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Regioselective Hydrothiolation of Alkenes Bearing Heteroatoms with Thiols Catalyzed by Palladium Diacetate

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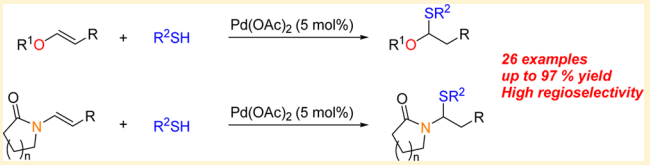
Supporting Information

ABSTRACT: In sharp contrast to many examples of transition-metal-catalyzed hydrothiolation of alkynes, the corresponding catalytic addition of thiols to alkenes has remained undeveloped. However, a novel Pd-catalyzed addition of thiols to alkenes bearing a heteroatom, such as oxygen and nitrogen, is found to proceed under mild conditions to give the corresponding Markovnikov adducts, regioselectively, in good yields.

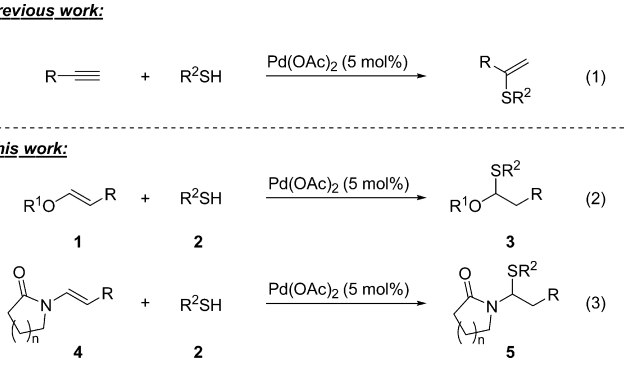


INTRODUCTION

Transition-metal-catalyzed addition reactions of heteroatom compounds have attracted much attention, as a variety of heteroatom functions can be introduced to organic molecules by this method with good atom economy, high efficiency, and high selectivity.[1] In parallel with these explorations, highly selective addition reactions of organosulfur compounds to unsaturated bonds have been developed using transition-metal catalysts.[2] Compounds containing sulfur functions are known as valuable feedstock chemicals, finding utility in applications such as synthetic intermediates, bioactive compounds, and functional materials.[3] However, examples of the transition-metal-catalyzed addition reaction of organosulfur compounds have been mostly limited to alkynes; thus, the development of a transition-metal-catalyzed addition to alkenes is strongly desired.[4−7] The difficulties associated with the catalytic addition of organosulfur compounds to alkenes can be attributed to the lower coordination ability of alkenes compared with that of alkynes, which in turn may contribute to catalyst poisoning.[8] However, functionalized alkenes bearing a heteroatom are expected to show stronger coordination to the catalyst through assistance of the heteroatom.

Thus, we have focused attention on alkenes bearing heteroatom as functional alkenes and have developed a novel Pd-catalyzed addition reaction of thiols with heteroatom-substituted alkenes, which proceeds with excellent regioselectivity to afford the corresponding Markovnikov adducts in good yield (Scheme 1). In general, radical addition reactions of thiols with alkenes are well-known to proceed in the *anti*-Markovnikov manner.[9] In sharp contrast, the present Pd-catalyzed hydrothiolation of alkenes affords Markovnikov-type adducts, regioselectively. Both methods are regio-complementary to each other.

Scheme 1. Palladium-Catalyzed Hydrothiolation



RESULTS AND DISCUSSION

We first examined the optimization of the addition reaction of benzenethiol (**2a**) to *n*-butyl vinyl ether (**1a**) in the presence of $Pd(OAc)_2$ as the catalyst (Table 1). When the reaction of *n*-butyl vinyl ether (**1a**) and benzenethiol (**2a**) was conducted at 45 °C for 20 h using 5 mol % $Pd(OAc)_2$, the Markovnikov-type hydrothiolation product (**3aa**) was obtained in 95% yield in a regioselective fashion without formation of an *anti*-Markovnikov-type adduct (entry 1). When the amount of $Pd(OAc)_2$ was decreased to 1 mol %, the desired hydrothiolation proceeded inefficiently (entry 2). In the absence of the Pd catalyst, a complex reaction mixture resulted, yielding 7% of Markovnikov-type adduct **3aa** and 18% of the corresponding *anti*-Markovnikov-type adduct (entry 3). Next, the optimization of reaction times and temperatures was examined. Results indicated that hydrothiolation proceeded well in shorter times under mild conditions (entries 4−7).

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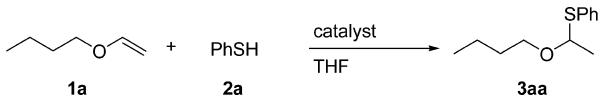
Table 1. Optimization of Hydrothiolation of Vinyl Ether[a]

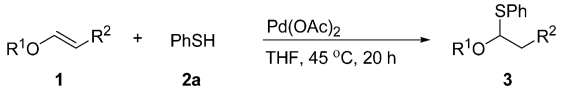


1a 2a 3aa

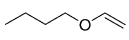
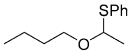
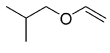
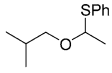
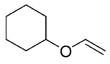
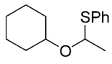
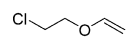
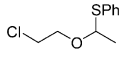
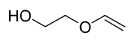
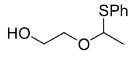
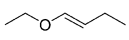
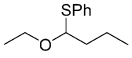
entry	catalyst	time, h	temp, °C	yield, %[b]
1	$Pd(OAc)_2$ (5 mol %)	20	45	95
2	$Pd(OAc)_2$ (1 mol %)	20	45	11
3	none	20	45	7[c]
4	$Pd(OAc)_2$ (5 mol %)	14	45	80
5	$Pd(OAc)_2$ (5 mol %)	5	45	85
6	$Pd(OAc)_2$ (5 mol %)	20	reflux	77
7	$Pd(OAc)_2$ (5 mol %)	20	30	83

[a]Reaction conditions: *n*-butyl vinyl ether (**1a**, 0.5 mmol), benzenethiol (**2a**, 0.5 mmol), THF (0.3 mL). [b]Determined by ^{1}H NMR analysis. [c]Accompanied by 18% of the *anti*-Markovnikov hydrothiolation adduct in the reaction mixture. In other entries, no formation of *anti*-adducts was observed.

Table 2. Hydrothiolation of Several Vinyl Ethers[a]



1 2a 3

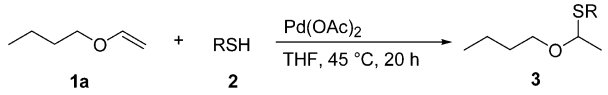
entry	substrate	1	product	3	yield, %[b]
1		**1a**		**3aa**	95
2		**1b**		**3ba**	85
3		**1c**		**3ca**	87
4		**1d**		**3da**	90
5		**1e**		**3ea**	57
6		**1f**		**3fa**	87
7		**1g**		**3ga**	88
8		**1h**		**3ha**	84

[a]Reaction conditions: vinyl ether (**1**, 0.5 mmol), benzenethiol (**2a**, 0.5 mmol), $Pd(OAc)_2$ (5 mol %), THF (0.3 mL), 45 °C, 20 h. [b]Isolated yield.

