HETEROCYCLES, Vol. 90, No. 2, 2015, pp. 1323 - 1331. © 2015 The Japan Institute of Heterocyclic Chemistry
Received, 8th July, 2014, Accepted, 1st October, 2014, Published online, 10th October, 2014
DOI: 10.3987/COM-14-S(K)80

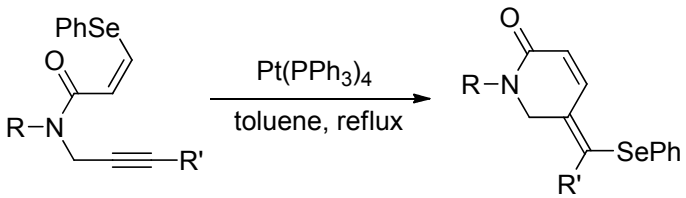
PALLADIUM CATALYZED INTRAMOLECULAR VINYLSELENATION AND VINYLTHIOLATION OF ALLENES

Susumu Tsuda,[1] Maiko Okuyama,[2] Shin-ichi Fujiwara,[1,*] Takanori Iwasaki,[2] Hitoshi Kuniyasu,[2] and Nobuaki Kambe[2,*]

[1]Department of Chemistry, Osaka Dental University, Hirakata, Osaka 573-1121, Japan, and [2]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka, 565-0871, Japan

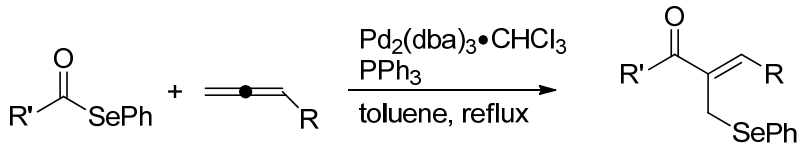
Abstract – Intramolecular vinylselenation of allenes **1a,b** proceeds in the presence of Pd(0) catalyst producing pyridin-2-one derivatives **2a,b** having a high degree of unsaturation as a sole product. This cyclization could also be applied to vinylthiolation and to the construction of seven-membered lactams.

Simultaneous addition of carbon and heteroatom units to carbon-carbon unsaturated bonds such as alkynes and allenes with the cleavage of carbon-heteroatom bond by transition metal complexes has attracted great interest in organic and organometallic chemistry.[1] In the cases of alkynes, the reaction proceeds in *syn*-selective manner to give multi-functionalized alkenyl heteroatom compounds. However the introduction of vinyl group as a carbon unit had been limited to the cases using strained substrates.[2] In 2008, we disclosed Pt(0)-catalyzed intramolecular *syn*-vinylselenation of alkynes leading to effective construction of a six-membered lactam framework (Scheme 1).[3] In this reaction an anion stabilizing group on the β-position of acyclic vinyl selenides would enhance oxidative addition to Pt(0) complex.[4]



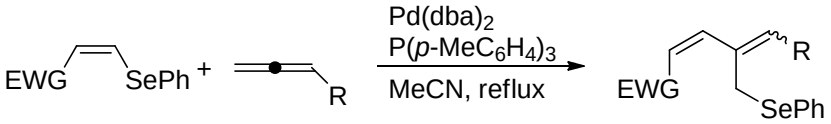
Scheme 1. Pt(0)-Catalyzed Intramolecular Vinylselenation of Alkynes

Allenes have been employed as versatile building blocks in organic synthesis.[5] However, there are only fewer examples of allene insertion into carbon-heteroatom bonds.[2a-b,6] In 2008, we reported carboselenation of allenes proceeded regioselectively providing allylic selenides (Scheme 2).[7,8]



Scheme 2. Pd(0)-Catalyzed Acylselenation of Allenes

Furthermore, we reported that vinylselenation of allenes proceeded when activated vinyl selenides were employed in the presence of Pd(0) complex as a catalyst to form 1,3-diene framework site- and regioselectively carrying the vinyl moiety at the inner carbon and the SePh group at the terminal carbon (Scheme 3).[9]

