

Note

Palladium-Catalyzed Markovnikov-Selective Hydroselenation of N-Vinyl Lactams with Selenols Affording N,Se-Acetals

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Palladium-Catalyzed Markovnikov-Selective Hydroselenation of *N*-Vinyl Lactams with Selenols Affording *N,Se*-Acetals

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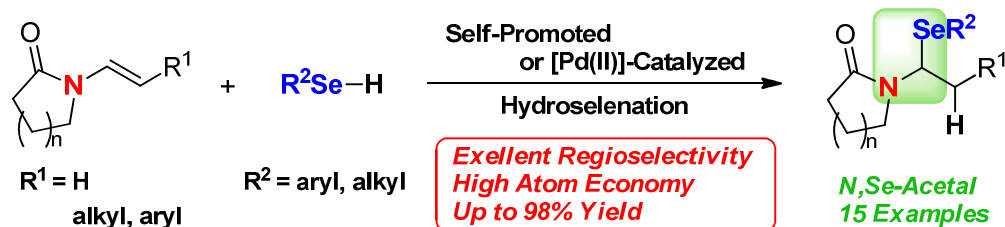
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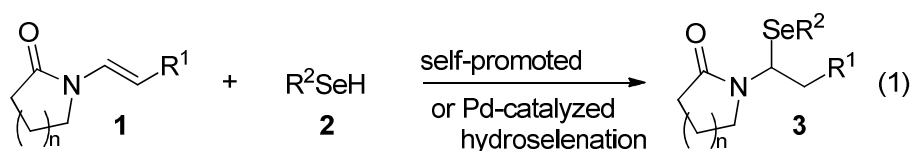
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ABSTRACT. The highly regioselective hydroselenation of *N*-vinyl lactams has been revealed to successfully afford the corresponding *N,Se*-acetals as Markovnikov adducts. In the case of terminal *N*-vinyl lactams, Markovnikov-selective hydroselenation proceeds efficiently in the absence of any catalyst (or additive), owing to the acidity of the selenols. In contrast, the self-promoted hydroselenation is inefficient with internal *N*-vinyl lactams. In the presence of palladium diacetate (Pd(OAc)₂), however, the desired hydroselenation of internal *N*-vinyl lactams proceeds efficiently to afford the corresponding *N,Se*-acetals.

KEYWORDS. Hydroselenation, Selenol, *N*-Vinyl lactam, Self-promoted addition, Palladium catalyst

A number of organoselenium compounds serve as synthetic intermediates, bioactive compounds, and functional materials.¹ Among them, *Se,Se*-, *O,Se*-, and *N,Se*-acetals are excellent synthetic intermediates as protecting groups for carbonyl and iminyl moieties, and especially, *Se,Se*-acetals have been used as practical umpolung species.² Selenium-containing acetals are usually prepared by the nucleophilic addition of selenols to carbonyl and iminyl groups. The regioselective addition of selenols to enol ethers and enamines is a promising alternative method to synthesize acetal derivatives. Herein, we report the Markovnikov-selective hydroselenation of *N*-vinyl lactams with selenols as an alternative approach towards *N,Se*-acetals (eq. 1).



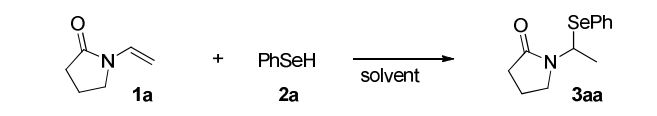
To date, numerous regioselective addition reactions of heteroatom-containing compounds such as boron, silicon, phosphorus, and sulfur to C-C unsaturated bonds have been developed, e.g., radical, ionic, and transition-metal-catalyzed additions.³ Although the addition of selenols to alkynes has been established in acid- or base-assisted ionic reactions, radical reactions, and transition-metal-catalyzed

1 reactions, the corresponding addition to alkenes has considerable limitations.^{4,5,6,7} In general, the radical
2 addition of selenols to alkenes gives *anti*-Markovnikov adducts regioselectively, and limited examples
3 of Markovnikov-selective hydroselenations are known.⁵ Although Markovnikov adducts may be
4 synthesized by transition-metal-catalyzed reactions, catalyst poisoning by selenols often hinders catalytic
5 reactions.^{7,8} Moreover, most known Markovnikov-selective hydroselenation reactions require additives,
6 such as Brønsted acids, to promote the addition. Very recently, we overcame similar limitation in
7 transition-metal-catalyzed hydrothiolations by using alkenes bearing alkoxy or amino group directly
8 bonded to carbon-carbon double bond.⁹

19 In this study, we found that selenols promote the hydroselenation of terminal *N*-vinyl lactams. This
20 self-promoted hydroselenation requires no additives; therefore, this method exhibits high atom economy.
21 Furthermore, the hydroselenation of internal *N*-vinyl lactams proceeds with excellent regioselectivity
22 (Markovnikov-selective) in the presence of palladium catalysts such as Pd(OAc)₂.

28 First, we investigated the addition of benzeneselenol to *N*-vinyl pyrrolidone, as a manageable terminal
29 *N*-vinyl lactam, without the addition of any additives (Table 1). When *N*-vinyl pyrrolidone (**1a**) was
30 reacted with benzeneselenol (**2a**) at 45 °C for 20 h in THF, the Markovnikov-type adduct was obtained
31 regioselectively in 93% yield without formation of *anti*-Markovnikov adduct (entry 1). When CH₃CN
32 and toluene were used as solvents, the yield of the desired hydroselenation product decreased (entries 2
33 and 3). The reaction in EtOH or in the absence of solvent was also examined to produce the
34 corresponding adduct in good yield, respectively (entries 4 and 5). Next, we examined the effects of
35 reaction time and temperature (entries 6-9). Furthermore, when the reaction in the presence of *p*-TsOH
36 as a strong acid was conducted, the desired hydrothiolation did not proceed (entry 10). This is probably
37 because *p*-TsOH promoted the polymerization of *N*-vinyl pyrrolidone. The results clearly indicated that
38 the optimal reaction conditions were 45 °C for 20 h in THF.

