Organic & Biomolecular Chemistry

REVIEW

Chiral sulfide and selenide catalysts for asymmetric halocyclizations and related reactions

Ryuichi Nishiyori, Taiki Mori, Ken Okuno and Seiji Shirakawa*

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

DOI: 10.1039/x0xx00000x

Asymmetric organocatalysis using well-designed artificial chiral molecular catalysts is one of the most reliable methods to create important chiral compounds in a highly enantioenriched form. A wide variety of efficient asymmetric transformations have been developed by utilizing well-designed chiral organocatalysts. Among the wide variety of organocatalysts, chiral amine and phosphine catalysts that utilize the characteristics of group 15 elements are the most extensively employed for asymmetric transformations. By comparison with chiral amine and phosphine catalysts, the use of chiral sulfide catalysts has remained limited and under-developed. The catalytic abilities of chiral sulfide organocatalysts were initially investigated using Corey-Chaykovsky-type asymmetric epoxidations and related reactions via the formation of sulfonium ylide intermediates. Unfortunately, the types of asymmetric reactions with chiral sulfide catalysts are limited in comparison with chiral amine-catalyzed asymmetric reactions, and development of other catalytic reactions using chiral sulfides is highly desired. Several research groups have recently discovered that newly designed chiral sulfide catalysts are quite effective for asymmetric halocyclizations. This review summarizes recent achievements in chiral sulfide-catalyzed enantioselective halocyclizations and halogenations. The asymmetric catalyses of related chiral selenides that are used in enantioselective halogenations are also introduced.

1. Introduction

The design and development of new artificial chiral molecular catalysts has progressed in the field of asymmetric organocatalysis over the past two decades.[1] A wide variety of efficient asymmetric transformations have been achieved by utilizing newly designed chiral organocatalysts. The catalytic abilities of chiral amine compounds, which are representative organocatalysts, have been the most extensively investigated in this field.[2] Among the effective chiral organocatalysts, chiral sulfides remain under-developed by comparison with other more-established versions such as chiral amine and phosphine organocatalysts.[3] The catalytic abilities of chiral sulfide organocatalysts were initially investigated via Corey-Chaykovsky-type asymmetric epoxidations (Scheme 1a).[4] Although several chiral sulfide molecules realized the catalytic highly enantioselective epoxidations[5] and related reactions[6] via the formation of chiral sulfonium ylide intermediates, the types of asymmetric reactions with chiral sulfide catalysts were still limited in comparison with chiral amine-catalyzed asymmetric reactions. In recent years, several research groups have discovered different methods for catalysis via the utilization of chiral sulfide catalysts.[7,8] Highly enantioselective halocyclizations of unactivated alkene substrates have been achieved using newly designed chiral sulfide catalysts (Scheme 1b). A key for the chiral sulfide-catalyzed halocyclizations is the formation of halosulfonium salt intermediates.[9] Herein we summarize recent advances in chiral sulfide organocatalysis for asymmetric halocyclizations and

Ryuichi Nishiyori was born in 1994, in Fukuoka, Japan. He studied environmental science at Nagasaki University, and obtained his bachelor's and master's degrees. He is currently doctoral course student in Nagasaki University. He was awarded JSPS fellow (DC1).

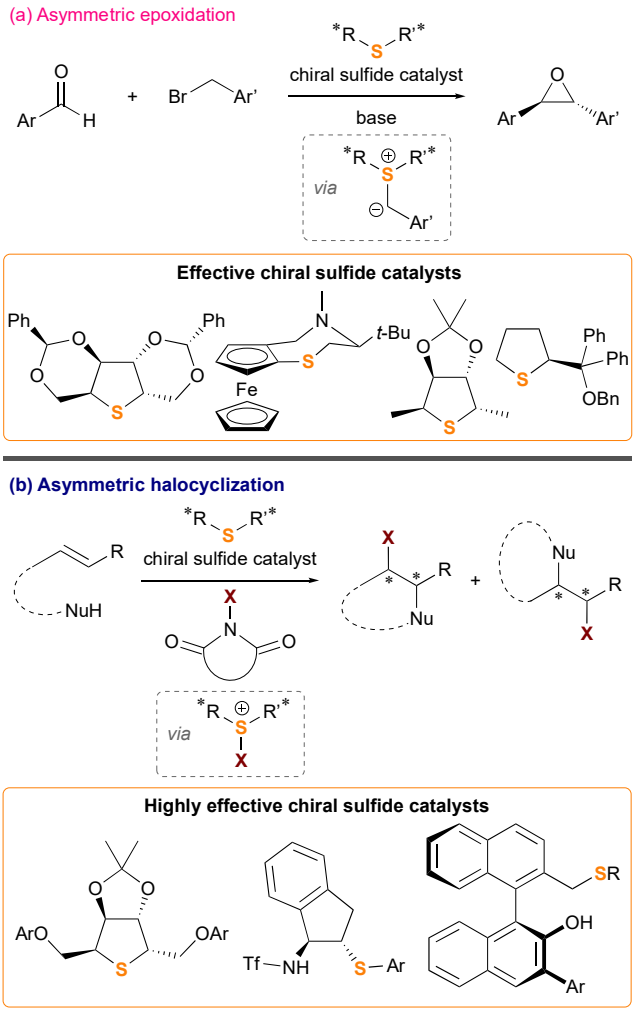
Taiki Mori was born in 2000, in Fukuoka, Japan. He entered Nagasaki University in 2019. He started on research of organic chemistry and green chemistry with Prof. Shirakawa in 2021.

Ken Okuno was born in 1996, in Nagasaki, Japan. He studied environmental science at Nagasaki University, and obtained his bachelor's and master's degrees. He is currently doctoral course student in Nagasaki University.

Department of Environmental Science, Graduate School of Fisheries and Environmental Sciences, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan. E-mail: seijishirakawa@nagasaki-u.ac.jp

† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

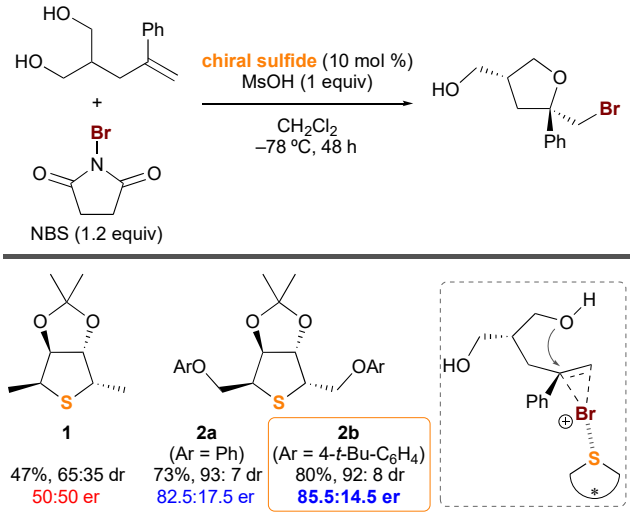
halogenations.[10] The related chiral selenide organocatalysts for asymmetric halocyclizations are also introduced.



Scheme 1 Effective chiral sulfide organocatalysts for asymmetric reactions.

2. Tetrahydrothiophene-type chiral sulfide and selenide catalysts

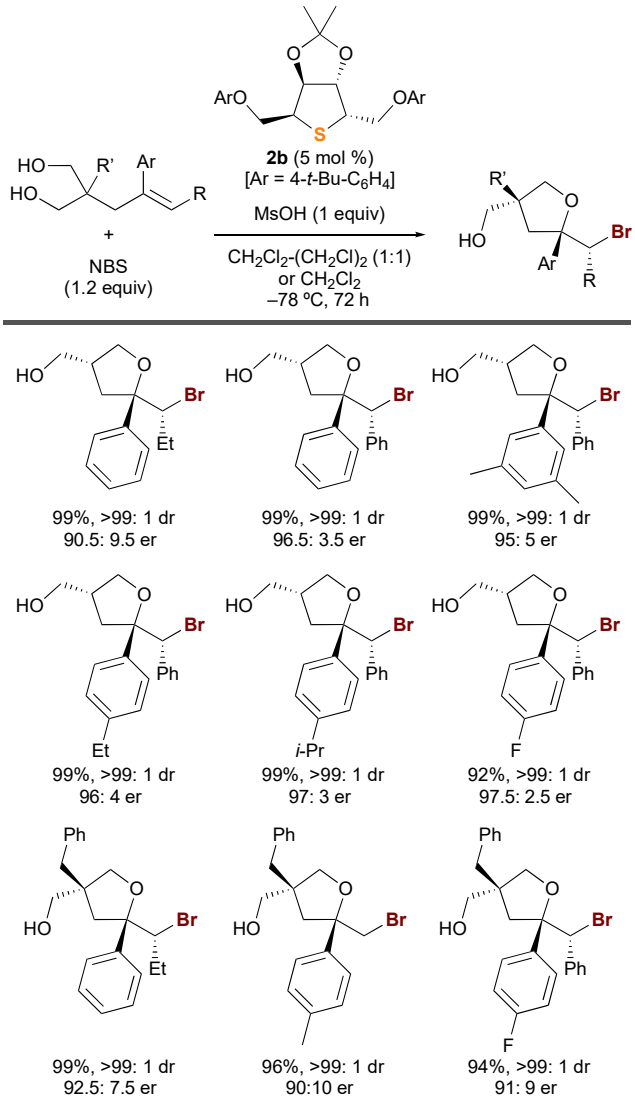
Based on the success of tetrahydrothiophene-type chiral sulfide catalysts in asymmetric epoxidations,[5] Yeung and co-workers have been interested in other forms of catalysis that can be accomplished using tetrahydrothiophene-type catalysts. They researched the novel catalytic abilities of tetrahydrothiophene-type chiral sulfides in the desymmetrizing bromoetherifications of alkenoic diols for the preparation of highly substituted chiral tetrahydrofurans (Scheme 2).[11] Although the reaction using a chiral sulfide **1**, which is an effective catalyst for asymmetric epoxidation,[5c] gave a bromoetherification product in racemic form, chiral tetrahydrothiophene catalysts **2** derived from D-mannitol provided a chiral tetrahydrofuran product in good diastereo- and enantioselectivities. This reaction is believed to be promoted via the activation of the alkene portion of a substrate by a chiral bromosulfonium salt intermediate.



