

# First regioselective iodocyclization of *O*-allylselenocarbamates

Dinesh R. Garud,<sup>a</sup> Masaki Makimura,<sup>a</sup> Hiromune Ando,<sup>b</sup> Hideharu Ishihara<sup>a</sup> and Mamoru Koketsu<sup>b,\*</sup>

<sup>a</sup>Department of Chemistry, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan

<sup>b</sup>Division of Instrumental Analysis, Life Science Research Center, Gifu University, Gifu 501-1193, Japan

Received 14 August 2007; revised 1 September 2007; accepted 6 September 2007

Available online 11 September 2007

**Abstract**—4-Alkyl-2-imino-1,3-oxaselenolanes were prepared in good yields with high regioselectivity under mild conditions by the reaction of selenocarbamates with I<sub>2</sub> or NIS. The resulting 4-alkyl-2-imino-1,3-oxaselenolanes on dehydrohalogenation gave 4-alkylidene-2-imino-1,3-oxaselenolanes. The formation of the (*Z*)- or (*E*)-isomer of 4-alkylidene-2-imino-1,3-oxaselenolanes, strongly depends on the configuration of the double bond of *O*-allylselenocarbamates.

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Recently many syntheses of compounds containing selenium have been studied and reported because of the interesting reactivities<sup>1</sup> and their potential biological activity.<sup>2</sup> 1,3-Selenolanes are found to have anticancer activity.<sup>3</sup> On the other hand, there are some drawbacks of the syntheses of selenium heterocycles as they often involve the use of toxic selenium reagents, which are difficult to handle and to store. The use of selenoureas<sup>4</sup> and isoselenocyanates,<sup>5</sup> respectively, proved to be among the most efficient methods for the introduction of selenium into heterocycles, as they are conveniently prepared<sup>6</sup> and relatively stable. Some years ago, we started a research program concerning the synthetic potential of isoselenocyanates as building blocks of selenium-containing heterocycles.<sup>7</sup> Recently, we described the synthesis of 2-imino-1,3-selenazolidines,<sup>8</sup> 2-selenoxoperhydro-1,3-selenazin-4-ones,<sup>9</sup> 2-selenoxo-1,3-selenazolidin-4-ones,<sup>9</sup> selenohydantoins,<sup>10</sup> and 1-thia-6-oxa-6a<sup>λ</sup>-seleno-3-azapentalene<sup>11</sup> from isoselenocyanates by the respective nucleophilic attack of N, Se, and C nucleophiles.

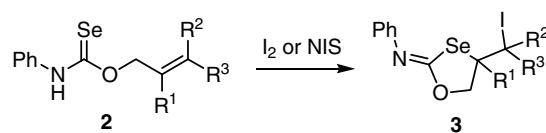
By way of contrast, no report on the synthesis of selenium-containing heterocycles from *N*-monoalkyl-*O*-allylselenocarbamates in the literature.<sup>12</sup> Iodocyclization of an unsaturated C–C bond with a wide variety of nucleophiles, including N, O, and S nucleophiles,

has been extensively studied<sup>13</sup> and has become a powerful tool for the construction of various heterocycles. In this letter, we describe the iodocyclization of *O*-allylselenocarbamates **2** using I<sub>2</sub> or NIS as the electrophile; this leads to 4-alkyl-2-imino-1,3-oxaselenolanes **3** in moderate to excellent yields (Scheme 1).

The starting *O*-allylselenocarbamates **2** for our approach were prepared from the isoselenocyanates **1** (Table 1).<sup>14</sup> The selenocarbamates **2c**, **2e**, and **2f** were sensitive to silica gel and were used for the next reaction without further purification.

Firstly, the reaction of **2a** (R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H) with 1.1 equiv of iodine in CH<sub>2</sub>Cl<sub>2</sub> was examined. To our delight the reaction took place readily at room temperature and the cyclization product **3a** was obtained in 40% yield after work-up of the reaction mixture. The structure of **3a** was elucidated by studies of IR, <sup>1</sup>H, <sup>13</sup>C, <sup>77</sup>Se NMR, COSY, HMQC, HMBC, NOESY, MS, HRMS, and elemental analysis.