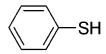
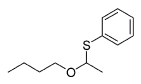
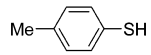
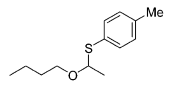
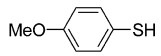
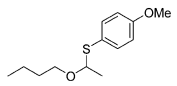
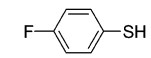
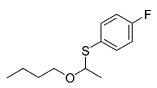
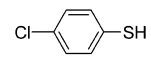
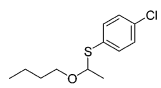
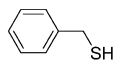
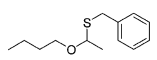
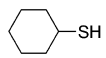
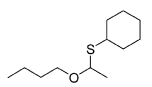
Next, the Pd-catalyzed hydrothiolation of several vinyl ethers was performed, the results of which are summarized in Table 2. In the cases of branched vinyl ethers **1b** and **1c**, the desired Markovnikov hydrothiolation products were obtained in 85% and 87% yields, respectively (entries 2 and 3). The reaction of vinyl ethers **1d** and **1e** bearing chloro and hydroxyl groups, respectively, afforded corresponding hydrothiolation products **3da** and **3ea** in good to moderate yields (entries 4 and 5). Interestingly, the reaction of internal vinyl ether **1f** also proceeded efficiently to yield the corresponding hydrothiolation product despite the generally known difficulty of the transition-metal-catalyzed reaction of internal alkenes (entry 6). Furthermore, cyclic vinyl ethers **1g** and **1h** were also tolerant to the hydrothiolation (entries 7 and 8).

We next examined the scope and limitations of this Pd-catalyzed hydrothiolation of vinyl ethers by using several thiols. The results of the reaction of *n*-butyl vinyl ether **1a** with several thiols (**2**) are summarized in Table 3. In the cases of

Table 3. Pd-Catalyzed Hydrothiolation Using Several Thiols[a]



1a 2 3

entry	RSH, 2	product	3	yield, %[b]
1	 **2a**		**3aa**	95
2	 **2b**		**3ab**	81
3	 **2c**		**3ac**	58
4	 **2d**		**3ad**	83
5	 **2e**		**3ae**	97
6	 **2f**		**3af**	35
7	 **2g**		**3ag**	39

[a]Reaction conditions: *n*-butyl vinyl ether (**1a**, 0.5 mmol), thiol (**2**, 0.5 mmol), $Pd(OAc)_2$ (5 mol %), THF (0.3 mL), 45 °C, 20 h. [b]Isolated yield.

benzenethiols bearing either electron-donating or -withdrawing groups, such as methyl, methoxy, fluoro, and chloro substituents on the aryl groups, the Pd-catalyzed Markovnikov hydrothiolation took place, affording the corresponding products **3ab**, **3ac**, **3ad**, and **3ae**, respectively, in good yields (entries 2−5). However, aliphatic thiols, such as phenylmethylthiol **2f** and cyclohexanethiol **2g**, gave low yields of the corresponding hydrothiolation products **3af** and **3ag** (entries 6 and 7).[10]

Highly selective hydrothiolation of alkenes bearing nitrogen functional groups is also of great interest as an application of the vinyl ether hydrothiolation to other functionalized alkenes. We chose *N*-vinyl lactams as alkenes bearing a nitrogen functional group for the Pd-catalyzed hydrothiolation. The lactam skeleton is a prominent structural feature found in a number of biologically active natural products.[11] Some of bioactive lactam compounds containing a *N*,*S*-acetal unit, such as penicillin, exhibit remarkable antibiosis. Therefore, the

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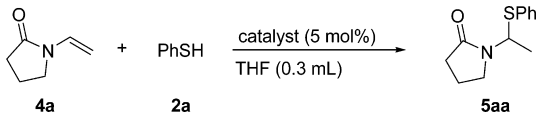
development of highly selective methods for the introduction of a sulfur group to lactam units is strongly desired.

We examined the optimization of the hydrothiolation reaction conditions by using *N*-vinyl pyrrolidinone as a manageable *N*-vinyl lactam (Table 4). When the reaction of

Table 4. Optimization of Hydrothiolation of *N*-Vinyl Lactam[a]



4a **2a** **5aa**

entry	catalyst	time, h	temp, °C	yield, %[b]
1	$Pd(OAc)_2$	20	45	94
2	$Pd(OAc)_2$ (1 mol %)	20	45	80
3	none	20	45	14
4	$Pd(PPh_3)_4$	20	45	16
5	$PdCl_2(PhCN)_2$	20	45	85
6	$PdCl_2(cod)$	20	45	77
7	$Pd(OAc)_2$	20	30	93
8	$Pd(OAc)_2$	14	45	81
9	$Pd(OAc)_2$	5	45	87

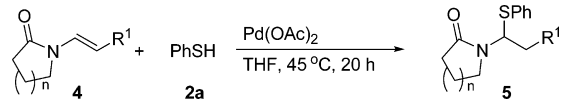
[a]Reaction conditions: *N*-vinyl lactam (**4a**, 0.5 mmol), benzenethiol (**2a**, 0.5 mmol), $Pd(OAc)_2$ (5 mol %), THF (0.3 mL), 45 °C, 20 h. [b]Isolated yield.

N-vinyl pyrrolidinone (**4a**) and benzenethiol (**2a**) was conducted at 45 °C for 20 h using 5 and 1 mol % $Pd(OAc)_2$, the Markovnikov-type hydrothiolation product (**5aa**) was obtained in 94% and 80% yields, respectively (entries 1 and 2). In the absence of $Pd(OAc)_2$, the desired hydrothiolation of *N*-vinyl lactam proceeded inefficiently (entry 3). The reaction using other palladium catalysts, such as $Pd(PPh_3)_4$, $PdCl_2(PhCN)_2$, and $PdCl_2(cod)$ was examined (entries 4−6). $PdCl_2(PhCN)_2$- and $PdCl_2(cod)$-catalyzed hydrothiolation yielded the desired Markovnikov-type adduct in moderate yield, whereas $Pd(PPh_3)_4$ did not catalyze the hydrothiolation of the *N*-vinyl lactam. Next, the hydrothiolation was conducted with varying temperature and time (entries 7−9). These results clearly indicate that the hydrothiolation of the *N*-vinyl lactam proceeded under mild conditions.