Scheme 2 Tetrahydrothiophene-type chiral sulfide catalysts for desymmetrizing bromoetherification.

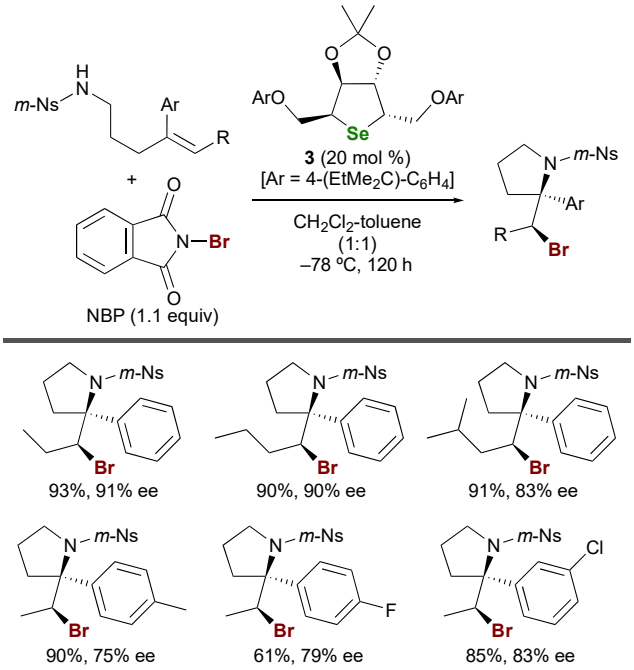
Optimized tetrahydrothiophene-type chiral sulfide catalyst **2b** has been used to test the substrate scope for the desymmetrizing bromoetherifications of alkenoic diols (Scheme 3).[11] Under the influence of sulfide catalyst **2b** (5 mol %), highly substituted tetrahydrofuran products have been obtained in excellent yields and diastereoselectivities with good to high enantioselectivities.

Seiji Shirakawa received his Ph.D. from Kyoto University under the guidance of Prof. Keiji Maruoka. He was awarded JSPS postdoctoral fellow to carry out postdoctoral work with Prof. James L. Leighton at Columbia University and Prof. Shū Kobayashi at The University of Tokyo. He was appointed as an assistant professor at Nihon University, and as an associate professor at Kyoto University. He is currently an associate professor in Nagasaki University since 2014. His current interests are organocatalysis, green chemistry, and planetary health.



Scheme 3 Catalytic asymmetric synthesis of highly substituted tetrahydrofurans.

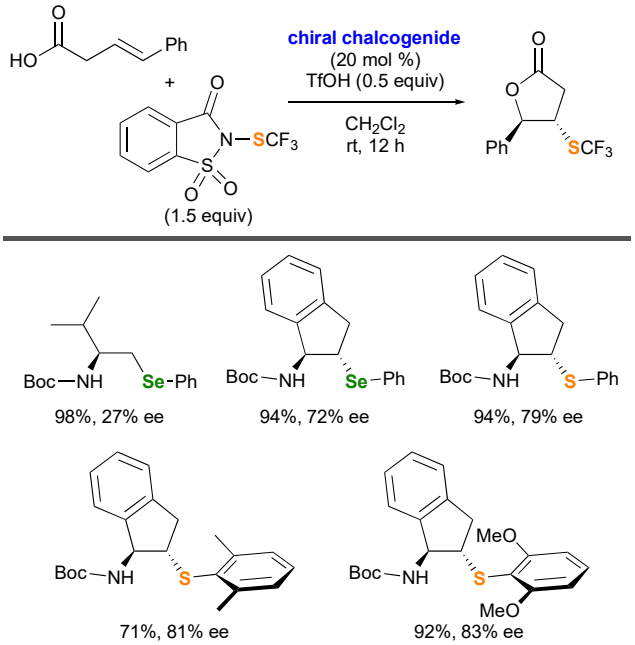
Yeung et al. also demonstrated the utility of related D-mannitol-derived chiral selenide catalyst **3** in asymmetric bromoaminocyclizations (Scheme 4).[12] Enantioselective bromoaminocyclizations of alkenoic amides were efficiently promoted by chiral selenide **3** to give chiral pyrrolidine products bearing a quaternary stereocenter in a highly stereoselective manner.



Scheme 4 D-Mannitol-derived chiral selenide catalyst for asymmetric bromoaminocyclization.

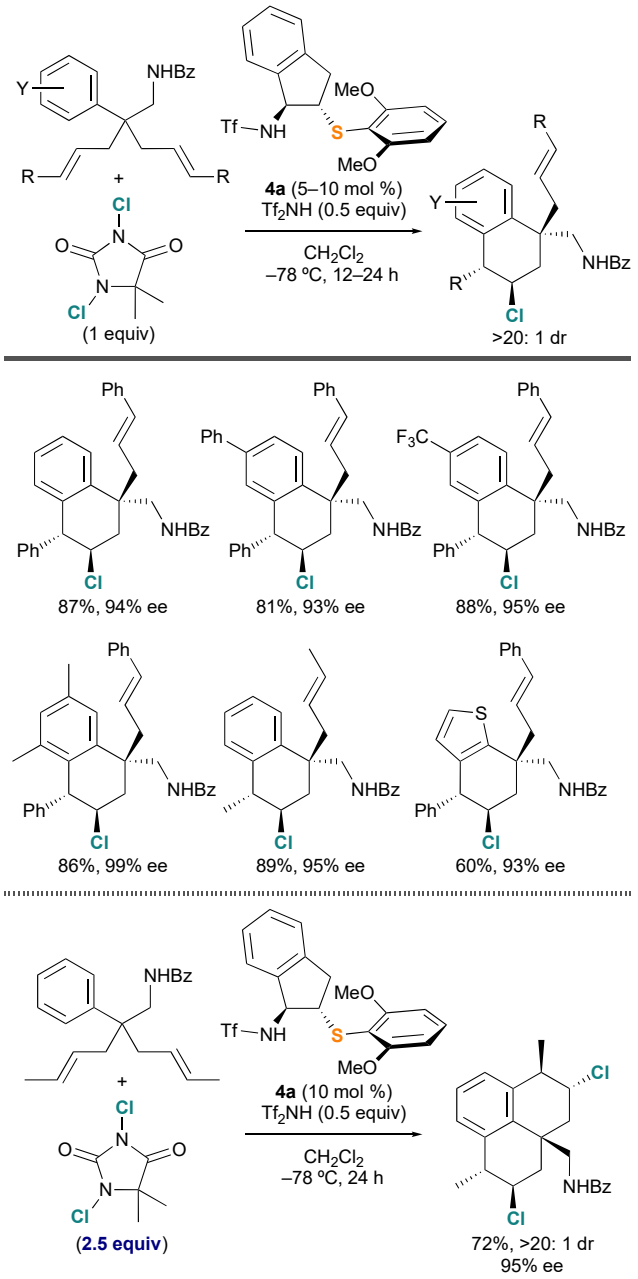
3. Indane-based chiral sulfide and selenide catalysts

Indane-based chiral chalcogenide catalysts bearing an amide moiety were developed by Zhao and co-workers.[8] The catalytic ability of indane-based chalcogenide catalysts was first examined in asymmetric thiolactonization (Scheme 5).[13] By comparison with acyclic chiral chalcogenide catalysts, conformationally fixed indane-based catalysts behaved as more effective catalysts in terms of enantioselectivity. In the present asymmetric thiolactonization, indane-based chiral sulfide catalysts provided better enantioselectivities than corresponding chiral selenide catalysts. Zhao et al. also reported other asymmetric thiofunctionalization reactions using indane-based chiral chalcogenide catalysts,[14] which were recently summarized in their personal account paper.[8]



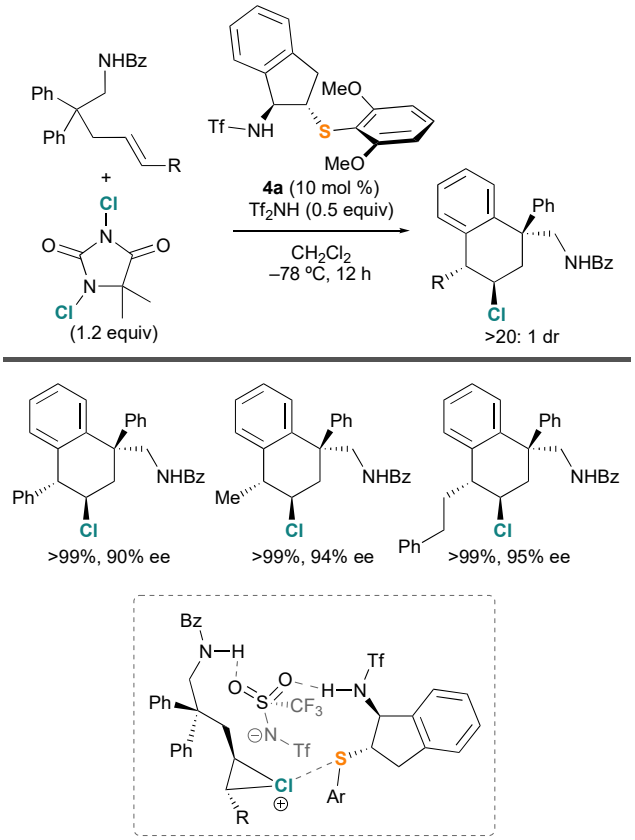
Scheme 5 Catalytic ability of indane-based chiral chalcogenides in asymmetric thiolactonization.

With an effective structural motif of chiral sulfide catalysts in hand, Zhao et al. examined chiral sulfide-catalyzed enantioselective chloro-carbocyclizations for the preparation of functionalized chiral tetralins (Scheme 6).[15] Desymmetrizing chloro-carbocyclizations of dialkenes were efficiently promoted using optimized indane-based chiral sulfide catalyst **4a** to yield the targeted highly substituted chiral tetralins in high enantioselectivities. The reaction system could be applied to the stereoselective construction of tricyclic compounds by the use of excess amounts of a chlorinating reagent. It should be noted that both sulfide catalyst and the acid additive, such as a bis(trifluoromethanesulfonyl)imide, were essential to promote the present chloro-carbocyclizations.



