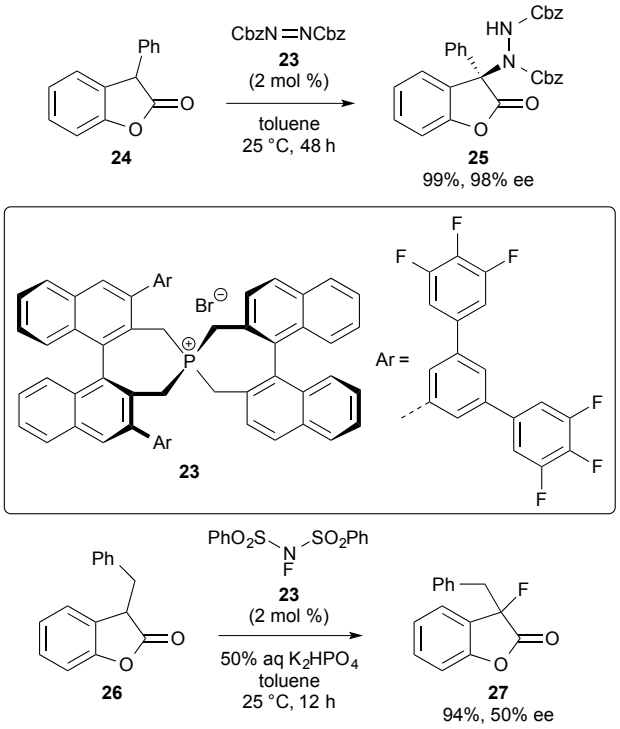
Scheme 5 Binaphthyl-modified tetraalkylphosphonium bromide-catalyzed aminations of β-keto esters.

To demonstrate the further utility of binaphthyl-modified quaternary phosphonium salt **15**, Maruoka and co-workers also examined asymmetric conjugate addition of 3-phenyloxindole **20a** under phase-transfer conditions (Scheme 6).[14] The reaction was efficiently promoted by catalyst **15** to give product **21a**, which was readily transformed to tricyclic compounds as important building blocks, in high yield and enantioselectivity. Catalyst **15** could also be applied to asymmetric Mannich reaction of 3-phenyloxindole **20a** to obtain product **22** with good enantioselectivity.



Scheme 6 Asymmetric conjugate addition and Mannich reactions of oxindole derivative.

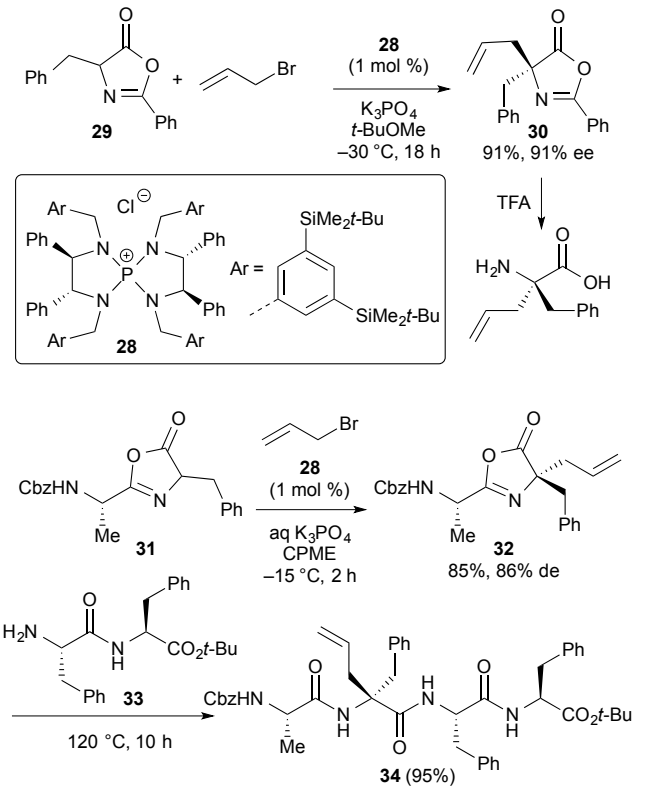
As related catalyst of **15**, spiro-type catalyst **23** was reported by Ma and co-workers (Scheme 7). The catalyst **23** was designed based on the binaphthyl-modified spiro-type tetraalkylammonium bromide catalyst developed by Maruoka.[4a] The catalyst ability of spiro-type phosphonium salt **23** was examined in asymmetric amination of benzofuranone derivative **24**. The amination was efficiently promoted by catalyst **23** under base-free homogeneous conditions to give product **25** in high yield and enantioselectivity.[15] Spiro-type catalyst **23** was also applied to asymmetric fluorination of benzofuranone derivative **26** under aqueous-organic biphasic phase-transfer conditions to obtain product **27** with moderate enantioselectivity.[16]



Scheme 7 Binaphthyl-modified spiro-type tetraalkylphosphonium bromide catalyst.

