

## Recent Advances in Molecular Space Chemistry

## Regular Article

## Chiral Bifunctional Selenide Catalysts for Asymmetric Iodolactonizations

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**1,1'-Bi-2-naphthol (BINOL)-derived chiral bifunctional sulfide and selenide catalysts that possess a hydroxy group are known to be effective catalysts for enantioselective bromolactonizations. When applied to asymmetric iodolactonizations of 4-pentenoic acids, these catalysts yield chiral  $\gamma$ -butyrolactone products that are important compounds in medicinal chemistry. Although chiral bifunctional selenides have shown good catalytic performances in enantioselective iodolactonizations, reactions with BINOL-derived chiral sulfide catalysts unexpectedly gave iodolactonization products in nearly racemic forms. The roles of chalcogenide moieties and hydroxy groups on bifunctional catalysts were investigated, and the importance of both a selenide moiety and a hydroxy group on chiral bifunctional selenide catalysts to achieve enantioselective iodolactonizations was clarified. An optimized chiral bifunctional selenide catalyst was applied to the asymmetric synthesis of chiral  $\gamma$ -butyrolactones and phthalides. Furthermore, the utility of chiral bifunctional selenides was also demonstrated in the catalytic enantioselective desymmetrizing iodolactonization of  $\alpha,\alpha$ -diallyl carboxylic acids.**

**Key words** asymmetric catalysis; halogenation; lactone; organocatalysis; selenium

## Introduction

The development of effective chiral catalysts for asymmetric halolactonizations of alkenyl carboxylic acids is an important research project in the field of asymmetric catalysis,<sup>1-7</sup> because the resultant optically active lactone products are important compounds in medicinal chemistry and in natural products chemistry.<sup>8-12</sup> Among the catalytic asymmetric halolactonizations using well-designed chiral catalysts, the reaction of 4-pentenoic acid derivatives **1** to give  $\gamma$ -butyrolactone products **2** has often been utilized as a benchmark reaction to examine the performance of chiral catalysts<sup>13-21</sup> (Fig. 1). In this context, we have recently developed 1,1'-bi-2-naphthol (BINOL)-derived chiral bifunctional chalcogenide catalysts for enantioselective bromolactonizations.<sup>22-30</sup> When our chiral bifunctional sulfide catalyst (*S*)-**3** was submitted to the bromolactonization of alkenyl carboxylic acid **1** as a benchmark reaction, the corresponding  $\gamma$ -butyrolactone product **2** (X = Br) was obtained in a highly enantioselective manner *via* the formation of a highly organized transition-state structure.<sup>28</sup> The related chiral bifunctional selenide catalyst (*S*)-**4** also served as an effective catalyst for the bromolactonization.<sup>26</sup> To expand the utility of our chiral bifunctional chalcogenide catalysts for asymmetric halolactonizations, we drew out an iodolactonization of **1** under the influence of our chiral bifunctional chalcogenides in this work. Surprisingly, however, asymmetric iodolactonization using chiral sulfide catalyst (*S*)-**3** provided  $\gamma$ -butyrolactone product **2** (X = I) in an almost racemic form. On the other hand, the reaction with chiral bifunctional sele-

nide catalyst (*S*)-**4** gave iodolactonization product **2** (X = I) in good enantioselectivity. Herein, we report the details of these unexpected tendencies between BINOL-derived chiral sulfide catalysts and selenide catalysts<sup>31,32</sup> in the enantioselective iodolactonizations of alkenyl carboxylic acids.

## Results and Discussion

Our initial aim was to compare the effects of chiral sulfide catalysts (*S*)-**3** and selenide catalysts (*S*)-**4** in the asymmetric iodolactonization of 4-phenyl-4-pentenoic acid **1a**<sup>13,16,18</sup> (Table 1). When a reaction of **1a** with *N*-iodosuccinimide (NIS) in dichloromethane was performed at  $-78^\circ\text{C}$  for 24 h in the absence of a catalyst, iodolactonization product **2a** was obtained in only an 8% yield. BINOL-derived chiral sulfide catalysts (*S*)-**3**, which were effective in the bromolactonization of **1a**, were used for iodolactonization with NIS. Although the reaction provided **2a** in moderate to good yields, almost no enantioselectivity was observed. On the other hand, the reactions using selenide catalysts (*S*)-**4** gave an optically active iodolactonization product **2a** with moderate to good levels of enantioselectivity. Among the examined BINOL-derived selenide catalysts, phenyl-substituted catalyst (*S*)-**4d** yielded product **2a** in a higher level of enantioselectivity (82:18 er). Several control experiments were performed to clarify the roles that the chalcogenide moiety and the hydroxy group exert on bifunctional catalysts. When iodolactonization was performed under the influence of hydroxy-protected sulfide catalyst (*S*)-**5**, the reaction was sluggishly promoted to give product **2a**

