Supporting Information for:

# Highly Selective Ring-Opening/Cross-Metathesis Reactions of Norbornene Derivatives using Selenocarbene Complexes as Catalysts

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## Experimental Section

**General Experimental Procedure and Materials.** All manipulations were performed under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was purified by passing successively through the columns of an activated copper catalyst (BASF, R3-11) and $P_2O_5$ (Merck, SICAPENT). NMR spectra were recorded on a Varian Mercury 300 ($^1$H NMR, 300.11 MHz; $^{13}$C NMR, 75.46 MHz; $^{31}$P NMR, 121.49 MHz) spectrometer. Chemical shifts are reported in $\delta$ (ppm), referenced to the $^1$H (of residual protons) and $^{13}$C signals of dueterated solvents or to the $^{31}$P signal of external 85% $H_3PO_4$. Mass spectra were measured with a Shimadzu QP-5000 GC-mass spectrometer (EI, 70 eV). GLC analysis was performed on a Shimadzu GC-14B instrument equipped with a FID detector and a capillary column CBP-1 (25 m ∞ 0.25 mm). Analytical TLC was carried out on Merck TLC aluminum sheets precoated with silica gel 60 $F_{254}$. Visualization was accomplished using UV light and/or a *p*-anisaldehyde charring solution. Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh).

$CH_2Cl_2$ was dried over $CaH_2$. Methanol was dried with $Mg(OMe)_2$. THF was dried over sodium benzophenone ketyl. These solvents were distilled and stored over activated molecular sieves (MS4A) under a nitrogen atmosphere. $CDCl_3$ was purified by passage through an alumina column, degassed by freeze–pump–thaw cycles, and stored over activated MS4A in the dark. Norbornene (**1**) was distilled from sodium prior to use. Phenyl vinyl ether (**2a**),[1] phenyl vinyl sulfide (**2b**),[2] phenyl vinyl selenide (**2c**),[3] phenyl vinyl telluride (**2d**),[4] $[Ru(=C=CHBu^t)Cl_2(PCy_3)_2]$ (**7**),[5] *exo*-5,6-bis(methoxycarbonyl)-7-oxanorbornene (**8**),[6] *exo*-*N*-methyl-7-oxanorbornene-2,3-dicarboximide (**10**),[7] *endo*-5,6-bis(methoxycarbonyl)norbornene (**12**),[8] *endo*-5,6-bis-{(*tert*-butyldimethylsilyloxy)methyl}norbornene (**14**),[9] and $[Ru(=CHPh)Cl_2(L)(PCy_3)]$ (L = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)[10] were synthesized according to the literatures. All other chemicals were obtained from commercial suppliers and used without further purification.

**Preparation of 4a–4d.** A typical procedure for synthesizing **4a** is as follows. To a solution of $[Ru(=CHPh)Cl_2(PCy_3)_2]$ (**6**) (412 mg, 0.501 mmol) in $CH_2Cl_2$ (8.4 mL) was added phenyl vinyl ether (**2a**) (66.2 mg, 0.551 mmol) with stirring at room temperature. The initially purple solution was gradually turned reddish brown. After 1 h, the mixture was concentrated by pumping to *ca.* 2 mL, and pentane (8 mL) was added at –78 °C to give red precipitate. The mother liquor was removed through a filter-paper-tipped cannula, and the residue was washed with pentane (3 mL ∞ 2) at –78 °C. The resulting solid was dissolved in $CH_2Cl_2$ (2 mL) at room temperature, and methanol (8 mL) was carefully layered on the $CH_2Cl_2$ solution. The solvent layers were allowed to stand at room temperature to form a red microcrystalline solid of **4a** (302 mg, 72% yield), which was analytically pure. Complexes **4b**–**4d** were similarly prepared using the corresponding vinyl chalcogenides. Analytically pure **4b** and **4c** were obtained as THF solvates after further recrystallization by cooling the saturated THF solutions.

