Supporting information

Desymmetrization of the 4-dimethylsiloxy-1,6-heptadiyne through sequential double silylformylation

Dominique Bonafoux and Iwao Ojima*

General methods and material: the ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-250 or Gemini 2300 using $CDCl_3$ as the internal standard. The IR spectra were measured with a Perkin-Elmer 1600 FT-IR spectrometer. Mass spectra and high resolution mass spectra were recorded by the Mass Spectrometry Facility, University of Illinois at Urbana-Champaign. Rhodium complex, Rh(acac)$(CO)_2$, was obtained from the Mitsubishi Chemical Corporation and use as received.

3-(Propynyl)-5-*exo*-(formylmethylene)-1,1-dimethyl-2-oxa-1-silacyclopentane (**2a**): In a 10 mL round bottomed flask under CO atmosphere, Rh(acac)$(CO)_2$ (0.48 mg, 0.0018 mmol) was dissolved in 2 mL of toluene and a solution of 4-dimethylsiloxy-1,6-heptadiyne (**1a**) (0.06g, 0.36 mmol) in toluene (3mL) was added. The flask was placed in a 300 mL stainless steel autoclave, pressurized with 10 atm of CO, and the reaction mixture stirred at room temperature for 16 h. The solvent was removed under vacuum to afford **2a** as a dark orange oil in 98% yield (determined by ^{1}HNMR using CH_2Cl_2 as external standard): ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 3H), 0.40 (s, 3H), 2.01 (t, 1H, J = 2.6 Hz), 2.37-2.98 (m, 4H), 4.21 (m, 1H), 6.77 (m, 1H), 9.53 (d, 1H, J = 4.12 Hz); ^{13}C NMR ($CDCl_3$) δ -1.1, -0.6, 27.4, 42.1, 70.5, 73.0, 80.2, 134.6, 171, 190; IR (neat) 2252 ($\nu_{C\equiv C}$), 1683 (ν_{CO}), 1592 ($\nu_{C=C}$); HRMS (CI) calcd for $C_{10}H_{15}O_2Si$ (MH^+) 195.0845, found 195.0841 (Δ = -0.4 ppm).

3-(But-2-ynyl)-5-*exo*-(formylpropylene)-1,1-dimethyl-2-oxa-1-silacyclopentane (**2b**): Product **2b** was obtained according to a procedure similar to that for **2a** at 60 °C and 20 atm of CO for 16 h. After purification by column chromatography on silica gel (hexanes/EtOAc = 5/1), **2b** was obtained as a light yellow oil in 82% yield : ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 3H), 0.37 (s, 3H), 1.75 (t, 1H, J = 2.4 Hz), 1.92 (s, 3H), 2.37-2.91 (m, 4), 4.19 (m, 1H), 9.44 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -0.1, 0.3, 13.5, 28.0, 39.8, 73.6, 75.0, 77.7, 142.3, 165.6, 192.3; IR (neat) 2359 ($\nu_{C\equiv C}$), 1681 (ν_{CO}), 1598 ($\nu_{C=C}$); HRMS (EI) calcd for $C_{12}H_{17}O_2Si$ (M^+-H) 221.0993, found 221.0998 (Δ = 0.4 ppm).

General procedure for the sequential double silylformylation of 4-dimethylsiloxy-1,6-heptadiyne (1a): In a 10 mL round bottomed flask, under CO atmosphere, Rh(acac)$(CO)_2$ (0.48 mg, 0.0018 mmol) was dissolved in toluene (2 mL) and a solution of 4-dimethylsiloxy-1,6-heptadiyne (**1a**) (0.06g, 0.36 mmol) in toluene (3 mL) and a silane (0.39 mmol,1.08 equiv) were added. The flask was placed in a 300 mL stainless steel autoclave, pressurized with 10 atm of CO and the reaction mixture was stirred at an appropriate temperature for an appropriate time (Table 1). The solvent was removed under vacuum to afford **4** in quantitative yield (Table 1).

3-((Z)-3-Dimethylphenylsilyl-2-formylprop-2-enyl)-5-*exo*-(formylmethylene)-1,1-dimethyl-2-oxa-1-silacyclopentane (**4a**): dark orange oil; ^1H NMR ($CDCl_3$) δ ppm 0.32 (s, 3H), 0.37 (s, 3H), 0.52 (s, 6H) 2.36-2.81 (m, 4H), 4.19 (m, 1H), 6.71 (m, 1H), 7.11 (s, 1H), 7.35-7.38 (m, 3H), 7.51-7.54 (m, 2H), 9.52 (d, 1H, J = 4.12 Hz), 9.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -1.0, -0.5, -0.1, 39.8, 43.0, 73.6, 127.7, 128.1, 129.5, 133.5, 134.6, 137.7, 152.5, 152.9, 171.6, 190.8, 193.0; IR (neat) 1680 (ν_{CO}), 1591 ($\nu_{C=C}$); HRMS (CI) calcd for $C_{19}H_{27}O_3Si_2$ (MH^+) 359.1498, found 359.1499 (Δ = 0.1 ppm).

3-((*Z*)-3-Triethylsilyl-2-formylprop-2-enyl)-5-*exo*-(formylmethylene)-1,1-dimethyl-2-oxa-1-silacyclopentane (**4b**): dark orange oil; ^1H NMR ($CDCl_3$) δ 0.28 (s, 3H), 0.34 (s, 3H), 0.72 (q, 6H, J = 7.7 Hz), 0.95 (t, 9H, J = 7.7 Hz), 2.33-2.77 (m, 4H), 4.14 (m, 1H), 6.69 (m, 1H), 6.91 (s, 1H), 9.49 (d,1H, J = 4.12 Hz), 9.71 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -2.6, -2.1, 2.8, 4.8, 37.2, 40.4, 71.1, 132.1, 150.4, 150.6, 169.2, 188.3, 188.9; IR (neat) 1683 (ν_{CO}), 1591 ($\nu_{C=C}$); HRMS (CI) calcd for $C_{17}H_{31}O_3Si_2$ (MH^+) 339.1807 found 339.1812 (Δ = 0.5 ppm).

