Efficient and Rapid C–Si Bond Cleavage in Supercritical Water

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General. ^1H and ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (^1H 300 MHz, ^{13}C 75 MHz) and JEOL A-500 (^1H 500 MHz, ^{13}C 125 MHz) spectrometers in CDCl_3 with chemical shifts referenced to internal standards (7.26 ppm ^1H , 77.0 ppm ^{13}C). EI and CI mass spectra were recorded on JMS-SX102A spectrometer. FAB mass spectra were recorded on JMS-HX110A spectrometer. Infrared spectra were recorded on Shimadzu FTIR-8100 spectrophotometer. Gel permeation chromatography was carried out with Japan Analytical Industry LC-918. Unless otherwise noted, all materials, anhydrous tetrahydrofuran (THF), and anhydrous diethyl ether (Et_2O) were obtained from commercial suppliers and used without further purification. Acetonitrile (CH_3CN) and triethylamine (Et_3N) were distilled over CaH_2 . *N,N*-Dimethylformamide (DMF) was distilled over P_2O_{10} . Ethyl acetate (EtOAc) was distilled over K_2CO_3 . *Cautionary Notes:* Although we have never experienced an accident, all reactions in supercritical water should be performed with great care due to the high temperature/pressure conditions.

Typical Procedure for the Reaction of Organosilicon Compounds in Supercritical Water. Unless otherwise noted, all reactions were performed in quartz amples placed in a stainless steel tube container in order to avoid any influence of stainless reactor (Houser's technique).¹ Quartz amples (inside diameter: 4.5 mm; thickness: 0.7 mm) of approximately 3 mL in total volume were used as the reactor vessels. An ample was filled with 0.1 mmol of organosilicon compound and 420 mg of water. After three freeze-pump-thaw cycles, the ample was immediately flame sealed and placed in a SUS316 stainless steel tube (volume: 11.85 mL; long: 145 mm; outside diameter: 12.7 mm). The stainless tube was used as a container to hold the ample during heating. To avoid breakage of the quartz ample due to the pressure increase, a calculated amount of water was added to the stainless tube to maintain balanced pressure. The temperature was monitored by a thermocouple inserted through the top end of the stainless tube container. The stainless tube was submerged in a dissolved salt bath ($\text{NaNO}_2/\text{KNO}_3$) whose temperature was controlled. After the specified time, the tube was removed and cooled in an ice bath. The reaction products were analyzed by standard methods such as capillary GC, GC-MS, and NMR. As for silicon-containing product, we observed the formation of silica-like solid after the reactions, although it has not been identified yet.

The reactions using **3** and **4** were carried out directly in the stainless reactor (SUS316).

(1) Houser, T. J.; Liu, X. *J. Supercrit. Fluids* **1996**, *9*, 167.

Synthesis of Starting Organosilicon Compounds.

(4-Butylphenyl)trimethylsilane (2)

To a solution of 1,4-dibromobenzene (12.76 g, 50.0 mmol) in Et₂O (100 mL) was added a solution of BuLi (50.0 mmol, 1.53 M) in hexane at -78°C and the reaction mixture was stirred at -78°C for 4 h. To this mixture was added chlorotrimethylsilane (6.18 g, 56.8 mmol) at -78°C and the reaction mixture was stirred for 10 min. After the mixture was stirred at room temperature for 2 h, H₂O was added to the mixture and organic phase was separated. The aqueous phase was extracted with Et₂O (three times) and the combined organic phase was washed with brine. Drying over MgSO₄ and removal of the solvents under reduced pressure afforded (4-bromophenyl)trimethylsilane quantitatively.

