Supporting Information

Cycloisomerization of Enynes via Rhodium Vinylidene Mediated Catalysis

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General: Unless otherwise noted, all reactions were conducted as described under an argon atmosphere using anhydrous solvent (either distilled or pass through activated alumina column or activated molecular sieves column). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using EM Science silica gel 60 F₂₅₄ plates and visualized by using UV light, anisaldehyde, ceric sulfate or potassium permanganate. Flash chromatography was performed on EM Science silica gel 60 (40-63 μ m) using the indicated solvent system. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 , unless otherwise noted, on a Varian Mercury 300 MHz or a Varian Inova 400 MHz spectrometer. Chemical shifts in ^1H NMR spectra were reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data for ^1H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz) and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift in ppm from the central peak of CDCl_3 (77.23 ppm). Infrared

(IR) spectra were recorded on a Nicolet 730 FT-IR spectrometer and reported in frequency of the absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained from the Princeton University Mass Spectrometry Facility.

Representative procedure using $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{P}(\text{4-F-Ph})_3$ (Condition A)

To a flame dried 1 dram glass vial equipped with screw-cap and Teflon septa was added $[\text{Rh}(\text{COD})\text{Cl}]_2$ (4.9 mg, 0.0099 mmol), $\text{P}(\text{4-F-Ph})_3$ (15.8 mg, 0.0499 mmol) and CH_3CN (0.50 mL). This mixture was stirred for 15 minutes before enyne **1** (42 mg, 0.20 mmol) in CH_3CN (0.50 mL) was added *via* syringe at 25 °C. The syringe was washed with CH_3CN (0.50 mL * 2). The resulting solution was then moved to a pre-heated sand bath (85 °C) and stirred for 24 h. After 24 h, the reaction mixture was loaded directly onto a silica gel column. Purification *via* flash column chromatography (petroleum ether: diethyl ether = 8:1) yielded **2** (36 mg, 0.17 mmol) as a colorless oil.

Representative procedure using Wilkinson's Catalyst $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (Condition B)

To a flame dried 1 dram glass vial equipped with screw-cap and Teflon septa, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (18.5 mg, 0.0200 mmol) and CH_3CN (0.50 mL) was added. To this mixture, enyne **13** (51 mg, 0.20 mmol) in CH_3CN (0.50 mL) was added *via* syringe at 25 °C. The syringe was washed with CH_3CN (0.50 mL * 2). The resulting solution was then moved to a pre-heated sand bath (85 °C) and stirred for 24 h. After 24 h, the reaction mixture was loaded directly onto a silica gel column. Purification *via* flash column chromatography (petroleum ether: diethyl ether = 40:1) yielded **14** (51 mg, 0.20 mmol) as a colorless oil.

5-Methylene-cyclohex-3-ene-1,1-dicarboxylic acid dimethyl ester (2, Eq 1). Following condition A, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (4.9 mg, 0.0099 mmol), $\text{P}(4\text{-F-Ph})_3$ (15.8 mg, 0.0499 mmol) and **1**¹ (42 mg, 0.20 mmol) was employed in DMF (2.0 mL, 0.10 M) to give **2** (36 mg, 0.17 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 8:1): IR (film) 3073, 2955, 1736, 1251, 1640, 1055 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.14 (dt, $J = 9.9, 2.0$ Hz, 1H), 5.76 (ddd, $J = 9.9, 5.4, 0.4$ Hz, 1H), 4.91 (m, 2H), 3.71 (s, 6H), 2.86 (t, $J = 1.5$ Hz, 2H), 2.69-2.67 (m, 2H); ^{13}C NMR (100MHz, CDCl_3) δ 171.3, 138.8, 128.8, 126.3, 113.6, 53.9, 52.7, 35.8, 30.9; HRMS (EI) Calc'd for $\text{C}_{11}\text{H}_{14}\text{O}_4$ [M^+] 210.0892, Found 210.0890.