**Ru{=C(H)OPh}$\mathbf{Cl_2(PCy_3)_2}$ (4a)**. Red solid (72% yield); $^1H$ NMR ($CDCl_3$): $\delta$ = 14.81 (s, 1H, Ru=CH), 7.38–7.31, 7.23–7.16, 7.11–7.04 (each m, 5H, Ph), 2.76–2.60, 2.06–1.92, 1.86–1.46, 1.38–1.12 (each m, 66H, Cy); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 274.4 (t, $^2J_{PC}$ = 10 Hz, Ru=C), 159.4 (s, *ipso*-C of Ph), 129.8, 125.3, 117.2 (each s, Ph), 31.9 (virtual triplet, $J_{app}$ = 9 Hz, $C^1$ of Cy), 29.6 (s, $C^{3,5}$ of Cy), 27.9 (virtual triplet, $J_{app}$ = 5 Hz, $C^{2,6}$ of Cy), 26.5 (s, $C^4$ of Cy); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 35.1 (s); elementary analysis calcd for $C_{43}H_{72}Cl_2OP_2Ru$: C 61.56, H 8.65; found: C 60.97, H 8.48.

**Ru{=C(H)SPh}$\mathbf{Cl_2(PCy_3)_2}$ (4b)**. Purple solid (68% yield); $^1H$ NMR ($CDCl_3$): $\delta$ = 17.65 (s, 1H, Ru=CH), 7.46–7.34 (m, 5H, Ph), 3.78–3.71 (m, 4H, THF), 2.74–2.56, 2.02–1.90, 1.86–1.48, 1.38–1.12 (each m, 66H, Cy), 1.89–1.84 (m, 4H, THF); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 280.5 (t, $^2J_{PC}$ = 9 Hz, Ru=C), 141.0 (s, *ipso*-C of Ph), 129.2, 129.1, 128.3 (each s, Ph), 67.9 (s, THF), 32.5 (virtual triplet, $J_{app}$ = 9 Hz, $C^1$ of Cy), 29.7 (s, $C^{3,5}$ of Cy), 27.7 (virtual triplet, $J_{app}$ = 5 Hz, $C^{2,6}$ of Cy), 26.4 (s, $C^4$ of Cy), 25.6 (s, THF); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 30.9 (s); elementary analysis calcd for $C_{43}H_{72}Cl_2P_2RuS \cdot C_4H_8O$: C 60.89, H 8.70; found: C 60.71, H 8.70.

**Ru{=C(H)SePh}$\mathbf{Cl_2(PCy_3)_2}$ (4c)**. Purple solid (77% yield); $^1H$ NMR ($CDCl_3$): $\delta$ = 18.50 (s, 1H, Ru=CH), 7.57–7.54, 7.36–7.33 (each m, 5H, Ph), 3.77–3.73 (m, 2H, THF), 2.67–2.59, 1.98–1.72, 1.58–1.50, 1.34–1.20 (each m, 66H, Cy), 1.88–1.84 (m, 2H, THF); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 285.7 (t, $^2J_{PC}$ = 8 Hz, Ru=C), 138.5 (s, *ipso*-C of Ph), 132.2, 129.2, 128.2 (each s, Ph), 67.9 (s, THF), 32.4 (virtual triplet, $J_{app}$ = 9 Hz, $C^1$ of Cy), 29.7 (s, $C^{3,5}$ of Cy), 27.7 (virtual triplet, $J_{app}$ = 5 Hz, $C^{2,6}$ of Cy), 26.5 (s, $C^4$ of Cy), 25.6 (s, THF); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 29.5 (s); elementary analysis calcd for $C_{43}H_{72}Cl_2P_2RuSe \cdot 0.5C_4H_8O$: C 57.62, H 8.17; found: C 57.55, H 8.09.

**Ru{=C(H)TePh}$\mathbf{Cl_2(PCy_3)_2}$ (4d)**. Brown solid (61% yield); $^1H$ NMR ($CDCl_3$): $\delta$ = 20.46 (s, 1H, Ru=CH), 7.85–7.78, 7.44–7.26 (each m, 5H, Ph), 2.63–2.50, 2.20–1.45, 1.35–1.25 (each m, 66H, Cy); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 279.8 (t, $^2J_{PC}$ = 7 Hz, Ru=C), 137.8 (s, *ipso*-C of Ph), 129.3, 128.0, 125.8 (each s, Ph), 32.3 (virtual triplet, $J_{app}$ = 9 Hz, $C^1$ of Cy), 29.6 (s, $C^{3,5}$ of Cy), 27.6 (virtual triplet, $J_{app}$ = 5 Hz, $C^{2,6}$ of

Cy), 26.4 (s, $C^4$ of Cy); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 26.3 (s); elementary analysis calcd for $C_{43}H_{72}Cl_2P_2RuTe$: C 54.33, H 7.63; found: C 54.50, H 7.68.