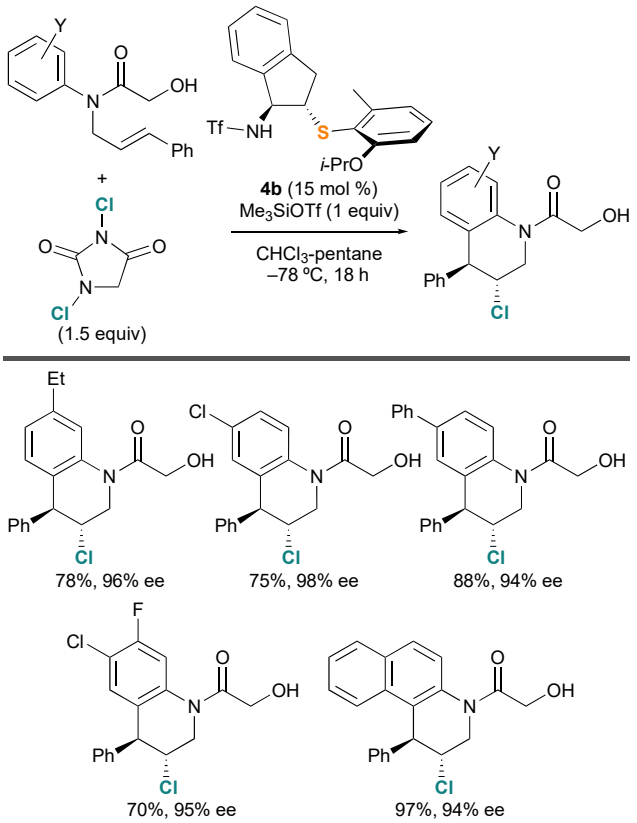
Scheme 6 Indane-based chiral sulfide-catalyzed desymmetrizing chloro-carbocyclizations of dialkenes.

The related asymmetric chloro-carbocyclizations of diaryl alkenes were also examined under the same catalytic conditions using sulfide **4a** (Scheme 7).[15] The targeted chiral tetralin products were obtained in high yields and enantioselectivities as a result of the Friedel-Crafts-type nucleophilic attack by one of the phenyl groups to the cyclic chloronium ion intermediate.



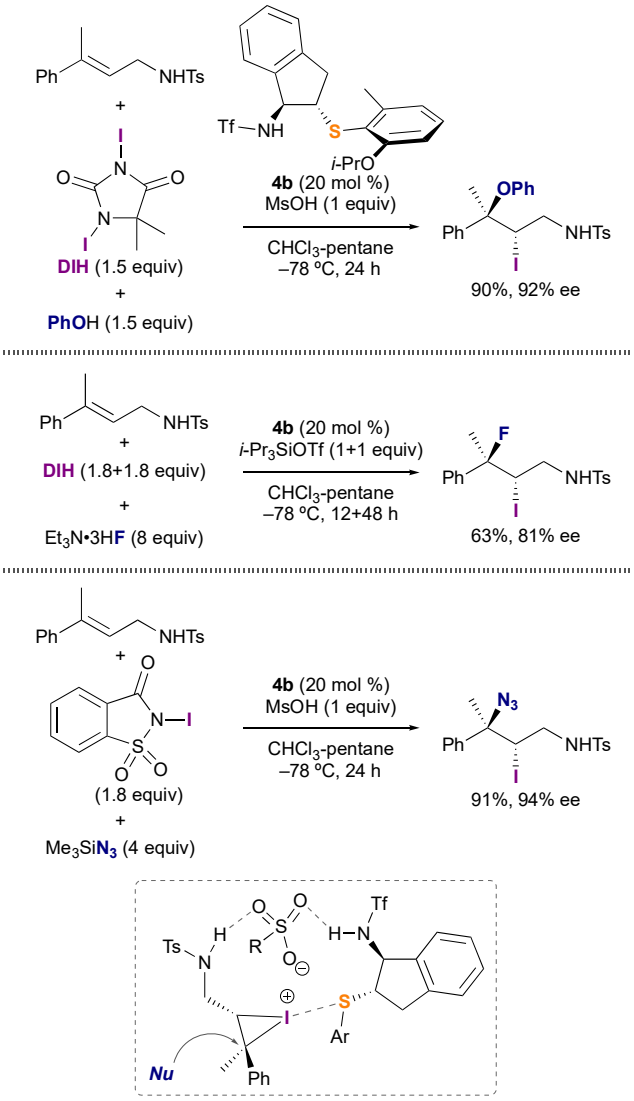
Scheme 7 Asymmetric chloro-carbocyclizations of diaryl alkenes using an indane-based chiral sulfide catalyst.

Catalytic asymmetric synthesis of chiral tetrahydroquinoline derivatives, which are important nitrogen heterocycles, was also realized via asymmetric chloro-carbocyclization using an indane-based chiral sulfide catalyst (Scheme 8).[16] Sulfide **4b** was used under the optimized reaction conditions to prepare functionalized chiral 1,2,3,4-tetrahydroquinolines in a highly enantioselective manner.



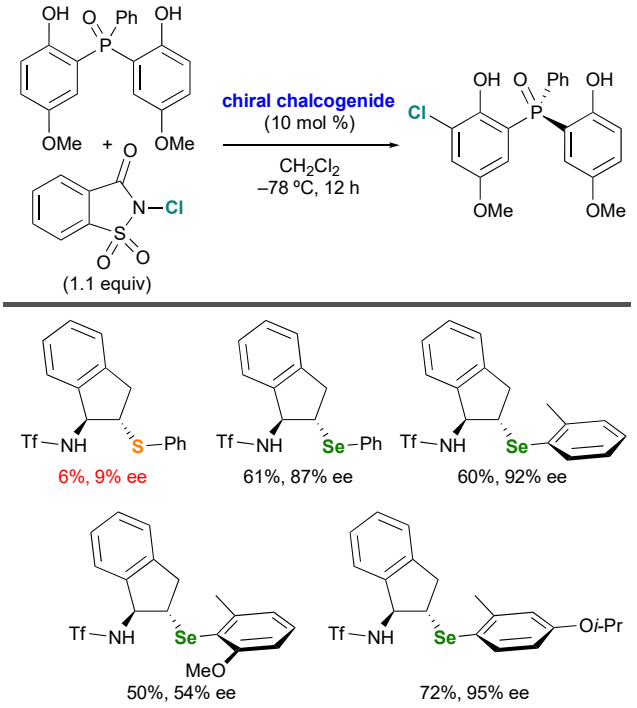
Scheme 8 Catalytic asymmetric chloro-carbocyclizations for the synthesis of chiral tetrahydroquinolines using an indane-based chiral sulfide.

The usefulness of indane-based chiral sulfide catalyst **4b** was further demonstrated in the intermolecular iodofunctionalizations of substituted allylamine derivatives (Scheme 9).[17] Phenol, fluoride, and azide were employed as nucleophiles with iodinating reagents to obtain difunctionalized products in good to high enantioselectivities. The formation of a well-organized transition-state structure, that includes methanesulfonate anion generated from methanesulfonic acid additive, is proposed on the basis of experimental results. The importance of the amide moiety as a hydrogen-bonding donor group on chiral sulfide catalyst is also clarified in this report.[17]



Scheme 9 Indane-based chiral sulfide-catalyzed intermolecular iodofunctionalizations of substituted allylamines.

The utility of related indane-based chiral selenide catalysts was demonstrated by Zhao and co-workers during the asymmetric synthesis of P-chiral phosphine oxides (Scheme 10).[18] Desymmetrizing chlorinations of achiral triarylphosphine oxides were performed under the influence of chiral chalcogenide catalysts. Although indane-based chiral sulfide showed low levels of catalytic activity in the present chlorination, the selenide version efficiently promoted desymmetrizing chlorination to provide P-chiral triarylphosphine oxide in a highly enantioenriched form. The formation of chloroselenonium salt intermediate was investigated in this report.[18]

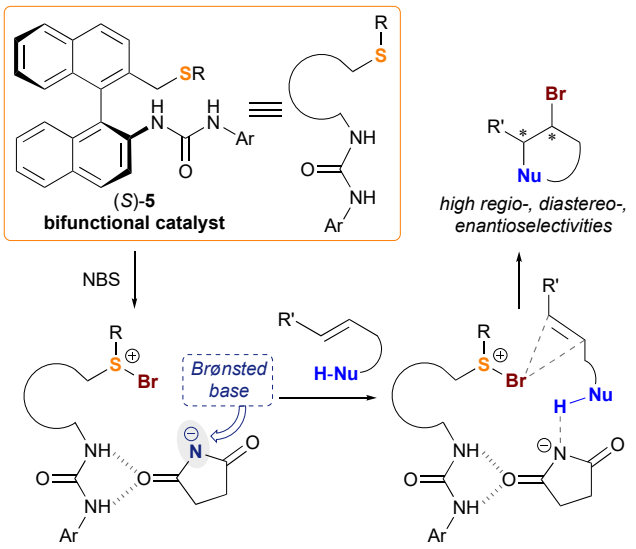


Scheme 10 Asymmetric synthesis of P-chiral phosphine oxide via indane-based chiral selenide-catalyzed chlorination.

