JOC The Journal of Organic Chemistry

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

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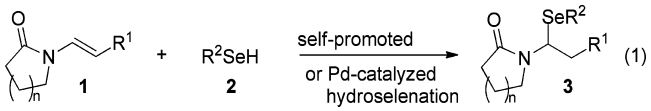
Supporting Information

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.

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 imino 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 toward *N,Se*-acetals (eq 1).

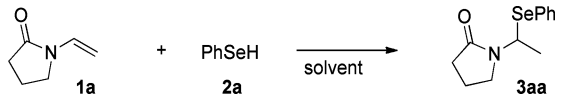


To date, numerous regioselective addition reactions of heteroatom-containing compounds such as boron, silicon, phosphorus, and sulfur to C−C unsaturated bonds have been developed, e.g., radical, ionic, and transition-metal-catalyzed additions.[3] Although the addition of selenols to alkynes has been established in acid- or base-assisted ionic reactions, radical reactions, and transition-metal-catalyzed reactions, the corresponding addition to alkenes has considerable limitations.[4−7] In general, the radical addition of selenols to alkenes gives *anti*-Markovnikov adducts regioselectively, and limited examples of Markovnikov-selective hydroselenations are known.[5] Although Markovnikov adducts may be synthesized by transition-metal-catalyzed reactions, catalyst poisoning by selenols often hinders catalytic reactions.[7,8] Moreover, most known Markovnikov-selective hydroselenation reactions require additives, such as Brønsted acids, to promote the addition. Very recently, we overcame similar limitation in transition-metal-catalyzed hydrothiolations by using alkenes bearing an alkoxyl or amino group directly bonded to the carbon−carbon double bond.[9]

In this study, we found that selenols promote the hydroselenation of terminal *N*-vinyl lactams. This self-promoted hydroselenation requires no additives; therefore, this method exhibits high atom economy. Furthermore, the hydroselenation of internal *N*-vinyl lactams proceeds with excellent regioselectivity (Markovnikov-selective) in the presence of palladium catalysts such as $Pd(OAc)_2$.

First, we investigated the addition of benzeneselenol to *N*-vinylpyrrolidone, as a manageable terminal *N*-vinyl lactam, without the addition of any additives (Table 1). When *N*-vinylpyrrolidone (**1a**) was reacted with benzeneselenol (**2a**) at

Table 1. Optimization of Hydroselenation of Terminal *N*-Vinylpyrrolidone[a]



entry	solvent	time, h	temp, °C	yield, %[b]
1	THF	20	45	93
2	CH_3CN	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*-vinylpyrrolidone (**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.

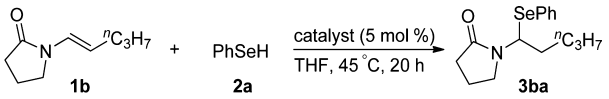
Received: October 21, 2015
Published: November 30, 2015

DOI: 10.1021/acs.joc.5b02431
J. Org. Chem. 2016, 81, 324−329

45 °C for 20 h in THF, the Markovnikov-type adduct was obtained regioselectively in 93% yield without formation of an *anti*-Markovnikov adduct (entry 1). When CH_3CN and toluene were used as solvents, the yield of the desired hydroselenation product decreased (entries 2 and 3). The reaction in EtOH or in the absence of solvent was also examined to produce the corresponding adduct in good yield, respectively (entries 4 and 5). Next, we examined the effects of reaction time and temperature (entries 6–9). Furthermore, when the reaction in the presence of *p*-TsOH as a strong acid was conducted, the desired hydroselenation did not proceed (entry 10). This is probably because *p*-TsOH promoted the polymerization of *N*-vinylpyrrolidone. The results clearly indicated that the optimal reaction conditions were 45 °C for 20 h in THF.

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,

Scheme 1. Optimization of Hydroselenation of Internal *N*-Vinylpyrrolidone



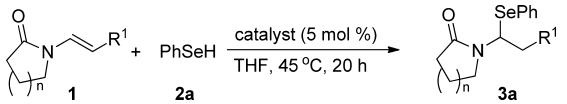
catalyst =		
	none	13%
	$Pd(OAc)_2$	91%
	$Pd(PPh_3)_4$	12%
	$PdCl_2(PhCN)_2$	57%
	$PdCl_2(cod)$	55%
	$PdCl_2(PPh_3)_2$	77%

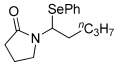
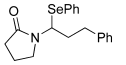
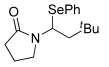
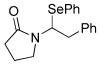
the desired Markovnikov hydroselenation proceeded very efficiently. When a low-valent palladium catalyst, $Pd(PPh_3)_4$, was employed, the hydroselenation product was obtained in only 12% yield. This result indicated that Pd(0) was not effective for the hydroselenation of internal *N*-vinyl lactams. Thus, the hydroselenation was examined in the presence of Pd(II) catalysts, such as $PdCl_2(PhCN)_2$, $PdCl_2(cod)$, and $PdCl_2(PPh_3)_2$. The tested Pd(II) complexes catalyzed the hydroselenation of internal *N*-vinyl lactam **1b** to produce Markovnikov-adduct **3ba** in moderate to good yields.

