Supporting Information for

Selenoimidoylation of Alcohols with Selenium and Isocyanides and Its

Application to the Synthesis of Selenium-Containing Heterocycles

Yoshiaki Asanuma[†], Shin-ichi Fujiwara^{,‡}, Tsutomu Shin-ike[‡], Nobuaki Kambe^{*,†}*

Department of Molecular Chemistry, Graduate School of Engineering, Osaka

University, Suita, Osaka 565-0871, Japan, and Department of Chemistry, Osaka Dental

University, Hirakata, Osaka 573-1121, Japan

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1-Methyl-2-butyl-3-cyclohexylselenocarbonimidate (4a)

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, $J = 7.3$ Hz, 3 H), 1.17-1.45 (m, 7 H), 1.58-1.75 (m, 7 H), 2.95 (t, $J = 7.4$ Hz, 2 H), 3.05-3.11 (m, 1 H), 3.77 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 23.0, 24.9, 25.1, 25.9, 33.3, 34.3, 55.6, 60.2, 149.4; IR (NaCl) 2930, 2854, 1652 (C=N), 1449, 1426, 1160, 1132, 1084 cm^{-1} ; MS (EI) m/z (relative intensity) 55 (33), 58 (95), 83 (47), 140 (100), 277 (M^+ , 2). Anal. calcd for $\text{C}_{12}\text{H}_{23}\text{NOSe}$: C, 52.17; H, 8.39; N, 5.07. Found: C, 51.98; H, 8.31; N, 5.26.

1-Methyl-2-butyl-3-(2,6-xylyl)selenocarbonimidate (4b).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, $J = 7.3$ Hz, 3 H), 1.36 (sext, $J = 7.4$ Hz, 2 H), 1.64 (quint, $J = 7.4$ Hz, 2 H), 2.13 (s, 6 H), 2.90 (t, $J = 7.3$ Hz, 2 H), 4.04 (s, 3 H), 6.89-7.01 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 18.2, 22.9, 25.2, 33.0, 56.5, 123.3, 127.8, 128.4, 144.6, 154.4; IR (NaCl) 2929, 2854, 1641 (C=N), 1449, 1169, 1134, 1083, 980 cm^{-1} ; MS (EI), m/z (relative intensity) 119 (9), 130 (19), 147 (51), 162 (100), 299 (M^+ , 21). Anal. calcd for $\text{C}_{14}\text{H}_{21}\text{NOSe}$: C, 56.37; H, 7.10; N, 4.70. Found: C, 56.42; H, 7.12; N, 4.87.

1,2-Dibutyl-3-cyclohexylselenocarbonimidate (4c).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.91-0.98 (m, 6 H), 1.08-1.46 (m, 9 H), 1.58-1.75 (m, 9 H), 2.94 (t, $J = 7.5$ Hz, 2 H), 3.03-3.08 (m, 1 H), 4.15 (t, $J = 6.5$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 14.0, 19.4, 23.1, 24.9, 25.2, 25.9, 31.0, 33.5, 34.3, 60.3, 68.0, 148.9; IR (NaCl) 2942, 2872, 1638 (C=N), 1592, 1459, 1234, 1157, 1092 cm^{-1} ; MS (CI), m/z (relative intensity) 83 (17), 126 (42), 182 (100), 246 (7), 320 ($\text{M}^+ + 1$, 51). Anal. calcd for $\text{C}_{15}\text{H}_{29}\text{NOSe}$: C, 56.59; H, 9.18; N, 4.40. Found: C, 56.93; H, 9.35; N, 4.69.

1,2-Dibutyl-3-(2,6-xylyl)selenocarbonimidate (4d).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.90 (t, $J = 7.4$ Hz, 3 H), 1.00, (t, $J = 7.3$ Hz, 3 H), 1.37 (sext, $J = 7.4$ Hz, 2 H), 1.50 (sext, $J = 7.5$ Hz, 2 H), 1.66 (quint, $J = 7.4$ Hz, 2 H), 1.80 (quint, $J = 7.1$ Hz, 2 H), 2.13 (s, 6 H), 2.88 (t, $J = 7.4$ Hz, 2 H), 4.46 (t, $J = 6.6$ Hz, 2 H), 6.88-7.00 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 14.0, 18.2, 19.4, 23.0, 25.2, 31.0, 33.2, 69.1, 123.2, 127.8, 128.5, 144.8, 153.7; IR (NaCl) 2958, 2872, 1634 (C=N), 1591, 1465, 1150, 1092, 763 cm^{-1} ; MS (EI), m/z (relative intensity)

57 (73), 119 (6), 148 (100), 204 (11), 341 (M^+ , 38). Anal. calcd for $C_{17}H_{27}NOSe$: C, 59.99; H, 8.00; N, 4.12. Found: C, 59.83; H, 8.05; N, 4.23.