4. BINOL-derived chiral bifunctional sulfide and selenide catalysts

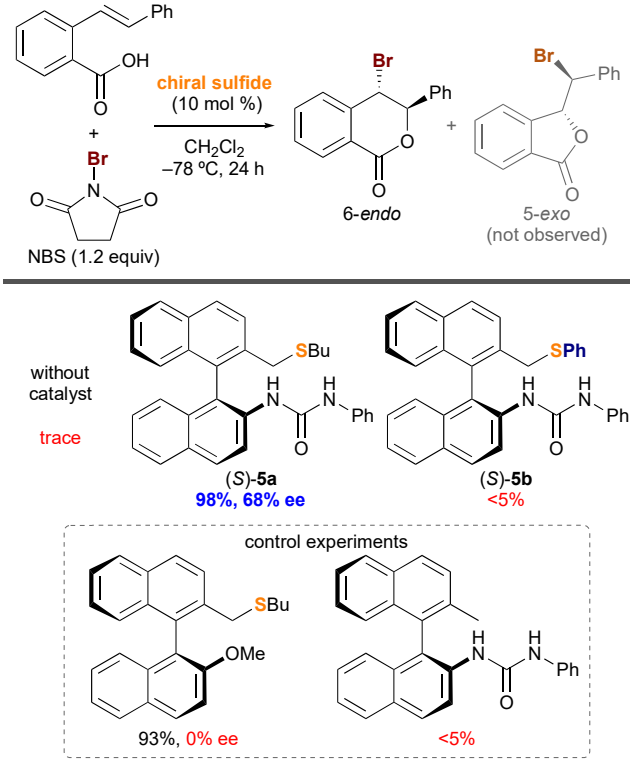
4-1. Urea-type chiral bifunctional sulfide and selenide catalysts

During the course of our study on the development of 1,1'-bi-2-naphthol (BINOL)-derived chiral bifunctional organocatalysts,[19] we became interested in the development of BINOL-derived chiral bifunctional sulfide catalysts for use in asymmetric halocyclizations. At first, we designed chiral bifunctional sulfide (*S*)-**5** bearing a urea moiety.[20] A working model of sulfide catalyst (*S*)-**5** in bromocyclization with *N*-bromosuccinimide (NBS) appears in Scheme 11. Basically, when the sulfide (*S*)-**5** is mixed with NBS, bromosulfonium succinimide is formed. The formations of halosulfonium salts have been studied in the literature.[9] The position of the generated succinimide anion is fixed by the urea moiety on the (*S*)-**5** via a hydrogen-bonding interaction. The alkene portion of the substrate is then activated by the bromosulfonium moiety to form a cyclic bromonium ion intermediate. Simultaneously, an acidic pro-nucleophilic moiety is activated by the succinimide anion, and this moiety serves as a Brønsted base to provide a well-organized transition-state. Highly stereoselective cyclization then proceeds to provide a corresponding bromocyclization product in regio-, diastereo-, and enantioselective manners.



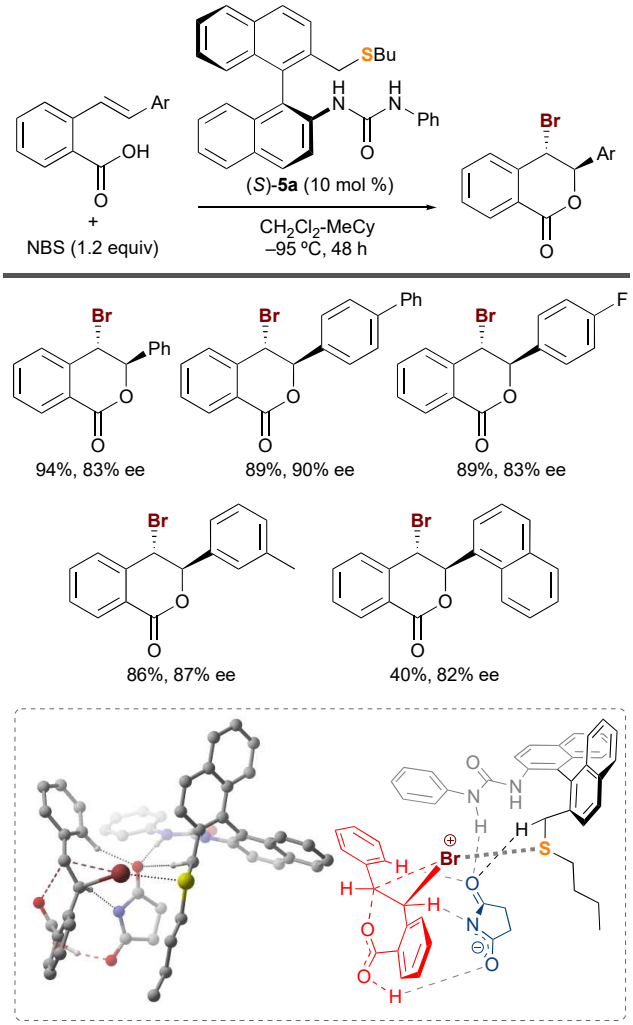
Scheme 11 Working model of a urea-type chiral bifunctional sulfide catalyst.

Our initial aim was to evaluate the catalytic ability of newly designed chiral bifunctional sulfide (*S*)-**5**. For this purpose, an asymmetric bromolactonization of a stilbene-type carboxylic acid was selected as a model reaction (Scheme 12).[20,21] When the bromolactonization of the stilbene-type carboxylic acid was performed with NBS at –78 °C for 24 hours in the absence of a catalyst, almost no reaction was observed. We were grateful to find that chiral bifunctional sulfide catalyst (*S*)-**5a** bearing a urea moiety efficiently promoted the bromolactonization to provide the 6-*endo*-cyclization product in a promising level of enantioselectivity. It should be noted that the rection proceeded with complete regioselectivity and that a 5-*exo*-cyclization product was not formed in our catalytic system. Interestingly, phenyl sulfide-type catalyst (*S*)-**5b** showed low catalytic activity under these reaction conditions. These results suggested that the electron density on the sulfur atom of catalyst (*S*)-**5a** is important to provide Lewis basicity sufficient for the promotion of the bromolactonization of stilbene-type carboxylic acid under the present reaction conditions. To clarify the importance of the bifunctional design of urea-type chiral sulfide catalyst (*S*)-**5a**, both a monofunctional sulfide catalyst and a urea catalyst were submitted to the bromolactonization as control experiments. The reaction using a monofunctional sulfide without a hydrogen-bonding donor group provided the targeted bromolactonization product in a high yield, but with no enantioselectivity. The urea catalyst without a sulfide moiety showed almost no catalytic activity. These results clearly prove the importance of the bifunctional feature of catalyst (*S*)-**5a** for the achievement of an efficient enantioselective bromolactonization of a stilbene-type carboxylic acid.



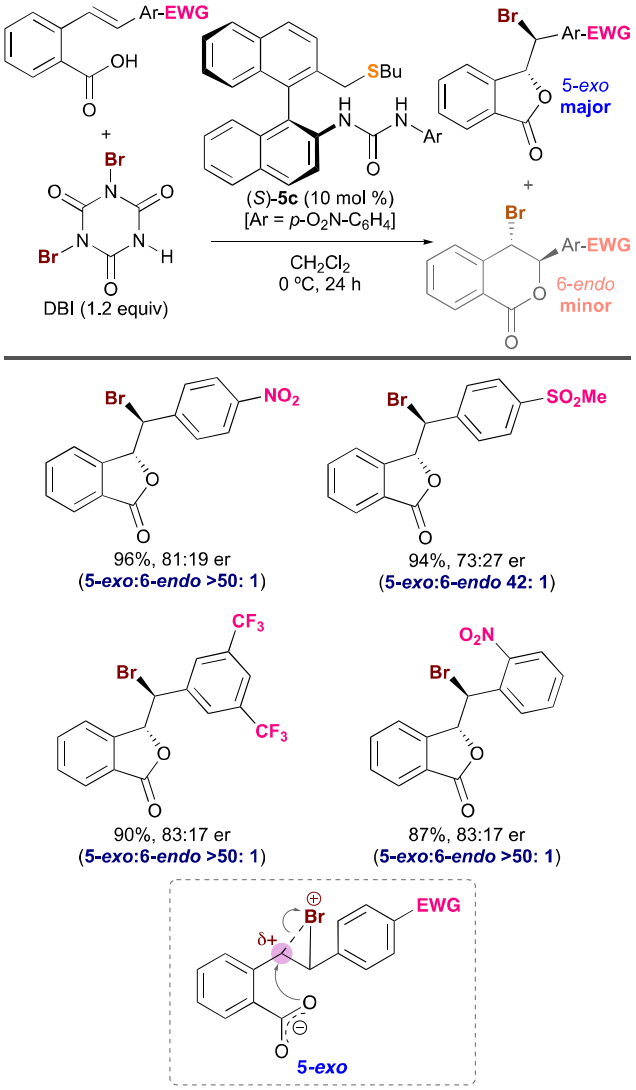
Scheme 12 Catalytic ability of urea-type chiral bifunctional sulfides to promote asymmetric bromolactonization.

With effective chiral bifunctional sulfide catalyst (*S*)-**5a** in hand, the substrate scope for asymmetric bromolactonizations of stilbene-type carboxylic acids was investigated under optimized reaction conditions (Scheme 13).[20] The targeted chiral 3,4-dihydoroisocoumarin products were obtained in highly regio-, diastereo-, and enantioselective manners. DFT calculations for the present reactions were also performed to gain insight into the origin of enantioselectivity.



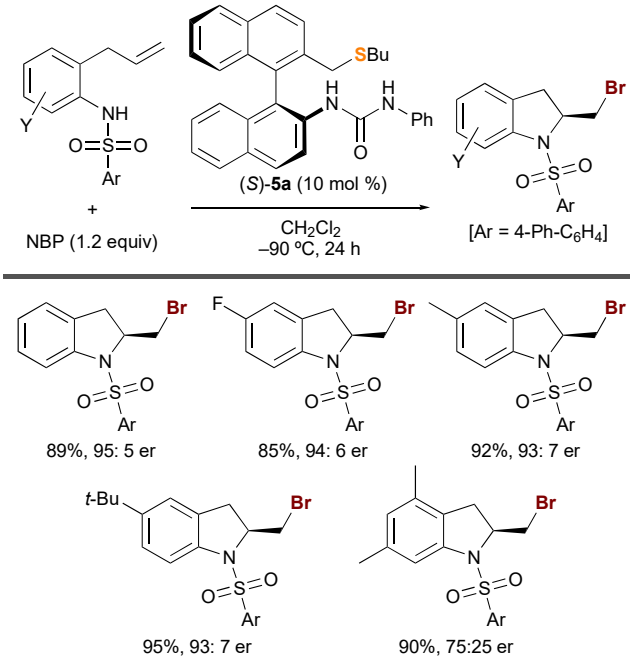
Scheme 13 Regio-, diastereo-, and enantioselective bromolactonizations of stilbene-type carboxylic acids.