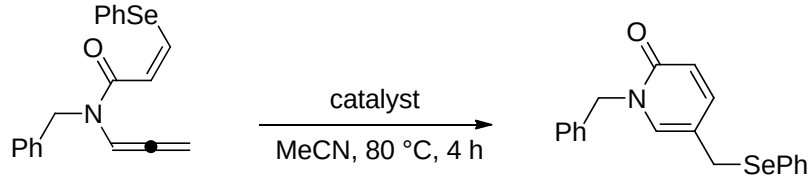


EWG = C(O)OEt, C(O)NEt_2

Scheme 3. Pd(0)-Catalyzed Vinylselenation of Allenes

Here we examined the intramolecular vinylselenation and –thiolation of allenes.[10] When an MeCN (0.3 mL) solution of **1a** (0.3 mmol), $Pd(dba)_2$ (5 mol%) and P(*p*-$MeC_6H_4)_3$ (10 mol%) was heated at 80 °C for 4 h, pyridin-2-one **2a** was obtained in 43% NMR yield (Table 1, run 1). $Pd(PPh_3)_4$ could also be employed as a catalyst to afford **2a** in a similar yield (run 2). Since unidentified by-products, probably arising from dimerization and/or oligomerization of **1a**, were detected in the resulting mixtures, the reaction was then carried out under more diluted conditions. As a result, the yield of **1a** was increased to 68% yield by the use of 3 mL of MeCN (run 3). As for the solvent, DMF also afforded **2a** in 53% yield; however, other solvents examined such as toluene, dioxane, and DMA were not suitable for this transformation giving the product in lower yields.[11] The yield of **2a** was further increased to 79% yield by

Table 1. Screening of Reaction Conditions



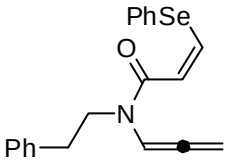
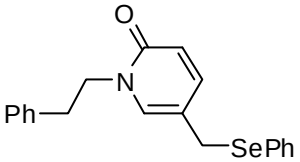
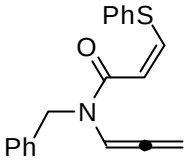
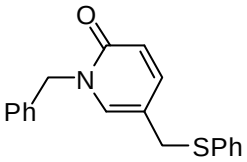
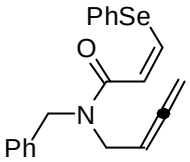
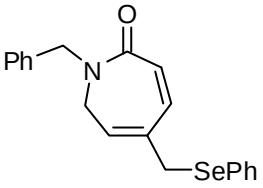
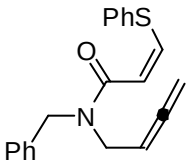
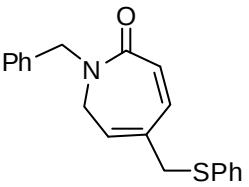
1a, 0.3 mmol **2a**

run	catalyst	MeCN	Isolated Yield (NMR Yield)
1	$Pd(dba)_2$ (5 mol%) P(*p*-$MeC_6H_4)_3$ (10 mol%)	0.3 mL	(43%)
2	$Pd(PPh_3)_4$ (5 mol%)	0.3 mL	(39%)
3	$Pd(PPh_3)_4$ (5 mol%)	3 mL	(68%)
4	$Pd(PPh_3)_4$ (20 mol%)	3 mL	69% (79%)

the use of 20 mol% of $Pd(PPh_3)_4$ (run 4). In contrast with vinylselenation of alkynes (Scheme 1), $Pt(PPh_3)_4$ was not effective in this transformation.

