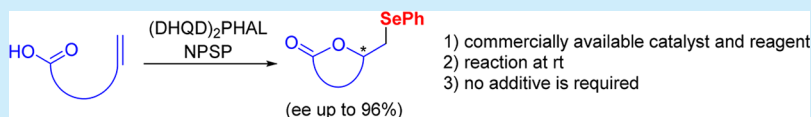


# Catalytic and Highly Enantioselective Selenolactonization

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**S** Supporting Information



**ABSTRACT:** An enantioselective selenolactonization of olefinic acids has been developed using (DHQD)<sub>2</sub>PHAL as the catalyst. Structurally simple and commercially available *N*-phenylselenophthalimide was used as the electrophilic selenium reagent. The corresponding selenolactones could be obtained with up to 96% ee.

Electrophilic functionalization of unactivated olefins through asymmetric catalysis has been a topic of great importance in organic chemistry in the past decades. A vast amount of asymmetric catalytic systems for epoxidation, dihydroxylation, aminohydroxylation, hydrogenations, and aziridination are well-documented in the literature.<sup>1</sup> In the past few years, there has also been a dramatic growth of asymmetric halogenation processes using various catalytic protocols.<sup>2</sup> A highly relevant class of reactions is the use of chalcogen electrophiles, including sulfur and selenium, in electrophilic chalcogen-functionalization processes.<sup>3</sup> This type of reaction is also considered as a complementary tool of co-halogenation as the chalcogen-containing molecules have apparently different synthetic utilities. Chemistry using thio and seleno compounds is also well-established.<sup>4</sup>

Significant efforts have been devoted to the development of chiral electrophilic selenium reagents in the stoichiometric enantioselective selenofunctionalization of unactivated olefins.<sup>5</sup> In sharp contrast, the catalytic enantioselective variant remains very uncommon. Recent reports by Denmark demonstrated excellent control of enantioselectivity in chiral Lewis-base-catalyzed sulfenofunctionalization reactions.<sup>6</sup> Intramolecular selenoetherification of olefinic alcohols with up to 70% ee was achieved when a similar protocol was applied.<sup>7</sup> In the report, the authors found that the phenylseleniranium ion could readily be racemized by olefin-to-olefin degeneration. A structurally unique reagent, *N*-(2-nitrophenylselenenyl)succinimide, was used as the electrophilic selenium source because the corresponding 2-nitrophenylseleniranium ion was found to be configurationally stable and can avoid extensive racemization. Very recently, Jacobsen and co-workers took advantage of the rapid racemization of the seleniranium ion and developed a highly enantioselective selenoetherification of olefinic phenols using a dynamic kinetic resolution strategy. In their report, the chiral squaramide/achiral sulfide Lewis base/PyHCl cocatalyst system together with the newly designed *N*-*p*-anisylselenenyl succinimide selenium reagent was employed.<sup>8</sup> However, to the best of our knowledge, there has been no report on the catalytic enantioselective selenolactonization. Herein, we disclose our recent finding on using a substoichiometric amount of

(DHQD)<sub>2</sub>PHAL as a bifunctional organocatalyst in the enantioselective selenolactonization of unactivated olefinic acids at room temperature, giving the corresponding selenolactones with up to 96% ee. This represents the first case of catalytic, asymmetric selenolactonization at a useful level of enantioselectivity.

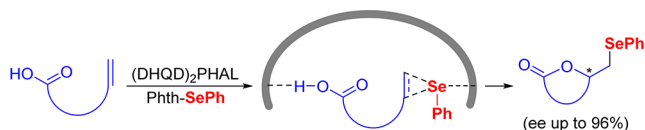
Development of enantioselective chalcogen-functionalization is challenging because there are three inherent difficulties: (1) racemization of the thiiranium or seleniranium ion through olefin-to-olefin degeneration; (2) nucleophilic partners (e.g., alcohol or carboxylic acid) may capture the thiiranium or seleniranium species and racemize it; and (3) Lewis basic chalcogen-containing products may capture the seleniranium ion and redeliver it to the olefin; this process is not necessary to be enantiospecific.<sup>9,10</sup> In one of the reports by Denmark and co-workers,<sup>9a</sup> it has been clearly demonstrated that both thiiranium and seleniranium ions could readily degenerate between olefins. When we compare thiiranium ions, seleniranium ions are far more configurationally unstable and their olefin-to-olefin transfer cannot be suppressed even at exceedingly low temperature; this might explain the extra difficulty in obtaining high enantioselectivity in catalytic enantioselective selenofunctionalization reactions.<sup>9</sup> In 1996, Toshimitsu and co-workers reported a potential solution to this problem in which a very bulky 2,4,6-tri-*tert*-butylphenyl group was introduced to provide steric protection to the chiral episeleniranium ion to suppress the racemization.<sup>10</sup> On the other hand, to avoid racemization of the chiral episeleniranium ion through the olefin-to-olefin degeneration or capturing by other nucleophiles, we decided to employ a bifunctional catalyst pocket that might potentially shield the configurationally unstable episeleniranium ion during the cyclization (Scheme 1).