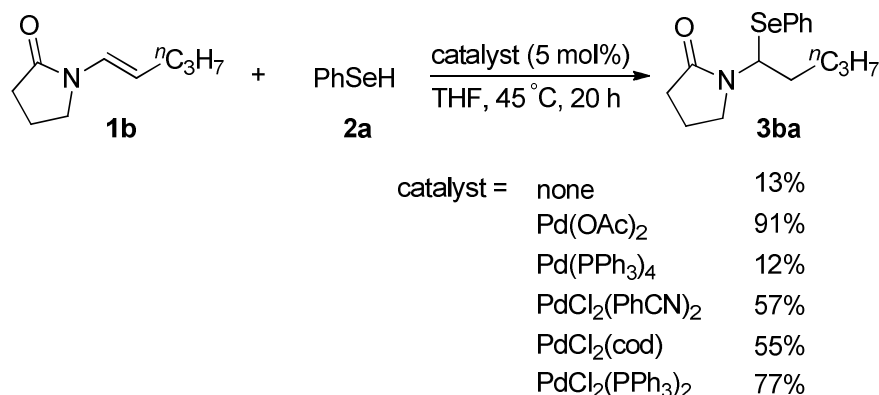
54 **Table 1. Optimization of Hydroselenation of Terminal *N*-Vinyl Pyrrolidone^a**



entry	solvent	time, h	temp., °C	yield, % ^b
1	THF	20	45	93
2	CH ₃ CN	20	45	60
3	toluene	20	45	27
4	EtOH	20	45	89
5	none	20	45	82
6	THF	6	45	73
7	THF	3	45	53
8	THF	20	reflux	93
9	THF	20	r.t.	67
10 ^c	THF	6	45	trace

^a Reaction conditions: *N*-vinyl pyrrolidone (**1a**, 0.5 mmol), benzeneselenol (**2a**, 0.5 mmol), and solvent (0.3 mL). ^b Determined by ¹H NMR analysis. ^c Reaction was conducted in the presence of *p*-TsOH as a strong acid.

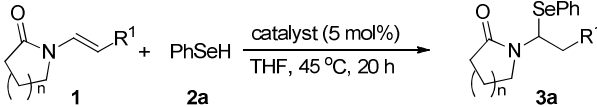












Next, the hydroselenation of internal *N*-vinyl lactams was conducted under similar reaction conditions (in the absence of additives); however, the corresponding hydroselenation product could not be obtained. Therefore, we examined the Pd-catalyzed hydroselenation of internal *N*-vinyl lactams (Scheme 1). When the 5 mol% of Pd(OAc)₂ was used as the catalyst, the desired Markovnikov hydroselenation proceeded very efficiently. When a low-valent palladium catalyst, Pd(PPh₃)₄, was employed, the hydroselenation product was obtained in only 12% yield. This result indicated that Pd(0) was not effective for the hydroselenation of internal *N*-vinyl lactams. Thus, the hydroselenation was examined in the presence of Pd(II) catalysts, such as PdCl₂(PhCN)₂, PdCl₂(cod), and PdCl₂(PPh₃)₂. The tested Pd(II) complexes catalyzed the hydroselenation of internal *N*-vinyl lactam **1b** to produce Markovnikov-adduct **3ba** in moderate to good yields.



Scheme 1. Optimization of Hydroselenation of Internal *N*-Vinyl Pyrrolidone

Next, the scope of viable *N*-vinyl lactams was examined under the optimized reaction conditions (Table 2). When terminal *N*-vinyl lactams **1a** and **1c** were used for the hydroselenation in the absence of a catalyst, the corresponding hydroselenation products **3aa** and **3ca** were obtained in 93% and 57% yields, respectively (entries 1 and 3). In the case of *N*-vinyl caprolactam **1c**, the yield was dramatically improved by the addition of 5 mol% of Pd(OAc)₂ (entry 4). In the case of internal *N*-vinyl lactams **1b**, **1d**, **1e**, and **1f**, the desired hydroselenation was ineffective in the absence of a catalyst (entries 5, 7, 9, 11). However, the Pd(OAc)₂-catalyzed hydroselenation proceeded successfully and the corresponding hydroselenation products were obtained in good to excellent yields (entries 6, 8, 10, 12). These results indicated that a Pd(II) catalyst was essential for the efficient hydroselenation of internal *N*-vinyl lactams.

Table 2. Hydroselenation of Several *N*-Vinyl Lactams ^a

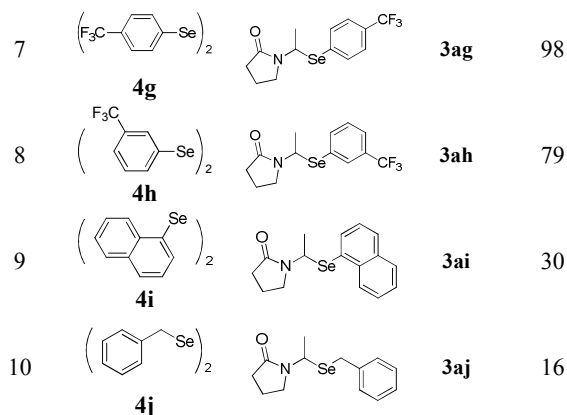
				
entry	catalyst	product	3	yield, % ^b
1	—		3aa	(93)
2	Pd(OAc) ₂		3aa	96
3	—		3ca	(57)
4	Pd(OAc) ₂		3ca	95
5	—		3ba	(13)
6	Pd(OAc) ₂		3ba	82
7	—		3da	(28)
8	Pd(OAc) ₂		3da	80
9	—		3ea	(7)
10	Pd(OAc) ₂		3ea	85
11	—		3fa	ND
12	Pd(OAc) ₂		3fa	50

^a Reaction conditions: *N*-vinyl pyrrolidone (**1**, 0.5 mmol), benzeneselenol (**2a**, 0.5 mmol), solvent (0.3 mL). ^b The yields in parenthesis are determined by ¹H NMR analysis.