During the course of extending the substrate scope for the asymmetric bromolactonizations of stilbene-type carboxylic acids, we found that 5-*exo*-cyclization products could be selectively obtained in reactions with substrates bearing electron-withdrawing substituents at one of the aryl units (Scheme 14).[22] After the optimization of a sulfide catalyst and reaction conditions were established, almost complete 5-*exo* selective reactions were achieved in several substrates possessing electron-withdrawing substituents. The 5-membered lactone products were selectively obtained in moderate enantioselectivities via bromolactonizations using sulfide catalyst (*S*)-**5c**.



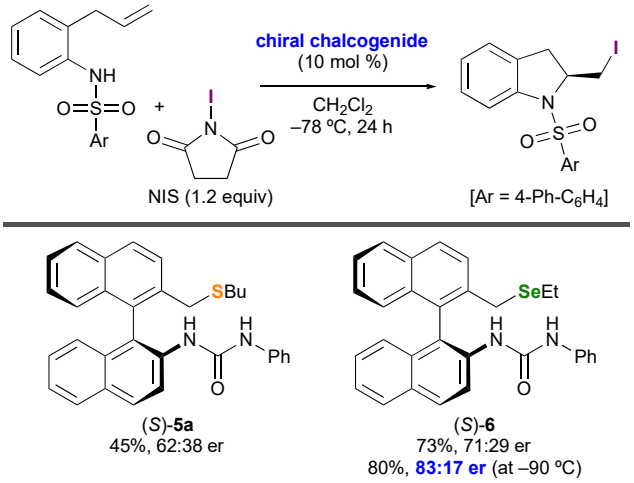
Scheme 14 Urea-type chiral bifunctional sulfide-controlled 5-*exo*-cyclizations of stilbene-type carboxylic acids.

Urea-type chiral bifunctional sulfide catalyst (*S*)-**5a** was also effective in the asymmetric bromoaminocyclizations that produced chiral indolines (Scheme 15).[23,24] 2-Substituted indoline products were obtained in good to high enantioselectivities under the optimized reaction conditions.



Scheme 15 Urea-type chiral bifunctional sulfide-catalyzed asymmetric bromoaminocyclizations.

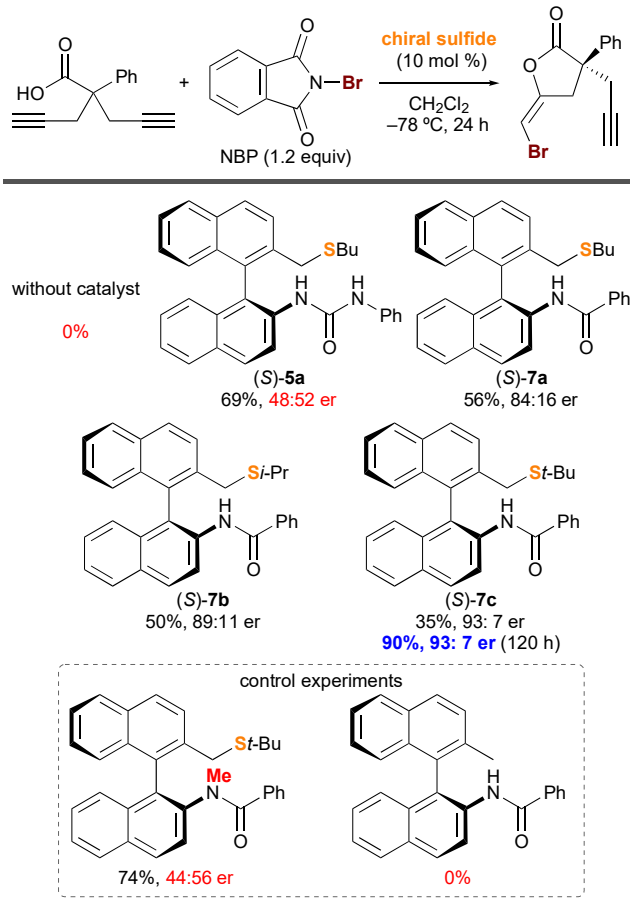
A related chiral selenide catalyst (*S*)-**6** bearing a urea moiety was also prepared (Scheme 16).[25] The utility of the chiral bifunctional selenide was demonstrated during asymmetric iodoaminocyclization. In the iodocyclization reactions, chiral bifunctional selenide catalysts provided enantioselectivities that were superior to those of chiral bifunctional sulfide catalysts.



Scheme 16 Utility of a urea-type chiral bifunctional selenide catalyst for asymmetric iodoaminocyclization.

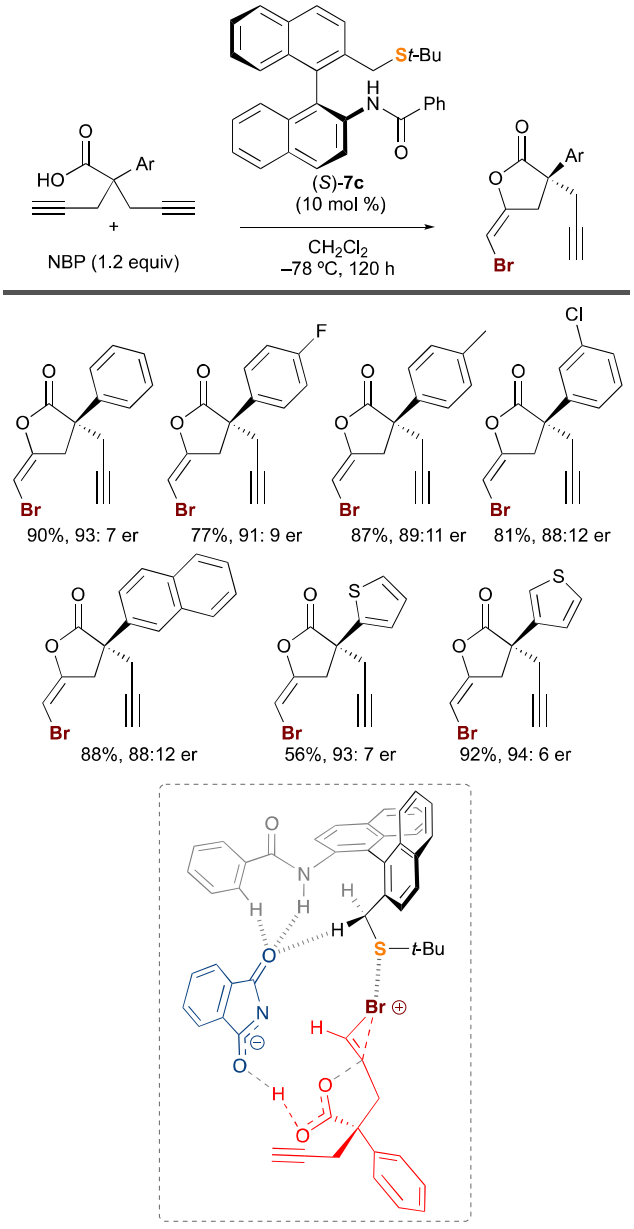
4-2. Amide-type chiral bifunctional sulfide catalysts

To expand the utility of BINOL-derived chiral bifunctional sulfide catalysts, next we examined asymmetric bromolactonizations uisng alkyne substrates. The enantioselective desymmetrizing bromolactonization of achiral α,α-dipropargyl carboxylic acid was selected as a model reaction to evaluate the catalytic ability of chiral bifunctional sulfides (Scheme 17).[26,27] The bromolactonization of α,α-dipropargyl carboxylic acid with NBP did not proceed in the absence of a catalyst when the reaction was let stand for 24 hours at –78 °C. Urea-type chiral sulfide (*S*)-**5a** did promote the reaction, however, and the targeted bromolactonization product was provided, albeit in quite low enantioselectivity. Fortunately, the reactions using newly prepared chiral bifunctional sulfide catalysts (*S*)-**7**, which possesses an amide group, promoted bromolactonization in good to high enantioselectivities. Control experiments for the present desymmetrizing bromolactonization of α,α-dipropargyl carboxylic acid were also performed to clarify the importance of the bifunctional design of amide-type chiral sulfide catalyst (*S*)-**7c**. The optimized chiral sulfide catalyst (*S*)-**7c** provided comparable (or better) results with previous reports using $(DHQD)_2PHAL$ catalyst,[27] which is a representative catalyst for asymmetric halolactonizations.



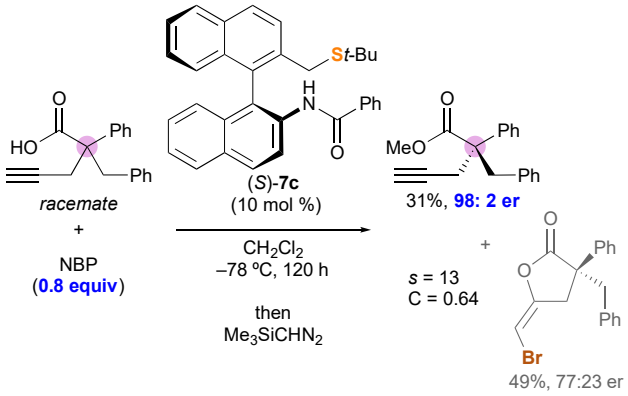
Scheme 17 Effects of chiral sulfide catalysts in the desymmetrizing bromolactonization of α,α-dipropargyl carboxylic acid.

The substrate scope for enantioselective desymmetrizing bromolactonizations of achiral α,α-dipropargyl carboxylic acids was investigated under the influence of chiral bifunctional sulfide (*S*)-**7c** (Scheme 18).[26] The corresponding α-quaternary γ-butyrolactone products were obtained in good to high enantioselectivities. A transition-state model of the present desymmetrizing bromolactonization was proposed based on DFT calculation.



Scheme 18 Amide-type chiral bifunctional sulfide-catalyzed desymmetrizing bromolactonizations of α,α-dipropargyl carboxylic acids.