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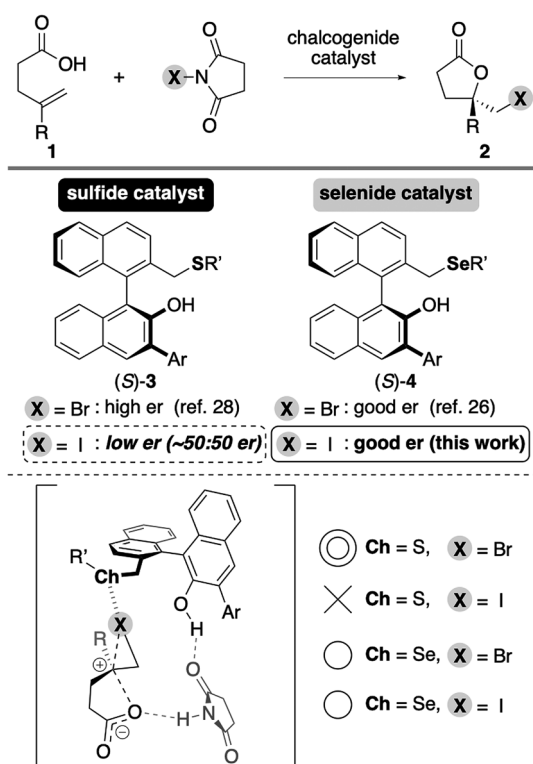
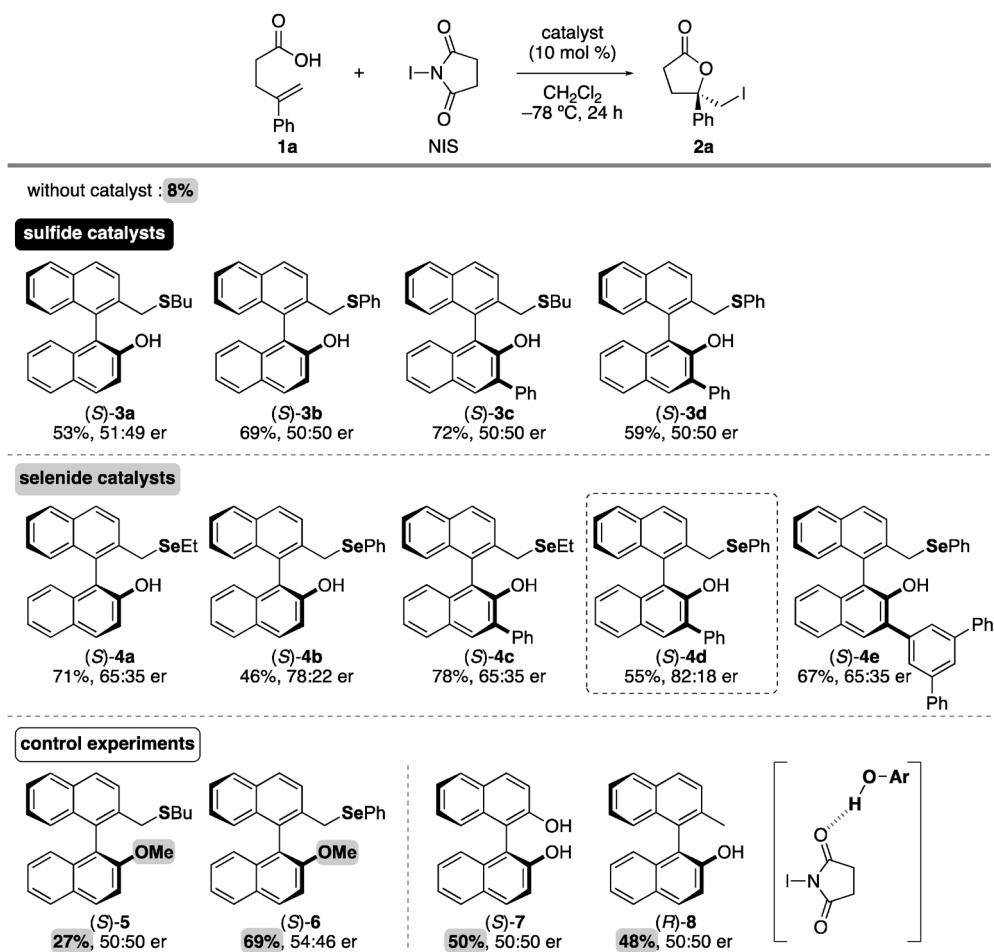