1-*sec*-Butyl-2-butyl-3-(2,6-xylyl)selenocarbonimidate (4e).

Yellow liquid; 1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, $J = 7.3$ Hz, 3 H), 1.01 (t, $J = 7.4$ Hz, 3 H), 1.32-1.41 (m, 5 H), 1.62-1.84 (m, 4 H), 2.13 (s, 3 H), 2.15 (s, 3 H), 2.86 (t, $J = 7.4$ Hz, 2 H), 5.31 (sext, $J = 6.2$ Hz, 1 H), 6.88-7.01 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.7, 13.5, 18.0, 18.1, 19.3, 22.8, 25.0 ($^1J_{Se-C} = 30.4$ Hz), 28.8, 33.1, 76.5, 123.0, 127.6, 128.4, 128.5, 144.8, 152.9; IR (NaCl) 2966, 1634 (C=N), 1591, 1463, 1377, 1234, 1150, 762 cm^{-1} ; MS (EI), m/z (relative intensity) 57 (40), 91 (13), 119 (32), 132 (27), 138 (13), 147 (100), 341 (M^+ , 37). Anal. calcd for $C_{17}H_{27}NOSe$: C, 59.99; H, 8.00; N, 4.12. Found: C, 59.79; H, 7.93; N, 4.27.

1-Allyl-2-butyl-3-cyclohexylselenocarbonimidate (4g).

Yellow liquid; 1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, $J = 7.3$ Hz, 3 H), 1.19-1.45 (m, 7 H), 1.58-1.75 (m, 7 H), 2.98 (t, $J = 7.4$ Hz, 2 H), 3.05-3.10 (m, 1 H), 4.66 (t, $J = 1.5$

Hz, 1 H), 4.67 (t, $J = 1.5$ Hz, 1 H), 5.18-5.21 (m, 1 H), 5.28-5.34 (m, 1 H), 5.93-6.03 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 23.0, 24.8, 25.2, 25.9, 33.3, 34.2, 60.2, 68.7, 117.1, 133.0, 148.2; IR (NaCl) 2929, 2854, 1639 (C=N), 1449, 1369, 1165, 1135, 1086 cm^{-1} ; MS (CI), m/z (relative intensity) 83 (26), 166 (100), 179 (30), 246 (39), 304 ($\text{M}^+ + 1$, 53). Anal. calcd for $\text{C}_{14}\text{H}_{25}\text{NOSe}$: C, 55.62; H, 8.34; N, 4.63. Found: C, 55.43; H, 8.38; N, 4.86.

1-Benzyl-2-butyl-3-cyclohexylselenocarbonimidate (4h).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.85 (t, $J = 7.3$ Hz, 3 H), 1.21-1.42 (m, 7 H), 1.59-1.77 (m, 7 H), 2.94 (t, $J = 7.5$ Hz, 2 H), 3.09-3.14 (m, 1 H), 5.20 (s, 2 H), 7.26-7.38 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.6, 23.0, 24.8, 25.3, 25.9, 33.4, 34.2, 60.3, 69.7, 127.5, 127.8, 127.9, 136.9, 148.5; IR (NaCl) 2928, 2854, 1644 (C=N), 1451, 1368, 1134, 1086, 984 cm^{-1} ; MS (EI), m/z (relative intensity) 55 (7), 91 (100), 216 (6), 228 (23), 353 (M^+ , 3). Anal. calcd for $\text{C}_{15}\text{H}_{27}\text{NOSe}$: C, 61.35; H, 7.72; N, 3.97. Found: C, 61.05; H, 7.74; N, 4.13

1-Benzyl-2-butyl-3-(2,6-xylyl)selenocarbonimidate (4i).

Colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.85 (t, $J = 7.3$ Hz, 3 H), 1.33 (sext, $J = 7.4$ Hz, 2 H), 1.65 (quint, $J = 7.5$ Hz, 2 H), 2.09 (s, 6 H), 2.92 (t, $J = 7.4$ Hz, 2 H), 5.50 (s, 2 H), 6.88-6.93 (m, 1 H), 6.99-7.01 (m, 2 H), 7.34-7.46 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.6, 18.1, 22.9, 25.3, 33.1, 70.6, 123.3, 127.78, 127.82, 128.1, 128.2, 128.4, 136.3, 144.6, 153.2; IR (NaCl) 2957, 1636 (C=N), 1591, 1464, 1207, 1135, 1093, 905 cm^{-1} ; MS (EI), m/z (relative intensity) 91 (100), 119 (3), 147 (6), 228 (5), 375 ($\text{M}^+ + 1$, 17); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{25}\text{NOSe}$ 375.1101, found 375.1106.