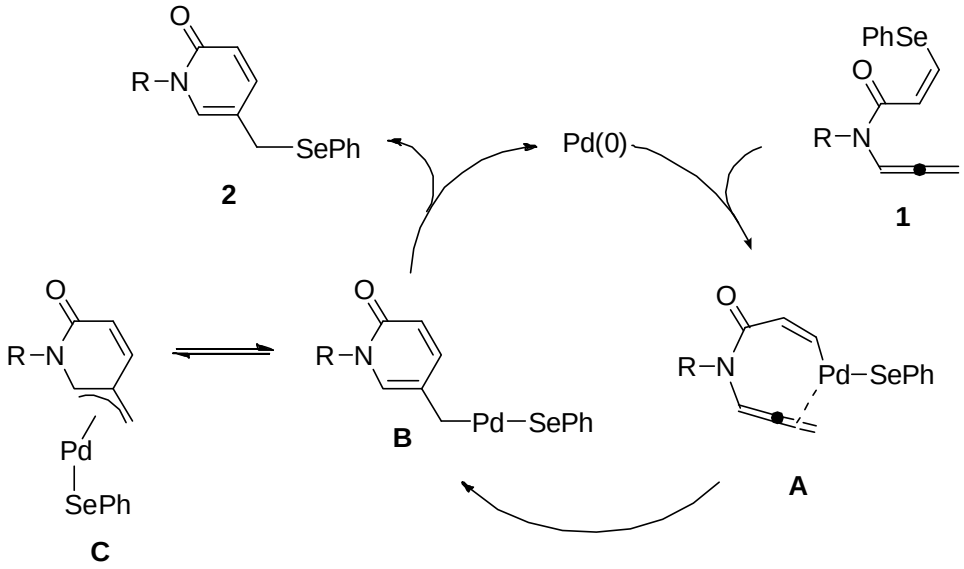
Table 2 summarizes the results obtained using several vinyl selenides and sulfides under the conditions of run 3 in Table 1. Vinyl selenide **1b** having a phenethyl group on the nitrogen atom afforded the pyridin-2-one **2b** in 43% yield (run 1). Vinyl sulfide **1c** also afforded **2c** albeit in a lower yield (run 2). When methylene group was introduced between the nitrogen atom and an allenyl group, seven-membered lactam **4a** was obtained in 17% yield. By the use of DMF as the solvent and rising the reaction temperature to 110 °C, the yield of **4a** was increased up to 50% (run 3). Similarly, lactam **4b** was obtained in 27% yield from vinyl sulfide **3b**. In all runs formation of other possible regioisomers was not confirmed. However, as mentioned above, unidentified dimer and/or oligomer of the substrates were formed as by-products.

Table 2. Pd(0)-Catalyzed Intramolecular Vinylselenation and Vinylthioation of Allenes

run	substrate	product, yield[a]
1	 **1b**	 **2b**, 43%
2	 **1c**	 **2c**, 14%
3[b]	 **3a**	 **4a**, 50%
4[b]	 **3b**	 **4b**, 27%

Conditions: substrate (0.3 mmol), $Pd(PPh_3)_4$ (5 mol%), MeCN (3 mL), 80 °C, 4 h. a) Isolated yield. b) DMF, 110 °C.

Although all our attempts to observe intermediates by NMR to shed light on the reaction mechanism failed, we would like to propose a reaction pathway involving σ-allylpalladium intermediate as depicted in Scheme 4. Thus, the first step is an oxidative addition of the *vinyl*–Se bond of vinyl selenides **1a,b** to Pd(0) giving rise to the allene-coordinated complexes **A**. Subsequent insertion of a distal C=C double bond of the coordinated allene into the *vinyl*–Pd bond generates the σ-allylpalladium species **B**, which may be in equilibrium with the π-allylpalladium species **C**. Reductive elimination leads to the six-membered lactams **2a,b**, and Pd(0) is regenerated. An alternative pathway via seleno-palladation cannot be ruled out yet, but the above pathway is in accord with DFT calculations we reported previously[7] for Pd(0)-catalyzed intermolecular acylselenation of allenes, where it was suggested that acyl-palladation to the terminal double bond of the allene was energetically the most favorable among the four possible reaction pathways.



Scheme 4. Plausible Reaction Pathways

In this transformation, four regioisomers can possibly be formed as the products. DFT calculations[12] were then performed to compare the relative stability of the products. As a result, **2a** was found to be more stable by at least 25.7 kcal/mol than other possible three regioisomers **5**, **6**, and **7** (Figure 1). Therefore **2a** was obtained as a sole product.