Fig. 1. Effects of Chiral Bifunctional Chalcogenide Catalysts in Asymmetric Halolactonizations

in a 27% yield and no enantioselectivity. On the other hand, hydroxy-protected selenide catalyst (S)-6 moderately promoted the iodolactonization of **1a** to provide **2a** in a 69% yield but in very low enantioselectivity. We also examined the reactions under the influence of simple BINOL (S)-7 and BINOL derivative (R)-8. Even in the reactions using the BINOL derivatives without a chalcogenide moiety, the iodolactonizations were moderately promoted, probably *via* the hydrogen-bonding activation of NIS.<sup>33</sup> In these reactions, the target iodolactonization products **2a** were obtained as racemates in moderate yields. These results could indicate that iodolactonizations using sulfide catalysts (S)-3 are promoted mainly by the effects of the hydroxy group on (S)-3, and that the sulfide catalysts (S)-3 cannot form an organized transition-state, as shown in Fig. 1. Based on the results in Table 1, we concluded that both the selenide moiety and the hydroxy group on the chiral bifunctional selenide catalysts (S)-4 are essential to achieve efficient enantioselective iodolactonizations.

To further explore the effect of the various functional groups on the reaction, we have carried out density functional theory (DFT) computations on some small model systems. We use the *r*<sup>2</sup>SCAN-3c method in combination with the solvation effect of dichloromethane incorporated using a continuum solvation model. First, in the absence of a catalyst, NIS reacts with **1a** to give **2a** with a concerted transition-state structure (Fig. 2); the calculated barrier for this reaction is 42 kJ mol<sup>-1</sup>. If the NIS reagent is replaced by the NIS-methanol hydrogen-

Table 1. Effect of Chiral Chalcogenide Catalysts



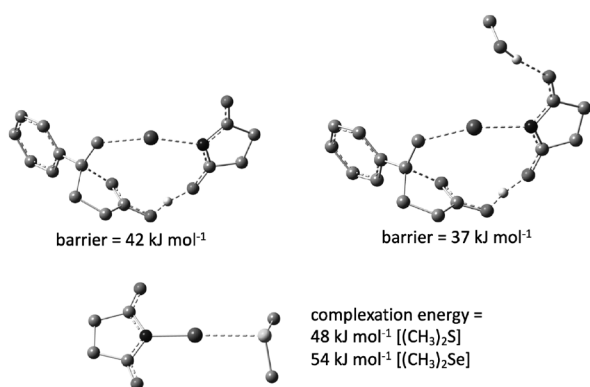
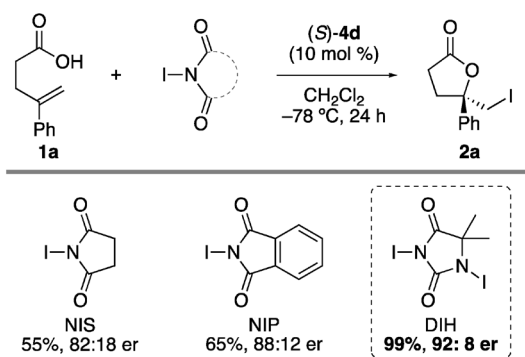


Fig. 2. Model Systems Used in Our DFT Computations, and Key Calculated Thermochemical Quantities