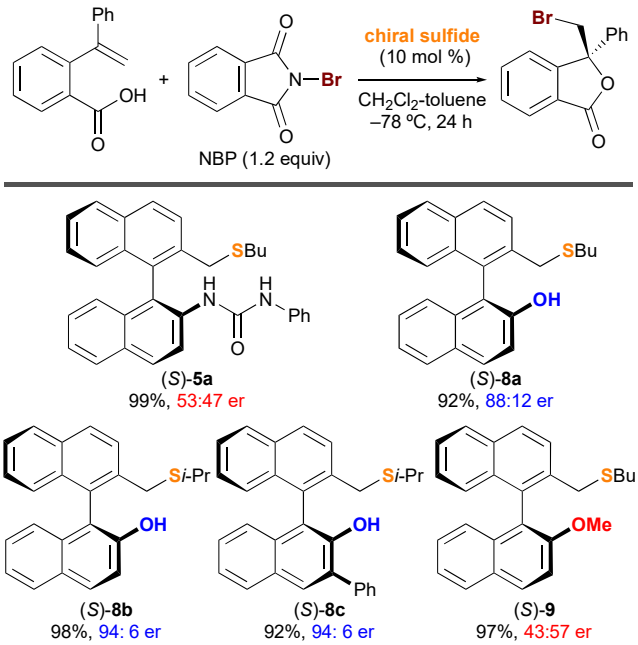
Based on the success of amide-type chiral bifunctional sulfide-catalyzed desymmetrizing bromolactonizations of α,α-dipropargyl carboxylic acids, the kinetic resolution of α-propargyl carboxylic acid bearing an all-carbon quaternary stereocenter was examined using sulfide catalyst (*S*)-**7c** (Scheme 19).[26] This is a challenging substrate for the catalytic kinetic resolution. The starting α-quaternary carboxylic acid, which was isolated as a methyl ester via treatment with trimethylsilyldiazomethane, was recovered in highly optically active form as a result of the kinetic resolution.



Scheme 19 Kinetic resolution of α-quaternary carboxylic acid via bromolactonization.

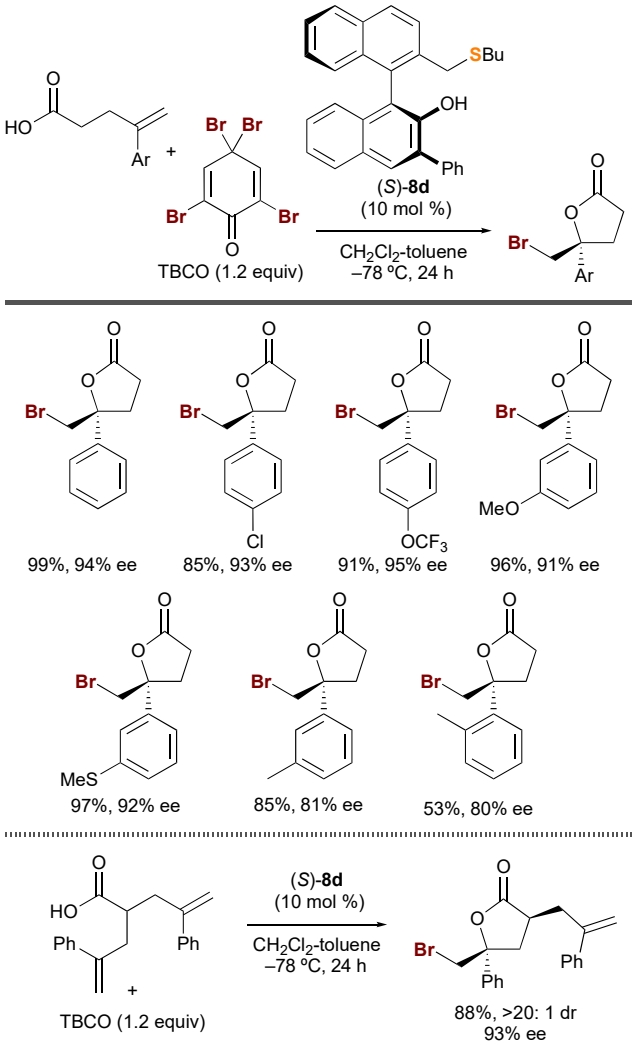
4-3. Hydroxy-type chiral bifunctional sulfide and selenide catalysts

In the course of our study on bifunctional sulfide-catalyzed asymmetric bromolactonizations, we became interested in the enantioselective synthesis of 3,3′-disubstituted phthalides possessing a chiral quaternary carbon center (Scheme 20).[28] Although urea-type chiral bifunctional sulfide (*S*)-**5a** showed poor enantioselectivity for this bromolactonization, re-designed bifunctional sulfide catalysts (*S*)-**8** bearing a hydroxy group largely improved the enantioselectivity to provide the targeted 3,3′-disubstituted phthalide product in highly enantioenriched form. The importance of the hydroxy group on sulfide catalyst (*S*)-**8** was established when a subsequent reaction using monofunctional sulfide catalyst (*S*)-**9** provided the product in low enantioselectivity.



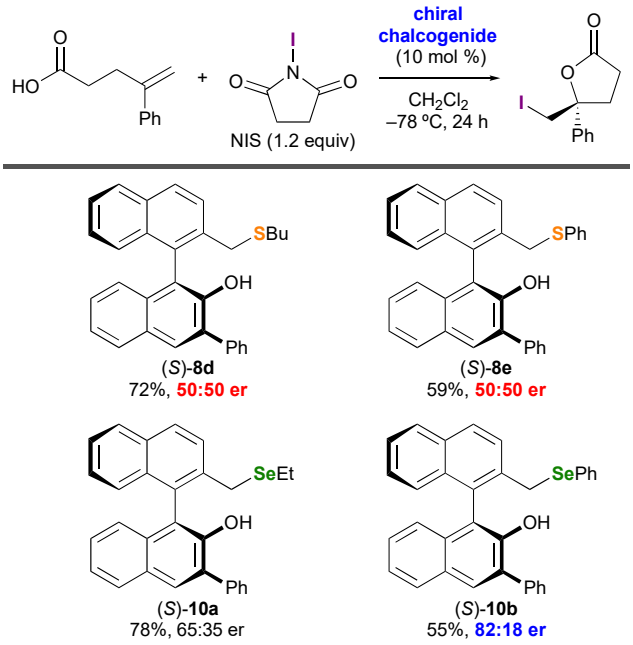
Scheme 20 Utility of hydroxy-type chiral bifunctional sulfide catalysts in the asymmetric synthesis of 3,3′-disubstituted phthalide.

The powerful potential of hydroxy-type chiral bifunctional sulfide catalysts (*S*)-**8** was further demonstrated by the highly enantioselective bromolactonization of 4-aryl-4-pentenoic acids,[29] which is one of the benchmark reactions in asymmetric halocyclizations (Scheme 21).[30] The highest levels of enantioselectivity yet reported for the asymmetric synthesis of γ-quaternary γ-butyrolactones via bromolactonizations have been observed by utilizing bifunctional sulfide (*S*)-**8d**. The present catalytic asymmetric reaction system could be applied to highly diastereo- and enantioselective desymmetrizing bromolactonizations.



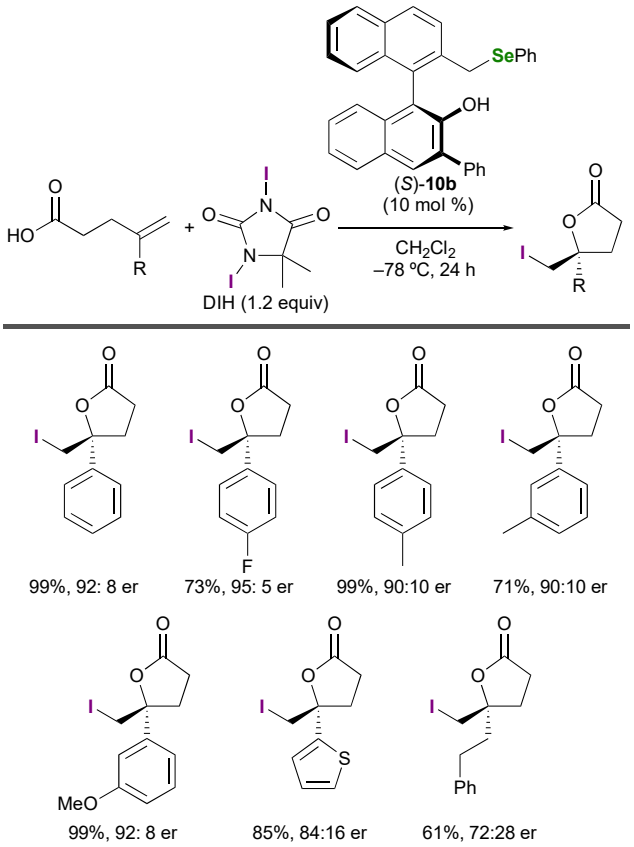
Scheme 21 Highly enantioselective synthesis of γ-quaternary γ-butyrolactones via hydroxy-type chiral bifunctional sulfide-catalyzed bromolactonizations.