3-((*Z*)-3-Dimethyl-*tert*-butylsilyl-2-formylprop-2-enyl)-5-*exo*-(formylmethylene)-1,1-dimethyl-2-oxa-1-silacyclopentane (**4c**): dark orange oil; ^1H NMR ($CDCl_3$) δ 0.19 (s, 3H), 0.20 (s, 3H), 0.26 (s, 3H), 0.33 (s, 3H), 0.9 (s, 9H), 2.30-2.77 (m, 4H), 4.12 (m, 1H), 6.68 (m, 1H), 6.97 (s, 1H), 9.48 (d, 1H, J = 4.12 Hz), 9.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -1.2, -0.6, 0.97, 4.8, 26.2, 39.9, 43.0, 73.5, 134.6, 153.4, 190.7, 193.3; IR (neat) 1685 (ν_{CO}), 1592 ($\nu_{C=C}$); HRMS (CI) calcd for $C_{17}H_{31}O_3Si_2$ (MH^+) 339.1811 found 339.1812 (Δ = 0.1 ppm).

General procedure of the reduction of aldehydes 2a or 4 obtained by silylformylation: To a solution of **2a** or **4** (0.36 mmol) in 5 mL of MeOH cooled down to 0 °C, was added $NaBH_4$ (13 mg, 0.36 mmol for **2a** or 26mg, 0.42 mmol for **4**). The reaction mixture was stirred 45 min at this temperature, quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. After evaporation of the solvent alcohols **3a** or **5** was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 30/1).

3-(Propynyl)-5-*exo*-(hydroxyethylidene)-1,1-dimethyl-2-oxa-1-silacyclopentane (**3a**): light orange oil; 70% yield; ^1H NMR ($CDCl_3$) δ 0.25 (s, 3H), 0.27 (s, 3H), 2.07 (t, 1H, J = 2.6 Hz), 2.29-2.62 (m, 4H), 3.81 (m, 1H), 4.53 (d, 2H, J = 1Hz), 6.54 (s (br), 1H); ^{13}C NMR ($CDCl_3$) δ 0.4, 27, 38.3, 69.3, 71.1, 71.3, 80.5, 137.6, 144; HRMS (CI) calcd for $C_{10}H_{17}O_2Si_1$ (MH^+) 197.0995 found 195.0998 (Δ = 0.3 ppm).

3-(3-Dimethylphenylsilyl-2-hydroxymethylprop-2-enyl)-5-*exo*-hydroxyethylidene-1,1-dimethyl-2-oxa-1-silacyclopentane (**5a**) : light orange oil; 56% yield; ^1H NMR ($CDCl_3$) δ 0.26 (s, 3H), 0.27 (s, 3H), 0.39 (s, 6H) 2.26-2.52 (m, 4H), 3.82 (m, 1H), 4.04 (dd, 2H, J_{AB} = 25.82 Hz), 4.53 (s, 2H), 5.68 (s, 1H), 6.51 (s, 1H), 7.34-7.36 (m, 3H), 7.52-7.55 (m, 2H), 9.52 (d, 1H, J = 4.12 Hz), 9.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -0.8, 0.5, 39.6, 46.0, 65.0, 70.6, 71.3, 128.0, 129.1, 129.8, 133.5, 138.3, 143.9, 155.8; HRMS (CI) calcd for $C_{19}H_{31}O_3Si_2$ (MH^+) 363.1807 found 363.1812 ($\Delta = 0.5$ ppm).

3-(3-Triethylsilyl-2-hydroxymethylprop-2-enyl)-5-*exo*-hydroxyethylidene-1,1-dimethyl-2-oxa-1-silacyclopentane (**5b**) : light orange oil; 74% yield; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 3H), 0.36 (s, 3H), 0.61 (q, 6H, J = 7.8 Hz), 0.93 (t, 9H, J = 7.8 Hz), 2.25-2.53 (m, 4H), 3.8 (m, 1H), 4.13 (dd, 2H, J_{AB} = 21.97 Hz), 4.53 (d, 2H, J = 1.6 Hz), 5.42 (s, 1H), 6.51 (s, 1H);^{13}C NMR ($CDCl_3$) δ 0.4, 0.5, 4.7, 7.5, 39.5, 46.4, 65.3, 70.8, 71.3 128.3, 138.3, 143.9, 155.0; HRMS (CI) calcd for $C_{17}H_{35}O_3Si_2$ (MH^+), 343.2124 found 343.2125 ($\Delta = 0.1$ ppm).

3-(3-Dimethyl-*tert*-butylsilyl-2-hydroxymethylprop-2-enyl)-5-*exo*-hydroxy-ethylidene-1,1-dimethyl-2-oxa-1-silacyclopentane (**5c**): light orange oil; 62% yield; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 3H), 0.26 (s, 3H), 0.27 (s, 3H), 0.88 (s, 9H), 2.26-2.53 (m, 4H), 3.82 (m, 1H), 4.16 (dd, 2H, J_{AB} = 28.43 Hz), 4.54 (d, 2H, J = 1.64 Hz), 5.52 (m, 1H), 6.5 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.0, 0.4, 26.3, 39.6, 46.7, 64.9, 71.0, 71.3, 129.2, 138.2, 143.7, 154.8; HRMS (CI) calcd for $C_{17}H_{33}O_3Si_2$ (M^+-H) 341.1963 found 341.1968 ($\Delta = 0.5$ ppm).