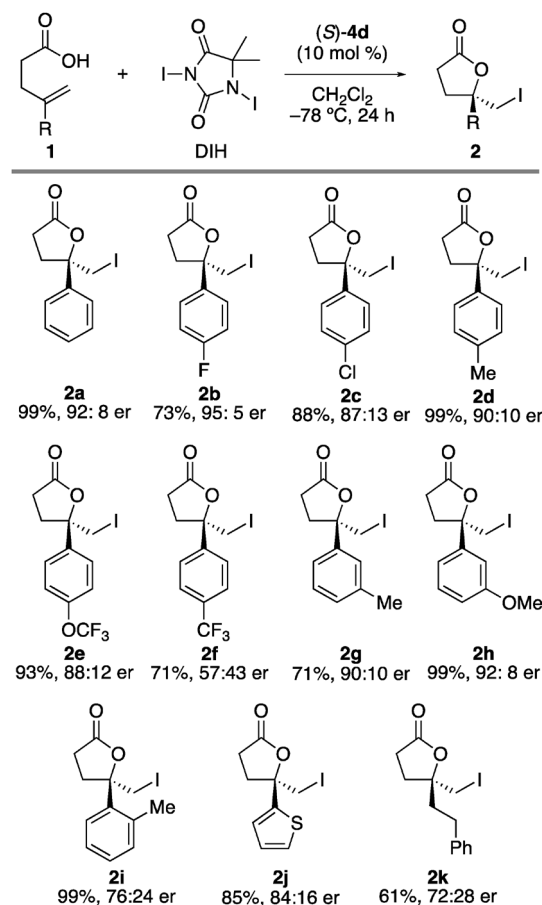
Table 2. Effect of Iodinating Reagents



bonded complex, the barrier is lowered to  $37\text{kJmol}^{-1}$ . To put this in perspective, the barrier for uncatalyzed bromination by NBS has a calculated barrier of  $36\text{kJmol}^{-1}$ ; we have in our preliminary experimental study found this reaction to proceed with good yield. Thus, our DFT barriers are qualitatively consistent with the catalytic effect of the OH groups in (*S*)-**3**, (*S*)-**4**, (*S*)-**7**, and (*R*)-**8**. Next, we discuss the effect of the sulfide and selenide moieties. The proposed mechanism involves the abstraction of iodine by the chalcogenide to form a reactive intermediate. We have examined the complexation energy of NIS with dimethyl sulfide and dimethyl selenide as an indicator for the ease of forming the iodinated chalcogenide intermediate. For the sulfide, the complexation energy is  $48\text{kJmol}^{-1}$ . In comparison, the binding with the selenide is stronger ( $54\text{kJmol}^{-1}$ ). This is consistent with the stronger catalytic effect of (*S*)-**6** than that of (*S*)-**5**. Overall, our results show a correlation between the observed catalytic activities and the calculated thermochemical quantities. To further rationalize the enantioselectivity would necessitate a thorough sampling of the conformational space of the catalytic transition-state structure, which we would consider in a separate study.

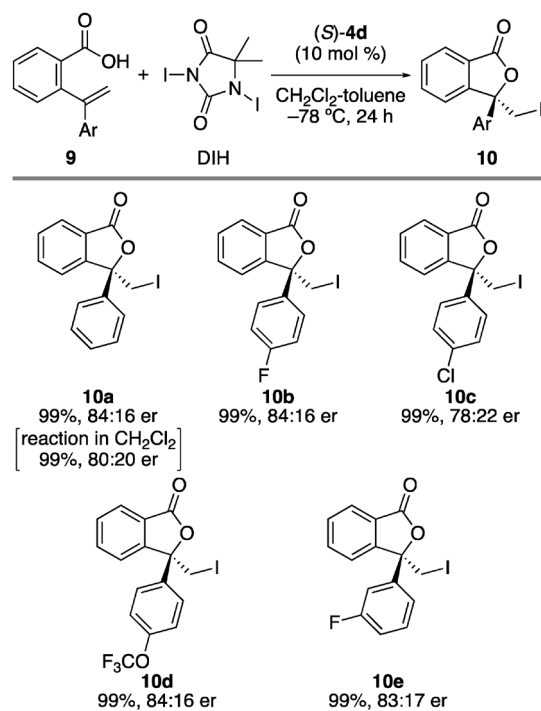
To improve enantioselectivity in the iodolactonization of 4-phenyl-4-pentenoic acid **1a** catalyzed by chiral bifunctional selenide (*S*)-**4d**, we next examined the effect of other iodinating reagents (Table 2). In a pleasing development, the reactions using *N*-iodophthalimide (NIP) and 1,3-diiodo-5,5-dimethylhydantoin (DIH) improved both the yields and the enantioselectivities. In particular, the iodolactonization of