To a solution of (4-bromophenyl)trimethylsilane (5.63 g, 24.7 mmol) in THF (50 mL) was added a solution of BuLi (29.6 mmol, 1.53 M) in hexane at room temperature. After the mixture was stirred at room temperature for 2 h, H₂O was added to the mixture and organic phase was separated. The aqueous phase was extracted with Et₂O (three times) and the combined organic phase was dried over MgSO₄. Removal of the solvents under reduced pressure and subsequent distillation afforded **2** (3.04 g, 60%) as colorless liquid: Bp $136^\circ\text{C}/27 \text{ mmHg}$. ¹H NMR (300 MHz) δ 0.25 (s, 9H), 0.93 (t, $J = 7.5 \text{ Hz}$, 3H), 1.30–1.45 (m, 2H), 1.55–1.65 (m, 2H), 2.60 (t, $J = 7.5 \text{ Hz}$, 2H), 7.19 (d, $J = 7.8 \text{ Hz}$, 2H), 7.44 (d, $J = 7.8 \text{ Hz}$, 2H). ¹³C NMR (75 MHz) δ -1.1 , 14.0 , 22.4 , 33.6 , 35.6 , 127.9 , 133.3 , 137.0 , 143.6 . HRMS (EI) m/z calcd for C₁₃H₂₂Si: 206.1491, found 206.1493. Anal. Calcd for C₁₃H₂₂Si: C, 75.65; H, 10.74. Found: C, 75.95; H, 10.84.

(*E*)-1-Dodecenyltrimethylsilane (3)

Compound **3** was prepared using the procedure developed by Chan.²

To a suspension of KOBu^t (8.41 g, 74.9 mmol) in hexane (40 mL) was added a solution of BuLi (75.0 mmol, 1.57 M) in hexane at 0°C and the mixture was stirred at 0°C for 10 min and at room temperature for 35 min. To this mixture were added Et₂O (50 mL) and allyltrimethylsilane (8.70 g, 76.1 mmol) at -78°C . After the mixture was stirred at 0°C for 1 h, a solution of 1-bromononane (15.63 g,

(2) Koumaglo, K.; Chan, T. H. *Tetrahedron Lett.* **1984**, 25, 717.

75.4 mmol) in Et₂O (20 mL) was added to the mixture at -78 °C. After the mixture was stirred at room temperature for 14 h, H₂O was added to the mixture and organic phase was separated. The organic phase was washed with *aq* Na₂S₂O₃ solution. Drying over MgSO₄ and removal of the solvents under reduced pressure afforded **3** (8.69 g, 48%) as colorless liquid: ¹H NMR (300 MHz) δ 0.04 (s, 9H), 0.88 (t, *J* = 6.9 Hz, 3H), 1.20–1.45 (m, 16H), 2.09 (td, *J* = 6.9, 6.3 Hz, 2H), 5.61 (dt, *J* = 18.3, 1.5 Hz, 1H), 6.02 (dt, *J* = 18.3, 6.3 Hz, 1H). ¹³C NMR (125 MHz) δ -1.1, 14.1, 22.7, 28.7, 29.2, 29.4, 29.5, 29.63, 29.64, 31.9, 36.8, 129.4, 147.4. HRMS (EI) *m/z* calcd for C₁₅H₃₂Si: 240.2273, found 240.2274. Anal. Calcd for C₁₅H₃₂Si: C, 74.91; H, 13.41. Found: C, 74.61; H, 13.70.

2-Dodecenyltrimethylsilane (**4**)

Compound **4** was prepared using the procedure developed by Tsuji.³

To a solution of vinylmagnesium bromide (60.0 mmol, 1.0 M) in THF was added decanal (7.86 g, 50.3 mmol) at 0 °C. After the mixture was stirred at 0 °C for 1 h and then at room temperature for 66 h, *aq* HCl solution was added to the mixture and organic phase was separated. The aqueous phase was extracted with Et₂O (four times). The combined organic phase was dried over MgSO₄. The removal of the solvents under reduced pressure and subsequent distillation afforded dodec-1-en-3-ol (7.92 g, 86%) as colorless liquid: Bp 82 °C/1.2 mmHg. ¹H NMR (300 MHz) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.15–1.40 (m, 14H), 1.45–1.60 (m, 3H), 4.09 (qt, *J* = 6.6, 1.2 Hz, 1H), 5.10 (dt, *J* = 10.5, 1.5 Hz, 1H), 5.22 (dt, *J* = 17.1, 1.5 Hz, 1H), 5.87 (ddd, *J* = 17.1, 10.5, 6.6 Hz, 1H).