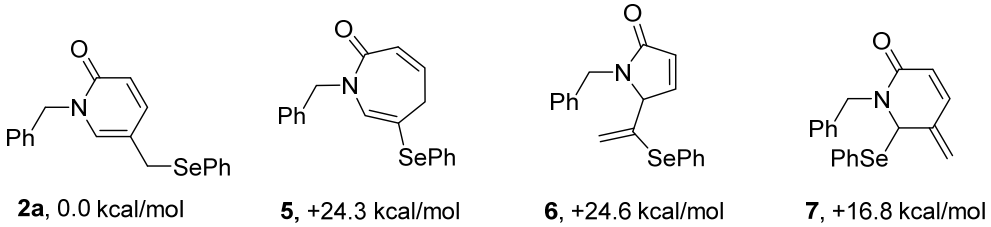


Figure 1. Possible Products and Energies Relative to **2a** Estimated by DFT Calculations

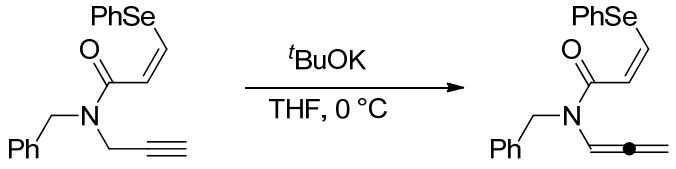
In summary, vinyl phenyl selenides and sulfides having an amide group at the vinylic β-carbon carrying an allene unit on its nitrogen atom underwent intramolecular vinylchalcogenation of a terminal double bond of the allene unit with perfect site- and regioselectivities in the presence of Pd(0) catalyst producing pyridin-2-one derivatives. As their homologues, 7-membered heterocycles were also obtained from the corresponding vinyl selenides having a methylene tether unit between an amide nitrogen and an allenyl carbon. A plausible reaction pathway accounting for the observed site- and regioselectivity was proposed.

EXPERIMENTAL

$Pd(PPh_3)_4$[13] and $Pt(PPh_3)_4$[14] were prepared according to the literature procedure. Alkynes, precursors of allenes, were prepared according to the procedure we previously reported.[3] Anhydrous solvents and other reagents were purchased from commercial source and used without further purification.

Melting points were measured using Stanford Research Systems OptiMelt MPA 100. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ALICE-400 (400 MHz and 100 MHz, respectively) spectrometer. The chemical shifts of ^1H and ^{13}C NMR spectra were recorded using Me_4Si (in $CDCl_3$) as an internal standard. IR spectra were determined on a JASCO Corporation FT/IR-4200 instrument equipped with ATR PRO450-S. Preparative TLC was conducted by using Wakogel B-5F silica gel (325 mesh). GC mass analyses (EI) were performed with a JEOL JMS-mate operating in the electron impact mode (70 eV) equipped with InertCap 5MS/NP column (I.D. 0.25 mm, Length 30 m, df 0.25 μm). High-resolution mass spectra (HRMS) and conventional mass spectra were obtained on a JEOL JMS-DX303 in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University or JEOL JMS-T100TD (DART). Elemental analyses were performed on Perkin Elmer 240C apparatus.

(Z)-*N*-Benzyl-3-(phenylseleno)-*N*-(propa-1,2-dienyl)acrylamide (1a): Typical Procedure for the Synthesis of Vinyl Selenides and Sulfides:



1a, 99%

Into a 50-mL Pyrex flask were placed (*Z*)-*N*-benzyl-*N*-prop-2-ynyl-3-phenylselenoacrylamide[3] (13.5 mmol) and THF (30 mL) under N_2. The mixture was cooled to 0 °C and ^{t}BuOK (0.30 g, 2.7 mmol) was added. The mixture was stirred at the same temperature for 20 min, then filtered through the celite pad with Et_2O, and volatiles were removed in vacuo. The residue was subjected to silica gel column chromatography (*n*-hexane/Et_2O/CH_2Cl_2 = 3/1/1) to afford (Z)-*N*-benzyl-3-(phenylseleno)-*N*-