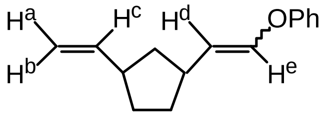
**Preparation of 5.** Phenyl vinyl selenide (**2c**) (0.290 g, 1.58 mmol) was added to a solution of $Ru(=CHPh)Cl_2(L)(PCy_3)$ (0.790 g, 0.931 mmol) in $CH_2Cl_2$ (16 mL) at room temperature. The resulting deep purple solution was stirred at room temperature for 6 h. All the volatiles were thoroughly removed by pumping. The solid residue was washed with MeOH (5 mL ∞ 3) and dried under vacuum to give analytically pure **5** (0.606 g, 70%) as reddish brown microcrystals.

$^1H$ NMR ($CDCl_3$): δ = 18.22 (s, 1H, Ru=CH), 7.25–7.12 (m, 5H, Ph), 6.97, 6.65 (each s, 4H, $C_6H_2$), 3.99–3.82 (m, 4H, $CH_2$ of dihydroimidazole ring), 2.61, 2.48 (each s, 12H, 2,6-Me of Mes), 2.30, 1.79 (each s, 6H, 4-Me of Mes), 2.30–2.17, 1.60–1.45, 1.18–0.95 (each m, 33H, $PCy_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 279.4–279.1 (br m, Ru=C), 216.9 (d, $^2J_{PC}$ = 77 Hz, Ru–$CN_2$), 139.0, 138.6, 138.5, 138.1, 137.5, 136.5, 134.0, 129.9, 129.4, 128.6, 128.3, 126.1 (each s, aromatic C of Mes and Ph), 52.2, 51.8 (each s, $NCH_2$), 31.9 (d, $^1J_{PC}$ = 16 Hz, $C^1$ of Cy), 29.0 (s, $C^{3,5}$ of Cy), 27.6 (d, $^2J_{PC}$ = 10 Hz, $C^{2,6}$ of Cy), 26.2 (s, $C^4$ of Cy), 21.1, 20.8 (each s, 4-Me of Mes), 19.7, 19.0 (each s, 2,6-Me of Mes); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.7 (s); elementary analysis calcd for $C_{46}H_{65}Cl_2N_2PRuSe$: C 59.54, H 7.06, N 3.02; found: C 58.82, H 7.01, N 2.96.

**Ring-Opening/Cross-Metathesis Reactions.** A typical procedure (Table 2, run 1) is as follows. To a solution of phenyl vinyl selenide (**2c**) (284 mg, 1.55 mmol) and *exo*-5,6-bis(methoxycarbonyl)-7-oxanorbornene (**8**) (328 mg, 1.55 mmol) in $CH_2Cl_2$ (6.2 mL) was added solid **4c** (28.1 mg, 31.2 μmol), and the resulting brown solution was stirred at room temperature. The reaction progress was followed by GLC. After 20 h, the solvent was removed by pumping to give brown oil, which was subjected to flash column chromatography. Elution with hexane/AcOEt (20/1) gave a purple fraction containing **4c** (28.0 mg), and further elution with hexane/AcOEt (5/1) afforded a colorless fraction containing **9**. Evaporation of the latter eluate gave analytically pure **9** (609 mg, 99% yield) as a colorless oil.

All the reactions listed in Tables 1 and 2 were similarly carried out. In runs 1–3 in Table 1, polymeric products were removed by pouring the reaction mixtures into a large amount of methanol (*ca*. 100 mL) followed by filtration.

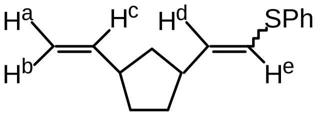
**Compound 3a.** Colorless oil (17% yield, *E*/*Z* = 15/85); TLC: $R_f$ 0.23 (hexane).



$^1H$ NMR ($CDCl_3$): δ = 7.34–7.28, 7.07–6.97 (each m, *E*- and *Z*-Ph), 6.44 (dd, *J* = 12.0, 0.9 Hz, *E*-$H^e$), 6.30 (dd, *J* = 6.0, 0.9 Hz, *Z*-$H^e$), 5.83 (ddd, *J* = 17.4, 9.9, 7.5 Hz, *E*-