To a solution of dodec-1-en-3-ol (9.22 g, 50.0 mmol), triethylamine (6.07 g, 60.0 mmol), and 4-(dimethylamino)pyridine (619 mg, 5.07 mmol) in CH₂Cl₂ (50 mL) was added trifluoroacetic anhydride (13.01 g, 61.9 mmol) at 0 °C. After the mixture was stirred at 0 °C for 2 h and then at room temperature for 2 h, H₂O was added to the mixture and organic phase was separated. The aqueous phase was extracted with CH₂Cl₂ (four times). The combined organic phase was dried over MgSO₄. The removal of the solvents under reduced pressure and subsequent distillation afforded 3-trifluoroacetoxy-1-dodecene (11.40 g, 81%) as colorless liquid: Bp 69 °C/1.1 mmHg. ¹H NMR (300 MHz) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.15–1.40 (m, 14H), 1.60–1.85 (m, 2H), 5.29 (d, *J* = 10.5 Hz, 1H), 5.35 (d, *J* = 17.4 Hz, 1H), 5.37 (q, *J* = 6.9 Hz, 1H), 5.80 (ddd, *J* = 17.4, 10.5, 6.9 Hz, 1H).

A solution of Pd(dba)₂ (345 mg, 0.60 mmol, 3 mol%), hexamethyldisilane (5.85 g, 40.0 mmol), and 3-trifluoroacetoxy-1-dodecene (5.63 g, 20.1 mmol) in THF (110 mL) was stirred at room temperature for 6 h. The removal of the solvents under reduced pressure and subsequent distillation afforded **4** (4.20 g,

87%, *E/Z* = 92/8) as colorless liquid: Bp 85–86 °C/0.8 mmHg. ¹H NMR (300 MHz) δ –0.02 (s, 9H), 0.88 (t, *J* = 6.9 Hz, 3H), 1.20–1.35 (m, 14H), 1.39 (d, *J* = 7.5 Hz, 2H), 1.96 (q, *J* = 6.9 Hz, 2H), 5.23 (dt, *J* = 15.1, 6.9 Hz, 1H), 5.36 (dt, *J* = 15.1, 7.5 Hz, 1H). ¹³C NMR (75 MHz) δ –2.0, 14.1, 22.6, 22.7, 29.1, 29.4, 29.5, 29.6, 30.0, 31.9, 32.8, 125.9, 129.0. HRMS (EI) *m/z* calcd for C₁₅H₃₂Si: 240.2273, found 240.2273

1-Dodecyldimethylsilanol (5)

Compound **5** was prepared using the procedure developed by Chang.⁴

To a suspension of Li (596 mg, 85.2 mmol) in Et₂O (20 mL) was added a solution of 1-bromododecane (10.63 g, 42.6 mmol) in Et₂O (30 mL) at 0 °C. The reaction mixture was stirred for 4 h, and chlorodimethylsilane (4.34 g, 45.9 mmol) was added to the mixture at 0 °C. After stirring the mixture at room temperature for 14 h, H₂O was added to the mixture and organic phase was separated. The organic phase was washed with brine. The aqueous phase was extracted with Et₂O (three times) and the combined organic phase was dried over MgSO₄. Removal of the solvents under reduced pressure and subsequent distillation afforded 1-dodecyldimethylsilane (6.24 g, 64%) as colorless liquid: Bp 84 °C/0.8 mmHg. ¹H NMR (300 MHz) δ 0.05 (d, *J* = 3.6 Hz, 6H), 0.50–0.62 (m, 2H), 0.88 (t, *J* = 6.9 Hz, 3H), 1.20–1.40 (m, 20H), 3.83 (heptet, *J* = 3.6 Hz, 1H).

The mixture of 1-dodecyldimethylsilane (6.23 g, 27.3 mmol), [RuCl₂(*p*-cymene)]₂ (334 mg, 0.55 mmol, 2 mol%), and H₂O (970 mg, 54.5 mmol) in CH₃CN (82 mL) was stirred at room temperature for 4 h under air. Removal of the solvents under reduced pressure and subsequent distillation afforded **5** (3.97 g, 60%) as colorless liquid: Bp 109 °C/0.8 mmHg. ¹H NMR (300 MHz) δ 0.12 (s, 6H), 0.55–0.63 (m, 2H), 0.88 (t, *J* = 6.9 Hz, 3H), 1.20–1.40 (m, 21H). ¹³C NMR (125 MHz) δ –0.3, 14.1, 17.8, 22.7, 23.1, 29.36, 29.38, 29.58, 29.65, 29.68, 29.7, 31.9, 33.4. HRMS (CI) *m/z* calcd for C₁₄H₃₃OSi [M+H]: 245.2301, found 245.2293.