(propa-1,2-dienyl)acrylamide (**1a**) in 99% yield as a s-*cis*/*trans* mixture: blown solid; mp 84.2-86.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (brs, 2 H, *major*), 4.82 (brs, 2 H, *minor*), 5.31-5.33 (two brs peaks overlapped, 2 H), 6.63 (d, *J* = 9.3 Hz, 1 H, *major*), 6.79 (m, 1 H), 6.88 (d, *J* = 9.3 Hz, 1 H, *mainor*), 7.18-7.83 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.9 (*minor*), 49.1 (*major*), 87.1 (*minor*), 88.0 (*major*), 100.0 (two peaks overlapped), 114.3 (*minor*), 114.8 (*major*), 126.1, 127.5, 128.1, 128.2, 128.4, 128.9, 129.4, 133.3, 134.0, 150.0 (*minor*), 150.7 (*major*), 165.5, 202.6; IR (KBr) 3040, 1952, 1616 (C=O), 1451, 1411, 1217 cm^{-1}; MS (EI), *m/z* (%) = 91 (59), 157 (28), 184 (100), 198 (42), 211 (21), 262 (31), 264 (64), 353 (20), 355 (M^+, 10). HRMS (EI) Calcd for $C_{19}H_{17}NOSe$: 355.0475. Found: 355.0474.

(Z)-*N*-Phenethyl-3-(phenylselano)-*N*-(propa-1,2-dienyl)acrylamide (1b): 74% (s-*cis*/*trans* mixture): blown solid; mp 57.2-59.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87-2.94 (m, 2 H), 3.70 (t, *J* = 8.0 Hz, 2 H, *major*), 3.80 (t, *J* = 8.0 Hz, 2 H, *minor*), 5.41 (d, *J* = 9.6 Hz, 2H, *minor*), 5.46 (d, *J* = 10.0 Hz, 2H, *major*), 6.60 (d, *J* = 10.0 Hz, 2H, *major*), 6.80 (d, *J* = 9.6 Hz, 2H, *minor*), 7.16-7.80 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.7 (*minor*), 34.9 (*major*), 46.5 (*minor*), 47.4 (*major*), 86.6 (*minor*), 87.3 (*major*) , 98.7 (*major*), 100.0 (*minor*), 114.1 (*major*), 114.3 (*minor*), 126.3, 126.7, 128.0, 128.4, 128.6, 128.7, 128.8, 128.9, 129.2, 133.1, 133.2, 134.0, 138.1, 139.1, 149.3 (*minor*), 150.0 (*major*), 164.8 (*major*), 165.0 (*minor*), 201.8 (*minor*), 202.5 (*major*); IR (neat) 3053, 3026, 2927, 2857, 1610 (C=O), 1551, 1452, 1409, 1261, 1170, 1020, 878, 783, 735, 692, 662 cm^{-1}; MS (EI), *m/z* (%) = 77 (19), 105 (100), 131 (12), 157 (19), 184 (20), 212 (80), 369 (M^+, 27). Anal. Calcd for $C_{20}H_{19}NOSe$: C, 65.22; H, 5.20; N, 3.80. Found: C, 64.98; H, 5.15; N, 3.69.

(Z)-*N*-Benzyl-3-(phenylthio)-*N*-(propa-1,2-dienyl)acrylamide (1c): 94% (s-*cis*/*trans* mixture): blown solid; mp 91.1-93.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (s, 2 H, *major*), 4.81 (brs, 2 H, *minor*), 5.32 (s, 2 H, *major*), 5.33 (s, 2 H, minor), 6.16 (d, *J* = 9.8 Hz, 1 H, *major*), 6.40 (d, *J* = 9.8 Hz, 1 H, *minor*), 6.80 (m, 1 H), 7.19-7.52 (m, 11 H), 7.78-7.81 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.6 (*minor*), 49.1 (major), 86.9 (*minor*), 87.8 (*major*), 99.7 (*major*), 100.1 (*minor*), 111.3 (*minor*), 111.6 (*major*), 126.0, 127.0, 127.4, 128.0, 128.2, 128.3, 128.8, 129.3, 131.0, 137.0 (*minor*), 137.2 (*major*), 149.2 (*major*), 150.0 (*major*), 164.8, 202.5; IR (KBr) 3061, 1951, 1619 (C=O), 1550, 1447, 1406, 1217, 1200, 949, 746, 738 cm^{-1}; MS (EI), *m/z* (%) = 91 (100), 109 (28), 163 (60), 198 (41), 216 (96), 307 (M^+, 25). HRMS (EI) Calcd for $C_{19}H_{17}NOS$: 307.1031. Found: 307.1035.