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*-vinylcaprolactam **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, and 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, and 12). These results indicated that a Pd(II) catalyst was essential for the efficient hydroselenation of internal *N*-vinyl lactams.

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

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



entry	catalyst	product	3	yield, %[b]
1	——		**3aa**	(93)
2	$Pd(OAc)_2$			96
3	——		**3ca**	(57)
4	$Pd(OAc)_2$			95
5	——		**3ba**	(13)
6	$Pd(OAc)_2$			82
7	——		**3da**	(28)
8	$Pd(OAc)_2$			80
9	——		**3ea**	(7)
10	$Pd(OAc)_2$			85
11	——		**3fa**	ND
12	$Pd(OAc)_2$			50

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

areneselenols by the reduction of the corresponding diaryl diselenides with diphenylphospine 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*-vinylpyrrolidone with various areneselenols in the absence of a Pd catalyst was successfully accomplished, as shown in Table 3. Diaryl diselenides bearing either an electron-donating group such as *p*-methoxy or electron-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).

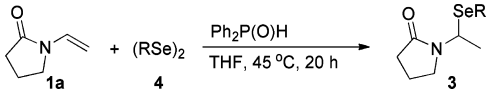
The Pd-catalyzed hydroselenation of *N*-vinylpyrrolidone **1a** using diphenyl diselenides and diphenylphosphine oxide was carried out (Scheme 2). When dinaphthyl diselenide **4i** and dibenzyl diselenide **4j** were employed, the yields of the desired hydroselenation products, **3ai** and **3aj**, were 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.

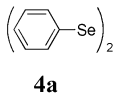
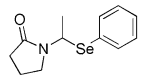
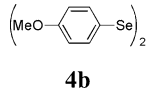
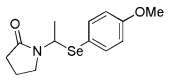
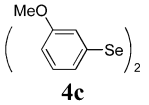
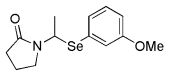
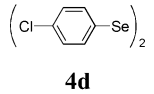
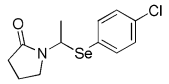
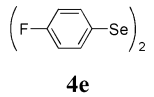
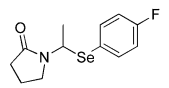
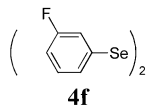
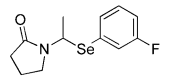
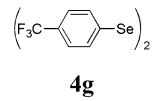
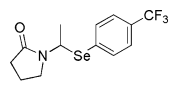
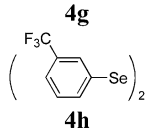
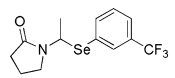
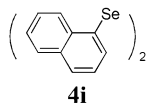
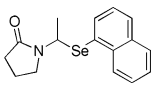
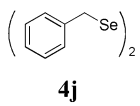
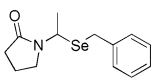
Finally, the hydroselenation of *N*-vinyl lactam was evaluated in the large scale reaction using 0.39 g of the *N*-vinylpyrrolidone. The reaction was completed in 48 h at 45 °C, and 92% of the isolated yield of the hydroselenation product was obtained selectively (Scheme 3). These *N*,*Se*-acetal derivatives can be transformed into the corresponding aldehydes under the radical reaction.[2f]

A plausible reaction pathway for the present hydroselenation of *N*-vinyl lactams is shown in Scheme 4. In the absence of the Pd-catalyst, first, the terminal *N*-vinyl lactam is easily protonated by selenol. Then, the generated cation of terminal