Deuterium Labeling Studies (Eq 2–4)

Eq 2. To a flame dried 1 dram glass vial equipped with screw-cap and Teflon septa was added $[\text{Rh}(\text{COD})\text{Cl}]_2$ (2.5 mg, 0.0050 mmol), $\text{P}(4\text{-F-Ph})_3$ (6.3 mg, 0.020 mmol) and DMF (0.50 mL). This mixture was stirred for 15 minutes before enyne **1a** (42 mg, 0.20 mmol) in DMF (0.50 mL) was added *via* syringe at 25 °C. The syringe was washed with DMF (0.50 mL * 2). The resulting solution was then moved to a pre-heated sand bath (85 °C) and stirred for 24 h. After 24 h, the reaction mixture was loaded directly onto a silica gel column. Purification *via* flash column chromatography (petroleum ether: diethyl ether = 8:1) yielded exclusively 5-Methylene-cyclohex-3-deuterio-3-ene-1,1-dicarboxylic acid dimethyl ester **2a** as a colorless oil in 83% yield (35 mg, 0.17 mmol) with 60% incorporation of deuterium as seen in the equation: IR (film) 3073, 2955, 1736, 1251, 1640, 1055 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.17-6.13 (m, 1H),

¹ Trost, B.M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 12491.

5.80-5.76 (m, 0.4H), 4.93-4.92 (m, 2H), 3.72 (s, 6H), 2.88 (t, $J = 1.4$ Hz, 2H), 2.69 (d, $J = 1.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) 171.4, 138.8, 128.6, 126.3 (t, $J = 22.5$ Hz), 113.6, 53.9, 52.7, 35.8; HRMS (EI) Calc'd for $\text{C}_{11}\text{H}_{13}\text{O}_4\text{D}$ [M^+] 211.0954, Found 211.0944.

The alkynyl deuterium label readily exchanges with residual water in these reaction conditions. In the following NMR study of eq 1 conducted in DMF- d_7 , a gradual increase in the HOD signal is observed, which appears at the right shoulder of the water peak (3.5 ppm).

Eq 3. To a flame dried 1 dram glass vial equipped with screw-cap and Teflon septa was added $[\text{Rh}(\text{COD})\text{Cl}]_2$ (2.5 mg, 0.0050 mmol), $\text{P}(4\text{-F-Ph})_3$ (6.3 mg, 0.020 mmol) and DMF (0.50 mL). This mixture was stirred for 15 minutes before enyne **1** (42 mg, 0.20 mmol) in DMF (0.50 mL) was added *via* syringe at 25 °C. The syringe was washed with DMF (0.50 mL * 2). The resulting solution was then moved to a pre-heated sand bath (85 °C) and stirred for 24 h. After 24 h, the reaction mixture was loaded directly onto a silica gel column. Purification *via* flash column

chromatography (petroleum ether: diethyl ether = 8:1) yielded exclusively 5-Methylene-cyclohex-4-deuterio-3-ene-1,1-dicarboxylic acid dimethyl ester **2b** as a colorless oil in 70% yield (29 mg, 0.14 mmol) with 94% incorporation of deuterium as seen in the equation: ^1H NMR (400 MHz, CDCl_3) δ 6.14 (m, 0.06H), 5.78 (t, J = 4.0 Hz, 1H), 4.93-4.91 (m, 2H), 3.72 (s, 6H), 2.86 (t, J = 1.5 Hz, 2H), 2.69 (d, J = 4.1 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) 171.4, 138.8, 128.6 (t, J = 22.5 Hz), 126.2, 113.6, 53.9, 52.7, 35.8; HRMS (EI) Calc'd for $\text{C}_{11}\text{H}_{13}\text{O}_4\text{D}$ [M^+] 211.0954, Found 211.0948.