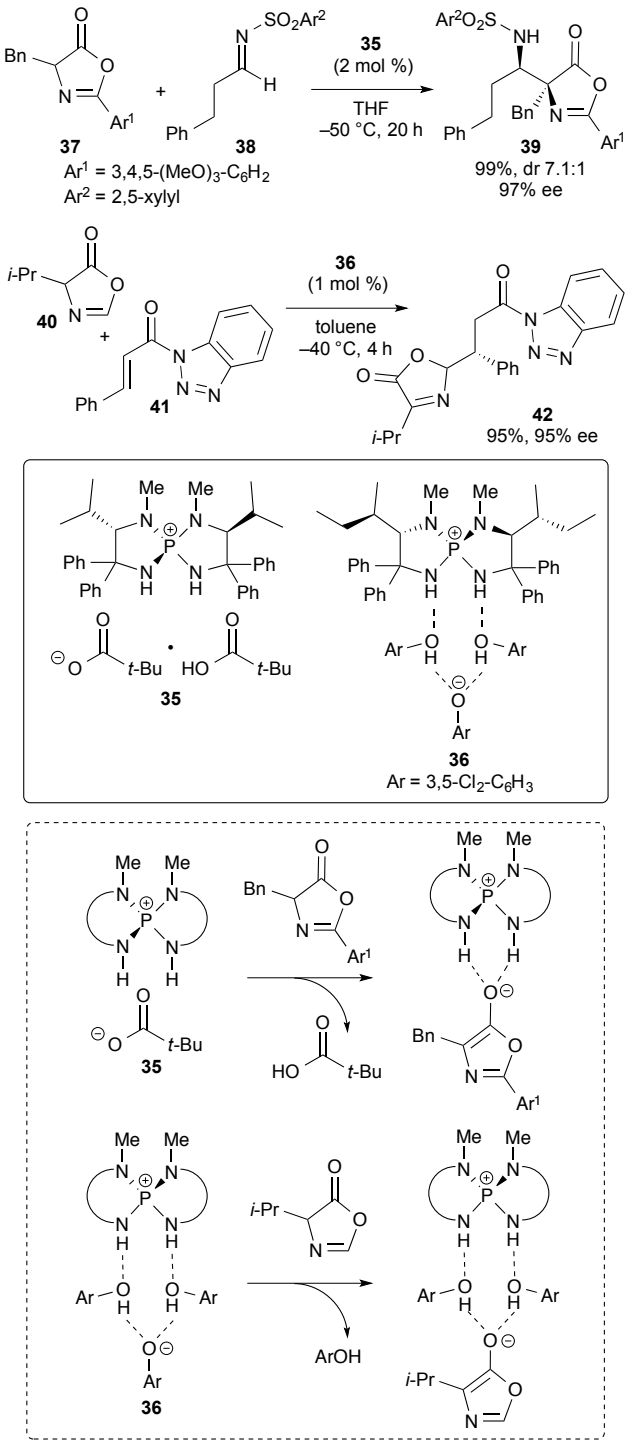
4. Chiral aminophosphonium salts

Ooi and co-workers have successfully demonstrated that *P*-spiro chiral tetraaminophosphonium salt **28** can function as an effective chiral phase-transfer catalyst for the highly enantioselective alkylation of azlactones derived from α-amino acids, such as **29**, as key substrates (Scheme 8).[17] The resulting alkylated azlactone **30** 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 **31** derived from dipeptide underwent stereoselective alkylation with high efficiency by the use of a chiral tetraaminophosphonium salt **28** as a phase-transfer catalyst, and the alkylated azlactone product **32** could be employed directly for peptide ligation with dipeptide **33** to give growing peptides **34**.[18] CPME (cyclopentyl methyl ether) is the solvent of choice to achieve high chemical yield and selectivity.



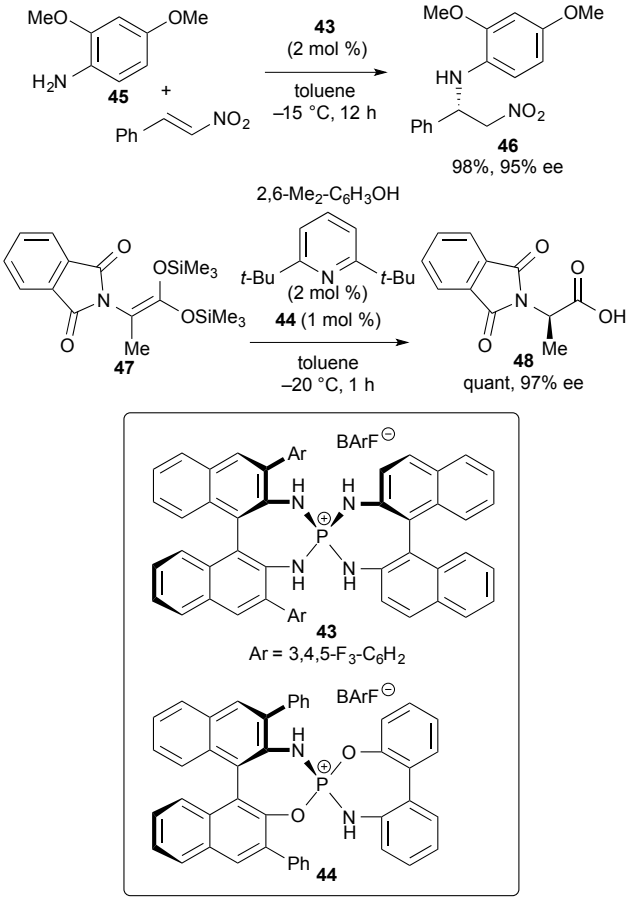
Scheme 8 *P*-Spiro tetraaminophosphonium salt as novel chiral phase-transfer catalyst.