Table 3. Substrate Scope in the Asymmetric Iodolactonization of 4-Pentenoic Acids **1**



**1a** with DIH under the influence of catalyst (*S*)-**4d** provided  $\gamma$ -butyrolactone product **2a** in high levels of yield and enantioselectivity (92:8 er).<sup>34,35</sup> The absolute configuration of **2a** was confirmed by comparison with reported data.<sup>16,18</sup>

With the optimum catalyst and iodinating reagent in hand, we investigated the substrate generality for an asymmetric iodolactonization of **1** with DIH under the influence of chiral bifunctional selenide catalyst (*S*)-**4d**<sup>36</sup> (Table 3). A series of aryl-substituted 4-pentenoic acids **1** were applied to enantioselective iodolactonization in an effort to obtain corresponding  $\gamma$ -butyrolactone products **2**. First, the effects of the functional groups at the *para* position of the aryl unit on **1** were examined. The iodolactonizations of halo-substituted substrates **1b** and **1c** gave products **2b** and **2c** in good yields and in good to high enantioselectivities. Methyl- and trifluoromethoxy-substituted substrates **1d** and **1e** were also applied to the reaction to obtain **2d** and **2e** in high yields and good enantioselectivities. Unfortunately, the iodolactonization with trifluoromethyl-substituted substrate **1f** gave product **2f** in low enantioselectivity. The aryl-substituted substrates **1** bearing functionalities at the *meta*- and *ortho*-positions were also examined. Although the *meta*-substituted products **2g** and **2h** were obtained in good levels of enantioselectivity, the *ortho*-substituted product **2i** was obtained in only moderate enantioselectivity. Heteroaromatic-substituted substrate **1j** was also applied to iodolactonization and provided **2j** in good levels of yield and enantioselectivity. The reaction with alkyl-

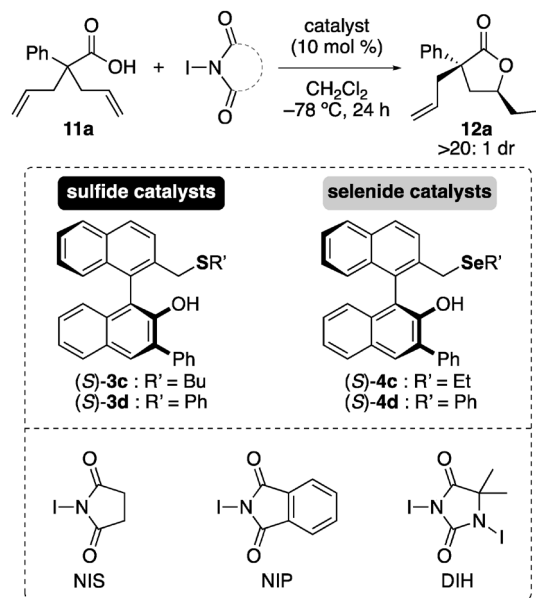
Table 4. Catalytic Asymmetric Synthesis of 3,3-Disubstituted Phthalides **10** via Iodolactonization

substituted substrate **1k** gave product **2k** in moderate levels of yield and enantioselectivity.

The chiral bifunctional selenide catalyst (*S*)-**4d** could also be applied to the asymmetric iodolactonizations of *o*-vinylbenzoic acid derivatives **9** to provide chiral phthalide products **10**<sup>24,37,38</sup> (Table 4). The reactions of substrates **9** were performed in a solvent mixture of dichloromethane–toluene, which provided better enantioselectivity for the iodolactonizations of substrates **9** by comparison with dichloromethane solvent. The target 3,3-disubstituted phthalide products **10** were obtained in high yields and in moderate to good levels of enantioselectivity.

