Supporting Information For

Ruthenium-Catalyzed Hydrosilylation of 1-Alkynes with Novel Regioselectivity

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Typical Procedure for Ruthenium-Catalyzed Hydrosilylation of 1-Alkynes (Reaction of 1-Heptyne and Trichlorosilane, Table 1, Entry 1)

To a solution of 1-heptyne (0.26 mL, 2.0 mmol) and Cp*$RuH_3(PPh_3)$ (30 mg, 0.06 mmol) in degassed toluene (1.0 mL) was added a solution of $HSiCl_3$ (1.0 *M* in degassed toluene, 3.0 mL, 3 mmol). The mixture was stirred at 80 °C for 24 h under argon. To the clear yellow reaction mixture was added CH_2Cl_2 (10 mL), Et_3N (2.4 mL, 18 mmol) and EtOH (1.0 mL, 18 mmol) at 0 °C, and the suspention was stirred at the same temperature for 1 h. The mixture was filtered through a celite plug and the filtrate was concentrated in vacuo. Bulb-to-bulb distillation of the residue (oven temp. 170 °C, 5 Torr) afforded a mixture of **2** and **3** as pale yellow liquid (410 mg, 79% yield). Preparative GLC of the distilled product (Silicone SE-30, 4.5 mm × 3 m, carrier gas: He (80 mL/min), 150 °C) could separate **2** from **3**. Spectral data of **2** (*si* = $(OEt)_3$): ^{1}H NMR (270 MHz) δ 5.71 (dt, *J*=3.4, 1.5 Hz, 1H), 5.62 (dt, *J*=3.4, 1.0 Hz, 1H), 3.81 (q, *J*=6.9 Hz, 6H), 2.13 (br t, *J*=7.7 Hz, 2H), 1.2–1.5 (m, 6H), 1.22 (t, *J*=6.9 Hz, 9H), 0.8–0.9 (m, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 143.7, 128.8, 58.3, 35.9, 31.6, 28.3, 22.4, 18.0, 13.9; ^{29}Si NMR (53.5 MHz, $CDCl_3$) δ –58.9; IR (neat) 2973, 2927, 1103, 1080, 958, 782 cm^{-1}; Anal. calcd for $C_{13}H_{28}O_3Si$: C, 59.95; H, 10.84. Found: C, 59.86; H, 11.02. The compound **3** consisted of (*E*)- and (*Z*)-isomers, and each of them could not be separated from **2**. The two isomers of **3** were assigned by comparing coupling patterns and constants of vinylic protons in ^{1}H NMR spectra. (*E*)-**3** (*si* = $(OEt)_3$): δ 6.42 (dt, *J*=18.8, 6.2 Hz, 1H), 5.40 (dt, *J*=18.8, 1.5 Hz, 1H) 2.27 (q, *J*=7.4 Hz, 2H). (*Z*)-**3** (*si* = $(OEt)_3$): δ 6.52 (dt, *J*=14.2, 7.4 Hz, 1H), 5.29 (dt, *J*=14.2, 1.3 Hz, 1H). Spectral data of (*E*)-**3** above, especially for vinylic and allylic protons, are comparable with reported ones of (*E*)-1-(triethoxysilyl)-1-butene:[1] ^{1}H NMR (100 MHz) δ *6.51* (dt, *J=19*, *5.6* Hz, 1H), *5.43* (dt, *J=19*, *1.6* Hz, 1H), 3.85 (q, 6H), *2.19* (m, *J=7*, 1.6, 5.6 Hz, 2H), 1.24 (t, 9H), 1.02 (t, 3H).

Spectral Data

2-(Diethoxymethylsilyl)-1-heptene (2 (*si* = $(OEt)_2Me$), Table 1, Entry 2): ^{1}H NMR (270 MHz) δ 5.67 (dt, *J*=3.1, 1.5 Hz, 1H), 5.53 (d, *J*=3.1 Hz), 3.76 (q, *J*=6.9 Hz, 4H), 2.13 (br t, *J*=7.8 Hz, 2H), 1.2–1.5 (m, 6H), 1.21 (t, *J*=6.9 Hz, 6H), 0.88 (m, 3H), 0.18 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 147.6, 127.2, 58.2, 35.5, 31.7, 28.5, 18.3, 14.0, -4.5; ^{29}Si NMR (53.5 MHz, $CDCl_3$) δ –18.1; IR (neat) 2971, 2927, 2875, 1105, 1081, 954, 820, 798, 765 cm^{-1}; Anal. calcd for $C_{12}H_{26}O_2Si$: C, 62.55; H, 11.37. Found: C, 62.46; H, 11.58.