At the outset of our trial, 4-phenyl-4-pentenoic acid (**1a**) was used as the substrate, and the commercially available *N*-phenylselenophthalimide (NPSP) **2** was used as the electrophilic selenium source. Various bifunctional organocatalysts were subjected to the investigation. Aminothiocarbamate **4**<sup>11</sup> and

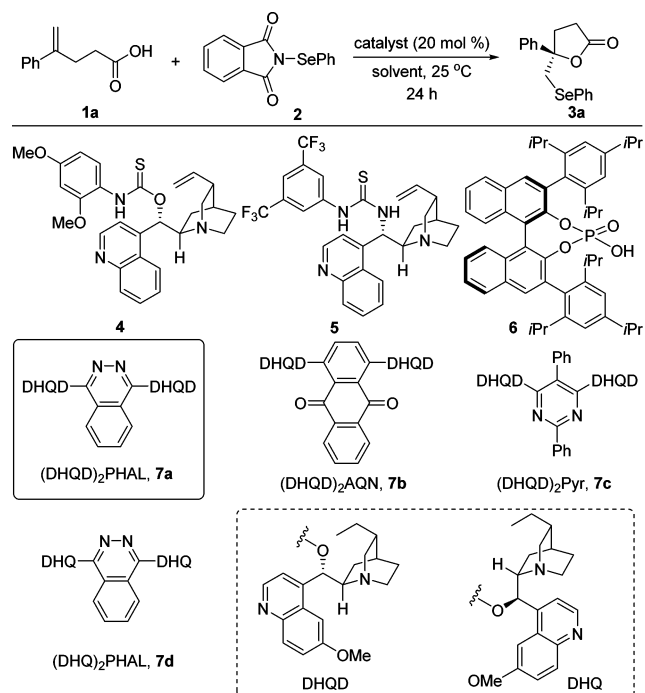
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## Scheme 1. Catalytic Enantioselective Selenolactonization



aminothiourea **5**,<sup>2</sup> which have shown excellent control in asymmetric halofunctionalization reactions, could not induce any enantioselectivity in the selenolactonization of **1a** (Table 1,

Table 1. Reaction Optimization<sup>a</sup>

entry	cat.	solvent	concn (M)	yield (%) <sup>b</sup>	ee (%)
1	4	CH <sub>2</sub> Cl <sub>2</sub>	0.1	91	0
2	5	CH <sub>2</sub> Cl <sub>2</sub>	0.1	48	0
3	6	CH <sub>2</sub> Cl <sub>2</sub>	0.1	23	0
4	7a	CH <sub>2</sub> Cl <sub>2</sub>	0.1	10	28
5	7a	(CH <sub>2</sub> Cl) <sub>2</sub>	0.1	67	68
6	7b	(CH <sub>2</sub> Cl) <sub>2</sub>	0.1	33	0
7	7c	(CH <sub>2</sub> Cl) <sub>2</sub>	0.1	51	4
8	7d	(CH <sub>2</sub> Cl) <sub>2</sub>	0.1	56	−49
9 <sup>c</sup>	7a	(CH <sub>2</sub> Cl) <sub>2</sub>	0.1	98	0
10 <sup>d</sup>	7a	(CH <sub>2</sub> Cl) <sub>2</sub>	0.1	99	0
11	7a	(CH <sub>2</sub> Cl) <sub>2</sub>	0.05	73	74
12	7a	(CH <sub>2</sub> Cl) <sub>2</sub>	0.02	77	84
13	7a	(CH <sub>2</sub> Cl) <sub>2</sub>	0.01	94	90
14	7d	(CH <sub>2</sub> Cl) <sub>2</sub>	0.01	82	−71