Eq 4. To a flame dried 1 dram glass vial equipped with screw-cap and Teflon septa, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (18.5 mg, 0.0200 mmol) and CH_3CN (0.50 mL) was added. To this mixture, enyne **1b** (21 mg, 0.10 mmol) and **3** (38 mg, 0.10 mmol) in CH_3CN (0.50 mL) was added *via* syringe at 25 °C. The syringe was washed with CH_3CN (0.50 mL * 2). The resulting solution was then moved to a pre-heated sand bath (85 °C) and stirred for 24 h. After 24 h, the reaction mixture was loaded directly onto a silica gel column. Purification *via* flash column chromatography (petroleum ether: diethyl ether = 40:1) yielded 5-Methylene-cyclohex-4-deuterio-3-ene-1,1-dicarboxylic acid dimethyl ester **2b** in 67% yield (14 mg, 0.067 mmol) with 94% incorporation of deuterium (identical result compared with **Eq 3**) while 5,5-Bis-(*tert*-butyl-dimethyl-silanyloxymethyl)-3-methylene-cyclohexene **4** was obtained in 95% yield (36 mg, 0.095 mmol) with no incorporation of deuterium: IR (film) 2955, 2926, 1471, 1256, 1083, 835, 775 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 6.11 (dt, J = 9.8, 2.1 Hz, 1H), 5.71 (m, 1H), 4.84 (s, 1H), 4.77 (s, 1H), 3.38 (s, 6H), 2.21 (t, J = 1.4 Hz, 2H), 1.99-1.97 (m, 2H), 0.89 (s, 18H), 0.02 (s, 12H); ^{13}C NMR (75MHz, CDCl_3) δ 141.5, 128.7, 128.0, 112.1, 65.1, 40.1, 34.3, 29.1, 25.9, 18.3, -5.6; HRMS (EI) Calc'd for $\text{C}_{17}\text{H}_{33}\text{O}_2\text{Si}_2$ [$\text{M}^+ - \text{C}(\text{CH}_3)_3$] 325.2019, Found 325.2029.

tert-Butyl-(2-methylene-cyclohex-3-enyloxy)-diphenyl-silane (6, Table 1, entry 1). Following condition A, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (4.9 mg, 0.0099 mmol), $\text{P}(4\text{-F-Ph})_3$ (15.8 mg, 0.0499 mmol) and **5**² (70 mg, 0.20 mmol) was employed in DMF (2.0 mL, 0.10 M) to give **6** (56 mg, 0.16 mmol) as a pale yellow oil after column chromatography (petroleum ether: diethyl ether = 40:1). Following condition B, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (18.5 mg, 0.0200 mmol) and **5**² (70 mg, 0.20 mmol) was employed in CH_3CN (2.0 mL, 0.10 M) to give **6** (54 mg, 0.15 mmol) as a pale yellow oil after column chromatography (petroleum ether: diethyl ether = 40:1): IR (film) 2930, 2857, 1427, 1111, 822, 701, 612 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.78-7.64 (m, 4H), 7.49-7.36 (m, 6H), 6.12 (dt, J = 9.7, 1.6 Hz, 1H), 5.74 (m, 1H), 5.08 (s, 1H), 4.86 (s, 1H), 4.40 (m, 1H), 2.25-2.20 (m, 1H), 1.79-1.66 (m, 1H), 1.11 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.6, 135.9, 129.5, 129.2, 128.0, 127.7, 127.5, 110.6, 71.2, 31.7, 27.0, 23.9, 19.4; HRMS (EI) Calc'd for $\text{C}_{23}\text{H}_{28}\text{OSi}$ [M^+] 348.1909, Found 348.1920.

3,3-Dimethyl-10-methylene-2,4-dioxaspiro[5.5]undec-8-ene (8, Table 1, entry 2). Following condition B, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (18.5 mg, 0.0200 mmol) and **7**³ (39 mg, 0.20 mmol) was employed in CH_3CN (2.0 mL, 0.10 M) to give **8** (35 mg, 0.18 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 20:1): IR (film) 2992, 2857, 1638, 1370, 1210,

² Adrio, J.; Rivero, M. R.; Carretero, J. C. *Chem. Eur. J.* **2001**, 7, 2435

1069, 881 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.13 (dt, $J = 9.8, 2.1$ Hz, 1H), 5.71 (dt, $J = 9.5, 5.1$ Hz, 1H), 4.90 (s, 1H), 4.87 (s, 1H), 3.57 (s, 4H), 2.27 (t, $J = 1.4$ Hz, 2H), 2.14-2.13 (m, 2H), 1.43 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.8, 129.0, 126.8, 113.3, 98.1, 68.2, 36.1, 32.4, 31.6, 24.4, 23.0; HRMS (EI) Calc'd for $\text{C}_{11}\text{H}_{15}\text{O}_2$ [$\text{M}^+ - \text{CH}_3$] 179.1072, Found 179.1077.