Catalytic asymmetric iodolactonizations of 4-aryl-4-pentenoic acids were also examined using hydroxy-type chiral bifunctional sulfide catalysts (*S*)-**8**, which were quite effective for bromolactonizations (Scheme 22).[29] Surprisingly, however, the asymmetric iodolactonization of 4-pheny-4-pentenoic acid using chiral sulfide catalysts (*S*)-**8d** or **8e** provided a corresponding γ-butyrolactone product in a racemic form. On the other hand, related hydroxy-type chiral selenide catalysts (*S*)-**10** showed good catalytic performance to give an iodolactonization product in moderate to good levels of enantioselectivity.[31]



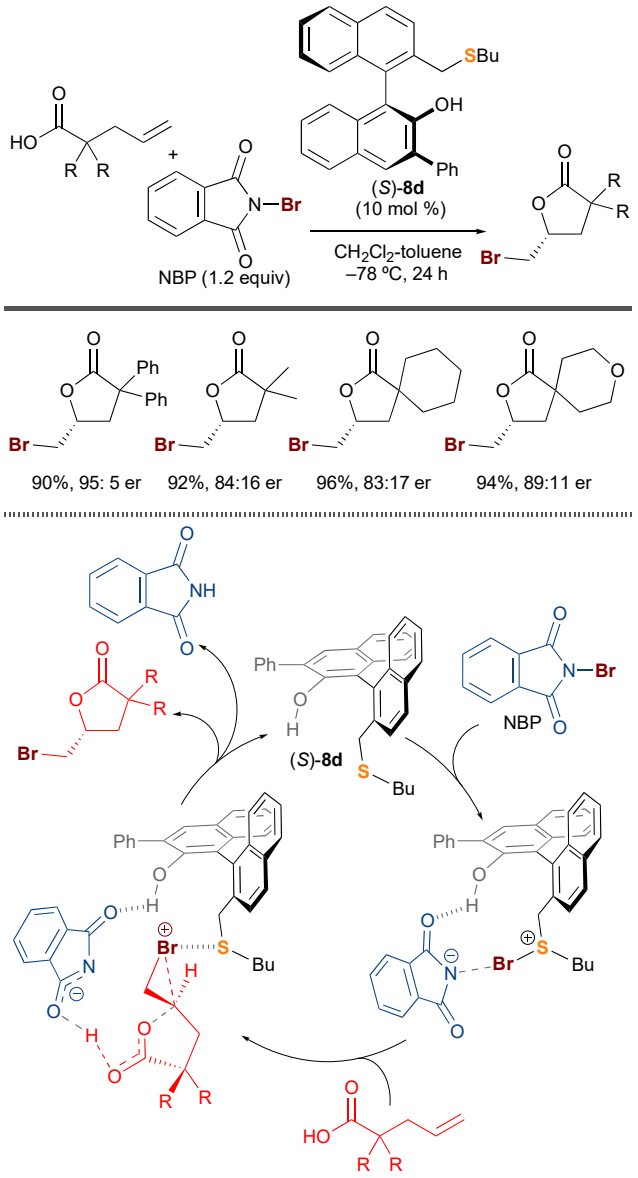
Scheme 22 Utility of hydroxy-type chiral bifunctional selenide catalysts in asymmetric iodolactonization.

The scope of substrates for the asymmetric iodolactonizations of 4-aryl-4-pentenoic acids was investigated under the optimized reaction conditions using chiral bifunctional selenide (*S*)-**10b** (Scheme 23).[31] Corresponding γ-quaternary γ-butyrolactone products were obtained in good enantioselectivities.



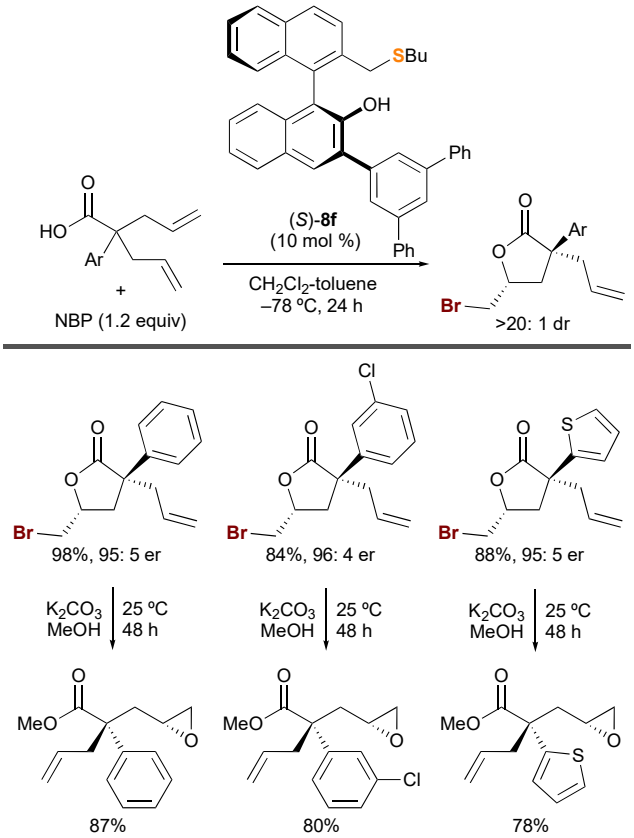
Scheme 23 Hydroxy-type chiral bifunctional selenide-catalyzed asymmetric iodolactonizations.

Despite numerous examples of the efficient asymmetric halolactonizations of γ- or δ-substituted γ,δ-alkenyl carboxylic acids,[30,32] sterically less-hindered α-allyl carboxylic acids remain to be challenging substrates for catalytic asymmetric halolactonization. In order to overcome this situation, we became interested in the development of chiral bifunctional sulfide-catalyzed highly enantioselective bromolactonizations of α-allyl carboxylic acid substrates (Scheme 24).[33] As a result of the asymmetric bromolactonizations of α-allyl carboxylic acids under the influence of sulfide catalyst (*S*)-**8d**, the targeted α,α-disubstituted γ-butyrolactone products were obtained in good enantioselectivities. Optically active α-spiro-γ-lactones could also be prepared using this method. The assumed catalytic cycle for the present asymmetric bromolactonizations of α-allyl carboxylic acids using chiral bifunctional sulfide catalyst (*S*)-**8d** was also discussed in this report.[33]



Scheme 24 Hydroxy-type chiral bifunctional sulfide-catalyzed enantioselective bromolactonizations of α-allyl carboxylic acids.

Catalytic asymmetric desymmetrizing bromolactonizations of α,α-diallyl carboxylic acids were also examined under the influence of optimized hydroxy-type chiral bifunctional sulfide catalyst (*S*)-**8f** (Scheme 25).[34] The target α-quaternary γ-butyrolactone products bearing an all-carbon quaternary stereocenter were obtained in highly diastereo- and enantioselective manners. The synthetic utility of obtained α-quaternary γ-butyrolactone products was demonstrated in the transformation to optically active α-quaternary esters possessing an epoxy group.



Scheme 25 Efficient asymmetric synthesis of α-quaternary lactones and esters via desymmetrizing bromolactonizations.

5. Conclusions

Recent advances in chiral sulfide and selenide organocatalysis for asymmetric halogenation reactions were summarized in this review. Re-designed tetrahydrothiophene-type chiral sulfide catalysts derived from D-mannitol were prepared by Yeung and co-workers. The tetrahydrothiophene-type chiral sulfide showed excellent catalytic performance in the asymmetric desymmetrizing bromoetherifications of alkenoic diols to obtain highly substituted chiral tetrahydrofuran products. Related D-mannitol-derived selenide catalysts were also prepared by Yeung et al. for highly stereoselective bromoaminocyclizations. Zhao and co-workers developed indane-based chiral sulfide and selenide catalysts. The high catalytic potential of indane-based chiral chalcogenides was initially established in the asymmetric thiofunctionalization reactions of alkenes. The developed indane-based chalcogenide catalysts were effective not only for halocyclizations but also for other important asymmetric halogenation reactions. Our group developed BINOL-derived chiral bifunctional sulfide and selenide catalysts. Several types of chiral bifunctional sulfide catalysts were designed to possess a hydrogen-bonding donor group. These catalysts realized highly enantioselective bromocyclizations of alkenoic and alkynoic acids. The importance of the bifunctional design of our BINOL-derived chiral sulfides was clarified in several control experiments. The utility of BINOL-derived selenide catalysts was demonstrated in iodocyclization reactions when they yielded products in enantioselectivities that were superior to those produced using sulfide catalysts. Although cinchona alkaloid derivatives are still most reliable asymmetric catalysts for halocyclizations, high potentials of chiral sulfide and selenide catalysts for halofunctionalizations were demonstrated. The chiral chalcogenide catalysts are now recognized as one of the powerful options for the catalytic asymmetric halocyclizations.

Only a portion of the potential for chiral sulfide and selenide catalysts has been showcased in this review. We believe that the full capabilities of chiral chalcogenide catalysts remain unexplored. The design and development of conceptually new chiral sulfide and selenide catalysts will further reveal the potential of chalcogenide organocatalysis.

Author Contributions

S.S. directed and wrote the initial manuscript. All authors discussed and commented on the manuscript. The manuscript was revised based on the authors opinions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

A portion of the research by our group on this topic was supported by JSPS KAKENHI Grant Numbers JP19K05480 (for S.S.) and JP21J20978 (for R.N.), by the Cooperative Research Program of "Network Joint Research Center for Materials and Devices" (20221027 for S.S.), by the Joint Usage/Research Center for Catalysis (22DS0140 and 23DS0163 for S.S.), by Kumagai Foundation for Science and Technology (for S.S.), by Fujimori Science and Technology Foundation (for S.S.), and by Naohiko Fukuoka Memorial Foundation (for S.S.). R.N. thanks JSPS for a research fellowship (DC1).

Notes and references

1 (*a*) P. I. Dalko and L. Moisan, *Angew. Chem., Int. Ed.*, 2001, **40**, 3726–3748; (*b*) P. I. Dalko and L. Moisan, *Angew. Chem., Int. Ed.*, 2004, **43**, 5138–5175; (*c*) D. W. C. MacMillan, *Nature*, 2008, **455**, 304–308; (*d*) M. H. Aukland and B. List, *Pure Appl. Chem.*, 2021, **93**, 1371–1381.

2 (*a*) B. List, *Chem. Commun.*, 2006, 819–824; (*b*) A. Erkkilä, I. Majander and P. M. Pihko, *Chem. Rev.*, 2007, **107**, 5416–5470; (*c*) S. Mukherjee, J. W. Yang, S. Hoffmann and B. List, *Chem. Rev.*, 2007, **107**, 5471–5569; (*d*) R. P. Wurz, *Chem. Rev.*, 2007, **107**, 5570–5595; (*e*) M. J. Gaunt and C. C. C. Johansson, *Chem. Rev.*, 2007, **107**, 5596–5605; (*f*) T. Kano and K. Maruoka, *Chem. Sci.*, 2013, **4**, 907–915.

3 (*a*) Y. Xiao, Z. Sun, H. Guo and O. Kwon, *Beilstein J. Org. Chem.*, 2014, **10**, 2089–2121; (*b*) Y. Wei and M. Shi, *Chem.–Asian J.*, 2014, **9**, 2720–2734.