1-(Diethoxymethylsilyl)-1-heptene (3 (*si* = $(OEt)_2Me$), Table 1, Entry 2): The two isomers of **3** were assigned by comparing coupling patterns and constants of vinylic protons in ^{1}H NMR spectra of a mixture of **2** and **3**. (*E*)-**3** (*si* = $(OEt)_2Me$): δ 6.30 (dt, *J*=19.0, 6.3 Hz, 1H), 5.52 (dt, *J*=19.0, 1.5 Hz, 1H). (*Z*)-**3** (*si* = $(OEt)_2Me$): δ 6.44 (dt, *J*=14.3, 7.5 Hz, 1H), 5.36 (dt, *J*=14.3, 1.2 Hz, 1H).

2-(Ethoxydimethylsilyl)-1-heptene (2 (*si* = $(OEt)Me_2$), Table 1, Entry 3): ^{1}H NMR (270 MHz) δ 5.62 (dt, *J*=3.0, 1.6 Hz, 1H), 5.41 (dt, *J*=3.0, 1.0 Hz, 1H), 3.63 (q, *J*=6.9 Hz, 2H), 2.13 (t, *J*=7.9 Hz, 2H), 1.2–1.5 (m, 6H), 1.18 (m, 3H), 0.18 (s, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 150.6, 125.5, 58.3, 35.6, 31.7, 28.6, 22.5, 18.4, 14.0, -2.0; ^{29}Si NMR (53.5 MHz, $CDCl_3$) δ 6.8; IR (neat) 3048, 2960, 2927, 1251, 1160, 1081, 946, 929, 833, 784 cm^{-1}; Anal. calcd for $C_{11}H_{24}OSi$: C, 65.92; H, 12.07. Found: C, 65.74; H, 12.28.

1-(Ethoxydimethylsilyl)-1-heptene (3 (*si* = $(OEt)Me_2$), Table 1, Entry 3): The two isomers of **3** were assigned by comparing coupling patterns and constants of vinylic protons in ^{1}H NMR spectra of a mixture of **2** and **3**. (*E*)-**3** (*si* = $(OEt)Me_2$): δ 6.38 (dt, *J*=18.5, 6.1 Hz). (*Z*)-**3** (*si* = $(OEt)Me_2$): δ 6.44 (dt, *J*=14.3, 7.5 Hz, 1H), 5.36 (dt, *J*=14.3, 1.2 Hz, 1H).

2-(Diethoxymethylsilyl)-1-octene (2 (*si* = $(OEt)_2Me$), Table 1, Entry 4): ^{1}H NMR spectrum of this compound was quite similar to that of 2-(diethoxymethylsilyl)-1-heptene described above. ^{1}H NMR (270 MHz) δ 5.67 (dt, *J*=3.3, 1.6 Hz, 1H), 5.54 (d, *J*=3.3 Hz, 1H), 3.76 (q, *J*=7.0 Hz, 4H), 2.13 (br t, *J*=7.7 Hz, 2H), 1.2–1.5 (m, 8H), 1.21 (t, *J*=7.0 Hz, 6H), 0.88 (m, 3H), 0.19 (s, 3H); IR (neat) 2927, 1081 cm^{-1}.

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[1] Green, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1519–1529.

(*Z*)-1-(Diethoxymethylsilyl)-1-octene (3 (*si* = $(OEt)_2Me$), Table 1, Entry 4): Stereochemistry of (*Z*)-**3** was determined by means of comparing coupling patterns and constants of vinylic protons in ^{1}H NMR spectra of a mixture of **2** and **3** with those of 1-(diethoxymethylsilyl)-1-heptene described above. ^{1}H NMR (270 MHz) δ 6.46 (dt, *J*=14.3, 7.4 Hz, 1H), 5.36 (dt, *J*=14.3, 1.3 Hz, 1H).

4-(Diethoxymethylsilyl)-4-penten-1-yl Acetate (2 (*si* = $(OEt)_2Me$), Table 1, Entry 5): ^{1}H NMR (270 MHz) δ 5.69 (dt, *J*=3.0, 1.5 Hz, 1H), 5.58 (d, *J*=3.0 Hz, 1H), 4.07 (t, *J*=6.7 Hz, 2H), 3.77 (q, *J*=7.0 Hz, 4H), 2.22 (t, *J*=7.9 Hz, 2H), 2.06 (s, 3H), 1.80 (tt, *J*=7.9, 6.7 Hz, 2H), 1.22 (t, *J*=6.9 Hz, 6H), 0.20 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 170.9, 146.1, 127.8, 63.9, 58.0, 31.6, 27.5, 20.7, 18.1, -4.9; IR (neat) 2973, 1743, 1241, 1103, 1078 cm^{-1}; Anal. calcd for $C_{12}H_{24}O_4Si$: C, 55.35; H, 9.29. Found: C, 55.29; H, 9.23.