<sup>a</sup>Reactions were carried out with olefinic acid **1a** (0.1 mmol), catalyst (0.02 mmol), and NPSP (**2**) (0.1 mmol) at 25 °C for 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>PhSeCl was used as the selenylating agent. <sup>d</sup>PhSeBr was used as the selenylating agent.

entries 1 and 2). BINOL-derived phosphoric acid **6** was also examined, and the reaction was sluggish with no enantioselectivity (Table 1, entry 3). Nevertheless, to our delight, it was found that (DHQD)<sub>2</sub>PHAL **7a** could offer the desired product with an appreciable amount of ee (28%) (Table 1, entry 4).

Interestingly, the ee was enhanced significantly when the solvent was changed to 1,2-dichloroethane (Table 1, entry 5).

A brief survey of other structural analogues, including (DHQD)<sub>2</sub>AQN and (DHQD)<sub>2</sub>Pyr, revealed that (DHQD)<sub>2</sub>PHAL **7a** remained a better catalyst for this reaction (Table 1, entries 5–8). The antipode of **3a** could be obtained in 49% ee when the pseudoenantiomeric catalyst **7d** was employed. Other commercially available reagents, including PhSeCl and PhSeBr, were also examined, but no ee was obtained (Table 1, entries 9 and 10). The ee could be increased when the reaction was conducted at a lower concentration environment; 90% ee of **3a** could be obtained at 0.01 M (Table 1, entries 11–13).

With the optimized conditions, we then expanded the substrate scope, and the results are shown in Table 2. In general,

Table 2. Asymmetric Selenolactonization of **1**<sup>a</sup>

entry	3, R	time (days)	yield % (ee %)
1	3b, 2-naphthyl	3	76 (86)
2	3c, 4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	3	87 (83)
3	3d, 4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	1	89 (61)
4	3e, 4-Cl-C <sub>6</sub> H <sub>4</sub>	3	85 (90)
5	3f, 4-F-C <sub>6</sub> H <sub>4</sub>	5	72 (93)
6	3g, 4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	5	65 (94)
7	3h, 3-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	3	79 (91)
8	3i, 3-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	3	64 (91)
9	3j, 3-Cl-C <sub>6</sub> H <sub>4</sub>	5	85 (92)
10	3k, 3,5-(CF <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	5	45 (96)
11	3l, 2-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	3	23 (47)
12	3m, 3-thienyl	3	83 (81)
13	3n, cyclohexyl	3	89 (16)

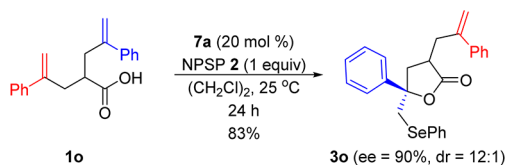
<sup>a</sup>Reactions were carried out with olefinic acid **1** (0.1 mmol), catalyst **7a** (0.02 mmol), and NPSP **2** (0.1 mmol) in 1,2-dichloroethane (10 mL). The yields were isolated yields.

the reactions were all performed smoothly with good yields and ee values. Aromatic-substituted acid substrates bearing electron-withdrawing chloro, fluoro, trifluoromethyl, and 3,5-bistrifluoromethyl substituents gave excellent ee (Table 2, entries 4–6, 9, and 10). The relatively low conversion in the formation of **3k** (55% of **1k** was recovered) could be attributed to the deactivated olefinic system. On the other hand, moderate ee values were obtained for the electron-donating *p*-methoxyphenyl- and *p*-methylphenyl-substituted substrates **1c** and **1d**, presumably due to the destruction of the episeleniranium ion through resonance (Table 2, entries 2 and 3). Nevertheless, the electron-rich *m*-methoxyphenyl and *m*-methylphenyl substrates **1h** and **1i** returned high enantioselectivity (Table 2, entries 7 and 8). Additionally, heteroaromatic substrate **1m** was found to be amenable to the catalytic asymmetric protocol and gave **3m** in good yield and ee (Table 2, entry 12). The *ortho*-methyl substrate **1l** gave low yield and ee of **3l**, probably due to the combination of adverse steric and electronic effects (Table 2, entry 11). While excellent yield of **3n** was obtained with the cyclohexyl substrate **1n**, the ee was undesirable under this catalytic protocol (Table 2, entry 13).