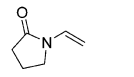
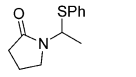
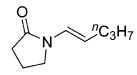
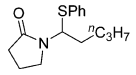
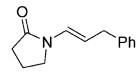
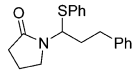
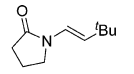
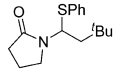
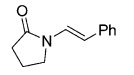
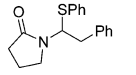
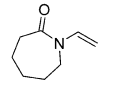
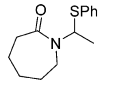
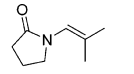
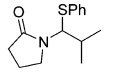
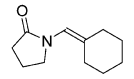
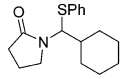
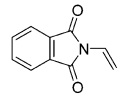
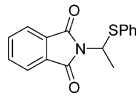
Next, under the optimized reaction conditions, the scope and limitation of the hydrothiolation of *N*-vinyl lactams was examined (Table 5). When internal *N*-vinyl lactams **4b** and **4c** were used for hydrothiolation, the corresponding hydrothiolation products were obtained in 73% and 69% yields, respectively (entries 2 and 3). In the case of branched and aromatic internal *N*-vinyl lactams **4d** and **4e**, the desired hydrothiolation proceeded in good to moderate yields (entries 4 and 5). The reaction of *N*-vinyl caprolactam **4f** took place efficiently to obtain a Markovnikov adduct regioselectively (entry 6). In the case of 1-(2-methylpropenyl)-2-pyrrolidinone **4g** and 1-cyclohexylidene-2-pyrrolidinone **4h**, however the desired reaction did not proceed at all. This is probably because the bulkiness of the alkene interrupted the approach of the Pd-sulfide complex to the alkenes. Moreover, the hydrothiolation using *N*-vinyl phthalimide **4i** as the substrate did not take place owing to the lower coordination ability of the nitrogen atom.

Furthermore, Pd-catalyzed hydrothiolations of the *N*-vinyl lactam using several thiols were performed, and the results are summarized in Table 6. Benzenethiols bearing either electron-donating or -withdrawing groups, such as the methyl, methoxy,

Table 5. Hydrothiolation of Several *N*-Vinyl Lactams[a]



4 **2a** **5**

entry	substrate	**4**	product	**5**	yield, %[b]
1		**4a**		**5aa**	94
2		**4b**		**5ba**	73
3		**4c**		**5ca**	69
4		**4d**		**5da**	71
5		**4e**		**5ea**	48
6		**4f**		**5fa**	87
7		**4g**		**5ga**	ND
8		**4h**		**5ha**	ND
9		**4i**		**5ia**	ND

[a]Reaction conditions: *N*-vinyl lactams (**4**, 0.5 mmol), benzenethiol (**2a**, 0.5 mmol), $Pd(OAc)_2$ (5 mol %), THF (0.3 mL), 45 °C, 20 h. [b]Isolated yield.

fluoro, and chloro group, afforded the corresponding hydrothiolation products **5ab**, **5ac**, **5ad**, and **5ae**, respectively (entries 2−5). In the case of aliphatic thiols, such as phenylmethylthiol **2f** and cyclohexanethiol **2g**, the desired hydrothiolation products were obtained in moderate to good yields (entries 6 and 7).[12]

To obtain insight into the present Pd-catalyzed hydrothiolation reaction, we examined the catalytic hydrothiolation of a vinyl ether using a preformed Pd-sulfide complex (Scheme 2). Initially, the Pd-sulfide complex was prepared by the reaction of $Pd(OAc)_2$ and benzenethiol (**2a**) according to the literature.[6] The reaction of *n*-butyl vinyl ether (**1a**) with benzenethiol (**2a**) in the presence of 5 mol % of Pd-sulfide complex **A** as a catalyst afforded the corresponding Markovnikov hydrothiolation product (**3aa**) in 85% yield. Furthermore, when the equimolar reaction of Pd-sulfide complex **A** with a vinyl ether was conducted, no hydrothiolation product was obtained at all. These results strongly suggest that Pd-sulfide complex **A** is a highly effective catalyst for the hydrothiolation of vinyl ethers and also thiol is essential for catalytic reaction.

Further investigations were conducted to acquire information on the hydrothiolation reaction. When a Lewis acid catalyst such as $Sc(OTf)_3$ was introduced to the reaction instead of the Pd catalyst, the desired hydrothiolation product was not obtained at all. This result indicates that the Pd catalyst did not

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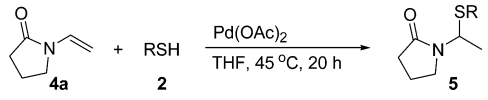
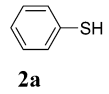
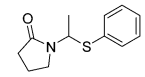
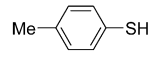
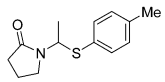
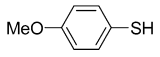
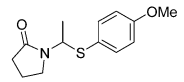
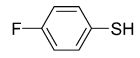
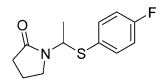
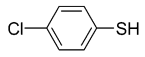
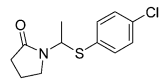
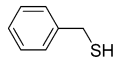
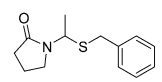
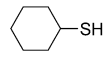
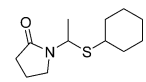
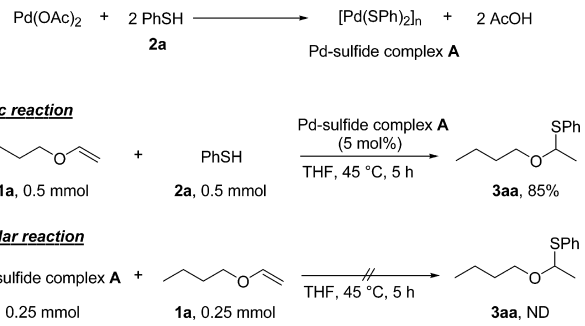
Table 6. Pd-Catalyzed Hydrothiolation Using Several Thiols[a]



entry	RSH, **2**	product	**3**	yield, %[b]
1	 **2a**		**5aa**	95
2	 **2b**		**5ab**	85
3	 **2c**		**5ac**	87
4	 **2d**		**5ad**	81
5	 **2e**		**5ae**	86
6	 **2f**		**5af**	72
7	 **2g**		**5ag**	59

[a]Reaction conditions: *N*-vinyl lactam (**4a**, 0.5 mmol), thiol (**2**, 0.5 mmol), $Pd(OAc)_2$ (5 mol %), THF (0.3 mL), 45 °C, 20 h. [b]Isolated yield.