2-(2,6-Xylyl)imino-4-phenylmethylen-1,3-oxaselenolane (10a)

White solid: mp. 114-115 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 2.18 (s, 6 H), 5.20 (d, $J = 0.8$ Hz, 2H), 6.93-7.33 (m, 9 H). NOE experiment, irradiation of methylene at δ 5.20 resulted in 10% enhancement of signal at δ 6.93 (vinyl); ^{13}C NMR (100 MHz, CDCl_3) δ 18.2, 78.0, 123.6, 124.1, 127.5, 127.7, 128.1, 128.5, 128.7, 131.3, 135.6, 146.8, 160.7; IR (KBr) 3425, 2917, 1685, 1672 (C=N), 1590, 1115, 1082, 1010 cm^{-1} ; MS (EI), m/z

(relative intensity) 91 (7), 115 (100), 147 (9), 196 (80), 343 (M^+ , 19). Anal. calcd for

$C_{18}H_{17}NOSe$: C, 63.16; H, 5.01; N, 4.09. Found: C, 62.87; H, 5.28; N, 4.19.

2-(2,6-Xylyl)imino-4-(*p*-tolyl)methylidene-1,3-oxaselenolane (10b).

Yellow solid: mp. 52-54 °C; 1H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 6 H), 2.31 (s, 3 H), 5.18 (s, 2 H), 6.90 (s, 1 H), 6.94-7.13 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 21.2, 77.7, 123.4, 123.8, 127.1, 127.9, 128.4, 129.0, 129.7, 132.5, 137.4, 146.6, 160.5; IR (KBr) 3324, 2919, 1667 (C=N), 1591, 1470, 1124, 1088, 1015 cm^{-1} ; MS (EI), m/z (relative intensity) 115 (21), 129 (76), 193 (18), 210 (100), 357 (M^+ , 36). Anal. calcd for $C_{19}H_{19}NOSe$: C, 64.04; H, 5.37; N, 3.93. Found: C, 63.81; H, 5.36; N, 4.09.

2-(2,6-Xylyl)imino-4-(*p*-methoxyphenyl)methylidene-1,3-oxaselenolane (10c).

Yellow solid: mp. 97-98 °C; 1H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 6 H), 3.77 (s, 3 H), 5.16 (s, 2 H), 6.82-7.11 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 55.1, 77.8, 113.8,

123.1, 123.9, 127.9, 128.0, 128.5, 128.58, 128.62, 128.7, 146.8, 158.8; IR (KBr) 3428, 2975, 1665 (C=N), 1511, 1252, 1088, 1007, 779 cm^{-1} ; MS (EI), m/z (relative intensity) 103 (10), 145 (89), 195 (12), 211 (22), 226 (100), 373 (M^+ , 22). Anal. calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_2\text{Se}$: C, 61.29; H, 5.14; N, 3.76. Found: C, 61.14; H, 5.06; N, 3.76.

2-(2,6-Xylyl)imino-4-(*p*-chlorophenyl)methylidene-1,3-oxaselenolane (10d).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 2.18 (s, 6 H), 5.19 (s, 2 H), 6.88 (s, 1 H), 6.96-7.36 (m, 7 H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.1, 77.8, 122.4, 124.2, 128.1, 128.2, 128.50, 128.56, 128.59, 132.5, 133.9, 146.6, 160.3; IR (NaCl) 3294, 2919, 1668 (C=N), 1590, 1490, 1089, 1011, 768 cm^{-1} ; MS (EI), m/z (relative intensity) 115 (26), 149 (26), 195 (100), 230 (24), 377 (M^+ , 24). Anal. calcd for $\text{C}_{18}\text{H}_{16}\text{ClNOSe}$: C, 57.39; H, 4.28; N, 3.72. Found: C, 57.50; H, 4.26; N, 3.50.

2-(2,6-Xylyl)imino-4-methylidene-1,3-oxaselenolane (10e).

Colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 2.17 (s, 6 H), 4.99 (s, 2H), 5.23 (q, J = 2.2 Hz, 1 H), 5.23 (q, J = 2.2 Hz, 1 H), 6.95 (t, J = 7.1 Hz, 1 H), 7.03 (d, J = 7.1 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.9, 77.0, 109.7, 123.9, 128.3, 136.0, 139.1, 146.8, 160.4; IR (NaCl) 2920, 1668 (C=N), 1626, 1591, 1471, 1085, 1020 cm^{-1} ; MS (EI), m/z (relative intensity) 119 (22), 147 (100), 267 (M^+ , 27). Anal. calcd for $\text{C}_{12}\text{H}_{13}\text{NOSe}$: C, 54.14; H, 4.92; N, 5.26. Found: C, 54.14; H, 4.85; N, 5.39.