The related *P*-spiro tetraaminophosphonium carboxylate **35** and phenoxide **36** were also developed by Ooi and co-workers, and these catalysts were utilized as chiral Brønsted base catalysts (Scheme 9). Highly stereoselective Mannich reaction of azlactone **37** with imine **38** to obtain product **39** was achieved by the employment of catalyst **35**.[19] Furthermore, catalyst **36** efficiently promoted the highly enantioselective conjugate addition of azlactone **40**, as an acyl anion equivalent, to α,β-unsaturated acylbenzotriazole **41**. The reaction gave product **42** with high enantioselectivity.[20] These catalysts recognized and activated the nucleophiles through the hydrogen-bonding network.



Scheme 9 *P*-Spiro tetraaminophosphonium carboxylate and phenoxide as chiral Brønsted base catalysts.

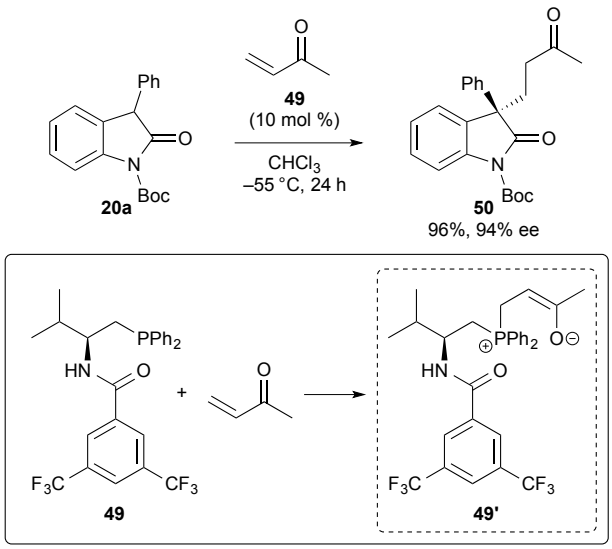
Furthermore, Ooi and co-workers developed binaphthyl-modified *P*-spiro aminophosphonium barfates **43** and **44**, and these catalysts behaved as chiral Brønsted acid catalysts (Scheme 10). Heterochiral tetraaminophosphonium barfate **43** could activate β-nitrostyrene to promote asymmetric conjugate amination with arylamine **45**, and amination product **46** could obtain in high yield and enantioselectivity.[21] Chiral diaminodioxaphosphonium barfate **44** was utilized as a chiral proton catalyst. The asymmetric protonation of ketene disilyl acetal **47** was efficiently promoted by catalyst **44** in the presence of catalytic amount of 2,6-di-*tert*-butylpyridine and 2,6-dimethylphenol as a stoichiometric proton source to give α-amino acid derivative **48** with high enantioselectivity.[22] These types of chiral Brønsted acid catalysts could also apply to other important asymmetric transformations.[23]



Scheme 10 Binaphthyl-modified *P*-spiro aminophosphonium barfates as chiral Brønsted acid catalysts.

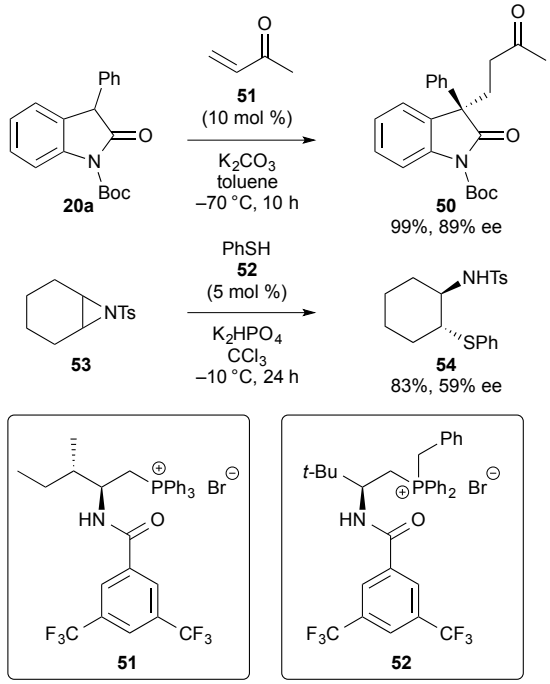
5. Amino acid-derived bifunctional phosphonium salts