(Z)-*N*-Benzyl-*N*-(buta-2,3-dienyl)-3-(phenylseleno)acrylamide (3a): 93% (s-*cis*/*trans* mixture): pale yellow solid; mp 51.7-53.3 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (brs, 2 H, *major*), 4.12 (brs, 2 H, *minor*), 4.61 (s, 2 H, *minor*), 4.70 (s, 2 H, *major*), 4.77-4.84 (two brs peaks overlapped, 2 H), 5.05 (t, *J* = 6.1 Hz, 1 H, *minor*), 5.24 (t, *J* = 6.6 Hz, 1 H, *major*), 6.65-6.75 (m, 1 H), 7.20-7.73 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.0 (*minor*), 44.5 (*major*), 48.0 (*major*), 49.6 (*minor*), 75.6, 114.3 (minor), 114.5 (*major*), 125.78 126.6, 126.8, 127.0, 127.7, 128.0, 128.4, 132.1, 133.4, 133.5, 136.0 (*minor*), 136.6 (major), 146.8 (major*Z*), 147.4 (*minor*), 166.3

(*major*), 166.4 (*minor*), 207.6 (*major*), 208.6 (*minor*); IR (KBr) 3023, 2982, 2906, 1959, 1624 (C=O), 1473, 1443, 1227, 788, 746 cm^{-1}; HRMS (EI) Calcd for $C_{20}H_{19}NOSe$: 369.0632. Found: 369.0633. Anal. Calcd for $C_{20}H_{19}NOSe$: C, 65.22; H, 5.20; N, 3.80. Found: C, 65.04; H, 5.19; N, 3.79.

(Z)-*N*-Benzyl-*N*-(buta-2,3-dienyl)-3-(phenylthio)acrylamide (3b): 58% (s-*cis*/*trans* mixture): white solid; mp 72.3-73.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (brs, 2 H, *major*), 4.11 (brs, 2 H, minor), 4.60 (s, 2 H, *minor*), 4.69 (s, 2 H, *major*), 4.75-4.85 (two brs peaks overlapped, 2 H), 5.05 (t, *J* = 9.6 Hz, 1 H, *minor*), 5.24 (t, *J* = 10.0 Hz, 1 H, *major*), 6.17-6.30 (m, 1 H), 7.15-7.69 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.6 (*minor*), 46.3 (*major*), 49.4 (major*Z*), 51.2 (minor), 87.2 (major), 87.8 (*minor*), 112.7 (minor), 112.9 (*major*), 127.3, 128.2, 128.3, 128.6, 128.7, 129.3, 129.4, 129.6, 130.0, 131.7, 137.7, 138.3, 138.4, 138.5, 148.5 (*major*), 149.1 (*minor*), 167.5 (*minor*), 167.7 (*major*), 209.4 (*major*), 210.4 (*minor*); IR (KBr) 1954, 1627 (C=O), 1561, 1472, 1445, 1228, cm^{-1}; MS (EI), *m/z* (%) = 91 (33), 163 (100), 321 (M^+, 79). HRMS (EI) Calcd for $C_{20}H_{19}NOS$: 321.1187. Found: 321.1182. Anal. Calcd for $C_{20}H_{19}NOS$: C, 74.73; H, 5.96; N, 4.36. Found: C, 74.44; H, 6.02; N, 4.31.

1-Benzyl-5-(phenylselenomethyl)-1*H*-pyridin-2-one (2a): Typical Procedure

Into a 3-mL flask equipped with a reflux condenser were placed $Pd(PPh_3)_4$ (0.015 mmol) and MeCN (0.3 mL) at room temperature under N_2. The mixture was stirred for 10 minutes, and vinyl selenide **1a** (0.3 mmol) was added. The mixture was refluxed at 80 ºC for 4 h, then filtered through the celite pad with CH_2Cl_2, and volatiles were removed in vacuo. After the yield was determined by ^{1}H NMR (68%), the crude product was purified by preparative recycling HPLC (eluted with $CHCl_3$) to afford **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 2 H), 4.96 (s, 2 H), 6.57 (d, *J* = 9.2 Hz, 1 H), 6.75 (s, 1 H), 7.13-7.37 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.7, 51.8, 116.7, 121.3, 127.9, 128.0, 128.6, 128.8, 129.0, 129.3, 134.8, 135.1, 136.1, 141.0, 161.8; IR (NaCl) 3032, 2924, 1661 (C=O), 1599, 1537, 1422, 1271, 832, 721 cm^{-1}; MS (EI), *m/z* (%) =91 (82), 198 (100), 355 (M^+, 1). HRMS (EI) Calcd for $C_{19}H_{17}NOSe$: 355.0475. Found: 355.0484.