To improve the yield of cyclization, different conditions were then screened. As shown in Table 2, CH<sub>2</sub>Cl<sub>2</sub> was a



Scheme 1.

**Keywords:** Selenium; Selenocarbamate; Isoselenocyanate; 1,3-Oxaselenolane.

\* Corresponding author. Tel./fax: +81 58 293 2619; e-mail: koketsu@gifu-u.ac.jp

**Table 1.** Synthesis of *O*-allylselenocarbamates **2**

Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Product	Yield <sup>a</sup> (%)
1	H	H	H	<b>2a</b>	94
2	Me	H	H	<b>2b</b>	91
3	H	<sup>n</sup> Pr	H	<b>2c</b>	— <sup>b</sup>
4	H	H	<sup>n</sup> Pr	<b>2d</b>	69
5	H	H	Ph	<b>2e</b>	— <sup>b</sup>
6	H	Me	Me	<b>2f</b>	— <sup>b</sup>

<sup>a</sup> Isolated yield.<sup>b</sup> The crude product was used for the next reaction without purification.

suitable solvent for the cyclization reaction. Furthermore, the reaction was influenced by the amount of iodine and the best result was obtained when 1.5 equiv of iodine was used (entry 4).

Under the optimized conditions, the reaction of other *O*-allylselenocarbamates **2** with iodine or NIS was investigated. The results are summarized in Table 3.<sup>15</sup> In most cases NIS was efficient and the corresponding 1,3-oxaselenolanes **3** were obtained in moderate to high yields. The reaction was strongly influenced by the substitution pattern on the allyl skeleton: unsubstituted *O*-allylselenocarbamates **2** at terminal position gave good to excellent yields (entries 1–4). The reaction of (*Z*)- or (*E*)-

**Table 2.** The reaction of **2a** with iodine under different conditions<sup>a</sup>

Entry	I <sub>2</sub> (equiv)	Solvent	Temp	Time (h)	Yield <sup>b</sup> (%)
1	1.1	CH <sub>2</sub> Cl <sub>2</sub>	rt	1	40
2	1.5	CH <sub>2</sub> Cl <sub>2</sub>	rt	0.5	40
3	1.5	CH <sub>2</sub> Cl <sub>2</sub>	–10 °C	0.5	54
4	1.5	CH <sub>2</sub> Cl <sub>2</sub>	–40 to –10 °C	2	77
5	1.5	CH <sub>3</sub> CN	–40 to –10 °C	2	60
6	1.5	THF	–40 to –10 °C	2	64
7	1.5	DMF	–40 to –10 °C	2	24

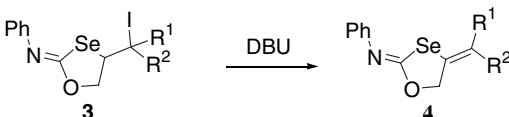
<sup>a</sup> The reaction was carried out using 0.5 mmol of **2a** as starting material.<sup>b</sup> Isolated yield.

allylselenocarbamates **2** with iodine gave very low yield (entries 5 and 7), however, the desired products **3c** and **3d** could be obtained in moderate yields when stronger electrophile NIS was used in the reaction instead of I<sub>2</sub> (entries 6 and 8). In the case of entries 9 and 10, the reaction was complicated and the products were isolated in traces. Bulky groups such as <sup>n</sup>Pr and Ph at  $\gamma$ -carbon may block the attack of iodine or selenium and make the yield lower. The reaction shows high regio- and stereo-selectivities for five-membered ring. In all reactions only five-membered 1,3-oxaselenolanes **3** were obtained. Recently, we reported the iodocyclization reaction of *N*-