Lu and co-workers reported amino acid-derived bifunctional chiral phosphine **49**-catalyzed asymmetric conjugate addition of 3-phenyloxindole **20a** to obtain product **50** in high yield and enantioselectivity (Scheme 11). The key of this catalytic system was in situ formation of phosphonium betaine **49'** by the reaction of phosphine **49** and methyl vinyl ketone as an electrophile for this reaction.[24]



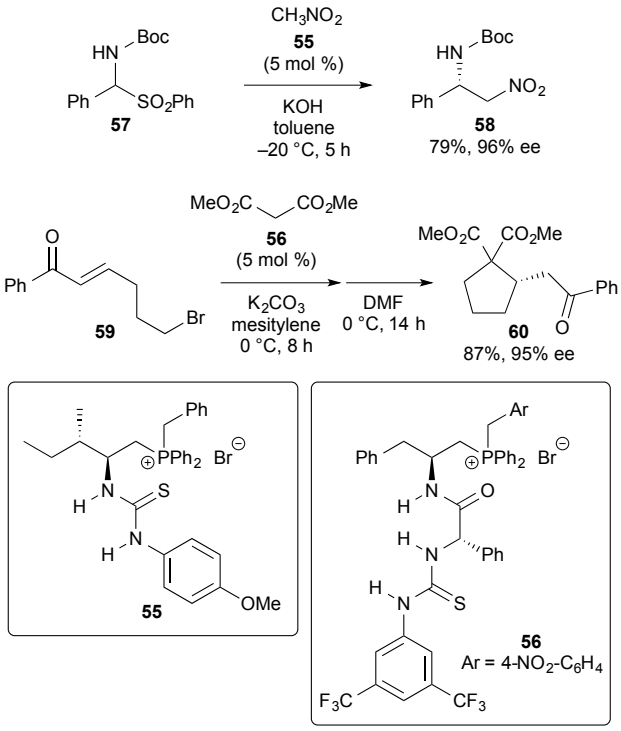
Scheme 11 In situ-generated chiral phosphonium betaine catalyst derived from amino acid.

Zhao and co-workers developed chiral bifunctional quaternary phosphonium bromides **51** and **52** derived from amino acids (Scheme 12). Chiral quaternary phosphonium bromide **51** possessing an amide moiety efficiently promoted asymmetric conjugate addition of 3-phenyloxindole **20a** under phase-transfer conditions to give conjugate adduct **50** in high yield and enantioselectivity.[25] The related catalyst **52** could apply to asymmetric desymmetrization of *meso*-aziridine **53** with thiophenol under phase-transfer conditions, and product **54** was obtained with moderate enantioselectivity.[26]



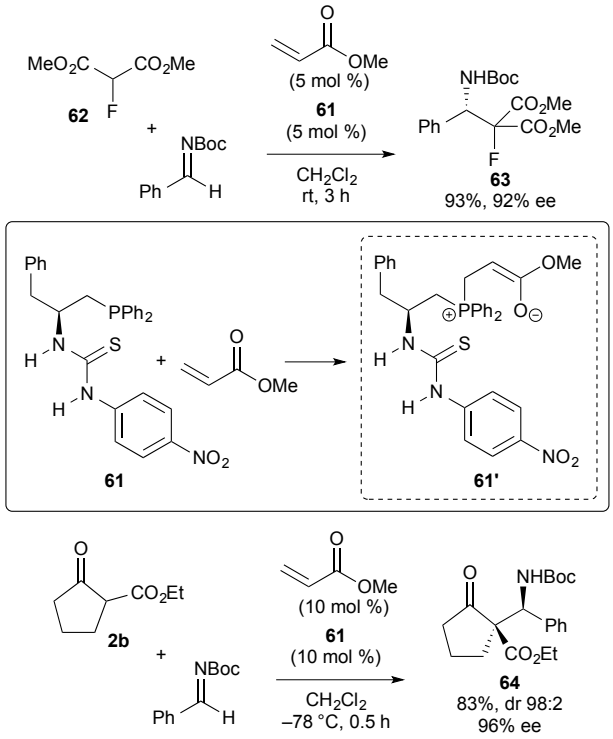
Scheme 12 Amino acid-derived chiral quaternary phosphonium bromides possessing an amide moiety.

As related catalysts, amino acid-derived chiral bifunctional quaternary phosphonium bromides **55** and **56** possessing a thiourea moiety were also developed by Zhao and co-workers (Scheme 13). Bifunctional phosphonium bromide catalyst **55** was used for asymmetric aza-Henry reaction of imine precursor **57** with nitromethane to give product **58** with high enantioselectivity.[27] The same highly enantioselective aza-Henry reaction was also achieved with amino acid-derived bifunctional chiral ammonium salt as the related catalyst.[28] Dipeptide-derived multifunctional phosphonium bromide **56** was effective catalyst for asymmetric cyclization via tandem Michael addition/intramolecular S_N2 reaction with substrate **59** and malonate.[29] As a result of the tandem reaction, cyclopentane derivative **60** was obtained in good yield with high enantioselectivity. In both cases, thiourea moiety of the catalyst was essential to achieve highly enantioselective reactions.