(6,6-Dimethyl-2-methylene-cyclohex-3-enyloxymethyl)-benzene (10, Table 1, entry 3).

Following condition A, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (4.9 mg, 0.0099 mmol), $\text{P}(4\text{-F-Ph})_3$ (15.8 mg, 0.0499 mmol) and **9**⁴ (46 mg, 0.20 mmol) was employed in DMF (2.0 mL, 0.10 M) to give **10** (41 mg, 0.18 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 20:1). Following condition B, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (18.5 mg, 0.0200 mmol) and **9**⁴ (46 mg, 0.20 mmol) was employed in CH_3CN (2.0 mL, 0.10 M) to give **10** (38 mg, 0.17 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 20:1): IR (film) 3026, 2930, 2855, 1452, 1060, 732, 695, 665 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.20 (m, 5H), 6.09 (d, $J = 9.9$ Hz, 1H), 5.79-5.74 (m, 1H), 5.10 (s, 1H), 4.96 (s, 1H), 4.64 (d, $J = 12.2$ Hz, 1H), 4.39 (d, $J = 12.2$ Hz, 1H), 3.40 (s, 1H), 2.32 (d, $J = 18.1$ Hz, 1H), 1.94 (dd, $J = 18.1, 5.3$ Hz, 1H), 1.08 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 139.2, 129.2, 128.1, 127.6, 127.1, 126.0, 114.5, 84.4, 69.8, 37.9, 36.5, 25.6, 25.2; HRMS (EI) Calc'd for $\text{C}_{16}\text{H}_{20}\text{O}$ [M^+] 228.1514, Found 228.1527.

³ Mori, M.; Saito, N.; Tanaka, D.; Takimoto, M.; Sato, M. *J. Am. Chem. Soc.* **2003**, *125*, 5606.

⁴ Prepared based on procedure in the following reference: Adrio, J.; Rivero, M. R.; Carretero, J. *C. Angew. Chem., Int. Ed.* **2000**, *39*, 2906

trans-4a-Benzyloxy-5-methylene-1,2,3,4,4a,5,8,8a-octahydro-naphthalene (12, Table 1, entry 4). Following condition A, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (4.9 mg, 0.0099 mmol), $\text{P}(4\text{-F-Ph})_3$ (15.8 mg, 0.0499 mmol) and **11**⁵ (51 mg, 0.20 mmol) was employed in DMF (2.0 mL, 0.10 M) to give **12** (46 mg, 0.18 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 40:1). Following condition B, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (18.5 mg, 0.0200 mmol) and **11**⁵ (51 mg, 0.20 mmol) was employed in CH_3CN (2.0 mL, 0.1 M) to give **12** (46 mg, 0.18 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 40:1): IR (film) 3026, 2930, 2855, 1452, 1060, 732, 695, 665 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.21 (m, 5H), 6.08 (dd, $J = 9.9, 2.4$ Hz, 1H), 5.89-5.85 (m, 1H), 5.09 (s, 2H), 4.28 (s, 2H), 2.46 (d, $J = 14.0$ Hz, 1H), 2.36-2.28 (m, 1H), 1.94 (td, $J = 18.3, 4.7$ Hz, 1H), 1.78-1.56 (m, 5H), 1.51-1.47 (m, 1H), 1.38-1.27 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 140.4, 128.4, 128.3, 128.0, 127.0, 126.6, 112.2, 73.8, 62.7, 42.0, 37.9, 30.1, 28.4, 25.9, 21.8; HRMS (EI) Calc'd for $\text{C}_{18}\text{H}_{22}\text{O}$ [M^+] 254.1671, Found 254.1655.

trans-8a-Benzyloxy-6-methylene-1,2,3,4,4a,5,6,8a-octahydro-naphthalene (14, Table 1, entry 5). Following condition B, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (18.5 mg, 0.0200 mmol) and **13**⁶ (51 mg, 0.20

⁵ Marson, C. M.; McGregor, J.; Khan, A.; Grinter, T. J. *J. Org. Chem.* **1998**, 63, 7833.