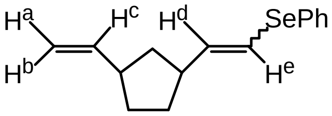
and *Z*-H$^{c}$), 5.38 (dd, *J* = 12.0, 6.2 Hz, *E*-H$^{d}$), 4.98 (ddd, *J* = 17.1, 1.8, 1.2 Hz, *E*- and *Z*-H$^{b}$), 4.88 (ddd, *J* = 9.9, 1.8, 0.9 Hz, *E*- and *Z*-H$^{a}$), 4.81 (dd, *J* = 9.0, 6.0 Hz, *Z*-H$^{d}$), 3.15–3.06, 2.59–2.48, 2.08–1.78, 1.53–1.37, 1.33–1.02 (each m, *E*- and *Z*-CH, CH$_2$); $^{13}$C{$^{1}$H} NMR (CDCl$_3$): δ = 158.1,143.4, 139.7, 129.8, 122.6, 118.4, 116.5, 112.6, 44.6, 41.3, 35.6, 32.8, 31.9; MS, *m*/*z* (rel intensity, %): *E*-isomer 214 (M$^{+}$, 2), 185 (4), 171 (2), 159 (2), 145 (4), 131 (9), 120 (100), 105 (31), 91 (64), 79 (91), 67 (71), 51 (59), 41 (92); *Z*-isomer 214 (M$^{+}$, 2), 185 (3), 171 (1), 159 (2), 145 (9), 131 (9), 120 (100), 105 (29), 91 (58), 79 (86), 67 (68), 51 (50), 41 (91); elementary analysis calcd for $C_{15}H_{18}O$: C 84.07, H 8.47; found: C 84.15, H 8.22.

**Compound 3b.** Colorless oil (63% yield, *E*/*Z* = 63/37); TLC: R$_f$ 0.30 (hexane).



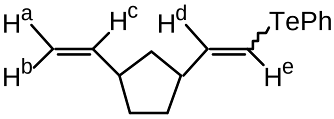
$^{1}$H NMR (CDCl$_3$): δ = 7.38–7.26, 7.24–7.13 (each m, *E*- and *Z*-Ph), 6.16 (d, *J* = 14.8 Hz, *E*-H$^{e}$), 6.15 (d, *J* = 9.7 Hz, *Z*-H$^{e}$), 6.00 (dd, *J* = 14.8, 7.7 Hz, *E*-H$^{d}$), 5.85 (ddd, *J* = 17.6, 10.3, 7.5 Hz, *Z*-H$^{c}$), 5.83 (ddd, *J* = 17.4, 10.3, 7.5 Hz, *E*-H$^{c}$), 5.81 (dd, *J* = 9.7, 9.1 Hz, *Z*-H$^{d}$), 5.02 (d, *J* = 17.4 Hz, *E*- and *Z*-H$^{b}$), 4.93 (d, *J* = 10.3 Hz, *E*- and *Z*-H$^{a}$), 2.78–2.50, 2.14–1.80, 1.60–1.41, 1.30–1.16 (each m, *E*- and *Z*-CH$_2$, CH); $^{13}$C{$^{1}$H} NMR (CDCl$_3$): δ = 142.9, 142.8, 141.3, 138.6, 136.5, 128.9, 128.6, 128.4, 126.0, 121.2, 119.3, 112.6, 44.3, 44.1, 43.7, 40.3, 40.2, 39.9, 32.0, 31.7, 31.5; MS, *m*/*z* (rel intensity, %): *E*-isomer 230 (M$^{+}$, 26), 201 (4), 175 (4), 136 (61), 120 (54), 105 (34), 91 (65), 79 (91), 67 (74), 41 (100); *Z*-isomer 230 (M$^{+}$, 21), 201 (3), 175 (3), 136 (55), 120 (48), 105 (32), 93 (49), 91 (61), 79 (87), 67 (72), 41 (100); elementary analysis calcd for $C_{15}H_{18}S$: C 78.21, H 7.88; found: C 78.62, H 8.01.