(*Z*)-5-(Diethoxymethylsilyl)-4-penten-1-yl Acetate (3 (*si* = $(OEt)_2Me$), Table 1, Entry 5): The compound **3** was assigned by comparing coupling patterns and constants of vinylic protons in ^{1}H NMR spectra of a mixture of **2** and **3**. (*Z*)-**3** (*si* = $(OEt)_2Me$): δ 6.42 (dt, *J*=14.1, 7.3 Hz).

3-(Diethoxymethylsilyl)-3-buten-1-yl Acetate (2 (*si* = $(OEt)_2Me$), Table 1, Entry 6): ^{1}H NMR (270 MHz) δ 5.76 (dt, *J*=2.8 Hz, 1H), 5.64 (dt, *J*=2.8 Hz, 1H), 4.18 (t, *J*=7.2 Hz, 2H), 3.77 (q, *J*=7.0 Hz, 4H), 2.48 (ddt, *J*=1.0, 1.0, 7.2 Hz, 2H), 2.03 (s, 3H), 1.21 (t, *J*=7.0 Hz, 6H), 0.20 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 170.9, 143.1, 130.0, 63.6, 58.2, 34.5, 20.9, 18.2, -4.8; IR (neat) 1743, 1103, 1078 cm^{-1}; Anal. calcd for $C_{11}H_{22}O_4Si$: C, 53.62; H, 9.00. Found: C, 53.35; H, 8.70.

(*Z*)-4-(Diethoxymethylsilyl)-3-buten-1-yl Acetate (3 (*si* = $(OEt)_2Me$), Table 1, Entry 6): The compound **3** was assigned by comparing coupling patterns and constants of vinylic protons in ^{1}H NMR spectra of a mixture of **2** and **3**. δ 6.42 (dt, *J*=14.2, 7.1 Hz, 1H), 5.54 (dt, *J*=14.2, 1.4 Hz, 1H).

2-(Diethoxymethylsilyl)-2-propen-1-yl Phenyl Ether (2 (*si* = $(OEt)_2Me$), Table 1, Entry 7): ^{1}H NMR (270 MHz) δ 7.33–7.20 (m, 2H), 6.97–6.85 (m, 3H), 6.04 (dt, *J*=2.6, 1.9 Hz, 1H), 5.76 (dt, *J*=2.9, 1.5 Hz, 1H), 4.66 (s, 2H), 3.82 (q, *J*=6.9 Hz, 4H), 1.24 (t, *J*=7.1 Hz, 6H), 0.28 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 158.6, 142.8, 129.3, 128.5, 120.5, 114.6, 70.5, 58.4, 18.2, -4.4; IR (neat)) 3062, 3041, 2973, 1105, 1081 cm^{-1}; Anal. calcd for $C_{13}H_{28}O_3Si$: C, 63.12; H, 8.32. Found: C, 62.95; H, 8.20.

3-(Diethoxymethylsilyl)-2-propen-1-yl Phenyl Ether (3 (*si* = $(OEt)_2Me$), Table 1, Entry 7): The compound **3** consisted of (*E*)- and (*Z*)-isomers, and each of them could not be separated from **2**. The two isomers of **3** were assigned by comparing coupling patterns and constants of vinylic protons in ^{1}H NMR spectra. (*E*)-**3** (*si* = $(OEt)_2Me$): δ 6.47 (dt, *J*=18.8, 4.2 Hz, 1H), 5.95 (dt, *J*=19.1, 1.8 Hz, 1H). (*Z*)-**3** (*si* = $(OEt)_2Me$): δ 6.66 (dt, *J*=15.1, 5.9 Hz, 1H), 5.68 (dt, *J*=14.7, 1.4 Hz, 1H).

2-(Diethoxymethylsilyl)-2-propen-1-yl 3-Methylbutyl Ether (2 (*si* = $(OEt)_2Me$), Table 1, Entry 8): ^{1}H NMR (270 MHz) δ 5.92 (m, 1H), 5.66 (m, 1H), 4.07 (s, 2H), 3.78 (q, *J*=6.9 Hz, 4H), 3.45 (t, *J*=6.9 Hz, 2H), 1.72 (m, 1H), 1.49 (q, *J*=6.9 Hz, 2H), 1.22 (t, *J*=6.9 Hz, 6H), 0.90 (d, *J*=6.6 Hz, 6H), 0.22 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 144.3, 127.6, 73.7, 68.9, 58.2, 38.5, 25.0, 22.6, 18.2, -4.4; IR (neat) 1103, 1081 cm^{-1}; Anal. calcd for $C_{13}H_{28}O_3Si$: C, 59.95; H, 10.84. Found: C, 59.01; H, 10.85.