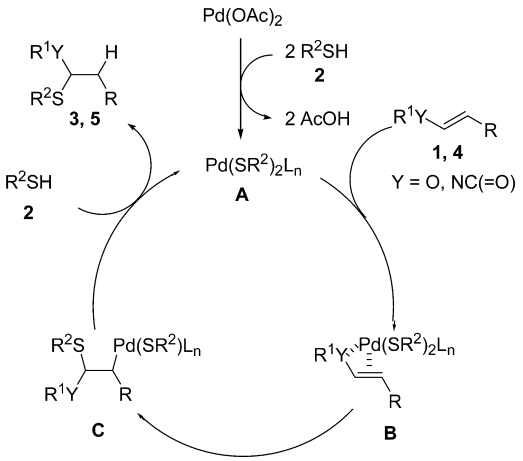
Scheme 2. Examination of the Effects of Pd Catalyst



serve in a Lewis acid capacity to catalyze the hydrothiolation. As another possibility, it was considered that AcOH generated from the reaction of $Pd(OAc)_2$ and benzenethiol might catalyze this hydrothiolation as a Brønsted acid. Thus, the reaction using AcOH as a protic acid was examined. However, the hydrothiolation reaction did not proceed.

Although the details of the reaction mechanism are not clear at present, a possible reaction pathway for the Pd-catalyzed hydrothiolation of heteroatom-substituted alkene with thiol **2** is shown in Scheme 3. We think heteroatoms on the alkene are of great importance for promotion of the hydrothiolation, because Pd-catalyzed hydrothiolation of normal alkenes did not proceed at all. Therefore, the $Pd(OAc)_2$ catalyst reacts with thiols to form Pd-sulfide complex **A**. Then, vinyl ether **1** coordinates to

Scheme 3. A Possible Reaction Pathway of Pd-Catalyzed Hydrothiolation of Heteroatom-Substituted Alkenes



Pd-sulfide complex **A**, providing Pd-sulfide-alkene complex **B**, where heteroatoms might coordinate to palladium, stabilizing complex **B**. Subsequent insertion generates palladium intermediate **C**. The following protonation of palladium intermediate **C** with thiol provides the Markovnikov hydrothiolation product regioselectively, with regeneration of Pd-sulfide complex **A**.[13]

CONCLUSION

In summary, we have developed a novel and highly selective Pd-catalyzed Markovnikov hydrothiolation of alkenes bearing heteroatom functional groups, which proceeds under mild conditions and affords the addition products in good yields; the nature of the thiol substrate is general and includes thiols previously reported as problematic in transition-metal-catalyzed reactions of alkenes. Internal and cyclic alkenes bearing a heteroatom are also shown to be compatible. In addition, the present hydrothiolation could produce *O,S*-acetals or *N,S*-acetals with a new stereogenic center in their structure. Therefore, application of this methodology toward the enantioselective hydrothiolation will be explored next, because these heteroacetals units are known as synthetic intermediates and bioactive products.[11,14] We believe that this reaction will open up a new field of transition-metal-catalyzed reactions of alkenes.

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all starting materials and catalysts were purchased from a commercial source and used without further purification. The following substrates were prepared by using dehydration condensation of pyrrolidinone and the corresponding aldehyde with *p*-TsOH: (*E*)-1-(1-pentenyl)-2-pyrrolidinone,[15] (*E*)-1-(3-phenyl-1-propenyl)-2-pyrrolidinone,[16] (*E*)-1-(3,3-dimethyl-1-butenyl)-2-pyrrolidinone,[16] (*E*)-1-styryl-2-pyrrolidinone,[15] 1-(2-methylpropenyl)-2-pyrrolidinone,[16] and 1-cyclohexylidene-2-pyrrolidinone.[16] THF as solvent and benzenethiol were used after distillation. ^1H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were taken in $CDCl_3$ with Me_4Si as an internal standard. Chemical shifts in ^1H 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 are reported in wave numbers (cm^{-1}). FAB mass spectra were obtained by employing double focusing mass spectrometers. Elemental

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analyses and EI mass spectra were performed in the analytical section of Osaka University.

General Procedure for Hydrothiolation of Heteroatom-Substituted Alkenes. In a two-necked 10 mL flask with a magnetic stirring bar under a N_2 atmosphere were placed $Pd(OAc)_2$ (0.025 mmol), freshly distilled THF (0.3 mL), heteroatom-substituted alkene (0.5 mmol), and thiol (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) provided the hydrothiolated product.

*1-(Phenylthio)ethyl Butyl Ether (**3aa**).* This compound was prepared from *n*-butyl vinyl ether (64.7 μL, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (105.1 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.38 (sext, *J* = 7.3 Hz, 2H), 1.50 (d, *J* = 6.3 Hz, 3H), 1.54−1.61 (m, 2H), 3.43 (td, *J* = 6.3 Hz, 9.0 Hz, 1H), 3.88 (td, *J* = 6.3 Hz, 9.0 Hz, 1H), 4.88 (q, *J* = 6.3 Hz, 1H), 7.24−7.31 (m, 3H), 7.46−7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 14.0, 19.5, 22.7, 31.6, 67.9, 84.8, 127.5, 128.8, 133.3, 133.8; IR (NaCl) 3071, 2959, 2932, 2870, 1582, 1481, 1439, 1369, 1315, 1261, 1111, 1026, 972, 910, 744 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{18}OS$: 210.1078. Found: 210.1080; Anal. Calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.63. Found: C, 68.41; H, 8.67.

*1-(Phenylthio)ethyl 2-methylpropyl Ether (**3ba**).* This compound was prepared from 2-methylpropyl vinyl ether (65.0 μL, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (89.6 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.92 (dd, *J* = 6.9 Hz, 8.2 Hz, 6H), 1.50 (d, *J* = 6.4 Hz, 3H), 1.86 (sept, *J* = 6.9 Hz, 1H), 3.21 (dd, *J* = 6.9 Hz, 9.2 Hz, 1H), 3.63 (dd, *J* = 6.9 Hz, 9.2 Hz, 1H), 4.89 (q, *J* = 6.4 Hz, 1H), 7.23−7.31 (m, 3H), 7.46−7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 19.5 (overlap), 22.4, 28.3, 74.7, 84.7, 127.3, 128.6, 133.2, 133.6; IR (NaCl) 3074, 2959, 2932, 2870, 1582, 1474, 1435, 1362, 1323, 1265, 1111, 1053, 1026, 891, 745, 691 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{18}OS$: 210.1078. Found: 210.1076.

*1-(Phenylthio)ethyl Cyclohexyl Ether (**3ca**).* This compound was prepared from cyclohexyl vinyl ether (70.9 μL, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following a general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (102.6 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.16−1.41 (m, 5H), 1.48 (d, *J* = 6.0 Hz, 3H), 1.49−1.57 (m, 1H), 1.67−1.75 (m, 2H), 1.84−1.90 (m, 2H), 3.73−3.80 (m, 1H), 5.01 (q, *J* = 6.0 Hz, 1H), 7.23−7.31 (m, 3H), 7.48−7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 23.2, 24.0, 24.2, 25.6, 31.1, 33.1, 74.8, 81.5, 127.4, 128.5, 132.9, 134.0; IR (NaCl) 3063, 2932, 2855, 1582, 1477, 1450, 1369, 1312, 1265, 1153, 1099, 1057, 1026, 972, 883, 745, 694, 621 cm^{-1}; Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53. Found: C, 70.92; H, 8.52.