**Compound 3c.** Colorless oil (92% yield, *E*/*Z* = 65/35); TLC: $R_f$ 0.30 (hexane).



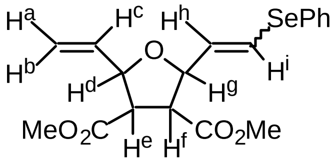
$^1$H NMR (CDCl$_3$): δ = 7.47–7.39, 7.28–7.17 (each m, *E*- and *Z*-Ph), 6.35 (dd, *J* = 15.3, 0.9 Hz, *E*-H$^e$), 6.34 (dd, *J* = 9.3, 0.9 Hz, *Z*-H$^e$), 6.07 (dd, *J* = 15.3, 7.8 Hz, *E*-H$^d$), 5.98 (dd, *J* = 9.3, 8.7 Hz, *Z*-H$^d$), 5.78 (ddd, *J* = 17.1, 10.2, 7.2 Hz, *E*- and *Z*-H$^c$), 4.96 (ddd, *J* = 17.1, 1.8, 1.2 Hz, *E*- and *Z*-H$^b$), 4.87 (ddd, *J* = 10.2, 1.8, 0.9 Hz, *E*- and *Z*-H$^a$), 2.92–2.83, 2.67–2.44, 2.07–1.76, 1.51–1.33, 1.24–1.03 (each m, *E*- and *Z*-CH$_2$, CH); $^{13}$C{$^1$H} NMR (CDCl$_3$): δ = 144.3, 142.9, 140.4, 131.5, 131.3, 129.1, 126.7, 118.6, 114.6, 112.6, 44.8, 44.1, 42.0, 40.2, 31.9, 31.8, 31.6, 31.5; MS, *m*/*z* (rel intensity, %): *E*-isomer 278 (M$^+$, 27), 276 (14), 184 (13), 158 (15), 115 (18), 105 (27), 93 (92), 92 (24), 91 (79), 80 (12), 79 (100), 78 (39), 77 (72), 67 (92), 66 (18), 65 (45), 55 (49), 53 (35), 51 (52); *Z*-isomer 278 (M$^+$, 24), 276 (12), 184 (14), 158 (13), 157 (16), 155 (13), 141 (12), 133 (13), 129 (28), 128 (17), 121 (45), 120 (22), 117 (13), 115 (19), 105 (27), 93 (92), 92 (24), 91 (78), 80 (12), 79 (100), 78 (35), 77 (73), 67 (93), 66 (18), 65 (43), 55 (46), 53 (33), 51 (50); elementary analysis calcd for $C_{15}H_{18}Se$: C 64.98, H 6.54; found: C 65.21, H 6.70.

**Compound 3d.** Colorless oil (34% yield, *E*/*Z* = 46/54); TLC: $R_f$ 0.25 (hexane).



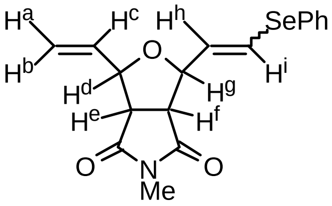
$^1$H NMR (CDCl$_3$): δ = 7.69–7.63, 7.30–7.18 (each m, *E*- and *Z*-Ph), 6.71 (dd, *J* = 15.9, 1.2 Hz, *E*-H$^e$), 6.65 (dd, *J* = 9.0, 0.9 Hz, *Z*-H$^e$), 6.35 (dd, *J* = 15.9, 7.5 Hz, *E*-H$^d$), 6.24 (dd, *J* = 9.0, 9.0 Hz, *Z*-H$^d$), 5.80 (ddd, *J* = 17.1, 10.2, 7.2 Hz, *E*- and *Z*-H$^c$), 4.90 (ddd, *J* = 17.1, 1.8, 0.9 Hz, *E*- and *Z*-H$^b$), 4.89 (ddd, *J* = 10.2, 1.8, 0.9 Hz, *E*- and *Z*-H$^a$), 2.74–2.45, 2.06–1.78, 1.52–1.43, 1.27–1.14 (each m, *E*- and *Z*-CH$_2$, CH); $^{13}$C{$^1$H} NMR (CDCl$_3$): δ = 152.7, 146.4, 142.9, 142.8, 137.9, 137.6, 137.1, 136.7, 129.5, 129.3, 128.0, 127.8, 127.5, 127.3, 114.1, 113.9, 112.6, 103.5, 96.6, 47.1, 46.4, 44.3, 44.1, 39.9, 31.8, 31.6, 31.5, 31.4; MS, *m*/*z* (rel intensity, %): *E*- and *Z*-isomer 328 (M$^+$, 22), 326 (20), 324 (13), 207 (12), 205 (12), 129 (25), 93 (83), 91 (65), 79 (95), 77 (97), 67 (100), 65 (38), 55 (53); elementary analysis calcd for $C_{15}H_{18}Te$: C 55.28, H 5.27; found: C 55.92, H 5.66.