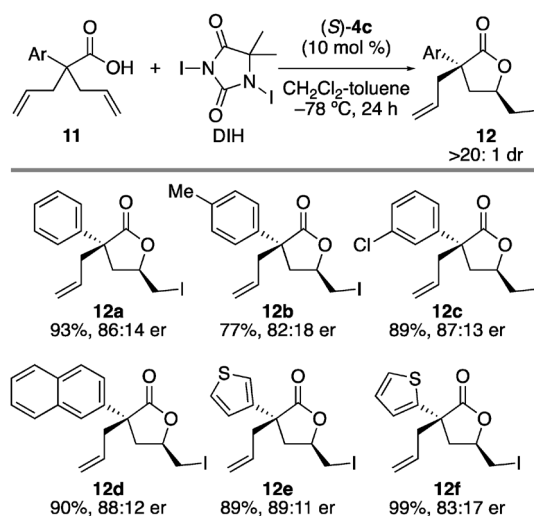
To demonstrate the further potential of our BINOL-derived chiral bifunctional chalcogenide catalysts for iodolactonizations, we next examined catalytic enantioselective desymmetrizing iodolactonization of  $\alpha,\alpha$ -diallyl carboxylic acid **11a**,<sup>29,39,40</sup> which provided  $\alpha$ -quaternary lactone **12a** with an all-carbon quaternary stereocenter<sup>41–45</sup> (Table 5). When desymmetrizing iodolactonizations of **11a** with NIS in dichloromethane were performed at  $-78^\circ\text{C}$  for 24 h under the influence of sulfide catalysts (*S*)-**3c** and **3d**, the target  $\alpha$ -quaternary  $\gamma$ -butyrolactone product **12a** was obtained in an almost racemic form (entries 1 and 2). On the other hand, the desymmetrizations of **11a** using chiral bifunctional selenide catalysts (*S*)-**4c** and **4d** provided **12a** in moderate enantioselectivities (entries 3 and 4). These trends between sulfide catalysts (*S*)-**3** and selenide catalysts (*S*)-**4** agreed with that seen in the iodolactonization of substrate **1a**, as shown in Table 1. The reaction conditions for the desymmetrizing iodolactonization of **11a** using selenide catalyst (*S*)-**4c** were further optimized to improve the enantioselectivity (entries 5–7). The highest enantioselectivity was observed in the reaction of **11a** with DIH in a dichloromethane–toluene mixed solvent (entry 7).

Selected substrates **11** were submitted to chiral selenide-

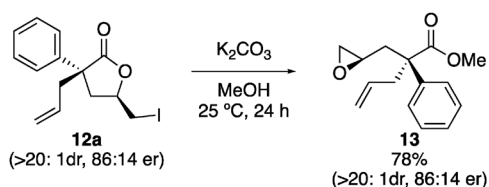
Table 5. Optimization of the Reaction Conditions in the Desymmetrizing Iodolactonization of **11a**<sup>a)</sup>

Entry	Catalyst	Iodinating reagent	Yield (%) <sup>b)</sup>	er <sup>c)</sup>
1	( <i>S</i> )- <b>3c</b>	NIS	97	52:48
2	( <i>S</i> )- <b>3d</b>	NIS	66	50:50
3	( <i>S</i> )- <b>4c</b>	NIS	62	72:28
4	( <i>S</i> )- <b>4d</b>	NIS	80	63:37
5	( <i>S</i> )- <b>4c</b>	NIP	96	81:19
6	( <i>S</i> )- <b>4c</b>	DIH	93	82:18
7 <sup>d)</sup>	( <i>S</i> )- <b>4c</b>	DIH	93	86:14

a) Reaction conditions: **11a** (0.10 mmol), iodinating reagent (0.12 mmol), catalyst (10 mol %, 0.010 mmol),  $\text{CH}_2\text{Cl}_2$  (2.0 mL),  $-78^\circ\text{C}$ , 24 h. b) Yield of isolated product **12a**. c) The enantiomeric ratio (er) was determined via HPLC analysis on a chiral stationary phase. d) The reaction was performed in a  $\text{CH}_2\text{Cl}_2$ -toluene mixed solvent (1.0 mL each).