The hydroselenation of *N*-vinyl lactams using several selenols was performed; the results are summarized in Table 3. Recently, we developed a convenient method to prepare areneselenols by the reduction of the corresponding diaryl diselenides with diphenylphosphine oxide. In general, selenols are air-sensitive and foul-smelling, and therefore, *in situ* generation and direct use are desired.¹⁰ By using this method, the hydroselenation of *N*-vinyl pyrrolidone with various areneselenols in the absence of a Pd catalyst was successfully accomplished, as shown in Table 3. Diaryl diselenides bearing either electron-donating group such as *p*-methoxy or -withdrawing groups such as *m*-methoxy, chloro, fluoro, and trifluoromethyl moieties, afforded the corresponding hydroselenation products **3ab**, **3ac**, **3ad**, **3ae**, **3af**, **3ag**, and **3ah**, respectively (entries 2–8). In the case of dinaphthyl diselenide, the desired hydroselenation product **3ai** was obtained in a moderate yield (entry 9). When dibenzyl diselenide as an aliphatic organoselenide was used for the hydroselenation, the corresponding hydroselenation product **3aj** was obtained in 16% yield (entry 10).

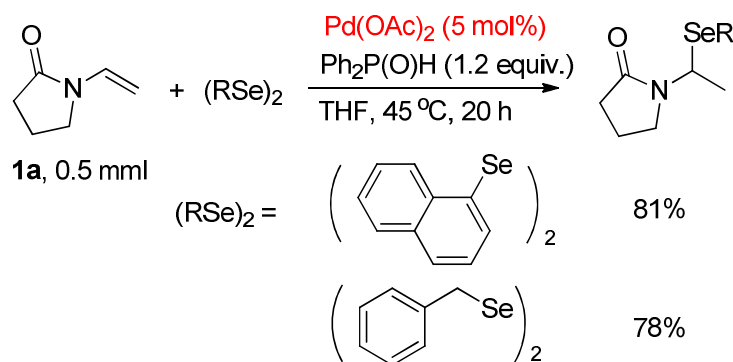
Table 3. Self-Promoted Hydroselenation of *N*-Vinyl Lactams Using Several Diselenides ^a

entry	(RSe) ₂ , 4	product	3	yield, %
1			3aa	94
2			3ab	79
3			3ac	85
4			3ad	70
5			3ae	64
6			3af	71



^a Reaction conditions: *N*-vinyl pyrrolidone (**1a**, 0.25 mmol), diselenide (**4**, 0.25 mmol), THF (0.15 mL), diphenylphosphine oxide (0.3 mmol), 45 °C, 20 h.

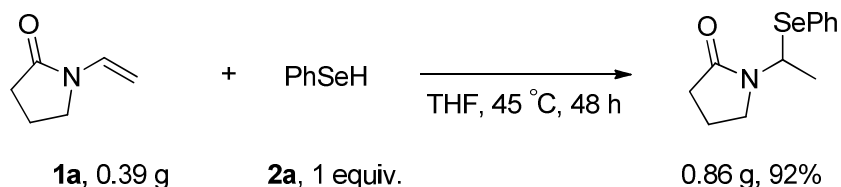
The Pd-catalyzed hydroselenation of *N*-vinyl pyrrolidone **1a** using diphenyl diselenides and diphenylphosphine oxide was carried out (Scheme 2). When dinaphthyl diselenide **4i** and dibenzyl diselenide **4j** were employed, the yields of the desired hydroselenation products, **3ai** and **3aj**, were dramatically improved. The results clearly indicated that the palladium diacetate-catalyzed hydroselenation in the presence of diselenides and diphenylphosphine oxide could serve as a convenient tool to synthesize *N*,*Se*-acetal derivatives.



Scheme 2. Pd-Catalyzed Hydroselenation of Terminal *N*-Vinyl Pyrrolidone Using Diselenides

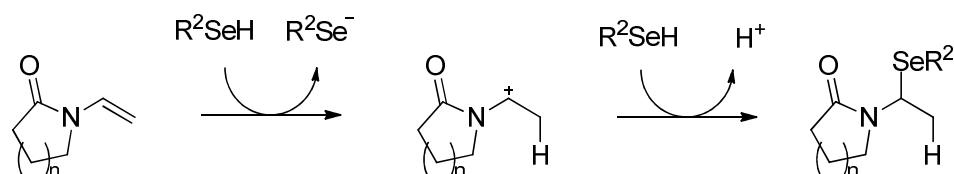
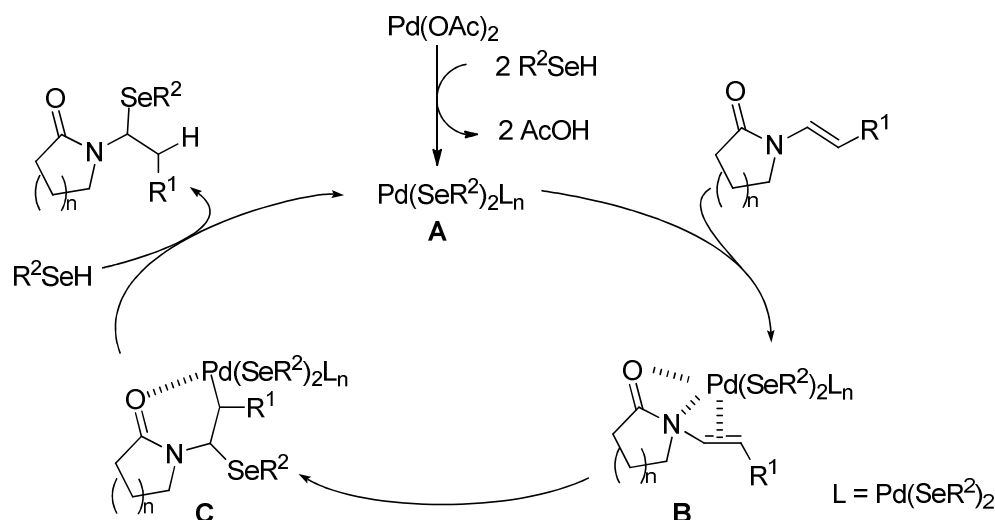
Finally, the hydroselenation of *N*-vinyl lactam was evaluated in the large scale reaction using 0.39 g of the *N*-vinyl pyrrolidone. The reaction was completed in 48 h at 45 °C and 92% of the isolated yield of