DOI: 10.1021/acs.joc.5b02431
J. Org. Chem. 2016, 81, 324–329

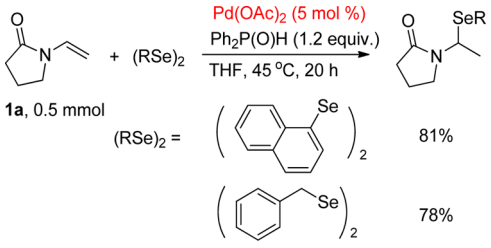
Table 3. Self-Promoted Hydroselenation of *N*-Vinyl Lactams Using Several Diselenides[a]



entry	$(RSe)_2$, **4**	product	**3**	yield, %
1	 **4a**		**3aa**	94
2	 **4b**		**3ab**	79
3	 **4c**		**3ac**	85
4	 **4d**		**3ad**	70
5	 **4e**		**3ae**	64
6	 **4f**		**3af**	71
7	 **4g**		**3ag**	98
8	 **4h**		**3ah**	79
9	 **4i**		**3ai**	30
10	 **4j**		**3aj**	16

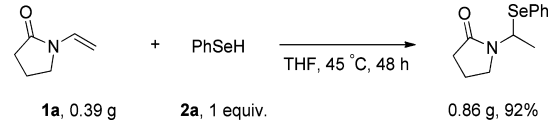
[a]Reaction conditions: *N*-vinylpyrrolidone (**1a**, 0.25 mmol), diselenide (**4**, 0.25 mmol), THF (0.15 mL), diphenylphosphine oxide (0.3 mmol), 45 °C, 20 h.

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

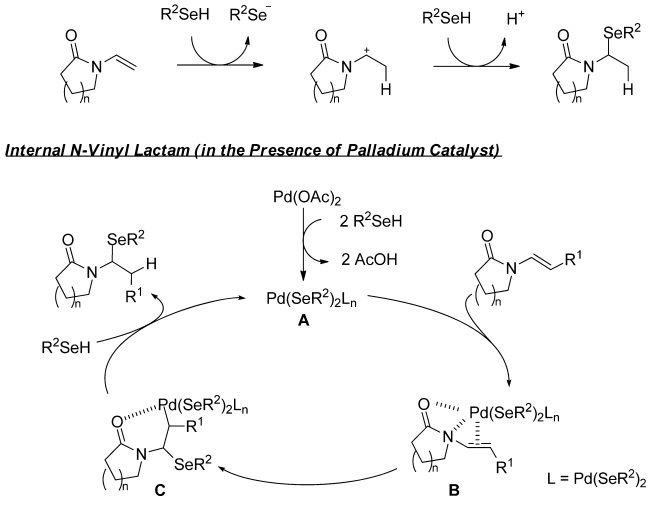


N-vinyl lactam is stabilized by electron donation from the nitrogen atom. Finally, selenol attacks the cation of terminal *N*-vinyl lactam to give the Markovnikov-type hydroselenation product regioselectively. In the case of the Pd-catalyzed hydroselenation, the $Pd(OAc)_2$ catalyst initially reacts 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 seleno-palladation 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**.

Scheme 3. Hydroselenation of *N*-Vinylpyrrolidone with Benzeneselenol on the Large Scale



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 diphenylphosphine oxide.

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all starting materials and catalysts were purchased form commercial sources and used without further purification. The following substrates were prepared by using dehydrative condensation of pyrrolidinone and the corresponding aldehydes 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, and (*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 CaH_2. ^1H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were taken in $CDCl_3$ with Me_4Si as an internal standard. ^{19}F NMR spectra (373 MHz) were taken in $CDCl_3$ with $CFCl_3$ as an external standard.

DOI: 10.1021/acs.joc.5b02431
J. Org. Chem. 2016, 81, 324–329

^{77}Se NMR spectra (75 MHz) were taken in $CDCl_3$ with Me_2Se as an external standard. Chemical shifts in ^{1}H NMR were measured relative to $CDCl_3$ and converted to δ (Me_4Si) values by using δ ($CDCl_3$) 7.26 ppm. Chemical shifts in ^{13}C NMR were measured relative to $CDCl_3$ and converted to δ (Me_4Si) values by using δ ($CDCl_3$) 77.00 ppm. IR spectra were reported in wavenumbers (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-neck 10 mL flask with a magnetic stirring bar under a N_2 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-neck 10 mL flask with a magnetic stirring bar under a N_2 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-neck 10 mL flask with a magnetic stirring bar under a N_2 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%); ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 17.3, 19.8, 30.8, 42.0, 49.4, 127.9, 128.6 (overlap), 135.3, 173.9; ^{77}Se NMR (75 MHz, $CDCl_3$, 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 $C_{12}H_{15}NOSe$ [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 benzeneselenol (53.1 μL, 0.5 mmol) following the general procedure of Pd-catalyzed hydroselenation of *N*-vinyl lactam. Isolated as a yellow oil (127.6 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 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; ^{77}Se NMR (75 MHz, $CDCl_3$, 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 $C_{15}H_{21}NONaSe$ [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 μL, 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%); ^{1}H 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}C{^{1}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 $C_{14}H_{19}NONaSe$ [M + 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 μL, 0.5 mmol) following the general procedure of Pd-catalyzed hydroselenation of *N*-vinyl lactam. Isolated as a yellow oil (143.3 mg, 80%); ^{1}H 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}C{^{1}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 $C_{19}H_{21}NONaSe$ [M + 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 μL, 0.5 mmol) following the general procedure of Pd-catalyzed hydroselenation of *N*-vinyl lactam. Isolated as a yellow oil (138.2 mg, 85%); ^{1}H 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}C{^{1}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 $C_{16}H_{23}NONaSe$ [M + 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%); ^{1}H 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}C{^{1}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 $C_{18}H_{19}NONaSe$ [M + 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%); ^{1}H 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}C{^{1}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 $C_{13}H_{17}NO_2NaSe$ [M + 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 μL, 0.25 mmol) and bis(3-methoxyphenyl) diselenide (93.1 mg, 0.25 mmol) and diphenylphosphine oxide (60.7 mg, 0.3 mmol) following