Scheme 13 Amino acid-derived chiral quaternary phosphonium bromides possessing a thiourea moiety.

Based on the method for asymmetric reactions using in situ-generated phosphonium betaine catalyst by Lu in Scheme 11,[24] Zhao and co-workers reported enantioselective reactions using in situ-generated phosphonium betaine catalyst **61'** possessing a thiourea moiety (Scheme 14). Highly enantioselective Mannich reaction with fluoromalonate **62** and benzaldehyde-derived *N*-Boc imine was achieved by in situ-generated catalyst **61'**, which was formed from chiral phosphine **61** and acrylate. As a result of the reaction, product **63** was obtained in high yield and enantioselectivity.[30] This catalyst system was also applied to asymmetric Mannich reaction of 2-oxocyclopentanecarboxylate **2b** to obtain product **64** with high stereoselectivity.[31]

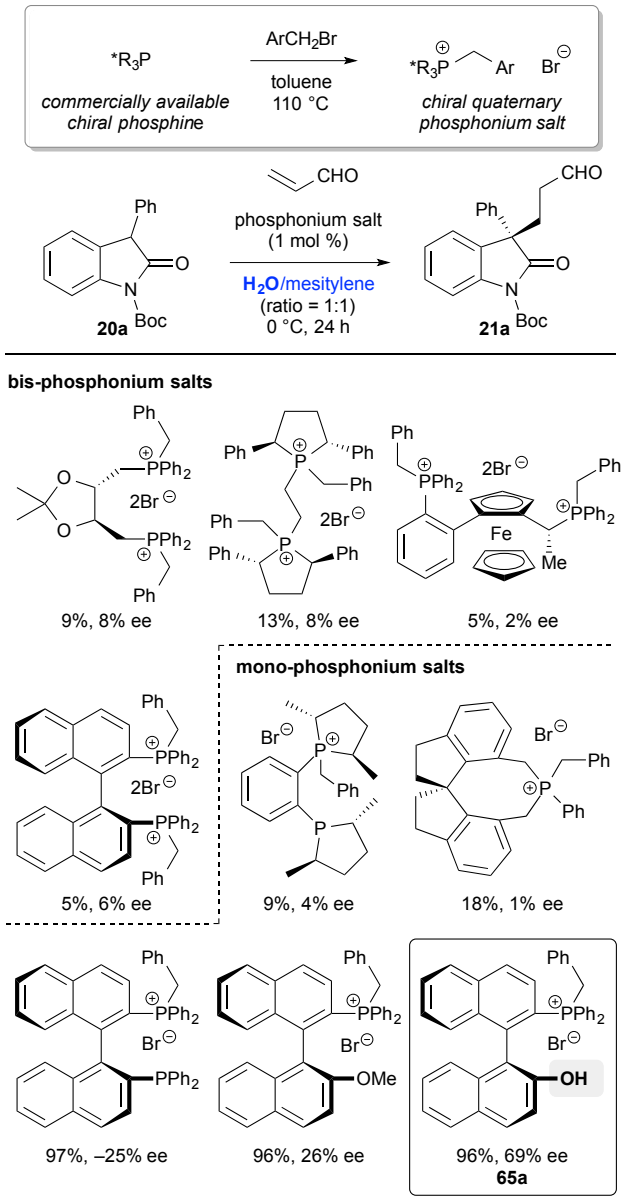


Scheme 14 In situ-generated chiral phosphonium betaine catalyst possessing a thiourea moiety.