the hydroselenation product was obtained selectively (Scheme 3). These *N*,*Se*-acetal derivatives can be transformed into the corresponding aldehydes under the radical reaction.^{2f}



Scheme 3. Hydroselenation of *N*-Vinyl Pyrrolidone with Benzeneselenol in the Large Scale

A plausible reaction pathway for the present hydroselenation of *N*-vinyl lactams is shown in Scheme 4. In the absence of the Pd-catalyst, firstly, the terminal *N*-vinyl lactam is easily protonated by selenol. Then, the generated cation of terminal *N*-vinyl lactam is stabilized by electron donation from nitrogen atom. Finally, selenol attacks the cation of terminal *N*-vinyl lactam to give the Markovnikov-type hydroselenation product regioselectively. In the case of the Pd-catalyzed hydroselenation, the Pd(OAc)₂ catalyst initially reacts with selenol to form Pd selenide complex **A**. Then, *N*-vinyl lactam coordinates to Pd selenide complex **A**, providing Pd selenide-alkene complex **B**, where heteroatoms might coordinate to palladium, thereby stabilizing complex **B**. Subsequent selenopalladation takes place regioselectively to generate palladium intermediate **C**. Protonation of palladium intermediate **C** with the selenol provides the Markovnikov hydroselenation product regioselectively, with regeneration of Pd selenide complex **A**.

Terminal *N*-Vinyl Lactam (in the Absence of Palladium Catalyst)**Internal *N*-Vinyl Lactam (in the Presence of Palladium Catalyst)****Scheme 4. A Possible Reaction Pathway for Hydroselenation of *N*-Vinyl Lactams**

In conclusion, the highly selective hydroselenation of *N*-vinyl lactams to produce *N*,*Se*-acetal derivatives was developed. The hydroselenation of terminal *N*-vinyl lactams proceeded smoothly to give Markovnikov-type adducts selectively. Palladium(II) diacetate catalyzed the hydroselenation of internal *N*-vinyl lactams, despite the inefficiency of the self-promoted hydroselenation. Furthermore, Markovnikov-selective hydroselenation was demonstrated using a series of areneselenols, which were generated *in situ* from the corresponding diselenides and diphenyl phosphine oxide.

Experimental Section**General Information.**

Unless otherwise stated, all starting materials and catalysts were purchased from commercial sources and used without further purification. The following substrates were prepared by using dehydrative

condensation of pyrrolidinone and the corresponding aldehyde with *p*-TsOH: (*E*)-1-(1-pentenyl)-2-pyrrolidinone, (*E*)-1-(3-phenyl-1-propenyl)-2-pyrrolidinone, (*E*)-1-(3,3-dimethyl-1-butenyl)-2-pyrrolidinone, (*E*)-1-styryl-2-pyrrolidinone.¹¹ The all diorganyl diselenides were synthesized according to the literature.¹² THF as solvent was used after distillation from CaH₂. ¹H NMR spectra (400 MHz), ¹³C NMR spectra (100 MHz) were taken in CDCl₃ with Me₄Si as an internal standard. ¹⁹F NMR spectra (373 MHz) were taken in CDCl₃ with CFC₃ as an external standard. ⁷⁷Se NMR spectra (75 MHz) were taken in CDCl₃ with Me₂Se as an external standard. Chemical shifts in ¹H NMR were measured relative to CDCl₃ and converted to δ (Me₄Si) values by using δ (CDCl₃) 7.26 ppm. Chemical shifts in ¹³C NMR were measured relative to CDCl₃ and converted to δ (Me₄Si) values by using δ (CDCl₃) 77.00 ppm. IR spectra were reported in wave numbers (cm⁻¹). ESI and EI mass spectra were obtained by employing double focusing mass spectrometers.

General Procedure for Self-Promoted Hydroselenation of *N*-Vinyl Lactams.

In a two-necked 10 mL flask with a magnetic stirring bar under N₂ atmosphere were placed freshly distilled THF (0.3 mL), *N*-vinyl lactam (0.5 mmol) and selenol (0.5 mmol). The reaction was conducted at 45 °C for 20 h, and then the resulting solution was concentrated in vacuo. The product was purified by preparative TLC (silica gel, eluent: hexane; AcOEt = 2:1) to afford the hydroselenation product.

General Procedure for Pd-Catalyzed Hydroselenation of *N*-Vinyl Lactams.

In a two-necked 10 mL flask with a magnetic stirring bar under N₂ atmosphere were placed Pd(OAc)₂ (5.6 mg, 0.025 mmol), freshly distilled THF (0.3 mL), *N*-vinyl lactam (0.5 mmol), and selenol (0.5 mmol), in that order. The reaction was conducted at 45 °C for 20 h, and then the resulting solution was filtered through Celite with ethyl acetate as an eluent. Concentration in vacuo, and purification by preparative TLC (silica gel, eluent: hexane; AcOEt = 2:1) provided the hydroselenation product.

General Procedure for Pd-Catalyzed Hydroselenation of *N*-Vinyl Lactam by Using Selenols Generated from Diselenides.