**Compound 9.** Colorless oil (99% yield, *E*/*Z* = 84/16); TLC: $R_f$ 0.20 (hexane/AcOEt = 10/1).



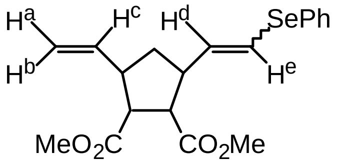
$^1$H NMR (CDCl$_3$): δ = 7.53–7.46, 7.32–7.26 (each m, *E*- and *Z*-Ph), 6.86 (dd, $^2J_{SeH}$ = 15.4 Hz, *J* = 15.3, 1.2 Hz, *E*-H$^i$), 6.76 (dd, *J* = 9.5, 0.9 Hz, *Z*-H$^i$), 6.09 (dd, *J* = 9.5, 7.4 Hz, *Z*-H$^h$), 5.96 (dd, *J* = 15.3, 6.4 Hz, *E*-H$^h$), 5.87 (ddd, *J* = 17.0, 10.4, 6.0 Hz, *E*- and *Z*-H$^c$), 5.44 (ddd, *J* = 17.0, 1.4, 1.4 Hz, *Z*-H$^b$), 5.39 (ddd, *J* = 17.0, 1.4, 1.4 Hz, *E*-H$^b$), 5.25 (ddd, *J* = 10.4, 1.3, 1.3 Hz, *Z*-H$^a$), 5.22 (ddd, *J* = 10.4, 1.3, 1.3 Hz, *E*-H$^a$), 5.09–5.04 (m, *Z*-H$^g$), 4.80–4.66 (m, *E*-H$^{d,g}$ and *Z*-H$^d$), 3.73, 3.72, 3.70 (s, *E*- and *Z*-CO$_2$Me), 3.25–3.06 (m, *E*- and *Z*-H$^{e,f}$); $^{13}$C{$^1$H} NMR (CDCl$_3$): δ = 171.1, 170.9, 136.3, 132.8, 132.3, 130.5, 129.3, 129.2, 127.5, 127.3, 126.7, 123.2, 117.6, 81.9, 81.6, 81.5, 79.3, 52.4, 52.2, 51.9; MS, *m*/*z* (rel intensity, %): *E*-isomer 396 (M$^+$, 2), 239 (20), 207 (24), 179 (11), 175 (14), 157 (11), 151 (10), 127 (57), 121 (19), 111 (18), 93 (12), 77 (17), 71 (13), 65 (15), 59 (40), 55 (100)); *Z*-isomer 396 (M$^+$, 2), 239 (19), 207 (24), 175 (13), 157 (11), 151 (11), 111 (16), 93 (12), 77 (15), 71 (13), 65 (16), 59 (38), 55 (100); elementary analysis calcd for $C_{18}H_{20}O_5Se$: C 54.59, H 5.10; found: C 54.78, H 5.20.

**Compound 11.** Orange oil (82% yield, *E*/*Z* = 72/28); TLC: $R_f$ 0.13 (hexane/AcOEt = 10/1).



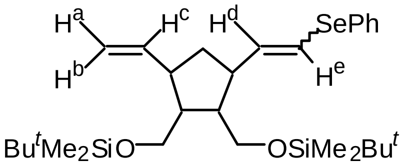
$^1$H NMR (CDCl$_3$): δ = 7.56–7.49, 7.33–7.28 (each m, *E*- and *Z*-Ph), 6.90 (dd, $^2J_{SeH}$ = 21.0 Hz, *J* = 15.4, 1.1 Hz, *E*-H$^i$), 6.84 (dd, *J* = 9.5, 0.9 Hz, *Z*-H$^i$), 6.22 (dd, *J* = 9.5, 7.3 Hz, *Z*-H$^h$), 6.05 (ddd, *J* = 17.2, 10.6, 6.0 Hz, *Z*-H$^c$), 5.98 (ddd, *J* = 16.5, 10.4, 5.0 Hz, *E*-H$^c$), 5.98 (dd, *J* = 15.4, 6.4 Hz, *E*-H$^h$), 5.50 (ddd, *J* = 17.2, 1.1, 1.1 Hz, *Z*-H$^d$), 5.43 (ddd, *J* = 16.5, 1.3, 1.1 Hz, *E*-H$^d$), 5.33 (ddd, *J* = 10.6, 1.1, 1.1 Hz, *Z*-H$^a$), 5.28 (ddd, *J* = 10.4, 1.1, 1.1 Hz, *E*-H$^a$), 4.78 (ddd, *J* = 7.3, 7.1, 0.9 Hz, *Z*-H$^g$), 4.51–4.40 (m, *E*-H$^{d,g}$ and *Z*-H$^d$), 3.41–3.23 (m, *E*- and *Z*-H$^{e,f}$), 3.03, 2.99 (each s, *E*- and *Z*-NMe); $^{13}$C{$^1$H} NMR (CDCl$_3$): δ = 175.8, 175.7, 135.8, 135.6, 133.3, 132.4, 131.2, 130.9, 129.8, 129.4, 129.3, 128.7, 127.8, 127.7, 127.5, 124.6, 118.3, 118.2, 82.3, 82.0, 79.6, 52.7, 52.4, 52.2, 52.1, 25.1, 25.0; MS, *m*/*z* (rel intensity, %): *E*-isomer 363 (M$^+$, 6), 206 (77), 157 (14), 121 (54), 93 (21), 77 (19), 66 (40), 55 (100); *Z*-isomer 363 (M$^+$, 7), 206 (82), 157 (14), 121 (53), 93 (24), 77 (19), 66 (39), 55 (100); elementary analysis calcd for $C_{17}H_{17}NO_3Se$: C 56.36, H 4.73, N 3.87; found: C 55.47, H 4.76, N 3.65.