6. Commercially available chiral phosphine-derived quaternary phosphonium bromides

6.1. Chiral phosphine ligand-derived bis- and mono-phosphonium salts

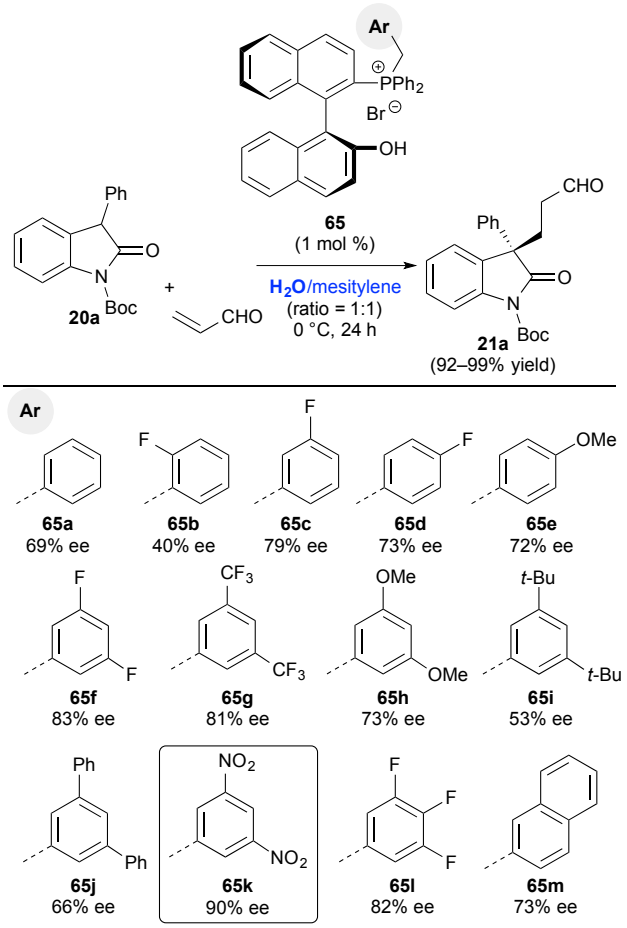
We also examined development of effective chiral quaternary phosphonium bromides as phase-transfer catalysts. Our approach for the discovery of effective chiral quaternary phosphonium salts relies on the use of commercially available chiral phosphine compounds as catalyst precursors. This approach allows facile construction of a catalyst library of chiral quaternary phosphonium salts with various structures (Scheme 15).[32,33] A catalyst library of chiral quaternary phosphonium salts with various structures was readily constructed by benzylation of corresponding commercially available phosphines. As a model reaction to examine the catalyst ability of these phosphonium salts, asymmetric conjugate addition of 3-phenyloxindole **20a** to acrolein under base-free neutral phase-transfer conditions as an environmentally benign reaction system was selected.[34] It is expected that phosphonium ylides are not formed from phosphonium salts under the base-free neutral phase-transfer conditions, and we can efficiently find the effective chiral quaternary phosphonium salt catalysts. Although chiral bis-phosphonium salts as phase-transfer catalysts for this conjugate addition showed low reactivities likely due to lack of lipophilicity of the catalysts,[34f] some of lipophilic mono-phosphonium salts efficiently promoted the reaction to afford the product **21a** in high yields. Among these catalysts, bifunctional catalyst **65a** possessing a hydroxy group at 2'-position of binaphthyl moiety showed good enantioselectivity (69% ee).



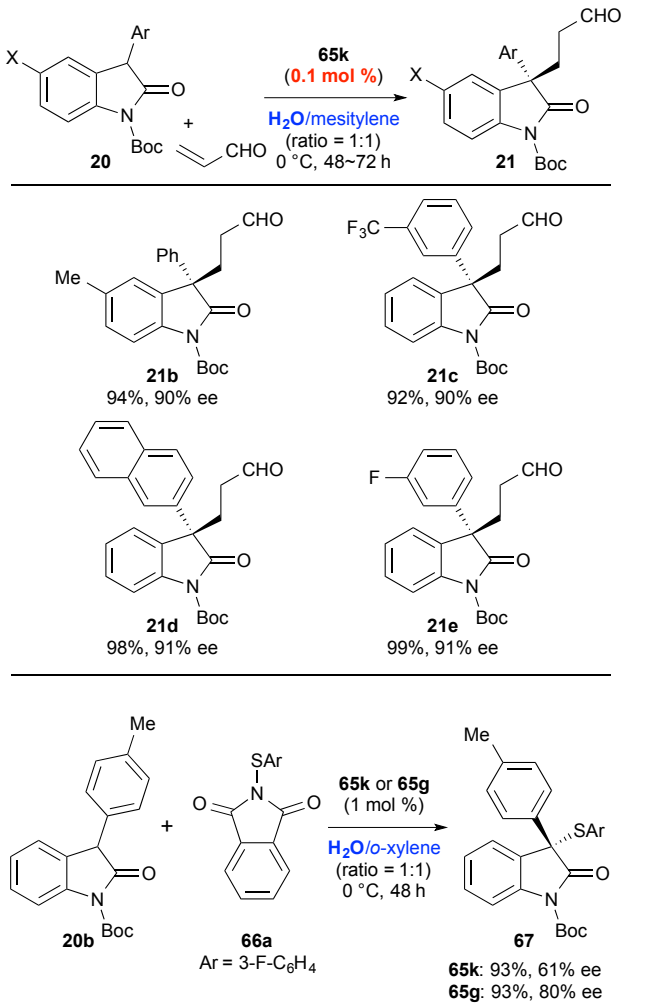
Scheme 15 Library of chiral quaternary phosphonium bromides.

6.2. MOP ligand-derived quaternary phosphonium salts possessing a hydroxy group

The structure of catalyst **65a** was further optimized by the introduction of various arylmethyl groups on the phosphorus (Scheme 16). A wide variety of arylmethyl bromides were employed to prepare a catalyst library with various electronic and steric environments, and the prepared catalysts **65a–m** were applied to asymmetric conjugate addition of 3-phenyloxindole **20a** with acrolein under base-free neutral phase-transfer conditions. The catalysts generally promoted the reaction efficiently, and introduction of nitro groups as a strong electron-withdrawing group at 3,5-positions of aryl moiety (**65k**) gave highest enantioselectivity (90% ee).



Scheme 16 Optimization of catalyst structure.



Scheme 17 Asymmetric conjugate additions and sulfenylation of 3-aryloxindoles.