In a two-necked 10 mL flask with a magnetic stirring bar under N₂ atmosphere were placed diphenylphosphine oxide (60.7 mg, 0.3 mmol), freshly distilled THF (0.15 mL), diselenide (0.25 mmol), and *N*-vinyl lactam (0.25 mmol). The reaction was conducted at 45 °C for 20 h, and then the resulting solution was filtered through Celite with ethyl acetate as an eluent. Concentration in vacuo, and purification by preparative TLC (silica gel, eluent: hexane; AcOEt = 2:1) provided the hydroselenation product.

1-[(1-Phenylseleno)ethyl]-2-pyrrolidinone (3aa):

This compound was prepared from 1-vinyl-2-pyrrolidinone (53.2 μL, 0.5 mmol) and benzeneselenol (53.1 μL, 0.5 mmol) following the general procedure of Pd-catalyzed hydroselenation of *N*-vinyl lactam. Isolated as a pale yellow oil (128.9 mg, 96%); ¹H NMR (400 MHz, CDCl₃, ppm) δ 1.57 (d, *J* = 6.9 Hz, 3H), 1.69–1.80 (m, 1H), 1.85–1.94 (m, 1H), 1.96–2.05 (m, 1H), 2.18–2.27 (m, 1H), 3.29–3.35 (m, 1H), 3.48–3.54 (m, 1H), 6.04 (q, *J* = 6.9 Hz, 1H), 7.22–7.30 (m, 3H), 7.54–7.56 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 17.3, 19.8, 30.8, 42.0, 49.4, 127.9, 128.6 (overlap), 135.3, 173.9; ⁷⁷Se NMR (75 MHz, CDCl₃, ppm) δ 409.7; IR (NaCl) 3510, 3055, 2976, 2879, 1696, 1576, 1477, 1410, 1352, 1283, 1184, 1021, 999, 952, 845, 740, 692 cm⁻¹; HRMS (EI) Calcd for C₁₂H₁₅NOSe [M]⁺: 269.0319, Found: 269.0324.

1-[(1-Phenylseleno)pentyl]-2-pyrrolidinone (3ba):

This compound was prepared from 1-(1-pentenyl)-2-pyrrolidinone (76.6 mg, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure of Pd-catalyzed hydrothiolation of *N*-vinyl lactam. Isolated as a yellow oil (127.6 mg, 82%); ¹H NMR (400 MHz, CDCl₃, ppm) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.24–1.37 (m, 4H), 1.58–1.75 (m, 1H), 1.76–2.02 (m, 4H), 2.18–2.26 (m, 1H), 3.20–3.26 (m, 1H), 3.46–3.52 (m, 1H), 5.91 (dd, *J* = 6.3 Hz, 9.1 Hz, 1H), 7.21–7.27 (m, 3H), 7.53–7.55 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 13.7, 17.4, 21.8, 29.0, 30.8, 33.2, 42.1, 54.5, 127.8, 128.6 (overlap), 135.3, 174.5; ⁷⁷Se NMR (75 MHz, CDCl₃, ppm) δ 391.4; IR (NaCl) 3472, 3061, 2956, 2930, 2871, 1685, 1577, 1476, 1410, 1363, 1265, 1160, 1112, 1072, 1022, 923, 843, 741, 692 cm⁻¹; HRMS (ESI) Calcd for C₁₅H₂₁NONaSe [M+Na]⁺: 334.0686, Found: 334.0681.

1-(1-Phenylseleno)ethyl-2-caprolactam (3ca):

This compound was prepared from 1-vinyl-2-caprolactam (69.6 mg, 0.5 mmol) and benzeneselenol (53.1 μ L, 0.5 mmol) following the general procedure of Pd-catalyzed hydroselenation of *N*-vinyl lactam. Isolated as a pale yellow oil (140.7 mg, 95%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.42–1.71 (m, 6H), 1.52 (d, J = 6.9 Hz, 3H), 2.26–2.41 (m, 2H), 3.26–3.28 (m, 1H), 3.42–3.48 (m, 1H), 6.62 (q, J = 6.9 Hz, 1H), 7.22–7.26 (m, 3H), 7.49–7.53 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 20.0, 23.1, 28.9, 29.7, 37.2, 43.9, 52.4, 127.4, 128.8, 128.9, 134.1, 175.3; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 408.3; IR (NaCl) 3515, 3049, 2928, 2855, 1642, 1476, 1437, 1410, 1363, 1308, 1259, 1226, 1193, 1144, 1082, 1022, 976, 928, 885, 846, 739, 691 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{19}\text{NONaSe}$ $[\text{M}+\text{Na}]^+$: 320.0530, Found: 320.0534.

1-[3-Phenyl-(1-phenylseleno)propyl]-2-pyrrolidinone (3da):

This compound was prepared from 1-(3-Phenyl-1-propenyl)-2-pyrrolidinone (112 mg, 0.5 mmol) and benzeneselenol (53.1 μ L, 0.5 mmol) following the general procedure of Pd-catalyzed hydroselenation of *N*-vinyl lactam. Isolated as a yellow oil (143.3 mg, 80%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.60–1.83 (m, 2H), 1.93–2.04 (m, 1H), 2.13–2.23 (m, 3H), 2.56–2.63 (m, 1H), 2.68–2.76 (m, 1H), 3.14–3.20 (m, 1H), 3.44–3.50 (m, 1H), 5.97 (dd, J = 6.3 Hz, 8.6 Hz, 1H), 7.15–7.29 (m, 8H), 7.54–7.55 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.4, 31.0, 33.7, 35.3, 42.4, 54.5, 126.1, 127.7, 128.0, 128.3, 128.4, 128.8, 135.5, 140.4, 174.7; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 394.7; IR (NaCl) 3500, 3062, 3018, 2938, 2878, 1684, 1602, 1496, 1490, 1476, 1437, 1409, 1361, 1283, 1265, 1222, 1071, 1022, 996, 907, 843, 741, 700 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{21}\text{NONaSe}$ $[\text{M}+\text{Na}]^+$: 382.0686, Found: 382.0684.