**Compound 13**. Pale yellow oil (96% yield, *E*/*Z* = 55/45); TLC: $R_f$ 0.19 (hexane/AcOEt = 10/1).



$^1H$ NMR ($CDCl_3$): δ = 7.48–7.44, 7.30–7.23 (each m, *E*- and *Z*-Ph), 6.49 (dd, *J* = 9.0, 0.7 Hz, *Z*-$H^e$), 6.47 (dd, *J* = 15.2, 0.7 Hz, *E*-$H^e$), 6.27 (pseudo t, *J* = 9.0 Hz, *Z*-$H^d$), 6.18 (dd, *J* = 15.2, 8.8 Hz, *E*-$H^d$), 5.89, 5.86 (each ddd, *J* = 17.0, 10.1, 5.0 Hz, *E*- and *Z*-$H^c$), 5.09, 5.06 (each ddd, *J* = 17.0, 1.6, 1.1 Hz, *E*- and *Z*-$H^b$), 5.02, 4.96 (each ddd, *J* = 10.1, 1.6, 0.8 Hz, *E*- and *Z*-$H^a$), 3.68, 3.65 (each s, *E*- and *Z*-$CO_2Me$), 3.51–3.39, 3.33–3.16, 3.14–3.02, 2.98–2.86, 2.27–1.97 (each m, *E*- and *Z*-CH, $CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.0, 172.5, 138.0, 137.7, 136.8, 131.9, 131.5, 129.2, 126.9, 121.2, 118.8, 116.2, 116.0, 51.6, 51.5, 51.2, 51.1, 51.0, 46.2, 46.0, 45.7, 42.5, 40.0, 36.7; MS, *m*/*z* (rel intensity, %): *E*-isomer 394 ($M^+$, 9), 275 (5), 237 (64), 205 (61), 177 (53), 157 (17), 149 (13), 145 (72), 133 (10), 129 (13), 117 (100), 91 (87), 77 (56), 65 (31), 59 (77), 51 (39); *Z*-isomer 394 ($M^+$, 10), 275 (5), 237 (61), 205 (58), 177 (69), 157 (15), 145 (67), 131 (11), 129 (10), 117 (100), 91 (93), 77 (58), 65 (32), 59 (82), 51 (38); elementary analysis calcd for $C_{19}H_{22}O_4Se$: C 58.02, H 5.64; found: C 58.99, H 5.94.