⁶ Prepared and characterized based on procedures in the following reference: Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2002**, 124, 5025.

mmol) was employed in CH₃CN (2.0 mL, 0.10 M) to give **14** (51 mg, 0.20 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 40:1): IR (film) 3026, 2930, 2854, 1595, 1444, 1088, 930, 884, 694 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.24 (m, 5H), 6.60 (d, *J* = 9.7 Hz, 1H), 5.84 (d, *J* = 9.8 Hz, 1H), 4.93 (m, 2H), 4.45 (s, 2H), 2.71 (m, 1H), 2.17 (dd, *J* = 14.6, 3.6 Hz, 1H), 2.09 (dd, *J* = 14.9, 3.5 Hz, 1H), 1.80-1.65 (m, 3H), 1.61-1.52 (m, 2H), 1.42-1.38 (m, 1H), 1.33 (dt, *J* = 13.8, 3.9 Hz, 1H), 1.23 (td, *J* = 13.8, 4.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 140.4, 133.3, 132.9, 128.0, 126.9, 126.8, 112.9, 70.9, 63.2, 43.9, 32.9, 32.5, 27.5, 26.0, 21.4; HRMS (EI) Calc'd for C₁₂H₁₈O₂ [M⁺] 254.1671, Found 254.1665.

cis-8a-Benzyloxy-6-methylene-1,2,3,4,4a,5,6,8a-octahydro-naphthalene (16, Table 1, entry 6). Following condition A, [Rh(COD)Cl]₂ (4.9 mg, 0.0099 mmol), P(4-F-Ph)₃ (15.8 mg, 0.0499 mmol) and **15**⁶ (51 mg, 0.20 mmol) was employed in DMF (2.0 mL, 0.10 M) to give **16** (34 mg, 0.13 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 40:1): IR (film) 3028, 2928, 2856, 1636, 1452, 1062, 1028, 883, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.24 (m, 5H), 6.30 (d, *J* = 9.9 Hz, 1H), 5.71 (d, *J* = 10.0 Hz, 1H), 4.95-4.93 (m, 2H), 4.51 (d, *J* = 11.3 Hz, 1H), 4.47 (d, *J* = 10.7 Hz, 1H), 2.75-2.63 (m, 1H), 2.31 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.10-2.04 (m, 1H), 1.94-1.87 (m, 1H), 1.80-1.61 (m, 3H), 1.59-1.49 (m, 1H), 1.40-1.30 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.1, 140.0, 132.7, 128.2, 127.3, 127.0, 126.3, 113.4, 75.0, 63.9, 37.5, 34.9, 32.8, 27.9, 23.1, 22.4; HRMS (EI) Calc'd for C₁₂H₁₈O₂ [M⁺] 254.1671, Found 254.1672.

3-Methylene-1-(toluene-4-sulfonyl)-1,2,3,6-tetrahydro-pyridine (18, Table 1, entry 7).

Following condition A, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (4.9 mg, 0.0099 mmol), $\text{P}(4\text{-F-Ph})_3$ (15.8 mg, 0.0499 mmol) and **17**⁷ (50 mg, 0.20 mmol) was employed in DMF (2.0 mL, 0.10 M) to give **18** (27 mg, 0.18 mmol) as a white solid after column chromatography (petroleum ether: diethyl ether = 2:1): IR (film) 3427, 2922, 2825, 1594, 1345, 1165, 885, 668 cm^{-1} ; m.p. 112-114 °C; ¹H NMR (400 MHz, CDCl_3) δ 7.68 (dt, J = 8.5, 1.9 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.14 (dt, J = 10.0, 2.2 Hz, 1H), 5.71 (dt, J = 8.1, 3.7 Hz, 1H), 4.93 (s, 1H), 4.92 (s, 1H), 3.83 (t, J = 1.2 Hz, 2H), 3.73 (dt, J = 2.3, 1.1 Hz, 2H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl_3) δ 143.6, 136.7, 133.5, 129.6, 127.8, 127.5, 124.7, 113.0, 48.2, 44.7, 21.5; HRMS (EI) Calc'd for $\text{C}_{13}\text{H}_{15}\text{NO}_2\text{S}$ [M^+] 249.0823, Found 249.0824.