1-[3,3-Dimethyl-(1-Phenylseleno)butyl]-2-pyrrolidinone (3ea):

This compound was prepared from 1-(3,3-dimethyl-1-butenyl)-2-pyrrolidinone (83.6 mg, 0.5 mmol) and benzeneselenol (53.1 μ L, 0.5 mmol) following the general procedure of Pd-catalyzed hydroselenation of *N*-vinyl lactam. Isolated as a yellow oil (138.2 mg, 85%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 0.93 (s, 9H), 1.54–1.65 (m, 2H), 1.77–1.94 (m, 3H), 2.08–2.16 (m, 1H), 3.29–3.35 (m,

1H), 3.45–3.51 (m, 1H), 6.19 (dd, $J = 2.7$ Hz, 10.9 Hz, 1H), 7.22–7.30 (m, 3H), 7.54–7.56 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.5, 29.2, 31.1, 31.8, 42.2, 45.4, 52.1, 128.0, 128.2, 128.7, 135.7, 174.3; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 405.3; IR (NaCl) 3512, 3057, 2952, 2906, 1692, 1575, 1476, 1437, 1410, 1366, 1283, 1265, 1147, 1069, 891, 843, 739, 691 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{23}\text{NONaSe}$ $[\text{M}+\text{Na}]^+$: 348.0843, Found: 348.0848.

1-[2-Phenyl-(1-phenylseleno)ethyl]-2-pyrrolidinone (3fa):

This compound was prepared from 1-styryl-2-pyrrolidinone (93.5 mg, 0.5 mmol) and benzeneselenol (53.1 μL , 0.5 mmol) following the general procedure of Pd-catalyzed hydroselenation of *N*-vinyl lactam. Isolated as a yellow oil (86.1 mg, 50%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.59–1.81 (m, 2H), 1.86–1.94 (m, 1H), 2.02–2.10 (m, 1H), 3.10–3.16 (m, 1H), 3.20–3.30 (m, 2H), 3.47–3.53 (m, 1H), 6.22 (dd, $J = 6.8$ Hz, 9.5 Hz, 1H), 7.20–7.30 (m, 8H), 7.54–7.56 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.5, 30.8, 39.8, 42.6, 54.7, 126.9, 127.7, 128.0, 128.5, 128.8, 129.1, 135.6, 136.9, 174.5; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 396.1; IR (NaCl) 3491, 3058, 3027, 2975, 1681, 1577, 1497, 1476, 1455, 1409, 1284, 1266, 1155, 1071, 1021, 984, 928, 845, 741, 693 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{19}\text{NONaSe}$ $[\text{M}+\text{Na}]^+$: 368.0530, Found: 368.0536.

1-[[1-(*p*-Methoxyphenyl)seleno]ethyl]-2-pyrrolidinone (3ab):

This compound was prepared from 1-vinyl-2-pyrrolidinone (26.6 μL , 0.25 mmol) and bis(4-methoxyphenyl) diselenide (93.0 mg, 0.25 mmol) and diphenylphosphine oxide (60.7 mg, 0.3 mmol) following the general procedure of hydroselenation of *N*-vinyl lactam by using selenols generated from diselenides. Isolated as a pale yellow oil (58.8 mg, 79%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.55 (d, $J = 7.3$ Hz, 3H), 1.74–1.85 (m, 1H), 1.88–2.07 (m, 2H), 2.20–2.28 (m, 1H), 3.30–3.36 (m, 1H), 3.51–3.57 (m, 1H), 3.78 (s, 3H), 5.95 (q, $J = 7.3$ Hz, 1H), 6.77–6.81 (m, 2H), 7.46–7.49 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.5, 19.8, 31.1, 42.1, 49.7, 55.2, 114.4, 118.2, 137.7, 159.9, 174.1; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 394.6; IR (NaCl) 3466, 3058, 2980, 2848, 1685, 1590, 1570, 1461, 1440, 1377, 1286, 1244, 1181, 1130, 1095, 1022, 998, 803, 753, 730, 698 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2\text{NaSe}$ $[\text{M}+\text{Na}]^+$: 322.0322, Found: 322.0323.

1-{{1-(*m*-Methoxyphenyl)seleno}ethyl}-2-pyrrolidinone (3ac):

This compound was prepared from 1-vinyl-2-pyrrolidinone (26.6 μ L, 0.25 mmol) and bis(3-methoxyphenyl) diselenide (93.1 mg, 0.25 mmol) and diphenylphosphine oxide (60.7 mg, 0.3 mmol) following the general procedure of hydroselenation of *N*-vinyl lactam by using selenols generated from diselenides. Isolated as a pale yellow oil (63.6 mg, 85%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.59 (d, J = 7.3 Hz, 3H), 1.72–1.83 (m, 1H), 1.87–1.98 (m, 1H), 2.02–2.11 (m, 1H), 2.22–2.31 (m, 1H), 3.31–3.37 (m, 1H), 3.49–3.55 (m, 1H), 3.79 (s, 3H), 6.08 (q, J = 7.3 Hz, 1H), 6.80–6.82 (m, 1H), 7.11–7.18 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.5, 20.0, 31.1, 42.2, 49.5, 55.3, 114.1, 119.9, 127.0, 129.1, 129.5, 159.5, 174.1; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 414.0; IR (NaCl) 3490, 3062, 2963, 2828, 1685, 1586, 1573, 1476, 1412, 1353, 1312, 1283, 1245, 1228, 1184, 1095, 1037, 991, 953, 840, 780, 689 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2\text{NaSe}$ $[\text{M}+\text{Na}]^+$: 322.0322, Found: 322.0326.