With the effective chiral quaternary phosphonium salt in hand, we studied the substrate generality of the asymmetric conjugate addition of various 3-aryloxindoles **20** to acrolein under base-free phase-transfer conditions (Scheme 17). To demonstrate the practicability of the present reaction, only 0.1 mol % of chiral catalyst **65k** was used in these asymmetric conjugate additions. The introduction of electron-withdrawing and electron-donating substituents to both the oxindole core and the 3-aryl group uniformly gave the products **21** in excellent yields with high enantioselectivities at low catalyst loading under base-free neutral phase-transfer conditions. To further expand the synthetic utility of quaternary phosphonium salts **65**, we also examined the asymmetric sulfenylation of 3-aryloxindole **20b** with *N*-(arylthio)phthalimide **66a** under base-free phase-transfer conditions. Although the reaction with catalyst **65k** gave a product **67** in moderate enantioselectivity, catalyst **65g** improved the enantioselectivity to give the sulfenylation product **67** in high yield with good enantioselectivity.

7. Binaphthyl-modified bifunctional phosphonium bromides possessing an amide or a urea group

In our study of new phosphonium salts in Schemes 15–17, we found that the hydroxy group of catalyst **65** was crucial for obtaining high enantioselectivity in the conjugate additions of 3-substituted oxindoles. Based on this observation, we became interested in the design of new bifunctional phosphonium salts, which possess an amide moiety instead of a hydroxy group. The acidity of the amide (NH) in these catalysts can be easily tuned by introducing different substituents to the nitrogen (X–R). Additionally, the steric environment of the amide-type bifunctional catalysts can be controlled by tuning the steric size of the R group on the amide moiety as well as the aryl methyl group on the phosphorus (Fig. 1).

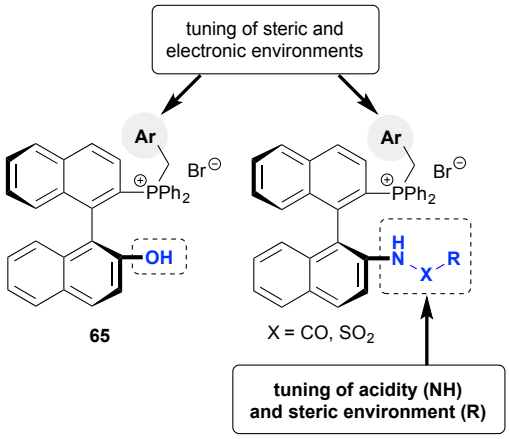
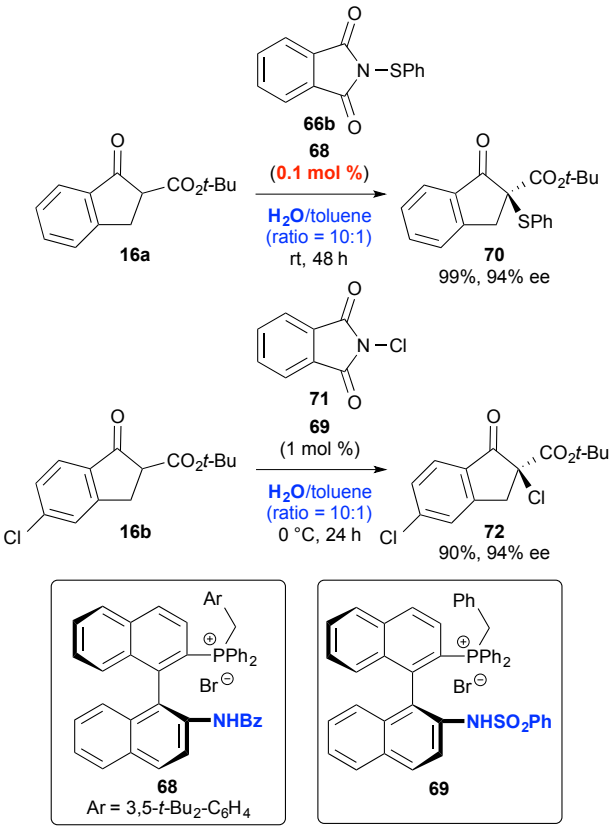


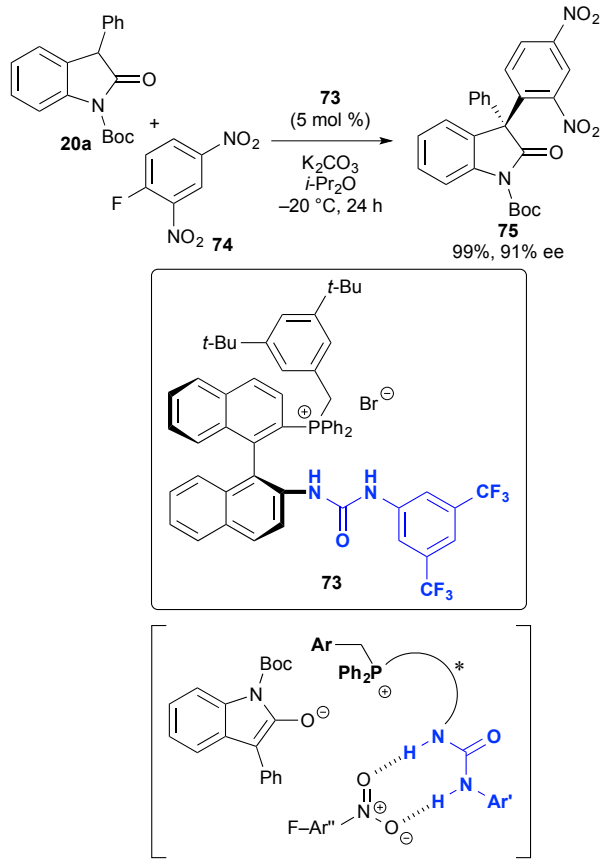
Fig. 1 Bifunctional quaternary phosphonium salts.