3-Methylene-6-pentyl-3,6-dihydro-2H-pyran (20, Table 1, entry 8). Following condition A, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (4.9 mg, 0.0099 mmol), $\text{P}(4\text{-F-Ph})_3$ (15.8 mg, 0.0499 mmol) and **19**⁷ (33 mg, 0.20 mmol) was employed in DMF (2.0 mL, 0.10 M) to give **20** (19 mg, 0.12 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 40:1). Following condition B, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (18.5 mg, 0.0200 mmol) and **19**⁷ (33 mg, 0.20 mmol) was employed in CH_3CN (2.0 mL, 0.10 M) to give **20** (17 mg, 0.11 mmol) as a colorless oil after column chromatography

⁷ Doucet, H.; Derrien, N.; Kabouche, Z.; Bruneau, C.; Dixneuf, P. H. *J. Organomet. Chem.* **1998**, 551, 151.

(petroleum ether: diethyl ether = 40:1): IR (film) 2928, 2858, 1457, 1260, 1092, 803 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.30 (dd, $J = 10.1, 2.3$ Hz, 1H), 5.80 (dd, $J = 10.1, 1.6$ Hz, 1H), 4.85 (d, $J = 0.7$ Hz, 1H), 4.80 (d, $J = 0.7$ Hz, 1H), 4.38 (d, $J = 13.4$ Hz, 1H), 4.23 (dt, $J = 13.4, 1.7$ Hz, 1H); 4.18-4.12 (m, 1H), 1.62-1.52 (m, 2H), 1.50-1.35 (m, 2H), 1.34-1.23 (m, 4H), 0.90 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 132.7, 126.4, 109.3, 74.0, 68.0, 35.0, 31.8, 25.0, 22.6, 14.0; HRMS (EI) Calc'd for $\text{C}_{11}\text{H}_{18}\text{O}$ [M^+] 166.1358, Found 166.1354.

2,2-Dimethyl-5-methylene-6-pentyl-5,6-dihydro-2H-[1,2]oxasiline (22, Table 1, entry 9).

Following condition A, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (4.9 mg, 0.0099 mmol), $\text{P}(4\text{-F-Ph})_3$ (15.8 mg, 0.0499 mmol) and **21**⁸ (42 mg, 0.20 mmol) was employed in DMF (2.0 mL, 0.10 M) to give **22** (41 mg, 0.20 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 40:1). Following condition B, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (18.5 mg, 0.0200 mmol) and **21**⁸ (42 mg, 0.20 mmol) was employed in CH_3CN (2.0 mL, 0.10 M) to give **22** (40 mg, 0.19 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 40:1): IR (film) 2956, 2931, 2860, 1552, 1496, 1251, 1079, 839, 795 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.98 (d, $J = 14.3$ Hz, 1H), 5.84 (dm, $J = 14.3$ Hz, 1H), 5.03 (m, 1H), 4.99 (m, 1H), 4.45 (dd, $J = 8.5, 5.3$ Hz, 1H), 1.82-1.74 (m, 1H), 1.64-1.57 (m, 1H), 1.54-1.44 (m, 1H), 1.39-1.20 (m, 5H), 0.90 (t, $J = 6.9$ Hz, 3H), 0.22 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.8, 146.5, 128.6, 115.7, 76.0, 37.2, 31.6, 25.6, 22.6, 14.0, 0.98, -0.32; HRMS (EI) Calc'd for $\text{C}_{12}\text{H}_{22}\text{OSi}$ [M^+] 210.1440, Found 210.1438.

⁸ Prepared by procedure in the following reference: Stork, G.; Keitz, P. F. *Tetrahedron Lett.* **1989**, 30, 6981.