*1-(Phenylthio)ethyl 2-Chloroethyl Ether (**3da**).* This compound was prepared from 2-chloroethyl vinyl ether (50.7 μL, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (97.3 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.52 (d, *J* = 6.4 Hz, 3H), 3.64 (t, *J* = 5.5 Hz, 2H), 3.73 (td, *J* = 5.5 Hz, 10.5 Hz, 1H), 4.11 (td, *J* = 5.5 Hz, 10.5 Hz, 1H), 4.97 (q, *J* = 6.4 Hz, 1H), 7.24−7.32 (m, 3H), 7.47−7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 22.2, 42.7, 67.6, 84.8, 127.7, 128.7, 132.4, 133.6; IR (NaCl) 3059, 2978, 2928, 2862, 1582, 1477, 1439, 1373, 1296, 1265, 1200, 1111, 1042, 1003, 968, 926, 814, 748, 694 cm^{-1}; Anal. Calcd for $C_{10}H_{13}ClOS$: C, 55.42; H, 6.05. Found: C, 55.29; H, 5.95.

*1-(Phenylthio)ethyl 2-Hydroxyethyl Ether (**3ea**).* This compound was prepared from 2-hydroxyethyl vinyl ether (45.0 μL, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (56.1 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.53 (d, *J* = 6.4 Hz, 3H), 2.02 (br, 1H), 3.55−3.60 (m, 1H), 3.75 (br, 2H), 3.95−4.00 (m, 1H), 4.97 (q, *J* = 6.4 Hz, 1H), 7.27−7.33 (m, 3H), 7.46−7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 22.3, 61.6, 68.8, 84.8, 127.7, 128.8, 132.5, 133.7; IR (NaCl) 3402, 3074, 2928, 1585, 1477, 1439, 1377, 1319, 1115, 1080, 937, 887, 829, 748, 694 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_{14}O_2S$: 198.0715. Found: 198.0713.

*1-(Phenylthio)butyl Ethyl Ether (**3fa**).* This compound was prepared from ethyl 1-butenyl ether (64.4 μL, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (91.3 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.89 (t, *J* = 7.3 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.48 (sext, *J* = 7.3 Hz, 2H), 1.66−1.81 (m, 2H), 3.48 (qd, *J* = 6.9 Hz, 9.1 Hz, 1H), 3.95 (qd, *J* = 6.9 Hz, 9.1 Hz, 1H), 4.70 (dd, *J* = 6.0 Hz, 7.3 Hz, 1H), 7.23−7.30 (m, 3H), 7.46−7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 13.6, 14.8, 19.5, 38.0, 63.4, 88.9, 127.3, 128.6, 133.4, 133.6; IR (NaCl) 3059, 2963, 2932, 2870, 1582, 1477, 1439, 1381, 1288, 1261, 1245, 1115, 1080, 1026, 972, 883, 829, 744, 690 cm^{-1}; Anal. Calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.63. Found: C, 68.27; H, 8.63.

*Tetrahydro-2-(phenylthio)pyran (**3ga**).* This compound was prepared from 2,3-dihydropyran (45.6 μL, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (85.5 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.57−1.69 (m, 3H), 1.78−1.89 (m, 2H), 1.99−2.06 (m, 1H), 3.55−3.60 (m, 1H), 4.14−4.19 (m, 1H), 5.20 (dd, *J* = 3.6 Hz, 5.9 Hz, 1H), 7.18−7.29 (m, 3H), 7.45−7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 21.6, 25.4, 31.5, 64.4, 85.2, 126.6, 128.7, 130.7, 135.3; IR (NaCl) 3063, 2940, 2858, 1582, 1477, 1439, 1339, 1323, 1261, 1188, 1103, 1076, 1038, 1007, 868, 810, 741, 691 cm^{-1}.

*Tetrahydro-2-(phenylthio)furan (**3ha**).* This compound was prepared from 2,3-dihydrofuran (37.7 μL, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (75.7 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.79−2.06 (m, 3H), 2.31−2.42 (m, 1H), 3.93−4.05 (m, 2H), 5.63−5.66 (m, 1H), 7.19−7.24 (m, 1H), 7.26−7.31 (m, 2H), 7.49−7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 24.8, 32.6, 67.2, 87.0, 126.7, 128.7, 131.0, 135.6; IR (NaCl) 3063, 2974, 2951, 2870, 1582, 1481, 1296, 1223, 1180, 1049, 907, 741, 691 cm^{-1}.

*1-[(p-Methylphenyl)thio]ethyl Butyl Ether (**3ab**).* This compound was prepared from *n*-butyl vinyl ether (64.7 μL, 0.5 mmol) and 4-methylbenzenethiol (62.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (90.3 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.38 (sext, *J* = 7.3 Hz, 2H), 1.47 (d, *J* = 6.4 Hz, 3H), 1.52−1.61 (m, 2H), 2.33 (s, 3 H), 3.42 (td, *J* = 6.4 Hz, 9.2 Hz, 1H), 3.89 (td, *J* = 6.4 Hz, 9.2 Hz, 1H), 4.82 (q, *J* = 6.4 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 13.9, 19.4, 21.1, 22.6, 31.5, 67.8, 84.8, 129.1, 129.4, 134.2, 137.6; IR (NaCl) 3017, 2959, 2932, 2870, 1738, 1493, 1458, 1396, 1315, 1265, 1241, 1107, 1088, 1049, 968, 907, 810, 756, 648 cm^{-1}; Anal. Calcd for $C_{13}H_{20}OS$: C, 69.59; H, 8.98. Found: C, 69.36; H, 8.80.

*1-[(p-Methoxylphenyl)thio]ethyl Butyl Ether (**3ac**).* This compound was prepared from *n*-butyl vinyl ether (64.7 μL, 0.5 mmol) and 4-methoxylbenzenethiol (61.5 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a pale yellow oil (69.8 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.39 (sext, *J* = 7.3 Hz, 2H), 1.43 (d, *J* = 6.4 Hz, 3H), 1.54−1.61 (m, 2H), 3.41 (td, *J* = 6.9 Hz, 9.2 Hz, 1H), 3.80 (s, 3H), 3.90 (td, *J* = 6.9 Hz, 9.2 Hz, 1H), 4.74 (q, *J* = 6.4 Hz, 1H), 6.82−6.86 (m, 2H), 7.38−7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 13.9, 19.4, 22.5, 31.5, 55.2, 68.0, 84.9, 114.2, 122.8, 136.4, 159.7; IR (NaCl) 2959, 2932, 2870, 1593, 1493, 1462, 1366, 1285, 1246, 1173, 1107, 1034, 907, 829, 648, 610 cm^{-1}; Anal. Calcd for $C_{13}H_{20}O_2S$: C, 64.96; H, 8.39. Found: C, 64.87; H, 8.45.