DOI: 10.1021/acs.joc.5b02431
J. Org. Chem. 2016, 81, 324−329

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%); ^{1}H 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}C{^{1}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 $C_{13}H_{17}NO_2NaSe$ [M + 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 μL, 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%); ^{1}H 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}C{^{1}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 $C_{12}H_{14}NONaClSe$ [M + 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 μL, 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 (91.4 mg, 64%); ^{1}H 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}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 17.5, 19.9, 31.0, 42.1, 50.0, 116.0 (d, $J_{C\text{-}F}$ = 21.0 Hz), 122.7 (d, $J_{C\text{-}F}$ = 2.9 Hz), 137.8 (d, $J_{C\text{-}F}$ = 8.6 Hz), 162.9 (d, $J_{C\text{-}F}$ = 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 $C_{12}H_{14}NOFNaSe$ [M + Na]$^+$: 310.0122, Found: 310.0125.

1-{[1-(m-Fluorophenyl)seleno]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%); ^{1}H 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}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 17.5, 20.0, 31.1, 42.2, 50.1, 115.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 121.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), 129.7 (d, $J_{C\text{-}F}$ = 6.7 Hz), 130.1 (d, $J_{C\text{-}F}$ = 7.6 Hz), 130.9 (d, $J_{C\text{-}F}$ = 2.9 Hz), 162.2 (d, $J_{C\text{-}F}$ = 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 $C_{12}H_{14}NOFNaSe$ [M + Na]$^+$: 310.0122, Found: 310.0130.

1-{[1-(p-Trifluoromethylphenyl)seleno]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%); ^{1}H 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}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 17.5, 20.1, 31.1, 42.3, 49.8, 124.0 (q, $J_{C\text{-}F}$ = 272.6 Hz), 125.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 129.7 (d, $J_{C\text{-}F}$ = 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 $C_{13}H_{14}NOF_3NaSe$ [M + Na]$^+$: 360.0090, Found: 360.0091.

1-{[1-(m-Trifluoromethylphenyl)seleno]ethyl}-2-pyrrolidinone (**3ah**). This compound was prepared from 1-vinyl-2-pyrrolidinone (26.6 μL, 0.25 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%); ^{1}H 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}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 17.3, 19.9, 30.9, 42.0, 50.4, 123.6 (q, $J_{C\text{-}F}$ = 271.8 Hz), 124.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 129.2, 131.0 (q, $J_{C\text{-}F}$ = 33.4 Hz), 131.8 (q, $J_{C\text{-}F}$ = 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 $C_{13}H_{14}NOF3NaSe$ [M + Na]$^+$: 360.0090, Found: 360.0091.

1-{[1-(1-Naphthyl)seleno]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%); ^{1}H 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}C{^{1}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 $C_{16}H_{17}NONaSe$ [M + Na]$^+$: 342.0373, Found: 342.0380.

1-{[(Phenylmethylseleno)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%); ^{1}H 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}C{^{1}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 $C_{13}H_{17}NONaSe$ [M + Na]$^+$: 306.0373, Found: 306.0375.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02431.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{77}Se NMR spectra of all compounds (PDF)

DOI: 10.1021/acs.joc.5b02431
J. Org. Chem. 2016, 81, 324−329

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research for JSPS Fellows (1381002900). T.T. thanks the Japan Society for the Promotion of Science for the Research Fellowship for Young Scientists.

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DOI: 10.1021/acs.joc.5b02431
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