1-{{1-(*p*-Chlorophenyl)seleno}ethyl}-2-pyrrolidinone (3ad):

This compound was prepared from 1-vinyl-2-pyrrolidinone (26.6 μ L, 0.25 mmol) and bis(4-chlorophenyl) diselenide (96.6 mg, 0.25 mmol) and diphenylphosphine oxide (60.7 mg, 0.3 mmol) following the general procedure of hydroselenation of *N*-vinyl lactam by using selenols generated from diselenides. Isolated as a pale yellow oil (53.0 mg, 70%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.58 (d, J = 6.8 Hz, 3H), 1.72–1.86 (m, 1H), 1.90–2.00 (m, 1H), 2.03–2.12 (m, 1H), 2.23–2.32 (m, 1H), 3.32–3.38 (m, 1H), 3.47–3.53 (m, 1H), 6.05 (q, J = 6.9 Hz, 1H), 7.21–7.23 (m, 2H), 7.47–7.49 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.5, 19.9, 31.0, 42.1, 49.9, 126.3, 129.0, 134.3, 136.6, 174.2; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 406.0; IR (NaCl) 3485, 3055, 2976, 2880, 1693, 1472, 1410, 1352, 1267, 1185, 1089, 1053, 1011, 953, 816, 730, 743 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{14}\text{NONaClSe}$ $[\text{M}+\text{Na}]^+$: 325.9827, Found: 325.9823.

1-{{1-(*p*-Fluorophenyl)seleno}ethyl}-2-pyrrolidinone (3ae):

This compound was prepared from 1-vinyl-2-pyrrolidinone (26.6 μ L, 0.25 mmol) and bis(4-fluorophenyl) diselenide (87.0 mg, 0.25 mmol) and diphenylphosphine oxide (60.7 mg, 0.3 mmol) following the general procedure of hydroselenation of *N*-vinyl lactam by using selenols generated from

diselenides. Isolated as a pale yellow oil (91.4mg, 64%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.57 (d, J = 6.8 Hz, 3H), 1.72–2.10 (m, 3H), 2.22–2.30 (m, 1H), 3.31–3.37 (m, 1H), 3.49–3.55 (m, 1H), 6.01 (q, J = 6.8 Hz, 1H), 6.92–6.98 (m, 2H), 7.51–7.55 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.5, 19.9, 31.0, 42.1, 50.0, 116.0 (d, $J_{\text{C-F}}$ = 21.0 Hz), 122.7 (d, $J_{\text{C-F}}$ = 2.9 Hz), 137.8 (d, $J_{\text{C-F}}$ = 8.6 Hz), 162.9 (d, $J_{\text{C-F}}$ = 248.0 Hz), 174.1; ^{19}F NMR (373 MHz, CDCl_3 , ppm) δ -112.8; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 402.4; IR (NaCl) 3466, 2979, 2889, 1685, 1583, 1486, 1458, 1412, 1285, 1268, 1223, 1184, 1157, 1089, 1012, 828, 743 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{14}\text{NOFNaSe}$ $[\text{M}+\text{Na}]^+$: 310.0122, Found: 310.0125.

1- $\{[1-(m\text{-Fluorophenyl})\text{seleno}]\text{ethyl}\}$ -2-pyrrolidinone (3af):

This compound was prepared from 1-vinyl-2-pyrrolidinone (26.6 μL , 0.25 mmol) and bis(3-fluorophenyl) diselenide (87.1 mg, 0.25 mmol) and diphenylphosphine oxide (60.7 mg, 0.3 mmol) following the general procedure of hydroselenation of *N*-vinyl lactam by using selenols generated from diselenides. Isolated as a pale yellow oil (50.8 mg, 71%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.59 (d, J = 6.8 Hz, 3H), 1.78–1.89 (m, 1H), 1.91–2.02 (m, 1H), 2.06–2.15 (m, 1H), 2.24–2.33 (m, 1H), 3.30–3.39 (m, 1H), 3.50–3.56 (m, 1H), 6.07 (q, J = 6.8 Hz, 1H), 6.96–7.01 (m, 1H), 7.20–7.35 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.5, 20.0, 31.1, 42.2, 50.1, 115.1 (d, $J_{\text{C-F}}$ = 21.0 Hz), 121.9 (d, $J_{\text{C-F}}$ = 21.0 Hz), 129.7 (d, $J_{\text{C-F}}$ = 6.7 Hz), 130.1 (d, $J_{\text{C-F}}$ = 7.6 Hz), 130.9 (d, $J_{\text{C-F}}$ = 2.9 Hz), 162.2 (d, $J_{\text{C-F}}$ = 250 Hz), 174.2; ^{19}F NMR (373 MHz, CDCl_3 , ppm) δ -111.9; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 418.2; IR (NaCl) 3491, 3068, 2977, 2881, 1693, 1591, 1471, 1411, 1352, 1284, 1263, 1210, 1185, 1053, 1000, 954, 858, 782, 743, 682 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{14}\text{NOFNaSe}$ $[\text{M}+\text{Na}]^+$: 310.0122, Found: 310.0130.

1- $\{[1-(p\text{-Trifluoromethylphenyl})\text{seleno}]\text{ethyl}\}$ -2-pyrrolidinone (3ag):

This compound was prepared from 1-vinyl-2-pyrrolidinone (26.6 μL , 0.25 mmol) and bis(4-trifluoromethylphenyl) diselenide (112.0 mg, 0.25 mmol) and diphenylphosphine oxide (60.7 mg, 0.3 mmol) following the general procedure of hydroselenation of *N*-vinyl lactam by using selenols generated from diselenides. Isolated as a pale yellow oil (82.2 mg, 98%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.62

(d, $J = 7.3$ Hz, 3H), 1.74–1.85 (m, 1H), 1.91–2.02 (m, 1H), 2.05–2.13 (m, 1H), 2.26–2.34 (m, 1H), 3.34–3.40 (m, 1H), 3.46–3.52 (m, 1H), 6.17 (q, $J = 7.3$ Hz, 1H), 7.48–7.50 (m, 2H), 7.64–7.66 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.5, 20.1, 31.1, 42.3, 49.8, 124.0 (q, $J_{\text{C-F}} = 272.6$ Hz), 125.6 (q, $J_{\text{C-F}} = 3.8$ Hz), 129.7 (d, $J_{\text{C-F}} = 33.4$ Hz), 133.6, 134.3, 174.3; ^{19}F NMR (373 MHz, CDCl_3 , ppm) δ -62.6; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 416.1; IR (NaCl) 3491, 3068, 2929, 2882, 1672, 1601, 1490, 1459, 1399, 1324, 1269, 1163, 1110, 1078, 1057, 1014, 954, 831, 775, 744 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{14}\text{NOF}_3\text{NaSe}$ $[\text{M}+\text{Na}]^+$: 360.0090, Found: 360.0091.