4 (*a*) V. K. Aggarwal and C. L. Winn, *Acc. Chem. Res.*, 2004, **37**, 611–620; (*b*) E. M. McGarrigle, E. L. Myers, O. Illa, M. A. Shaw, S. L. Riches and V. K. Aggarwal, *Chem. Rev.*, 2007, **107**, 5841–5883.

5 (*a*) C. L. Winn, B. R. Bellenie and J. M. Goodman, *Tetrahedron Lett.*, 2002, **43**, 5427–5430; (*b*) S. Minière, V. Reboul, P. Metzner, M. Fochi and B. F. Bonini, *Tetrahedron: Asymmetry*, 2004, **15**, 3275–3280; (*c*) M. Davoust, J.-F. Brière, P.-A. Jaffrès and P. Metzner, *J. Org. Chem.*, 2005, **70**, 4166–4169; (*d*) H.-Y. Wu, C.-W. Chang and R.-J. Chein, *J. Org. Chem.*, 2013, **78**, 5788–5793.

6 (*a*) V. K. Aggarwal, E. Alonso, G. Fang, M. Ferrara, G. Hynd and M. Porcelloni, *Angew. Chem., Int. Ed.*, 2001, **40**, 1433–1436; (*b*) X.-M. Deng, P. Cai, S. Ye, X.-L. Sun, W.-W. Liao, K. Li, Y. Tang, Y.-D. Wu and L.-X. Dai, *J. Am. Chem. Soc.*, 2006, **128**, 9730–9740; (*c*) O. Illa, M. Arshad, A. Ros, E. M. McGarrigle and V. K. Aggarwal, *J. Am. Chem. Soc.*, 2010, **132**, 1828–1830; (*d*) M.-T. Huang, H.-Y. Wu and R.-J. Chein, *Chem. Commun.*, 2014, **50**, 1101–1103; (*e*) Y.-C. Guo, K.-W. Chiu and R.-J. Chein, *J. Org. Chem.*, 2023, **88**, 559–572.

7 M. H. Gieuw, Z. Ke and Y.-Y. Yeung, *Chem. Rec.*, 2017, **17**, 287–311.

8 L. Liao and X. Zhao, *Acc. Chem. Res.*, 2022, **55**, 2439–2453.

9 (*a*) G. E. Wilson, Jr, *Tetrahedron*, 1982, **38**, 2597–2625; (*b*) S. A. Snyder, D. S. Treitler and A. P. Brucks, *Aldrichimica Acta*, 2011, **44**, 27–40; (*c*) S. A. Snyder and D. S. Treitler, *Org. Synth.*, 2011, **88**, 54–69; (*d*) C. A. Taylor and S. A. Snyder, *Org. Synth.*, 2020, **97**, 339–354.

10 (*a*) A. Castellanos and S. P. Fletcher, *Chem.–Eur. J.*, 2011, **17**, 5766–5776; (*b*) S. E. Denmark, W. E. Kuester and M. T. Burk, *Angew. Chem., Int. Ed.*, 2012, **51**, 10938–10953; (*c*) U. Hennecke, *Chem.–Asian J.*, 2012, **7**, 456–465; (*d*) S. Zheng, C. M. Schienebeck, W. Zhang, H.-Y. Wang and W. Tang, *Asian J. Org. Chem.*, 2014, **3**, 366–376; (*e*) J. M. J. Nolsøe and T. V. Hansen, *Eur. J. Org. Chem.*, 2014, 3051–3065; (*f*) R. Kristianslund, J. E. Tungen and T. V. Hansen, *Org. Biomol. Chem.*, 2019, **17**, 3079–3092; (*g*) K. D. Ashtekar, A. Jaganathan, B. Borhan and D. C. Whitehead, *Org. React.*, 2021, **105**, 1–266; (*h*) S. Liu, B.-Q. Zhang, W.-Y. Xiao, Y.-L. Li and J. Deng, *Adv. Synth. Catal.*, 2022, **364**, 3974–4005.

11 (*a*) Z. Ke, C. K. Tan, F. Chen and Y.-Y. Yeung, *J. Am. Chem. Soc.*, 2014, **136**, 5627–5630; (*b*) Z. Ke, C. K. Tan, Y. Liu, K. G. Z. Lee and Y.-Y. Yeung, *Tetrahedron*, 2016, **72**, 2683–2689.

12 F. Chen, C. K. Tan and Y.-Y. Yeung, *J. Am. Chem. Soc.*, 2013, **135**, 1232–1235.

13 X. Liu, R. An, X. Zhang, J. Luo and X. Zhao, *Angew. Chem., Int. Ed.*, 2016, **55**, 5846–5850.

14 (*a*) X. Liu, Y. Liang, J. Ji, J. Luo and X. Zhao, *J. Am. Chem. Soc.,* 2018, **140**, 4782–4786; (*b*) J. Luo, Q. Cao, X. Cao and X. Zhao, *Nat. Commun.*, 2018, **9**, 527; (*c*) Y. Liang and X. Zhao, *ACS Catal.*, 2019, **9**, 6896–6902; (*d*) Y. Liang, J. Ji, X. Zhang, Q. Jiang, J. Luo and X. Zhao, *Angew. Chem., Int. Ed.*, 2020, **59**, 4959–4964; (*e*) Y. Zhang, Y. Liang and X. Zhao, *ACS Catal.*, 2021, **11**, 3755–3761.

15 Q. Cao, J. Luo and X. Zhao, *Angew. Chem., Int. Ed.*, 2019, **58**, 1315–1319.

16 J. Luo, Y. Zhang, F. Zhong and X. Zhao, *CCS Chem.,* 2022, **4**, 1486–1498.

17 L. Liao, X. Xu, J. Ji and X. Zhao, *J. Am. Chem. Soc.,* 2022, **144**, 16490–16501.

18 R. Guo, Z. Liu and X. Zhao, *CCS Chem.,* 2020, **2**, 2617–2628.

19 (*a*) S. Liu, N. Suematsu, K. Maruoka and S. Shirakawa, *Green Chem.,* 2016, **18**, 4611–4615; (*b*) S. Liu, K. Maruoka and S. Shirakawa, *Angew. Chem., Int. Ed.*, 2017, **56**, 4819–4823.

20 R. Nishiyori, A. Tsuchihashi, A. Mochizuki, K. Kaneko, M. Yamanaka and S. Shirakawa, *Chem.–Eur. J.*, 2018, **24**, 16747–16752.

21 (*a*) J. Chen, L. Zhou, C. K. Tan and Y.-Y. Yeung, *J. Org. Chem.,* 2012, **77**, 999–1009; (*b*) T. Chen and Y.-Y. Yeung, *Org. Biomol. Chem.,* 2016, **14**, 4571–4575.

22 A. Tsuchihashi and S. Shirakawa, *Synlett*, 2019, **30**, 1662–1666.

23 T. Nakamura, K. Okuno, K. Kaneko, M. Yamanaka and S. Shirakawa, *Org. Biomol. Chem.,* 2020, **18**, 3367–3373.

24 S.-N. Yu, Y.-L. Li and J. Deng, *Adv. Synth. Catal.*, 2017, **359**, 2499–2508.

25 K. Okuno, T. Nakamura and S. Shirakawa, *Asian J. Org. Chem.*, 2021, **10**, 655–659.

26 K. Okuno, M. Hiraki, B. Chan and S. Shirakawa, *Bull. Chem. Soc. Jpn.*, 2022, **95**, 52–58.

27 (*a*) M. Wilking, C. Mück-Lichtenfeld, C. G. Daniliuc and U. Hennecke, *J. Am. Chem. Soc.,* 2013, **135**, 8133–8136; (*b*) M. Wilking, C. G. Daniliuc and U. Hennecke, *Chem.–Eur. J.,* 2016, **22**, 18601–18607.

28 M. Okada, K. Kaneko, M. Yamanaka and S. Shirakawa, *Org. Biomol. Chem.,* 2019, **17**, 3747–3751.

29 R. Nishiyori, M. Okada, J. R. J. Maynard and S. Shirakawa, *Asian J. Org. Chem.*, 2021, **10**, 1444–1448.

30 (*a*) D. C. Whitehead, R. Yousefi, A. Jaganathan and B. Borhan, *J. Am. Chem. Soc.*, 2010, **132**, 3298–3300; (*b*) L. Zhou, C. K. Tan, X. Jiang, F. Chen and Y.-Y. Yeung, *J. Am. Chem. Soc.*, 2010, **132**, 15474–15476; (*c*) D. H. Paull, C. Fang, J. R. Donald, A. D. Pansick and S. F. Martin, *J. Am. Chem. Soc.*, 2012, **134**, 11128–11131; (*d*) R. Nishiyori, J. R. J. Maynard and S. Shirakawa, *Asian J. Org. Chem.*, 2020, **9**, 192–196; (*e*) Y.-C. Chan, X. Wang, Y.-P. Lam, J. Wong, Y.-L. S. Tse and Y.-Y. Yeung, *J. Am. Chem. Soc.*, 2021, **143**, 12745–12754.

31 R. Nishiyori, K. Okuno, B. Chan and S. Shirakawa, *Chem. Pharm. Bull.*, 2022, **70**, 599–604.

32 (*a*) D. W. Klosowski, J. C. Hethcox, D. H. Paull, C. Fang, J. R. Donald, C. R. Shugrue, A. D. Pansick and S. F. Martin, *J. Org. Chem.*, 2018, **83**, 5954–5968; (*b*) Y. Nishikawa, Y. Hamamoto, R. Satoh, N. Akada, S. Kajita, M. Nomoto, M. Miyata, M. Nakamura, C. Matsubara and O. Hara, *Chem.–Eur. J.*, 2018, **24**, 18880–18885.

33 T. Mori, K. Abe and S. Shirakawa, *J. Org. Chem.*, 2023, **88**, (DOI: 10.1021/acs.joc.2c02283).

34 M. Hiraki, K. Okuno, R. Nishiyori, A. A. Noser and S. Shirakawa, *Chem. Commun.*, 2021, **57**, 10907–10910.