Chloro(1-dodecyl)dimethylsilane (6)

To a solution of dichlorodimethylsilane (21.4 g, 165.8 mmol) in THF (40 mL) was added a solution of 1-dodecylmagnesium bromide (78 mmol, 1.56 M) in THF at room temperature. After stirring the

(3) Tsuji, Y.; Funato, M.; Ozawa, M.; Ogiyama, H.; Kajita, S.; Kawamura, T. *J. Org. Chem.* **1996**, *61*, 5779.

(4) Lee, M.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2000**, *122*, 12011.

mixture at room temperature for 16 h, hexane (60 mL) was added to the mixture. Filtration through Celite®, removal of the solvents under reduced pressure, and distillation afforded **6** (17.6 g, 86%) as colorless liquid: Bp 105 °C/0.25 mmHg. ¹H NMR (300 MHz) δ 0.40 (s, 6H), 0.75–0.85 (m, 2H), 0.88 (t, *J* = 6.9 Hz, 3H), 1.20–1.45 (m, 20H). ¹³C NMR (125 MHz) δ 1.7, 14.1, 19.0, 22.7, 23.0, 29.3, 29.4, 29.5, 29.66, 29.68, 29.69, 31.9, 33.0. HRMS (EI) *m/z* calcd for C₁₄H₃₁SiCl: 262.1884, found 262.1885.

1-Dodecyl(ethoxy)dimethylsilane (**7**)

To a solution of imidazole (1.71 g, 25.2 mmol) and ethanol (1.18 g, 25.6 mmol) in DMF (45 mL) was added **6** (6.67 g, 25.4 mmol) at 0 °C. After stirring the mixture at room temperature for 19 h, brine was added to the mixture and organic phase was separated. The aqueous phase was extracted with Et₂O (three times) and the combined organic phase was dried over MgSO₄. Removal of the solvents under reduced pressure and subsequent distillation afforded **7** (3.97 g, 57%) as colorless liquid: Bp 102 °C/1.1 mmHg. ¹H NMR (300 MHz) δ 0.08 (s, 6H), 0.50–0.62 (m, 2H), 0.87 (t, *J* = 6.6 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.20–1.40 (m, 20H), 3.65 (q, *J* = 7.2 Hz, 2H). ¹³C NMR (125 MHz) δ –2.1, 14.1, 16.4, 18.5, 22.7, 23.2, 29.4 (two carbons), 29.59, 29.66, 29.69, 29.71, 31.9, 33.5, 58.2. IR (neat) 2957, 2924, 2855, 1466, 1458, 1250, 1109, 1082, 947, 839, 779 cm^{–1}. HRMS (CI) *m/z* calcd for C₁₆H₃₇OSi [M+H]: 273.2614, found 273.2614.

1,3-Di(1-dodecyl)-1,1,3,3-tetramethyldisiloxane (**8**).

To a solution of **5** (717 mg, 2.93 mmol) and triethylamine (296 mg, 2.93 mmol) in EtOAc (3 mL) was added **6** (828 mg, 2.93 mmol) at room temperature. After stirring the mixture at room temperature for 22 h, H₂O was added to the mixture and organic phase was separated. The aqueous phase was extracted with Et₂O (five times) and the combined organic phase was dried over MgSO₄. Removal of the solvents under reduced pressure and subsequent silica gel chromatography (hexane) afforded **8** (1.13 g, 82%) as colorless oil: ¹H NMR (300 MHz) δ 0.02 (s, 12H), 0.45–0.55 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 6H), 1.20–1.35 (m, 40H). ¹³C NMR (125 MHz) δ 0.4, 14.1, 18.4, 22.7, 23.3, 29.40, 29.45, 29.65, 29.70, 29.74, 29.76, 32.0, 33.5. HRMS (CI) *m/z* calcd for C₂₈H₆₃OSi₂ [M+H]: 471.4417, found 471.4423.

1-(1-Dodecyl)-1,1,2,2,2-pentamethyldisilane (**9**).