*1-[(p-Fluorophenyl)thio]ethyl Butyl Ether (**3ad**).* This compound was prepared from *n*-butyl vinyl ether (64.7 μL, 0.5 mmol) and 4-fluorobenzenethiol (53.3 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (95.7 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.38 (sext, *J* = 7.3 Hz, 2H), 1.45 (d, *J* = 6.4 Hz, 3H), 1.54−1.63 (m, 2H), 3.42 (td, *J* = 6.4 Hz, 9.1 Hz, 1H), 3.88 (td, *J* = 6.4

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Hz, 9.1 Hz, 1H), 4.80 (q, J = 6.4 Hz, 1H), 6.96−7.02 (m, 3H), 7.42−7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 13.8, 19.4, 22.4, 31.5, 67.9, 84.6, 115.7 (d, J_{C-F} = 22.0 Hz), 127.6 (d, J_{C-F} = 3.8 Hz), 136.2 (d, J_{C-F} = 8.6 Hz), 162.7 (d, J_{C-F} = 247.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ −113.9; IR (NaCl) 2959, 2932, 2870, 1894, 1740, 1589, 1489, 1462, 1396, 1369, 1265, 1227, 1157, 1107, 1088, 1034, 972, 907, 829, 760 cm^{-1}; Anal. Calcd for $C_{12}H_{17}FOS$: C, 63.12; H, 7.50. Found: C, 62.98; H, 7.56.

*1-[(p-Chlorophenyl)thio]ethyl Butyl Ether (**3ae**).* This compound was prepared from *n*-butyl vinyl ether (64.7 μL, 0.5 mmol) and 4-chlorobenzenethiol (72.3 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (118.6 mg, 97%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.92 (t, J = 7.3 Hz, 3H), 1.38 (sext, J = 7.3 Hz, 2H), 1.47 (d, J = 6.4 Hz, 3H), 1.53−1.64 (m, 2H), 3.42 (td, J = 6.9 Hz, 9.0 Hz, 1H), 3.85 (td, J = 6.9 Hz, 9.0 Hz, 1H), 4.85 (q, J = 6.4 Hz, 1H), 7.25 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 13.8, 19.4, 22.4, 31.4, 67.7, 84.5, 128.7, 131.5, 133.6, 134.9; IR (NaCl) 2959, 2932, 2870, 1570, 1474, 1389, 1373, 1315, 1269, 1111, 1092, 1015, 972, 907, 822, 741, 625 cm^{-1}; Anal. Calcd for $C_{12}H_{17}ClOS$: C, 58.88; H, 7.00. Found: C, 58.65; H, 6.88.

*1-(Phenylmethylthio)ethyl Butyl Ether (**3af**).* This compound was prepared from *n*-butyl vinyl ether (64.7 μL, 0.5 mmol) and phenylmethylthiol (58.6 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a colorless oil (39.2 mg, 35%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.93 (t, J = 7.3 Hz, 3H), 1.39 (sext, J = 7.3 Hz, 2H), 1.52 (d, J = 6.3 Hz, 3H), 1.51−1.59 (m, 2H), 3.41 (td, J = 6.3 Hz, 9.1 Hz, 1H), 3.61 (td, J = 6.4 Hz, 9.1 Hz, 1H), 3.45 (d, J = 13.1 Hz, 1H), 3.79 (d, J = 13.1 Hz), 4.64 (q, J = 6.3 Hz, 1H), 7.19−7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 13.9, 19.5, 22.1, 31.7, 32.6, 66.4, 80.6, 126.8, 128.4, 128.9, 138.8; IR (NaCl) 3028, 2959, 2932, 2866, 1597, 1489, 1454, 1369, 1265, 1231, 1103, 1030, 972, 907, 764, 702, 629 cm^{-1}.

*1-(Cyclohexylthio)ethyl Butyl Ether (**3ag**).* This compound was prepared from *n*-butyl vinyl ether (64.7 μL, 0.5 mmol) and 4-methylbenzenethiol (61.2 μL, 0.5 mmol) following the general procedure for hydrothiolation of vinyl ethers. Isolated as a pale yellow oil (42.7 mg, 39%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.93 (t, J = 7.3 Hz, 3H), 1.21−1.43 (m, 8H), 1.51−1.63 (m, 5H), 1.72−1.75 (m, 2H), 1.93−2.02 (m, 2H), 2.81−2.89 (m, 1H), 3.44 (td, J = 6.4 Hz, 9.2 Hz, 1H), 3.63 (td, J = 6.4 Hz, 9.2 Hz, 1H), 4.78 (q, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 13.9, 19.4, 22.6, 25.7, 31.7, 34.5, 35.0, 41.4, 66.1, 80.6; IR (NaCl) 2928, 2855, 1447, 1369, 1312, 1265, 1204, 1103, 1034, 999, 973, 907, 887, 772, 741, 637 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{24}OS$: 216.1548. Found: 216.1549.

*1-[(1-Phenylthio)ethyl]-2-pyrrolidinone (**5aa**).* This compound was prepared from 1-vinyl-2-pyrrolidinone (53.2 μL, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a pale yellow oil (104.4 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.48 (d, J = 6.9 Hz, 3H), 1.76−1.83 (m, 1H), 1.86−1.96 (m, 1H), 2.04−2.12 (m, 1H), 2.22−2.30 (m, 1H), 3.28−3.34 (m, 1H), 3.52−3.58 (m, 1H), 5.89 (q, J = 6.9 Hz, 1H), 7.20−7.30 (m, 3H), 7.39−7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 17.5, 18.7, 31.0, 41.1, 54.2, 127.3, 128.6, 132.0, 132.8, 174.3; IR (NaCl) 3495, 3071, 2986, 2881, 1686, 1585, 1481, 1458, 1416, 1350, 1269, 1200, 1092, 1065, 1018, 953, 926, 837, 748, 694 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{15}NOS$: 221.0874. Found: 221.0875.

*1-[(1-Phenylthio)pentyl]-2-pyrrolidinone (**5ba**).* 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 for hydrothiolation of *N*-vinyl lactam. Isolated as a yellow oil (96.3 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.90 (t, J = 6.9 Hz, 3H), 1.25−1.42 (m, 4H), 1.68−1.97 (m, 4H), 2.04−2.12 (m, 1H), 2.24−2.32 (m, 1H), 3.20−3.26 (m, 1H), 3.52−3.58 (m, 1H), 5.73 (dd, J = 5.7 Hz, 9.4 Hz, 1H), 7.19−7.29 (m, 3H), 7.38−7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 13.8, 17.7, 22.0, 28.5, 31.1, 32.2, 41.3, 58.8, 127.2, 128.7, 132.0, 132.9, 174.8; IR (NaCl) 3441, 3049, 2931, 2861, 1685, 1583, 1486, 1458, 1412, 1348, 1281, 1265, 1186, 1091, 1025, 928, 745, 692 cm^{-1}; HRMS (FAB) Calcd for $C_{15}H_{22}NOS$ [M + H]$^+$: 264.1422. Found: 264.1425.