1- $\{[1-(m\text{-Trifluoromethylphenyl})\text{seleno}]\text{ethyl}\}$ -2-pyrrolidinone (3ah):

This compound was prepared from 1-vinyl-2-pyrrolidinone (26.6 μL , 0.5 mmol) and bis(3-trifluoromethylphenyl) diselenide (112.0 mg, 0.25 mmol) and diphenylphosphine oxide (60.7 mg, 0.3 mmol) following the general procedure of hydroselenation of *N*-vinyl lactam by using selenols generated from diselenides. Isolated as a pale yellow oil (66.5 mg, 79%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.60 (d, $J = 7.3$ Hz, 3H), 1.76–1.87 (m, 1H), 1.92–2.09 (m, 2H), 2.22–2.31 (m, 1H), 3.33–3.39 (m, 1H), 3.51–3.57 (m, 1H), 6.09 (q, $J = 7.3$ Hz, 1H), 7.37–7.41 (m, 1H), 7.53–7.55 (m, 1H), 7.76–7.81 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.3, 19.9, 30.9, 42.0, 50.4, 123.6 (q, $J_{\text{C-F}} = 271.8$ Hz), 124.7 (q, $J_{\text{C-F}} = 3.8$ Hz), 129.2, 131.0 (q, $J_{\text{C-F}} = 33.4$ Hz), 131.8 (q, $J_{\text{C-F}} = 2.9$ Hz), 138.9, 174.1; ^{19}F NMR (373 MHz, CDCl_3 , ppm) δ -62.6; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 417.0; IR (NaCl) 3490, 3062, 2988, 2889, 1694, 1495, 1458, 1414, 1322, 1271, 1165, 1126, 1098, 1069, 993, 895, 798, 695 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{14}\text{NOF}_3\text{NaSe}$ $[\text{M}+\text{Na}]^+$: 360.0090, Found: 360.0091.

1- $\{[1-(1\text{-Naphthyl})\text{seleno}]\text{ethyl}\}$ -2-pyrrolidinone (3ai):

This compound was prepared from 1-vinyl-2-pyrrolidinone (26.6 μL , 0.25 mmol) and bis(1-naphthyl) diselenide (103.1 mg, 0.25 mmol) and diphenylphosphine oxide (60.7 mg, 0.3 mmol) following the general procedure of hydroselenation of *N*-vinyl lactam by using selenols generated from diselenides. Isolated as a pale yellow oil (23.8 mg, 30%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.49–1.64 (m, 1H), 1.61 (d, $J = 6.8$ Hz, 3H), 1.75–1.86 (m, 2H), 2.07–2.16 (m, 1H), 3.25–3.31 (m, 1H), 3.43–3.49 (m, 1H), 6.03 (q, $J = 6.8$ Hz, 1H), 7.35–7.39 (m, 1H), 7.47–7.59 (m, 2H), 7.80–7.90 (m, 3H), 8.49–8.51 (m, 1H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.3, 20.2, 30.8, 42.4, 50.4, 125.6, 126.1, 126.7, 127.9, 128.0, 128.6, 129.5, 133.8, 135.2, 135.9, 173.9; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 339.8; IR (NaCl) 3473, 3051, 2964, 2881, 1681, 1587, 1557, 1500, 1456, 1411, 1374, 1313, 1269, 1182, 1099, 1020, 957, 798, 771 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{17}\text{NONaSe}$ $[\text{M}+\text{Na}]^+$: 342.0373, Found: 342.0380.

1- $\{[(\text{Phenylmethylseleno})\text{ethyl}]\}$ -2-pyrrolidinone (3aj):

This compound was prepared from 1-vinyl-2-pyrrolidinone (26.6 μL , 0.25 mmol) and bis(phenylmethyl) diselenide (85.0 mg, 0.25 mmol) and diphenylphosphine oxide (60.7 mg, 0.3 mmol) following the general procedure of hydroselenation of *N*-vinyl lactam by using selenols generated from diselenides. Isolated as a pale yellow oil (11.1 mg, 16%); ^1H NMR (400 MHz, CDCl_3 , ppm) δ 1.47 (d, J = 6.9 Hz, 3H), 1.57–1.68 (m, 1H), 1.84–1.95 (m, 1H), 2.15–2.24 (m, 1H), 2.28–2.37 (m, 1H), 3.22–3.28 (m, 1H), 3.38–3.44 (m, 1H), 3.75 (d, J = 12.7 Hz, 1H), 3.86 (d, J = 12. Hz, 1H), 5.91 (q, J = 6.9 Hz, 1H), 7.17–7.20 (m, 1H), 7.25–7.34 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 17.3, 20.3, 28.0, 31.5, 42.0, 47.0, 125.5, 126.6, 128.4, 128.7, 174.4; ^{77}Se NMR (75 MHz, CDCl_3 , ppm) δ 352.9; IR (NaCl) 3478, 3024, 2975, 2926, 1685, 1494, 1452, 1412, 1350, 1313, 1268, 1178, 1096, 1054, 1029, 956, 759, 730 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{17}\text{NONaSe}$ $[\text{M}+\text{Na}]^+$: 306.0373, Found: 306.0375.

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Supporting Information Available: ^1H NMR, ^{13}C NMR, ^{19}F NMR, and ^{77}Se NMR spectra of all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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