**Table 3.** Synthesis of 1,3-oxaselenolanes **3** via iodocyclization of **2**<sup>a</sup>

Entry	Selenocarbamate	Electrophile	Product	Yield <sup>b</sup> (%)
1		I <sub>2</sub>		77
2		NIS		77
3		I <sub>2</sub>		79
4		NIS		88
5		I <sub>2</sub>		Trace
6		NIS		46 <sup>c</sup>
7		I <sub>2</sub>		Trace
8		NIS		64
9		NIS		Trace
10		NIS		Trace

<sup>a</sup> The reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub> using 1.0 equiv of **2** and 1.5 equiv of I<sub>2</sub> at –40 °C to –10 °C or 1.0 equiv of NIS at –40 °C to rt.<sup>b</sup> Isolated yield based on **2**.<sup>c</sup> Yield was calculated based on corresponding **1**.

**Table 4.** Synthesis of cis and trans isomer of 2-imino-4-methylidene-1,3-oxaselenolanes **4**<sup>a</sup>


Entry	Substrate	Time (h)	Product	Yield <sup>b</sup> (%)
1		3	<b>4a</b> 	99
2		1	<b>4b</b> 	94
3		3	<b>4c</b> 	67
4		1	<b>4d</b> 	67

<sup>a</sup> The reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

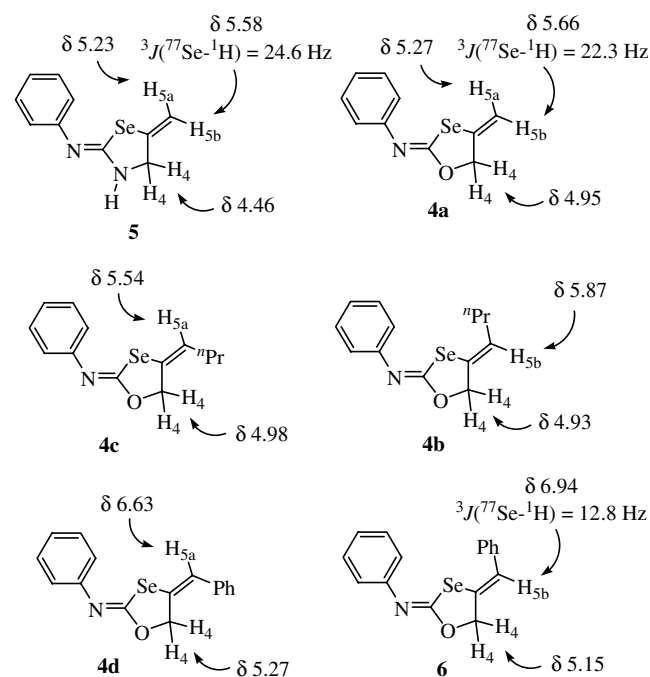
<sup>b</sup> Isolated yield based on **3**.

allylselenoureas with iodine to give six-membered ring.<sup>16</sup> In the present reaction, the reaction at  $-80\text{ }^{\circ}\text{C}$  also resulted in the formation of only five-membered ring compound **3** while formation of six-membered ring compounds had not been observed.

Next, the presence of the iodine allowed us the further structural elaboration, most notable by dehydrohalogenation reaction using DBU. For example, when compound **3a** was treated with DBU, the corresponding 4-methylidene-2-imino-1,3-oxaselenolane **4a** was isolated in excellent yield (Table 4, entry 1).<sup>17</sup> Interestingly, when 1,3-oxaselenolane, obtained from (*Z*)-*O*-allylselenocarbamate, was used in the reaction, the (*Z*)-geometry of the C=C double bond was retained in the final product **4b** (entry 2). To our delight treatment of 1,3-oxaselenolanes, obtained from (*E*)-*O*-allylselenocarbamates, with DBU afforded *E*-conformers **4c** and **4d** (entries 3 and 4). The geometry of the double bond was confirmed by <sup>1</sup>H, <sup>13</sup>C, <sup>77</sup>Se NMR, COSY, HMQC, HMBC, NOESY, and spectroscopic analysis.