*1-[3-Phenyl-(1-Phenylthio)propyl]-2-pyrrolidinone (**5ca**).* This compound was prepared from 1-(3-Phenyl-1-propenyl)-2-pyrrolidinone (112 mg, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a yellow oil (107.0 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.66−1.84 (m, 2H), 2.00−2.26 (m, 4H), 2.59−2.66 (m, 1H), 2.74−2.81 (m, 1H), 3.14−3.20 (m, 1H), 3.50−3.56 (m, 1H), 5.80 (dd, J = 6.0 Hz, 9.2 Hz, 1H), 7.17−7.30 (m, 8H), 7.38−7.40 (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 17.6, 31.0, 33.0, 34.3, 41.4, 58.9, 126.1, 127.4, 128.2, 128.4, 128.8, 132.2, 132.6, 140.5, 174.9; IR (NaCl) 3500, 3061, 3024, 2942, 1685, 1585, 1501, 1489, 1411, 1359, 1283, 1265, 1082, 1027, 908, 838, 745, 693 cm^{-1}; HRMS (FAB) Calcd for $C_{19}H_{22}NOS$ [M + H]$^+$: 312.1422. Found: 312.1417.

*1-[3,3-Dimethyl-(1-Phenylthio)butyl]-2-pyrrolidinone (**5da**).* This compound was prepared from 1-(3,3-dimethyl-1-butenyl)-2-pyrrolidinone (83.6 mg, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a yellow oil (98.3 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.97 (s, 9H), 1.57 (dd, J = 3.2 Hz, 14.7 Hz, 1H), 1.61−1.70 (m, 1H), 1.74−1.87 (m, 2H), 1.90−1.99 (m, 1H), 2.09−2.20 (m, 1H), 3.26−3.32 (m, 1H), 3.50−3.56 (m, 1H), 5.94 (dd, J = 3.2 Hz, 9.6 Hz, 1H), 7.20−7.28 (m, 3H), 7.40−7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 17.7, 29.3, 31.3, 31.3, 41.2, 44.7, 56.3, 127.5, 128.6, 132.3, 132.6, 174.4; IR (NaCl) 3492, 3057, 2953, 2878, 1691, 1582, 1476, 1411, 1362, 1283, 1266, 1153, 1020, 933, 895, 843, 744, 692 cm^{-1}; Anal. Calcd for $C_{16}H_{23}NOS$: C, 69.27; H, 8.36; N, 5.05. Found: C, 69.00; H, 8.38; N, 5.13.

*1-[2-Phenyl-(1-phenylthio)ethyl]-2-pyrrolidinone (**5ea**).* This compound was prepared from 1-styryl-2-pyrrolidinone (93.5 mg, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a yellow oil (70.9 mg, 48%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.65−1.81 (m, 2H), 1.95−2.12 (m, 2H), 2.99−3.05 (m, 1H), 3.16−3.29 (m, 2H), 3.53−3.59 (m, 1H), 6.05 (dd, J = 6.9 Hz, J = 9.2 Hz, 1H), 7.21−7.31 (m, 8H), 7.39−7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 17.7, 30.9, 38.9, 41.7, 59.4, 126.9, 127.5, 128.4, 128.7, 128.8, 132.2, 132.6, 136.4; IR (NaCl) 3491, 3068, 3024, 2969, 1690, 1646, 1583, 1482, 1456, 1438, 1410, 1265, 1157, 1078, 1025, 993, 929, 926, 746, 697 cm^{-1}; HRMS (FAB) Calcd for $C_{18}H_{20}NOS$ [M + H]$^+$: 298.1266. Found: 298.1261.

*1-(1-Phenylthio)ethyl-2-caprolactam (**5fa**).* This compound was prepared from 1-vinyl-2-caprolactam (69.6 mg, 0.5 mmol) and benzenethiol (51.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a yellow oil (108.0 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.38−1.66 (m, 6H), 1.42 (d, J = 6.9 Hz, 3H), 2.32−2.43 (m, 2H), 3.27−3.33 (m, 1H), 3.41−3.47 (m, 1H), 6.05 (q, J = 6.9 Hz, 1H), 7.15−7.19 (m, 1H), 7.23−7.27 (m, 2H), 7.33−7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 19.0, 23.1, 28.9, 29.7, 37.3, 42.5, 55.7, 126.4, 128.6, 130.0, 133.9, 175.5; IR (NaCl) 3512, 3050, 2929, 2854, 1640, 1477, 1438, 1412, 1366, 1310, 1183, 1147, 1094, 1059, 923, 888, 846, 743, 691 cm^{-1}; Anal. Calcd for $C_{14}H_{19}NOS$: C, 67.43; H, 7.68; N, 5.62. Found: C, 67.17; H, 7.87; N, 5.68.

*1-{[1-(p-Methylphenyl)thio]ethyl}-2-pyrrolidinone (**5ab**).* This compound was prepared from 1-vinyl-2-pyrrolidinone (53.2 μL, 0.5 mmol) and 4-methylbenzenethiol (62.1 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a pale yellow oil (100.6 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.47 (d, J = 6.8 Hz, 3H), 1.75−1.98 (m, 2H), 2.05−2.13 (m, 1H), 2.22−2.30 (m, 1H), 2.30 (s, 3H), 3.28−3.34 (m, 1H), 3.56−3.62 (m, 1H), 5.82 (q, J = 6.8 Hz, 1H), 7.08 (d, J = 7.7 Hz, 2H), 7.28−7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 17.6, 18.7, 21.0, 31.1, 41.1, 54.7, 129.0, 129.5, 132.7, 137.7, 174.3; IR (NaCl) 3499, 2974, 2951, 1928, 2885, 1693, 1493, 1458, 1412, 1350, 1265, 1200, 1099, 1088, 1061, 957, 810, 691 cm^{-1}; HRMS (FAB) Calcd for $C_{13}H_{18}NOS$ [M + H]$^+$: 236.1109. Found: 236.1123.