3-(Diethoxymethylsilyl)-2-propen-1-yl 3-Methylbutyl Ether (3 (*si* = $(OEt)_2Me$), Table 1, Entry 8: The two isomers of **3** were assigned by comparing coupling patterns and constants of vinylic protons in ^{1}H NMR spectra. (*E*)-**3** (*si* = $(OEt)_2Me$): δ 6.29 (dt, *J*=19.5, 6.1 Hz). (*Z*)-**3** (*si* = $(OEt)_2Me$): δ 6.42 (dt, *J*=14.2, 7.3 Hz, 1H), 5.43 (d, *J*=14.2 Hz, 1H).

1-(Diethoxymethylsilyl)-1-phenylethene (2 (*si* = $(OEt)_2Me$), Table 1, Entry 9): ^{1}H NMR (270 MHz) δ 7.2-7.6 (m, 5H), 6.08 (d, *J*=2.9 Hz, 1H), 5.87 (d, *J*=2.9 Hz), 3.80 (q, *J*=6.9 Hz, 4H), 1.22 (t, *J*=6.9 Hz, 6H), 0.27 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 147.0, 142.5, 130.1, 128.3, 126.8, 58.5, 18.2, -4.2. IR (neat) 3058, 3073, 2973, 1259, 1103, 1078 cm^{-1}. Anal. calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 65.85; H, 8.47.

1-(Diethoxymethylsilyl)-2-phenylethene (3 (*si* = $(OEt)_2Me$), Table 1, Entry 9):The two isomers of **3** were assigned by comparing coupling patterns and constants of vinylic protons in ^{1}H NMR spectra of a mixture of **2** and **3**. Only separable signals are shown below. (*E*)-**3** (*si* = $(OEt)_2Me$): δ 7.11 (d, *J*=19.3 Hz, 1H), 6.31 (d, *J*=19.3 Hz, 1H), 0.29 (s, 3H). (*Z*)-**3** (*si* = $(OEt)_2Me$): δ 7.41 (d, *J*=15.6 Hz, 1H), 5.72 (d, *J*=15.6 Hz, 1H), 0.10 (s, 3H).

(*E*)-1-(Diethoxymethylsilyl)-3,3-dimethyl-1-butene (3 (*si* = $(OEt)_2Me$), Table 1, Entry 10): ^{1}H NMR (270 MHz) δ 6.29 (d, *J*=19.1 Hz, 1H), 5.43 (d, *J*=19.1 Hz, 1H), 3.76 (q, *J*=7.0 Hz, 4H), 1.22 (t, *J*=7.0 Hz, 6H), 1.01 (s, 9H), 0.18 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 161.9, 116.7, 58.1, 35.2, 28.8, 18.3, -4.3; IR (neat) 1079, 804 cm^{-1}.

2-(Diethoxymethylsilyl)-3,3-dimethyl-1-butene (2 (*si* = $(OEt)_2Me$), Table 1, Entry 10): The compound **2** was assigned by comparing coupling patterns and constants of vinylic protons in ^1H NMR spectra of a mixture of **2** and **3**. ^1H NMR (270 MHz) δ 5.73 (d, *J*=2.1 Hz, 1H), 5.55 (d, *J*=2.1 Hz, 1H), 3.75 (q, *J*=7.0 Hz, 4H), 1.22 (m, 6H) 1.11 (s, 9H), 0.22 (s, 3H).

1-(Diethoxymethylsilyl)-1-(trimethylsilyl)ethene (2 (*si* = $(OEt)_2Me$), Table 1, Entry 11): ^1H NMR (270 MHz) δ 6.48 (d, *J*=5.2 Hz, 1H), 6.37 (d, *J*=5.2 Hz), 3.73 (q, *J*=7.0 Hz, 4H), 1.20 (t, *J*=7.0 Hz, 6H), 0.16 (s, 3H), 0.09 (s.9H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 150.4, 143.1, 58.0, 18.2, -0.9, -3.8; IR (neat) 1105, 1079 cm^{-1};

(*E*)-1-(Diethoxymethylsilyl)-2-(trimethylsilyl)ethene (3 (*si* = $(OEt)_2Me$), Table 1, Entry 11): The compound **3** was assigned by comparing coupling patterns and constants of vinylic protons in ^1H NMR spectra of a mixture of **2** and **3**. ^1H NMR (270 MHz) δ 6.85 (d, *J*=22.9 Hz, 1H), 6.43 (d, *J*=22.9 Hz, 1H), 3.77 (q, *J*=6.9 Hz, 4H), 1.22 (t, *J*=6.9 Hz, 6H), 0.19 (s, 3H), 0.06 (s, 9H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 155.8, 143.3, 58.2, 18.2, -1.7, -4.9.