Recently, we found very important spectral feature in the <sup>1</sup>H NMR spectra of 5-methylidene-2-phenylimino-1,3-selenazolidine **5** (Fig. 1).<sup>8</sup> The selenium coupling (<sup>3</sup>J<sub>77Se-1H</sub>) with trans-proton (H<sub>5b</sub> proton in **5**) was observed exclusively, while such a coupling with the cis-proton (H<sub>5a</sub> proton in **5**) was not observed. Also the cis-proton is upfield as compared to trans-proton. Similar spectral features were found in compound **4a**. The structures of compounds **4b** and **4c** were confirmed by comparison with compound **5** and **4a**. For the comparative studies, the (*Z*)-isomer of compound **4d**, that is, compound **6** was prepared by the reaction of 3-phenyl-2-propyn-1-ol with phenyl isoselenocyanate. Our current report confirms this important spectral feature (see: Ref. 8).

Kambe et al. reported the synthesis of 4-alkylidene-2-imino-1,3-oxaselenolanes **4** by the reaction of alk-2-yn-

**Figure 1.**

1-ols with selenium and isocyanides via intramolecular cycloaddition reaction.<sup>18</sup> The reactions gave only (*Z*)-isomer. Also the addition of selenolate ions to the triple bond gives (*Z*)-products only.<sup>19</sup> The formation of the product with (*E*)-configuration was not reported to date due to its difficulty in preparation. Our current report opens a new route for the synthesis of (*E*)-4-methylidene-2-imino-1,3-oxaselenolanes **4**.

In conclusion, we report the iodocyclization reaction of *O*-allylselenocarbamates to give five-membered ring 1,3-oxaselenolanes, which on treatment with DBU resulted in the formation (*Z*)- or (*E*)-4-alkylidene-2-imino-1,3-

oxaselenolanes selectively. Further investigation into the scope and limitations of this novel iodocyclization is underway.

### Acknowledgments

This work was supported by a Grant-in-Aid for Science Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (Nos. 15550030 and 17550099) to which we are grateful.