To a suspension of Mg (609 mg, 25.1 mmol) in Et₂O (7 mL) was added a solution of 1-bromododecane (6.31 g, 25.3 mmol) in Et₂O (6 mL) at 0 °C and the mixture was stirred at room temperature for 4 h. Chloropentamethyldisilane (4.19 g, 25.1 mmol) was then added to the reaction mixture at room temperature. After stirring the mixture at room temperature for 12 h, *aq* HCl solution was added to the reaction mixture and organic phase was separated. The aqueous phase was extracted with Et₂O (five times) and the combined organic phase was dried over MgSO₄. Removal of the solvents under reduced pressure and subsequent distillation afforded **9** (4.10 g, 54%) as colorless liquid: Bp 121 °C/1.1 mmHg. ¹H NMR (300 MHz) δ 0.01 (s, 6H), 0.04 (s, 9H), 0.50–0.60 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H), 1.20–1.35 (m, 20H). ¹³C NMR (125 MHz) δ –4.3, –2.0, 14.1, 14.9, 22.7, 24.6, 29.4 (two carbons), 29.64, 29.68, 29.71, 29.73, 31.9, 33.8. HRMS (EI) *m/z* calcd for C₁₇H₄₀Si₂: 300.2669, found 300.2666.

1-Dodecyltrimethylsilane (10).

To a suspension of Li (418 mg, 60.2 mmol) in Et₂O (10 mL) was added a solution of 1-bromododecane (7.63 g, 30.6 mmol) in Et₂O (10 mL) at 0 °C and the mixture was stirred at 0 °C for 2 h. Chlorotrimethylsilane (3.80 g, 35.0 mmol) was then added to the reaction mixture at 0 °C. After stirring the mixture at room temperature for 10 h, H₂O was added to the reaction mixture and organic phase was separated. The aqueous phase was extracted with Et₂O (three times) and the combined organic phase was dried over Na₂SO₄. Removal of the solvents under reduced pressure and subsequent distillation afforded **10** (2.28 g, 31%) as colorless liquid: Bp 86 °C/1.0 mmHg. ¹H NMR (300 MHz) δ –0.04 (s, 9H), 0.42–0.50 (m, 2H), 0.88 (t, *J* = 6.9 Hz, 3H), 1.20–1.35 (m, 20H). ¹³C NMR (75 MHz) δ –1.6, 14.1, 16.7, 22.7, 23.9, 29.39, 29.43, 29.64, 29.67, 29.70, 29.74, 31.9, 33.7. HRMS (EI) *m/z* calcd for C₁₄H₃₁Si [M–Me]: 227.2195, found 227.2197. Anal. Calcd for C₁₅H₃₄Si: C, 74.29; H, 14.13. Found: C, 74.45; H, 14.26.

2-Dodecyltrimethylsilane (11).

To a suspension of Mg (246 mg, 10.1 mmol) in THF (3 mL) were added a few drops of 1,2-dibromoethane and then a solution of 2-bromododecane (2.49 g, 10.0 mmol) in THF (3 mL) at room temperature and the mixture was stirred at room temperature for 1 h. Chlorotrimethylsilane (1.20 g, 11.0 mmol) and CuCN⁵ (50.2 mg, 0.55 mmol) were then added to the reaction mixture at 0 °C. After stirring the mixture at room temperature for 16 h, *aq* NaOH solution was added to the reaction mixture at 0 °C and organic phase was separated. The aqueous phase was extracted with Et₂O (three times) and the combined organic phase was dried over MgSO₄. Removal of the solvents under reduced pressure and subsequent gel permeation chromatography afforded **11** (534 mg, 22%) as colorless liquid: ¹H NMR (500 MHz) δ -0.07 (s, 9H), 0.51–0.58 (m, 1H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H), 1.00–1.30 (m, 18H). ¹³C NMR (125 MHz) δ -3.2, 14.0, 14.1, 19.5, 22.7, 28.6, 29.4, 29.67, 29.71, 29.75, 29.83, 31.7, 31.9. IR (neat) 2955, 2855, 1489, 1466, 1248, 855, 833, 749, 689 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₅H₃₄Si: 242.2430, found 242.2435. Anal. Calcd for C₁₅H₃₄Si: C, 74.29; H, 14.13. Found: C, 74.18; H, 13.90.

1-Dodecyltriethylsilane (**12**).