Table 6. Substrate Scope in the Desymmetrizing Iodolactonization of  $\alpha,\alpha$ -Diallyl Carboxylic Acids **11**

catalyzed desymmetrizing iodolactonizations under the optimized reaction conditions (Table 6). The target  $\alpha$ -quaternary  $\gamma$ -butyrolactone products **12** were obtained in good to high yields and in good levels of enantioselectivity. It should be

Chart 1. Synthesis of Optically Active  $\alpha$ -Quaternary Ester **13**

mentioned that products **12** were obtained in a highly diastereoselective fashion in all cases listed in Table 6.

The synthetic utility of optically active  $\gamma$ -butyrolactone product **12a** was demonstrated in a transformation to  $\alpha$ -quaternary ester **13**<sup>29)</sup> (Chart 1). The compound **12a** was treated with potassium carbonate in methanol to give a methyl ester **13** that would possess epoxide as a useful functional group. It is noteworthy that this transformation proceeded with a complete retention of the stereochemistry.

## Conclusion

We reported the unexpected tendencies between chiral sulfide catalysts and selenide catalysts during asymmetric iodolactonizations. BINOL-derived chiral bifunctional selenides bearing a hydroxy group served as efficient catalysts in enantioselective iodolactonizations of 4-pentenoic acids to give optically active  $\gamma$ -butyrolactone products in good enantioselectivities. Unexpectedly, however, the reactions using related chiral sulfide catalysts provided the iodolactonization products as racemates. The roles of the chalcogenide moiety and of the hydroxy group on the BINOL-derived bifunctional catalysts were investigated, and we concluded that both the selenide moiety and the hydroxy group on chiral bifunctional selenide catalysts are essential in order to achieve an efficient enantioselective iodolactonization. The utility of BINOL-derived chiral bifunctional selenide catalysts was further demonstrated in the asymmetric syntheses of chiral phthalides and  $\alpha$ -quaternary lactones *via* enantioselective iodolactonizations. Further applications of chiral bifunctional selenide catalysts to other asymmetric transformations are currently underway by our group.

## Experimental

### General Procedure for Asymmetric Iodolactonizations

A solution of alkenyl carboxylic acid substrate [**1**, **9**, or **11**] (0.10 mmol) and chiral selenide catalyst [(*S*)-**4d** or (*S*)-**4c**] (10 mol %, 0.010 mmol) in dichloromethane (2 mL) [or dichloromethane (1 mL)–toluene (1 mL)] was cooled to  $-78^\circ\text{C}$ . After stirring for 10 min at  $-78^\circ\text{C}$ , 1,3-diiodo-5,5-dimethylhydantoin (DIH) (0.12 mmol) was added to the cooled reaction solution. The reaction mixture was stirred for 24 h at  $-78^\circ\text{C}$ . After 24 h, the reaction mixture was quenched with saturated aqueous  $\text{Na}_2\text{SO}_3$  (4 mL) at  $-78^\circ\text{C}$  and stirred for 10 min at  $-78^\circ\text{C}$ . The quenched reaction mixture was diluted with dichloromethane (2 mL) and water (2 mL). The mixture was then warmed to room temperature. The organic materials were extracted with dichloromethane three times (5 mL  $\times$  3). The combined extracts were dried over  $\text{Na}_2\text{SO}_4$  and concentrated. [The  $^1\text{H-NMR}$  analysis of the crude reaction mixture was performed at this stage to confirm diastereoselectivities of products **12**.] The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate as eluent) to

give iodolactonization product [**2**, **10**, or **12**]. The enantioselectivities of the products were determined by HPLC analysis on a chiral stationary phase.

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**Conflict of Interest** The authors declare no conflict of interest.

**Supplementary Materials** This article contains supplementary materials.

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- 34) When the iodolactonization of **1a** was performed with 0.6 equivalent of DIH under the influence of catalyst (*S*)-**4d**, iodolactonization product **2a** was obtained in a 75% yield with a 92:8 er. See also, Chart S1 in Supplementary Materials.
- 35) When the iodolactonization of **1a** using DIH (1.2 equiv) and catalyst (*S*)-**4d** was performed in the presence of I<sub>2</sub> (0.3 equiv) as an additive, iodolactonization product **2a** was obtained in a 99% yield with a 94:6 er. See also, Chart S1 in Supplementary Materials.
- 36) Part of the catalyst (*S*)-**4d** (approx. 40%) could be recovered after the iodolactonizations.
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