1-Phenylethyl-5-(phenylselenomethyl)-1*H*-pyridin-2-one (2b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (t, *J* = 7.7 Hz, 2 H), 3.69 (s, 2 H), 3.96 (t, *J* = 7.7 Hz, 2 H), 6.52-6.55 (m, 2 H), 7.12-7.42 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.6, 35.1, 51.5, 116.1, 121.0, 126.7, 128.0, 128.6, 128.8, 129.1, 134.8, 135.7, 137.8, 141.0, 161.6; IR (neat) 3058, 3025, 2935, 1661 (C=O), 1596, 1536, 1477, 1438, 1353, 1266, 1144, 832, 737, 692 cm^{-1}; MS (EI), *m/z* (%) = 77 (6), 105 (55), 108 (16), 212 (100), 369 (M^+, 1). HRMS(EI) calcd for $C_{20}H_{19}NOSe$: 369.0632. Found: 369.0631.

1-Benzyl-5-(phenylthiomethyl)-1*H*-pyridin-2-one (2c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 2 H), 5.06 (s, 2 H), 6.59 (d, *J* = 9.2 Hz, 1 H), 6.90 (s, 1 H), 6.90-7.70 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.4, 51.9, 115.58, 115.60, 115.61, 127.3 (four

peaks overlapped), 127.35, 127.37, 128.0, 128.9, 129.0 (two peaks overlapped), 131.7, 140.8, 162.0; IR (NaCl) 2918, 2849, 1666 (C=O), 1598, 1539, 1439, 725, 694 cm^{-1}; MS (EI), *m/z* (%) = 91 (92), 198 (100), 307 (M^+, 5). HRMS (EI) Calcd for $C_{19}H_{17}NOS$: 307.1031. Found: 307.1025.

1-Benzyl-5-(phenylselenomethyl)-1,7-dihydroazepin-2-one (4a)

^1H NMR (400 MHz, $CDCl_3$) δ 2.86 (d, *J* = 6.8 Hz, 2 H), 3.58 (s, 2 H), 4.76 (s, 2 H), 5.29 (t, *J* = 6.8 Hz, 1 H), 5.92 (d, *J* = 9.3 Hz, 1 H), 6.24 (d, *J* = 9.3 Hz, 1 H), 7.17-7.38 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 37.2, 51.0, 116.5, 120.0, 127.4, 127.5 (two peaks overlapped), 128.6, 128.9, 131.1, 134.1, 136.2, 136.9, 166.8; IR (NaCl) 3335, 3031, 1660 (C=O), 1600, 1475, 1437, 1391 cm^{-1}; MS (EI), *m/z* (%) = 91 (100), 369 (M^+, 9). HRMS (EI) Calcd for $C_{20}H_{19}NOSe$: 369.0632. Found: 369.0627.

1-Benzyl-5-(phenylthiomethyl)-1,7-dihydroazepin-2-one (4b)

^1H NMR (400 MHz, $CDCl_3$) δ 3.59 (s, 2 H), 4.75 (s, 2 H), 5.43 (t, *J* = 7.0 Hz, 1 H), 5.92 (d, *J* = 9.0 Hz, 1 H), 6.25 (d, *J* = 9.0 Hz, 1 H), 7.15-7.75 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.2, 39.0, 51.0, 116.2, 120.7, 126.8, 127.5 (two peaks overlapped), 128.0, 128.6, 128.8, 128.9, 130.8, 131.2, 135.5, 137.0, 167.0; IR (NaCl) 3031, 2925, 1661 (C=O), 1601, 1393, 1265, 1159, 1026, 740 cm^{-1}; MS (CI) *m/z* (relative intensity, %) 322 (M^{+1}, 100). HRMS (CI) calcd for $C_{20}H_{20}NOS$: 322.1266. Found 322.1271.