To a suspension of Li (406 mg, 58.5 mmol) in Et₂O (10 mL) was added a solution of 1-bromododecane (7.25 g, 29.1 mmol) in Et₂O (10 mL) at 0 °C and the mixture was stirred at 0 °C for 2 h. Chlorotriethylsilane (4.87 g, 32.3 mmol) was then added to the reaction mixture at 0 °C. After stirring the mixture at room temperature for 16 h, H₂O was added to the reaction mixture and organic phase was separated. The aqueous phase was extracted with Et₂O (three times) and the combined organic phase was dried over MgSO₄. Removal of the solvents under reduced pressure and subsequent distillation afforded **12** (5.08 g, 61%) as colorless liquid: Bp 114 °C/1.0 mmHg. ¹H NMR (300 MHz) δ 0.45–0.48 (m, 2H), 0.49 (q, *J* = 7.8 Hz, 6H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 7.8 Hz, 9H), 1.20–1.30 (m, 20H). ¹³C NMR (125 MHz) δ 3.4, 7.5, 11.3, 14.1, 22.7, 23.9, 29.4 (two carbons), 29.66, 29.69, 29.73, 29.76, 32.0, 34.0. HRMS (EI) *m/z* calcd for C₁₆H₃₅Si [M–Et]: 255.2508, found 255.2504.

1-Dodecyltriisopropylsilane (**13**).

To a suspension of Li (283 mg, 40.8 mmol) in Et₂O (8 mL) was added a solution of 1-bromododecane

(5) Lennon, P. J.; Mack, D. P.; Thompson, Q. E. *Organometallics* **1989**, *8*, 1121.

(5.08 g, 20.4 mmol) in Et₂O (8 mL) at 0 °C and the mixture was stirred at 0 °C for 3 h. To this mixture were added triisopropylsilyl triflate (6.87 g, 22.4 mmol) and then hexamethylphosphoramide (8 mL) at 0 °C. After stirring the mixture at 0 °C for 2 h and then at room temperature for 15 h, H₂O was added to the reaction mixture and organic phase was separated. The aqueous phase was extracted with Et₂O (three times) and the combined organic phase was dried over MgSO₄. Filtration through a short silica gel pad (hexane), removal of the solvents under reduced pressure, and subsequent distillation afforded **13** (1.51 g, 23%) as colorless liquid: Bp 132 °C/0.9 mmHg. ¹H NMR (300 MHz) δ 0.50–0.60 (m, 2H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.95–1.00 (m, 3H), 1.02 (s, 18H), 1.20–1.40 (m, 20H). ¹³C NMR (125 MHz) δ 9.4, 11.0, 14.1, 18.9, 22.7, 24.3, 29.3, 29.4, 29.68 (two carbons), 29.73, 29.74, 32.0, 34.5. IR (neat) 2959, 2924, 1464, 884, 733, 693, 656 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₈H₃₉Si [M–Pr]: 283.2821, found 283.2813. Anal. Calcd for C₂₁H₄₆Si: C, 77.21; H, 14.19. Found: C, 77.04; H, 14.45.

Tetra(1-dodecyl)silane (**14**).

To a suspension of Li (304 mg, 43.8 mmol) in Et₂O (10 mL) was added a solution of 1-bromododecane (5.51 g, 22.1 mmol) in Et₂O (10 mL) at 0 °C and the mixture was stirred at 0 °C for 5 h. To this mixture was added tetrachlorosilane (538 mg, 3.17 mmol) at 0 °C. After stirring the mixture at 0 °C for 1 h and then at room temperature for 70 h, H₂O was added to the reaction mixture and organic phase was separated. The aqueous phase was extracted with Et₂O (three times) and the combined organic phase was dried over MgSO₄. Removal of the solvents under reduced pressure, and subsequent gel permeation chromatography afforded **14** (1.81 g, 81%) as colorless oil. ¹H NMR (300 MHz) δ 0.40–0.50 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 12H), 1.20–1.35 (br, 80H). ¹³C NMR (125 MHz) δ 12.5, 14.1, 22.7, 23.9, 29.34, 29.40, 29.66, 29.70, 29.74, 29.76, 32.0, 33.9. IR (neat) 2922, 2853, 1466, 766, 722 cm⁻¹. HRMS (EI) *m/z* calcd for C₃₆H₇₅Si [M–C₁₂H₂₅]: 535.5638, found 535.5637.