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 (Scheme 18).[35] The reaction between *tert*-butyl 1-oxo-2-indanecarboxylate **16a** and *N*-(phenylthio)phthalimide **66b** in H_2O/toluene (ratio = 10:1) took place in the presence of catalyst **68** (0.1 mol %) possessing a benzamide group at 25 °C over 48 h, affording the sulfenylation product **70** in excellent yield with high enantioselectivity (94% ee). Various 1-oxo-2-indanecarboxylates and *N*-(arylthio)phthalimides could be applied to this highly enantioselective sulfenylation under base-free neutral phase-transfer conditions at low catalyst loading. 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 **16b** and *N*-chlorophthalimide **71** with benzamide-substituted catalyst **68** gave a product **72** in moderate enantioselectivity, benzenesulfonamide-substituted catalyst **69** improved the enantioselectivity to give the chlorination product **72** in high yield and enantioselectivity. 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. Various β-keto esters could be employed for the chlorination with catalyst **69**, and products were obtained with good to high enantioselectivities.



Scheme 18 Asymmetric sulfenylation and chlorination with bifunctional quaternary phosphonium bromides possessing an amide moiety.

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.[36] 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 **20a** and electron deficient aryl fluoride **74** under the influence of chiral bifunctional phosphonium bromides as phase-transfer catalysts (Scheme 19).[37] Although catalysts **65**, **68**, and **69** possessing a hydroxy group or an amide group gave arylation product **75** in low to moderate enantioselectivities, the reaction with newly-designed chiral bifunctional quaternary phosphonium bromide **73** possessing a urea moiety gave product **75** in high yield and enantioselectivity. It is expected that the urea moiety of catalyst **73** interacts with nitroarene **74** through double hydrogen-bonding, giving rise to a well organized transition states that provides high stereocontrol.



Scheme 19 Asymmetric S_NAr reaction with bifunctional quaternary phophonium bromide possessing a urea moiety.

8. Conclusions

Development of chiral quaternary phosphonium salts for environmentally benign asymmetric transformations was summarized in this review. Although a pioneering example of chiral quaternary phosphonium salt as a phase-transfer catalyst was reported by Manabe in 1998,[6] the research on chiral quaternary phosphonium salts proceeded slowly in comparison with chiral quaternary ammonium salts. In 2008, the first successful example of highly enantioselective phase-transfer reactions catalyzed by quaternary phosphonium salt was reported by Maruoka.[11] After this report, the research on effective chiral quaternary phosphonium salts became a hot topic in the field of organocatalysis, and various effective phosphonium salt catalysts have been developed in the last several years. Chiral aminophosphonium salt catalysts, developed by Ooi, were used not only as phase-transfer catalysts but also as Brønsted base and acid catalysts.[17–23] As other types of chiral quaternary phosphonium salt, Zhao reported bifunctional catalysts derived from amino acids.[25–29] Our group also reported an efficient approach for the discovery of effective chiral quaternary phosphonium salts relies on the use of commercially available chiral phosphine compounds as catalyst precursors.[32] These catalysts were successfully applied to highly enantioselective reactions under base-free neutral phase-transfer conditions as an environmentally benign reaction system.[34] Although prominent advantages of chiral phosphonium salts in comparison with chiral ammonium salts are not clear at this stage, the high potential ability of chiral quaternary phosphonium salts can be recognized in this review. Further development of new chiral phosphonium salt catalysts will be examined, and the catalysts will achieve environmentally benign asymmetric transformations in the near future.

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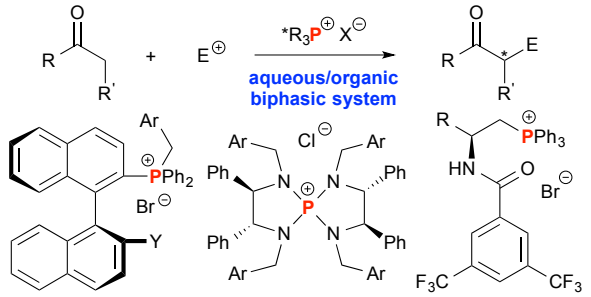
Graphical abstract



Development of chiral quaternary phosphonium salt catalysts for environmentally benign asymmetric phase-transfer reactions was summarized.