*1-{[1-(p-Methoxylphenyl)thio]ethyl}-2-pyrrolidinone (**5ac**).* This compound was prepared from 1-vinyl-2-pyrrolidinone (53.2 μL, 0.5

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mmol) and 4-methoxybenzenethiol (61.5 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a pale yellow oil (109.2 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.45 (d, *J* = 6.9 Hz, 3H), 1.77−1.98 (m, 2H), 2.04−2.12 (m, 1H), 2.21−2.29 (m, 1H), 3.28−3.34 (m, 1H), 3.57−3.63 (m, 1H), 3.77 (s, 3H), 5.74 (q, *J* = 6.9 Hz, 1H), 6.79−6.83 (m, 2H), 7.33−7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 17.5, 18.5, 31.0, 41.0, 55.0, 55.3, 114.2, 123.0, 135.3, 159.6, 174.2; IR (NaCl) 3483, 2974, 2889, 2835, 1686, 1593, 1493, 1458, 1416, 1354, 1285, 1246, 1200, 1177, 1103, 1057, 1030, 957, 930, 829, 745, 683 cm^{-1}; Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 61.83; H, 7.00; N, 5.58.

1-{[1-(p-Fluorophenyl)thio]ethyl}-2-pyrrolidinone (**5ad**). This compound was prepared from 1-vinyl-2-pyrrolidinone (53.2 μL, 0.5 mmol) and 4-fluorobenzenethiol (53.3 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a pale yellow oil (97.1 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.48 (d, *J* = 6.9 Hz, 3H), 1.76−2.00 (m, 2H), 2.05−2.13 (m, 1H), 2.23−2.32 (m, 1H), 3.29−3.35 (m, 1H), 3.54−3.60 (m, 1H), 5.82 (q, *J* = 6.9 Hz, 1H), 6.94−7.00 (m, 2H), 7.31−7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 17.5, 18.6, 30.9, 41.0, 55.0, 115.8 (d, J_{C-F} = 21.1 Hz), 127.9 (d, J_{C-F} = 2.9 Hz), 134.9 (d, J_{C-F} = 8.6 Hz), 162.4 (d, J_{C-F} = 248.2 Hz), 174.3; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ −113.2; IR (NaCl) 3483, 2978, 2932, 2885, 1686, 1589, 1489, 1458, 1416, 1354, 1269, 1223, 1157, 1092, 1057, 1015, 957, 930, 833, 745, 683 cm^{-1}; Anal. Calcd for $C_{12}H_{14}FNOS$: C, 60.23; H, 5.90; N, 5.85. Found: C, 60.03; H, 5.97; N, 5.84.

1-{[1-(p-Chlorophenyl)thio]ethyl}-2-pyrrolidinone (**5ae**). This compound was prepared from 1-vinyl-2-pyrrolidinone (53.2 μL, 0.5 mmol) and 4-chlorobenzenethiol (72.3 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a pale yellow oil (109.4 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.49 (d, *J* = 6.9 Hz, 3H), 1.75−1.86 (m, 1H), 1.89−2.00 (m, 1H), 2.09−2.18 (m, 1H), 2.25−2.33 (m, 1H), 3.29−3.35 (m, 1H), 3.50−3.56 (m, 1H), 5.88 (q, *J* = 6.9 Hz, 1H), 7.22−7.25 (m, 2H), 7.31−7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 17.5, 18.7, 30.1, 41.0, 54.3, 128.8, 131.4, 133.2, 133.4, 174.3; IR (NaCl) 3479, 3078, 2978, 2882, 1686, 1574, 1477, 1458, 1412, 1354, 1266, 1204, 1096, 1011, 957, 822, 744, 687, 644 cm^{-1}; Anal. Calcd for $C_{12}H_{14}ClNOS$: C, 56.35; H, 5.52; N, 5.48. Found: C, 56.13; H, 5.43; N, 5.50.

1-{[1-(Phenylmethylthio]ethyl}-2-pyrrolidinone (**5af**). This compound was prepared from 1-vinyl-2-pyrrolidinone (53.2 μL, 0.5 mmol) and phenylmethylthiol (58.6 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a yellow oil (85.3 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.35 (d, *J* = 7.3 Hz, 3H), 1.42−1.54 (m, 1H), 1.77−1.88 (m, 1H), 2.06−2.14 (m, 1H), 2.24−2.32 (m, 1H), 3.15−3.21 (m, 1H), 3.34−3.40 (m, 1H), 3.63 (d, *J* = 14.2 Hz, 1H), 3.73 (d, *J* = 14.2 Hz, 1H), 5.61 (q, *J* = 7.3 Hz, 1H), 7.19−7.23 (m, 1H), 7.26−7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 17.1, 19.1, 31.3, 35.8, 40.8, 52.8, 126.7, 128.2, 128.4, 138.4, 174.5; IR (NaCl) 3503, 3028, 2974, 2928, 2882, 1686, 1597, 1493, 1454, 1416, 1350, 1312, 1269, 1196, 1061, 1026, 957, 918, 849, 768, 710, 640 cm^{-1}; Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.34; H, 7.28; N, 5.95. Found: C, 65.95; H, 7.35; N, 6.01.

1-(1-Cyclohexylthio)ethyl-2-pyrrolidinone (**5ag**). This compound was prepared from 1-vinyl-2-pyrrolidinone (53.2 μL, 0.5 mmol) and cyclohexylthiol (61.2 μL, 0.5 mmol) following the general procedure for hydrothiolation of a *N*-vinyl lactam. Isolated as a pale yellow oil (67.1 mg, 59%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.22−1.38 (m, 5H), 1.38 (d, *J* = 6.9 Hz, 3H), 1.55−1.58 (m, 1H), 1.71−1.80 (m, 3H), 1.98−2.06 (m, 2H), 2.10−2.14 (m, 1H), 2.42 (t, *J* = 8.2 Hz, 2H), 2.50−2.61 (m, 1H), 3.27−3.33 (m, 1H), 3.61−3.66 (m, 1H), 5.61 (q, *J* = 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 17.7, 19.5, 25.6, 25.7, 26.0, 31.5, 33.3, 34.0, 40.9, 42.9, 50.4, 174.2; IR (NaCl) 3510, 2974, 2928, 2851, 1686, 1497, 1447, 1412, 1265, 1196, 1061, 995, 953, 929, 888, 849, 748, 694 cm^{-1}; HRMS (FAB) Calcd for $C_{12}H_{22}NOS$ $[M + H]^+$: 228.1422. Found: 228.1420.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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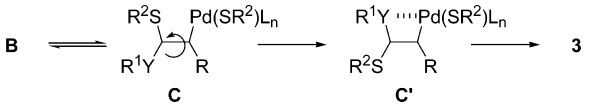
(12) The results indicated that hydrothiolation of *N*-vinyl lactams proceed more efficiently, probably because protonation of palladium intermediate from the *N*-vinyl lactam may proceed easily compared with the case of vinyl ether.
(13) An alternative reaction mechanism, which proceeds via palladium intermediate **C**′, is possible as shown below. Although we try to obtain some information about the reaction intermediates, clear evidence could not be obtained. Palladium intermediate **C** immediately converts to **C**′ due to stabilization by intramolecular coordination of the ether oxygen atom. We think this stabilization prevents *β*-elimination of **C** from taking place. The subsequent protonation of palladium intermediate **C**′ with thiol provides the Markovnikov hydrothiolation product selectively.



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