4-Methylidene-2-selenoxo-3-(2,6-xylyl)-1,3-oxolidine (11e).

White solid: mp. 138-139 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 2.19 (s, 6 H), 4.01 (q, J = 2.9 Hz, 1H), 4.39 (q, J = 2.9 Hz, 1 H), 5.34 (t, J = 2.9 Hz, 2 H), 7.20 (d, J = 7.6 Hz, 2 H), 7.30 (t, J = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.6, 73.1, 84.9, 128.8, 130.0, 131.9, 135.9, 141.2, 190.0; IR (KBr) 2921, 1768, 1682, 1661 (C=N), 1472, 1396, 1238, 1209 cm^{-1} ; MS (EI), m/z (relative intensity) 130 (28), 144 (48), 158 (91), 267 (M^+ , 27). Anal. calcd for $\text{C}_{12}\text{H}_{13}\text{NOSe}$: C, 54.14; H, 4.92; N, 5.26. Found: C, 54.42; H, 4.89; N, 5.33.

2-(2,6-Xylyl)imino-4-ethylidene-1,3-oxaselenolane (10f).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 1.64 (d, $J = 6.5$ Hz, 3H), 2.17 (s, 6 H), 4.95 (s, 2H), 5.89 (q, $J = 6.5$ Hz, 1 H), 6.96 (t, $J = 7.1$ Hz, 1 H), 7.30 (d, $J = 7.1$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.0, 18.5, 76.0, 119.0, 123.8, 127.9, 128.4, 132.0, 147.0, 160.0; IR (NaCl) 3308, 2943, 1667 (C=N), 1592, 1471, 1440, 1148, 1106 cm^{-1} ; MS (EI), m/z (relative intensity) 53 (69), 119 (22), 134 (100), 147 (47), 281 (M^+ , 44).
Anal. calcd for $\text{C}_{13}\text{H}_{15}\text{NOSe}$: C, 55.72; H, 5.40; N, 5.00. Found: C, 55.96; H, 5.44; N, 5.25.

2-(2,6-Xylyl)imino-4-methyl-5-phenyl-1,3-oxaselenenole (12g).

Yellow solid: mp. 105-106 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 2.11 (s, 3 H), 2.18 (s, 6 H), 7.24-7.27 (m, 2 H), 7.35-7.43 (m, 2 H), 7.47-7.51 (m, 2 H), 7.65-7.70 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 9.7, 17.9, 122.8, 124.9, 126.5, 128.5, 128.62, 128.65, 129.9, 132.3, 135.5, 146.0, 173.6; IR (KBr) 3454, 2917, 1752, 1657 (C=N), 1478, 1379, 1298,

1180 cm^{-1} ; MS (EI), m/z (relative intensity) 105 (13), 193 (12), 234 (17), 262 (100), 343

(M^+ , 80). HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{17}\text{NOSe}$ 343.0475, Found 343.0472.

2-Cyclohexylimino-4-phenylmethylidene-1,3-oxaselenolane (10h).

White solid: mp. 123-124 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 1.17-1.92 (m, 10 H), 2.65 (m, 1 H), 4.95 (s, 2 H), 6.94 (t, $J = 1.6$ Hz, 1 H), 7.27-7.42 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 24.6, 25.4, 33.7, 65.9, 75.4, 123.2, 127.4, 127.5, 128.3, 131.3, 135.7, 155.3; IR (KBr) 3417, 2938, 1678 (C=N), 1629, 1449, 1059, 996, 753 cm^{-1} ; MS (EI), m/z (relative intensity) 55 (7), 102 (4), 115 (100), 196 (63), 321 (M^+ , 5). HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{19}\text{NOSe}$ 321.0632, Found 321.0623.

2-(2,6-Xylyl)imino-4-methylidene-1,3-oxaselenane (17).

Yellow solid: mp. 119 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 2.19 (s, 6 H), 2.97 (t, $J = 5.7$ Hz, 2 H), 3.93 (s, 1 H), 4.33 (s, 1 H), 4.50 (t, $J = 5.7$ Hz, 2 H), 7.15 (d, $J = 7.3$ Hz, 2 H), 7.24 (dd, $J = 8.3, 6.8$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.5, 27.7, 67.3, 97.3,

128.5, 128.6, 134.6, 136.7, 139.2, 187.3; IR (KBr) 3444, 2967, 1648 (C=N), 1475, 1408, 1309, 1242, 1176 cm^{-1} ; MS (EI), m/z (relative intensity) 70 (31), 77 (17), 281 (M^+ , 100).
Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NOSe}$: C, 55.72; H, 5.40; N, 5.00. Found: C, 55.65; H, 5.42; N, 4.81.

¹H and ¹³C NMR Charts of Products

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ORTEP Diagram of 10a