2,2-Dimethyl-5-methylene-7-styryl-2,5,6,7-tetrahydro-[1,2]oxasilepine (24, Table 1, entry 10). To a flame dried 1 dram glass vial equipped with screw-cap and Teflon septa, Rh(PPh₃)₃Cl (37 mg, 0.040 mmol) and toluene (0.50 mL) was added which was then moved to a pre-heated sand bath (85 °C). To this mixture, enyne **21** (51 mg, 0.20 mmol) in CH₃CN (1.5 mL) was slowly added *via* syringe pump at a flow rate of 0.15 mL/h. Upon termination of the slow addition, resulting mixture was stirred additionally for 14 h. After 14 h, the reaction mixture was loaded directly onto a preparative TLC (silica gel) plate. Eluting twice (petroleum ether: diethyl ether = 20:1) yielded **22** (39 mg, 0.15 mmol) as a colorless oil: IR (film) 3025, 2959, 2852, 1566, 1437, 1252, 1118, 838, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.20 (m, 5H), 7.00 (d, *J* = 14.9 Hz, 1H), 6.60 (dd, *J* = 15.8, 1.2, Hz, 1H), 6.25 (dd, *J* = 15.8, 6.0, 1H), 5.73 (d, *J* = 14.8, 1H), 5.18-5.16 (m, 2H), 4.72-4.68 (m, 1H), 2.85 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.72 (ddd, *J* = 15.0, 7.3, 0.9 Hz, 1H), 0.31 (s, 3H), 0.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.8, 146.1, 137.0, 132.0, 129.1, 128.4, 127.4, 126.5, 121.6, 74.9, 44.5, 1.7, 0.8; HRMS (EI) Calc'd for C₁₆H₂₀OSi [M⁺] 256.1283, Found 256.1286.

(5,5-Bis-phenylmethoxymethyl-3-methylene-cyclohex-1-enylselanyl) benzene (26, Eq 5).

Following condition B, Rh(PPh₃)₃Cl (37.0 mg, 0.0400 mmol) and **25**⁹ (98 mg, 0.20 mmol) was

⁹ Prepared from the corresponding enyne by the procedure found in the following reference: Bieber, L. W.; da Silva, M. F.; Menezes, P. H. *Tetrahedron Lett.* **2004**, 45, 2735.

employed in toluene (2.0 mL, 0.10 M) to give **26** (50 mg, 0.10 mmol) as a light yellow oil after column chromatography (petroleum ether: diethyl ether = 80:1): IR (film) 3029, 2918, 2851, 1577, 1453, 1206, 1099, 735 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.55-7.50 (m, 2H), 7.37-7.21 (m, 13H), 5.96 (s, 1H), 5.65 (s, 1H), 5.20 (s, 1H), 4.54 (s, 4H), 3.46 (s, 4H), 2.51 (s, 2H), 2.37 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.8, 134.5, 133.8, 130.6, 129.2 (*2), 128.3, 128.2, 127.4(*2), 127.2, 118.1, 73.7, 73.3, 47.4, 39.7, 39.6; HRMS (EI) Calc'd for $\text{C}_{29}\text{H}_{30}\text{O}_2\text{Se}$ [M^+] 490.1411, Found 490.1425.

2,2,3-Trimethyl-5-methylene-6-pentyl-5,6-dihydro-2H-[1,2]oxasiline (28, Eq 6). Following condition B, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (37.0 mg, 0.0400 mmol) and **27**⁸ (42 mg, 0.20 mmol) was employed in toluene (2.0 mL, 0.10 M) to give **28** (27 mg, 0.13 mmol) as a colorless oil after column chromatography (petroleum ether: diethyl ether = 40:1): IR (film) 2957, 2859, 1577, 1435, 1252, 1078, 782 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.64 (t, J = 0.7 Hz, 1H), 4.90 (s, 1H), 4.89 (t, J = 0.7 Hz, 1H), 4.41 (dd, J = 8.4, 5.3 Hz, 1H), 1.82 (dd, J = 1.0, 0.6 Hz, 3H), 1.80-1.70 (m, 1H), 1.60-1.44 (m, 3H), 1.38-1.25 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H), 0.22 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.0, 140.7, 138.1, 113.2, 76.4, 37.5, 31.6, 25.7, 22.6, 20.4, 14.1, -0.34, -1.65; HRMS (EI) Calc'd for $\text{C}_{13}\text{H}_{24}\text{OSi}$ [M^+] 224.1596, Found 224.1588.

NOE Data for compound **28**

NOE for Irradiation at 6.64 ppm

NOE irradiation at 1.82 ppm