### References and notes

- (a) Ogawa, A.; Sonoda, N. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 6, p 461; (b) Ogawa, A.; Sonoda, N. *Rev. Heteroat. Chem.* **1994**, *10*, 43; (c) Guziec, F. S., Jr.; Guziec, L. J. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, 1995; Vol. 6, p 587; (d) Dell, C. P. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, 1995; Vol. 5, p 565; (e) Krief, A. In *Comprehensive Organometallic Chemistry*; Abel, W. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 11, p 515; (f) *Organoselenium Chemistry: A Practical Approach*; Back, T. G., Ed.; Oxford University Press: Oxford, 1999; p 999.
- (a) Kumar, Y.; Green, R.; Borysko, K. Z.; Wise, D. S.; Wotring, L. L.; Townsend, L. B. *J. Med. Chem.* **1993**, *36*, 3843; (b) Kumar, Y.; Green, R.; Wise, D. S.; Wotring, L. L.; Townsend, L. B. *J. Med. Chem.* **1993**, *36*, 3849; (c) Koketsu, M.; Ishihara, H.; Hatsu, M. *Res. Commun. Mol. Pathol. Pharmacol.* **1998**, *101*, 179; (d) Koketsu, M.; Ishihara, H.; Wu, W.; Murakami, K.; Saiki, I. *Eur. J. Pharm. Sci.* **1999**, *9*, 157; (e) Wu, W.; Murakami, K.; Koketsu, M.; Yamada, Y.; Saiki, I. *Anticancer Res.* **1999**, *19*, 5375; (f) Cho, S. I.; Koketsu, M.; Ishihara, H.; Matsushita, M.; Nairn, A. C.; Fukazawa, H.; Uehara, Y. *Biochim. Biophys. Acta.* **2000**, *1475*, 207.
- (a) Du, J.; Surzhykov, S.; Lin, J. S.; Newton, M. G.; Cheng, Y. C.; Schinazi, R. F.; Chu, C. K. *J. Med. Chem.* **1997**, *40*, 2991; (b) Chu, C. K.; Ma, L.; Olgen, S.; Pierra, C.; Du, J.; Gumina, G.; Gullen, E.; Cheng, Y. C.; Schinazi, R. F. *J. Med. Chem.* **2000**, *43*, 3906.
- See the review: Koketsu, M.; Ishihara, H. *Curr. Org. Synth.* **2006**, *3*, 439–455.
- See the review: Garud, D. R.; Koketsu, M.; Ishihara, H. *Molecules* **2007**, *12*, 504–535.
- (a) Barton, D. H. R.; Parekh, S. I.; Tajbakhsh, M.; Theodorakis, E. A.; Tse, C.-L. *Tetrahedron* **1994**, *50*, 639–654; (b) Bakhsh, M. T.; Behshtiha, Y. S.; Heravi, M. M. *J. Chem. Soc. Pak.* **1996**, *18*, 159–162.
- (a) Koketsu, M.; Yamamura, Y.; Ishihara, H. *Heterocycles* **2006**, *68*, 1191–1200; (b) Koketsu, M.; Yamamura, Y.; Ando, H.; Ishihara, H. *Heterocycles* **2006**, *68*, 1267–1273; (c) Koketsu, M.; Otsuka, T.; Ishihara, H. *Heterocycles* **2006**, *68*, 2107–2112.
- Koketsu, M.; Sakai, T.; Kiyokuni, T.; Garud, D. R.; Ando, H.; Ishihara, H. *Heterocycles* **2006**, *68*, 1607–1615.
- Koketsu, M.; Yamamura, Y.; Ishihara, H. *Synthesis* **2006**, 2738–2742.
- Koketsu, M.; Takahashi, A.; Ishihara, H. *J. Heterocyclic Chem.* **2007**, *44*, 79–81.
- Koketsu, M.; Otsuka, T.; Swenson, D.; Ishihara, H. *Org. Biomol. Chem.* **2007**, *5*, 613–616.
- Only one report from *N*-dialkyl-*O*-alkylselenocarbamates has been published recently concerning the synthesis of a 1,3-oxaselenolium salts. See: Perst, H. *Sci. Synthesis* **2002**, *11*, 93–95.
- See the review: Frederickson, M.; Grigg, R. *Org. Prep. Proced. Int.* **1997**, *29*, 33.