More importantly, we were delighted to realize that the catalytic protocol could also be applied in the desymmetrization—asymmetric selenolactonization of diene carboxylic acid **1o**,

affording **3o** in 90% ee with 12:1 dr (Scheme 2). The absolute configuration of lactones **3** was assigned to be *R* based on an X-ray crystallographic study of **3a**.

### Scheme 2. Catalytic Enantioselective Selenolactonization and Desymmetrization of **1o**



After the substrate scope expansion, the effect of catalyst loading on the reaction was investigated. It was found that 10 mol % of (DHQD)<sub>2</sub>PHAL could also promote the selenolactonization with 86% ee (Table 3, entry 1). Unexpectedly, increasing the

Table 3. Catalyst Loading Study<sup>a</sup>

entry	7a (mol %)	yield (%)	ee (%)
1	10	91	86
2	20	94	90
3	50	79	90
4	100	60	90

<sup>a</sup>Reactions were carried out with olefinic acid **1a** (0.1 mmol), catalyst **7a**, and NPSP **2** (0.1 mmol) in 1,2-dichloroethane (10 mL). The yields were isolated yields.

catalyst loading to 50 mol % suppressed the reaction rate, while the enantioselectivity was maintained (Table 3, entry 2 vs 3). The reaction efficiency was further suppressed in the presence of 1 equiv of (DHQD)<sub>2</sub>PHAL (Table 3, entry 4).

These unusual phenomena prompted us to further examine the interactions among substrate **1**, NPSP **2**, and catalyst **7a** using <sup>1</sup>H NMR.<sup>12</sup> The results are summarized as follows: (1) Upon mixing 1:1 of acid substrate **1a** and (DHQD)<sub>2</sub>PHAL **7a** in CD<sub>2</sub>Cl<sub>2</sub>, the protons H<sub>a</sub>–H<sub>d</sub> in **1a** shifted upfield while the methylene protons adjacent to the N atom of quinuclidine in **7a** exhibited a slight downfield shift (~0.1 ppm), which could be the result of the formation of a hydrogen-bonding complex between **1a** and **7a**. Since H<sub>g</sub> also exhibited a downfield shift, an interaction between the phthalazine and the proton might be present (Figure 1, **7a-H**).<sup>13</sup> (2) The shift pattern of H<sub>a</sub>–H<sub>f</sub> has no significant change for the **1a**/2/**7a** (1:1:1) mixture. In

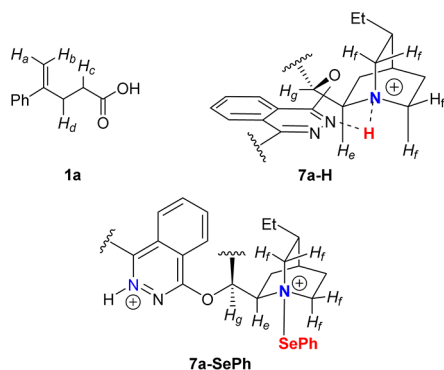
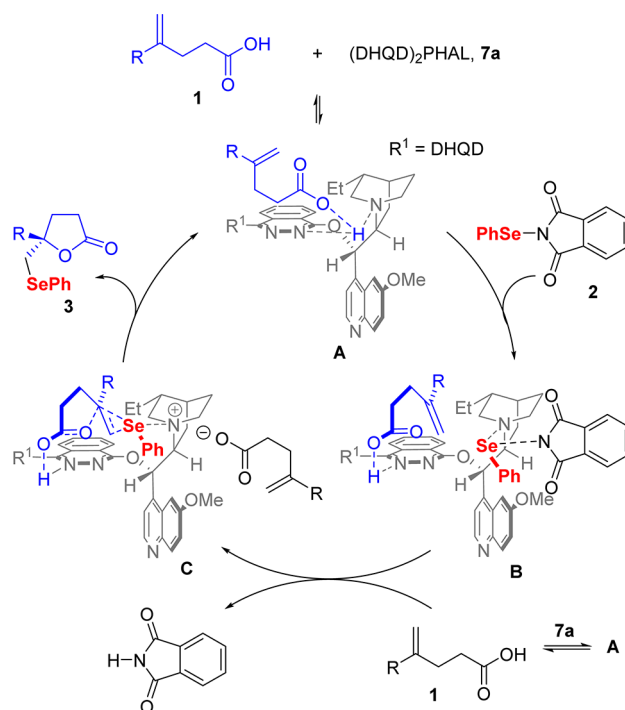