REFERENCES AND NOTES

1. For recent reviews, (a) M. Tanaka and R. Hua. *Pure Appl*. *Chem*., 2002, **74**, 181; (b) H. Kuniyasu and N. Kambe, *Chem*. *Lett*., 2006, **35**, 1320; (c) S. Fujiwara, M. Toyofuku, H. Kuniyasu, and N. Kambe, *Pure Appl*. *Chem*., 2010, **82**, 565 and references cited therein.
2. (a) D. Sayferth, M. L. Shannon, S. C. Vick, and T. F. O. Lim, *Organometallics,* 1985, **4**, 57; (b) H. Saso and W. Ando, *Chem*. *Lett*., 1988, 1567; (c) N. Choi, Y. Kabe, and W. Ando, *Tetrahedron Lett*., 1991, **32**, 4573; (d) J. Liu, X. Sun, M. Miyazaki, L. Liu, C. Wang, and Z. Xi, *J*. *Org*. *Chem*., 2007, **72**, 3137.
3. M. Toyofuku, S. Fujiwara, T. Shin-ike, H. Kuniyasu, and N. Kambe, *J*. *Am*. *Chem*. *Soc*., 2008, **130**, 10504.
4. (a) H. Kuniyasu, A. Ohtaka, T. Nakazono, M. Kinomoto, and H. Kurosawa, *J*. *Am*. *Chem*. *Soc*., 2000, **122**, 2375; (b) H. Kuniyasu, T. Kato, M. Inoue, J. Terao, and N. Kambe, *J*. *Organomet*. *Chem*., 2006, **691**, 1873.
5. For recent reviews, see: (a) S. Ma, *Chem. Rev*., 2005, **105**, 2829; (b) S. Ma, *Acc. Chem. Res.*, 2003, **36**, 701; (c) *Modern Allene Chemistry*, ed. by N. Krause and A. S. K. Hashmi, Wiley-VCH, Weinheim, 2004.
6. (a) N. Chatani, T. Takeyasu, and T. Hanafusa, *Tetrahedron Lett*., 1986, **27**, 1841; (b) R. Hua and M. Tanaka, *Tetrahedron Lett*., 2004, **45**, 2367; (c) E. Shirakawa, Y. Nakao, and T. Hiyama, *Chem*.

Commun., 2001, 263; (d) E. Shirakawa, Y. Nakao, T. Tsuchimoto, and T. Hiyama, *Chem*. *Commun*., 2002, 1962; (e) Y. Nakao, E. Shirakawa, T. Tsuchimoto, and T. Hiyama, *J*. *Organomet*. *Chem*., 2004, **689**, 3701.

7. M. Toyofuku, E. Murase, S. Fujiwara, T. Shin-ike, H. Kuniyasu, and N. Kambe, *Org*. *Lett*., 2008, **10**, 3957.
8. For intramolecur version: M. Toyofuku, E. Murase, H. Nagai, S. Fujiwara, T. Shin-ike, H. Kuniyasu, and N. Kambe, *Eur*. *J*. *Org*. *Chem*., 2009, 3141.
9. S. Fujiwara, M. Okuyama, S. Tsuda, T. Iwasaki, H. Kuniyasu, and N. Kambe, *Tetrahedron*, 2012, **68**, 10523.
10. A preliminary result was mentioned in a review on carbochalcogenation of unsaturated bonds, see ref. 1c.
11. Solvents examined and the yields of **2a** shown in parentheses were as follows: DMF (53%), DMSO (39%), DMA (30%), NMP (22%), dioxane (9%), toluene (9%), PhCN (9%), and DCE (<1%).
12. Calculations were carried out using the Gaussian 09W set of programs with the B3LYP functional, the 6-31G(d) basis set for all nonmetallic atoms (H, C, O, N) and the LANL2DZ basis set for Se. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09 Revision A.02 Gaussian, Inc.: Wallingford, CT, 2009.
13. J. R. Malpass, D. A. Hemmings, A. L. Wallis, S. R. Fletcher, and J. Patel, *J*. *Chem*. *Soc*., *Perkin Trans*. *1*, 2001, 1044.
14. L. Malatesta and C. Cariello, *J*. *Chem*. *Soc*., 1958, 2323.