- Synthesis procedure and spectral data of selected compounds. *N*-Phenyl-*O*-allylselenocarbamate (**2a**): To a solution of NaH (270 mg, 6.75 mmol) in THF (1 mL) was added a solution of allyl alcohol **1a** (0.3 mL, 4.5 mmol) in THF (1 mL) at 0 °C under argon. The resulting mixture was stirred for 20 min at 0 °C. To this, a solution of phenyl isoselenocyanate (548 mg, 3.0 mmol) in THF (1 mL) was added slowly and stirring was continued for additional 10 min at 0 °C. After the completion of the reaction, the reaction mixture was quenched with ice water and extracted with ethyl acetate, washed with saturated NH<sub>4</sub>Cl, and brine. The combined organic layer was dried over sodium sulfate, filtered, and evaporated in vacuo. The residue was chromatographed on silica gel using diethyl ether/hexane (1:10) as eluent to give **2a** as white solid (678 mg, 94%). Mp 79.9–81.1 °C; IR (KBr) 3172, 1596 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.20 (d, 2 H, *J* = 7.5 Hz), 5.31 (d, 1H, *J* = 10.3 Hz), 5.40 (d, 1H, *J* = 17.2 Hz), 6.00–6.08 (m, 1H), 7.19–7.35 (m, 5H), 9.65 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 76.6, 119.6, 121.8, 125.9, 129.1, 130.8, 136.8, 190.5; <sup>77</sup>Se NMR (95 MHz, CDCl<sub>3</sub>): δ 278.4; EIMS: *m/z* = 241 [M<sup>+</sup>]. Anal. Calcd for C<sub>10</sub>H<sub>11</sub>NOSe: C, 50.01; H, 4.62; N, 5.83. Found: C, 50.27; H, 4.71, N, 5.90.
- Synthesis procedure and spectral data of selected compounds. (*4R*\*)-4-[(1*S*\*)-1-Iodobutyl]-2-phenylimino-1,3-oxaselenolane **3d**: Method A: To a solution of **2d** (56.4 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added I<sub>2</sub> (76.4 mg, 0.3 mmol) at -40 °C. After stirring at this temperature for 1 h, the reaction mixture was warmed to -10 °C and stirring was continued for additional 30 min. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and NaHCO<sub>3</sub>. The organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated in vacuo. The residue was chromatographed on silica gel using ether/hexane (1:9) as eluent to give traces of compound **3d**. Method B: To a solution of **2d** (112 mg, 0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added NIS (90 mg, 0.4 mmol) at -40 °C. After stirring at this temperature for 10 min, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and NaHCO<sub>3</sub>. The organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated in vacuo. The residue was chromatographed on silica gel using ether/hexane (1:9) as eluent to give compound **3d** (104 mg, 64%). Mp 69.4–70.0 °C; IR (KBr) 1659 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.90 (t, 3H, *J* = 7.2 Hz), 1.38–1.47 (m, 1H), 1.55–1.65 (m, 2H), 1.71–1.78 (m, 1H), 4.26 (dt, 1H, *J* = 2.3, 9.2 Hz), 4.38 (m, 1H), 4.49 (dd, 1H, *J* = 5.7, 10.3 Hz), 4.62 (dd, 1H, *J* = 5.7, 10.3 Hz), 6.94 (d, 2H, *J* = 7.4 Hz), 7.13 (t, 1H, *J* = 7.4 Hz), 7.32 (t, 2H, *J* = 7.4 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 13.0, 22.2, 37.2, 42.6, 52.7 (<sup>1</sup>*J*<sub>77Se-13C</sub> = 58.8 Hz), 77.8, 120.7, 124.7, 129.2, 149.6, 160.4; <sup>77</sup>Se NMR (95 MHz, CDCl<sub>3</sub>): δ 405.9; EI-MS: *m/z* = 409 [M<sup>+</sup>]; HRMS: *m/z* = 409.9521, calcd for C<sub>13</sub>H<sub>17</sub>INOSe, found 409.9538 [M<sup>+</sup>+H]. (*4R*\*)-4-[(1*R*\*)-1-Iodobutyl]-2-phenylimino-1,3-oxaselenolane **3c**: Method A: IR (KBr) 1658 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.93 (t, 3H, *J* = 7.2 Hz), 1.29–1.39 (m, 1H), 1.62–1.77 (m, 3H), 4.34 (m, 1H), 4.46 (dd, 1H, *J* = 5.7, 10.3 Hz), 4.56 (m, 1H), 4.61 (dd, 1H, *J* = 4.0, 10.3 Hz),