Figure 1. <sup>1</sup>H NMR study of the reaction mixture.

addition, the solution remained clear, and the selenolactonization was sluggish after 12 h in CD<sub>2</sub>Cl<sub>2</sub>, indicating that the reaction was suppressed. (3) For the <sup>1</sup>H NMR study of a mixture of **1a**/2/**7a** at a 1:1:0.2 ratio, which mimics the catalytic protocol, H<sub>e</sub> and H<sub>f</sub> demonstrated an appreciable downfield shift (~0.4 ppm) while the chemical shift of H<sub>a</sub>–H<sub>d</sub> was similar to that of the 1:1:1 mixture of **1a**/2/**7a**. In addition, a white precipitate of phthalimide was formed gradually, and the selenolactonization proceeded smoothly. These observations could be attributed to a change in the environment close to the quinuclidine. A possible explanation is that the quinuclidine's basic nitrogen might coordinate to the selenium reagent while the acid substrate might interact with the phthalazine's nitrogen (Figure 1, **7a-SePh**). Precipitation of phthalimide suggested that the counteranion might be the carboxylate of **1a**.

Consolidating these results, we attempted to establish a plausible mechanistic picture, as depicted in Scheme 3. We

Scheme 3. Plausible Mechanism of the (DHQD)<sub>2</sub>PHAL-Catalyzed Asymmetric Selenolactonization



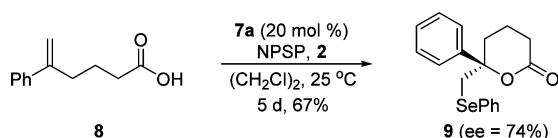
speculate that olefinic acid **1** might interact with **7a** to form the hydrogen-bonding complex **A**. Subsequent interaction of **A** with NPSP **2** could give the quinuclidine–NPSP complex **B**. Since no ee was observed when (DHQD)<sub>2</sub>AQN **7b** was used, the phthalazine's nitrogen might play a key role in the reaction, potentially interacting with the carboxylic acid moiety.<sup>13</sup> As shown in the above-mentioned results, the 1:1:1 mixture of **1a**/2/**7a** (a mimic of species **B**) could not undergo the selenolactonization smoothly, indicating that the selenium in **B** might not be electrophilic enough to drive the reaction. Thus, we suspect that species **B** might be further activated with another carboxylic acid **1** to give ionic species **C**, together with the elimination of a molecule of phthalimide, which might be the reason for the gradual generation of phthalimide precipitate in the 1:1:0.2 mixture of **1a**/2/**7a**. Species **C**, which contains a more electrophilic selenium, could then trigger the cyclization to give the desired product **3**.<sup>6d</sup> On the other hand, excess **7a** (under a



high catalyst loading condition) would trap acid **1** and slow the formation of species **C**, hence suppressing the reaction while the enantioselectivity could be maintained. It appears that a large catalyst pocket was required for this transformation to induce high enantioselectivity (Table 1); a possible explanation is that the catalyst might shield the seleniranium ion from racemization through the olefin-to-olefin degeneration.<sup>10</sup> Alternatively, the seleniranium ion could racemize rapidly, and intermediate **C** could be energetically more favorable through a dynamic kinetic resolution pathway.<sup>8</sup> A more detailed study is underway to further elucidate the whole reaction mechanism.

To further extend the scope, we examined the selenolactonization of **8**. Preliminary unoptimized results indicate that this catalytic protocol is potentially applicable to other skeletons in which **9** could be obtained in 74% ee (Scheme 4).

**Scheme 4. Preliminary Study on the Selenolactonization of 8**



In summary, we have developed a catalytic and highly enantioselective selenolactonization reaction. Further optimization of this catalytic protocol to other substrates with different skeletons is in progress.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures, characterization data for all new compounds, and CIF file of the X-ray structure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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