**Compound 15**. Colorless oil (91% yield, *E*/*Z* = 58/42); TLC: $R_f$ 0.33 (hexane/AcOEt = 20/1).



$^1H$ NMR ($CDCl_3$): δ = 7.49–7.40, 7.30–7.21 (each m, *E*- and *Z*-Ph), 6.40 (d, *J* = 9.0 Hz, *Z*-$H^e$), 6.37 (d, *J* = 15.3 Hz, *E*-$H^e$), 6.26 (dd, *J* = 15.3, 8.4 Hz, *E*-$H^d$), 6.18 (pseudo t, *J* = 9.0 Hz, *Z*-$H^d$), 5.93, 5.90 (each ddd, *J* = 17.1, 9.9, 7.8 Hz, *E*- and *Z*-$H^c$), 4.98 (d, *J* = 17.1 Hz, *E*- and *Z*-$H^b$), 4.93 (d, *J* = 9.9 Hz, *E*- and *Z*-$H^a$), 3.72–3.63 (m, *E*- and *Z*-$OCH_2$), 3.14–3.02, 2.91–2.65, 2.42–2.21, 2.09–1.95, 1.74–1.61 (each m, *E*- and *Z*-CH, $CH_2$), 0.89 (s, *E*- and *Z*-$SiMe_2\mathit{Bu}^t$), 0.05, 0.04 (each s, *E*- and *Z*-$Si\mathit{Me}_2Bu^t$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 142.8, 140.7, 140.6, 138.2, 131.6, 131.3, 129.1, 126.7, 126.5, 119.3, 115.4, 114.2, 114.1, 61.1, 61.0, 48.1, 47.5, 47.4, 47.1, 45.7, 45.6, 45.4, 42.8, 38.4, 37.5, 26.0, 18.2, –5.4; elementary analysis calcd for $C_{29}H_{50}O_2SeSi_2$: C 61.56, H 8.91; found: C 61.37, H 8.81.

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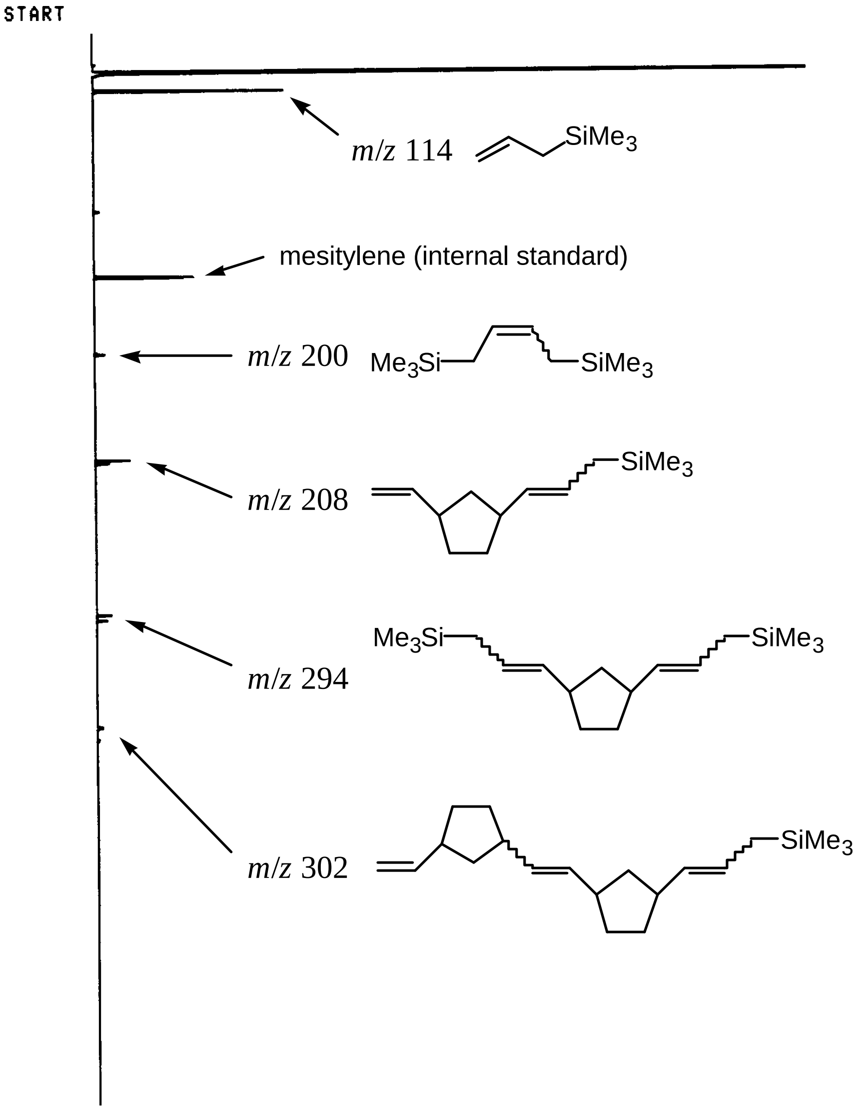

**Figure S1.** GCMS chart of the volatile products from the reaction of norbornene (**1**) with allyltrimethylsilane catalyzed by [Ru(=CHPh)$Cl_2$($(PCy_3)_2$] (**6**).