- 6.95 (d, 2H,  $J = 7.4$  Hz), 7.14 (t, 1H,  $J = 7.4$  Hz), 7.32 (t, 2H,  $J = 7.4$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.9, 23.4, 37.3, 38.6, 53.0 ( $^1J_{77\text{Se}-^{13}\text{C}} = 58.8$  Hz), 73.5, 120.7, 124.7, 129.3, 149.9, 161.2;  $^{77}\text{Se}$  NMR (95 MHz,  $\text{CDCl}_3$ ):  $\delta$  394.8; CI-MS:  $m/z = 409$  [ $\text{M}^+$ ]; HRMS:  $m/z = 409.9521$ , calcd for  $\text{C}_{13}\text{H}_{17}\text{INOSe}$ , found 409.9486 [ $\text{M}^+\text{H}$ ].
16. Koketsu, M.; Kiyokuni, T.; Sakai, T.; Ando, H.; Ishihara, H. *Chem. Lett.* **2006**, 35, 626–627.
17. Synthesis procedure and spectral data of selected compounds. (*Z*)-4-Butylidene-2-phenylimino-1,3-oxaselenolane (**4b**): To a solution of **3c** (61.8 mg, 0.15 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.5 mL) was added DBU (34  $\mu\text{L}$ , 0.23 mmol) and the resulting reaction mixture was stirred for 1 h at rt under argon. The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and washed with water and brine. The combined organic layer was dried over sodium sulfate, filtered, and evaporated in vacuo. The residue was chromatographed on silica gel using diethyl ether/hexane (1:6) as eluent to give **4b** (40.0 mg, 94%). IR (KBr) 2958, 1654, 1592, 1117  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.88 (t, 3H,  $J = 7.4$  Hz), 1.38–1.48 (m, 2H), 1.94 (q, 2H,  $J = 7.4$  Hz), 4.92 (d, 2H,  $J = 1.1$  Hz), 5.84–5.91 (m, 1H), 6.96 (d, 2H,  $J = 7.4$  Hz), 7.14 (t, 1H,  $J = 7.4$  Hz), 7.32 (t, 2H,  $J = 7.4$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.6, 21.8, 35.7, 75.6, 120.9, 124.6, 124.7, 129.2, 131.3, 149.8, 161.1;  $^{77}\text{Se}$  NMR (95 MHz,  $\text{CDCl}_3$ ):  $\delta$  344.9; FAB-MS:  $m/z = 282$  [ $\text{M}^+\text{H}$ ]. Anal. Calcd for  $\text{C}_{13}\text{H}_{15}\text{NOSe}$ : C, 55.72; H, 5.40; N, 5.00. Found: C, 55.58; H, 5.46; N, 4.86. (*E*)-4-Butylidene-2-phenylimino-1,3-oxaselenolane (**4c**): IR (KBr) 2958, 1663, 1592, 1115  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.82 (t, 3H,  $J = 7.4$  Hz), 1.39–1.48 (m, 2H), 2.08 (q, 2H,  $J = 7.4$  Hz), 4.99 (d, 2H,  $J = 1.1$  Hz), 5.51–5.57 (m, 1H), 6.95 (d, 2H,  $J = 7.4$  Hz), 7.13 (t, 1H,  $J = 7.4$  Hz), 7.32 (t, 2H,  $J = 7.4$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.6, 22.3, 32.2, 72.7, 120.9, 124.6, 126.4, 128.9, 129.2, 149.9, 161.4;  $^{77}\text{Se}$  NMR (95 MHz,  $\text{CDCl}_3$ ):  $\delta$  376.6; FAB-MS:  $m/z = 282$  [ $\text{M}^+\text{H}$ ]; HRMS:  $m/z = 282.0398$ , calcd. for  $\text{C}_{13}\text{H}_{16}\text{NOSe}$ , found 282.0419 [ $\text{M}^+\text{H}$ ]. Anal. Calcd for  $\text{C}_{13}\text{H}_{15}\text{NOSe}$ : C, 55.72; H, 5.40; N, 5.00. Found: C, 55.57; H, 5.50; N, 4.77.
18. Asanuma, Y.; Fujiwara, S.; Shin-ike, T.; Kambe, N. *J. Org. Chem.* **2004**, 69, 4845–4848.
19. (a) Ramazani, A.; Morsali, A.; Ganjeie, B.; Kazemizadeh, A. R.; Ahmadi, E. *Phosphorus, Sulfur Silicon Relat. Elem.* **2005**, 180, 2439–2442; (b) Ramazani, A.; Kazemizadeh, A. R.; Ganjeie, B.; Ahmadi, E. *Asian J. Chem.* **2005**, 17, 2371–2374; (c) Ramazani, A.; Morsali, A.; Ganjeie, B.; Kazemizadeh, A. R.; Ahmadi, E.; Kempe, R.; Hertle, I. Z. *Naturforsch.* **2005**, 60b, 569–571; (d) Koketsu, M.; Kanoh, K.; Ishihara, H. *Heterocycles* **2006**, 68, 2627–2633.