New and Efficient One-Pot Procedure for the Preparation of Unsymmetrical Silicon Tethers

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Supporting Information

General Methods. Reactions were carried out under argon, with magnetic stirring and degassed solvents when necessary unless otherwise noted. Ether and THF were distilled from sodium/benzophenone under nitrogen before use. CH_2Cl_2 , toluene and DMF were dried and distilled from CaH_2 . Propargylic and allylic alcohols were distilled under reduced pressure after drying over K_2CO_3 and filtering. Solid reagents were dried *in vacuo* (0.5 to 0.1 mmHg). - Thin layer chromatography (TLC) was performed on Merck 60 F₂₅₄ silica gel. Merck Geduran SI 60 A silica gel (35-70 μm) was used for column chromatography according to Still's method.¹ PE and EE refer to petroleum ether and Et_2O . Chemical shifts are given in ppm, referenced to the residual proton resonances of the solvents ($\delta = 7.26$ for CDCl_3 ; $\delta = 7.16$ for C_6D_6). Coupling constants (J) are given in Hertz (Hz). The terms m, s, d, t, q, quint refer to multiplet, singlet, doublet, triplet, quartet, quintet; br means that the signal is broad. - Elemental analysis were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie - Low resolution mass spectra (MS) and high resolution mass spectra (HRMS) were measured by Service de spectrométrie de masse de l'Ecole Normale Supérieure – Paris.

General procedure for the preparation of the silaketals

To a solution of 10 mmol of alcohol **1a-e** (1 equiv) in 10 mL of CH_2Cl_2 were added triethylamine (11 mmol, 1.1 equiv), 122 mg of DMAP (1 mmol, 0.1 equiv) and 1.7 mL of chlorodiisopropylsilane (1.51 g, 10 mmol, 1 equiv) or 1.1 mL of chlorodimethylsilane (0.94 g, 10 mmol, 1 equiv). The mixture was stirred at room temperature until completion of the reaction by TLC. This solution was then transferred under argon with filtration in another flask and NBS (1.96 g, 11 mmol, 1.1 equiv) was added slowly. The resulting mixture was stirred until completion of the reaction by TLC. Finally the preceding solution was added to a solution of 10 mmol of alcohol **4a-c** (1 equiv) in presence of 1.53 mL of triethylamine (11 mmol, 1.1 equiv), and 122 mg of DMAP (1 mmol, 0.1 equiv) in 10 mL of CH_2Cl_2 . The mixture was stirred at room temperature until completion of the reaction by TLC.

After concentration *in vacuo*, the residue was precipitated in pentane and filtered on a silica gel pad (EP/EE 95/5) and furnished the silaketals **5a-d** or **6** as colorless oils.

Allyloxy-(4-*tert*-butylphenoxy)-diisopropylsilane (5a): 2.72 g ; 85%.

¹ Still, W. C.; Khan, M.; Mitra, A. J. *J. Org. Chem.* **1978**, 43, 2423-2425.

Allyloxy-diisopropyl-(3-phenyl-allyloxy)-silane (5b): 2.62 g; 86%.

(5,5-Bis-methoxymethyl-octa-2,7-diynyloxy)-but-2-ynyloxy-diisopropyl-silane (5c): 2.78 g; **71 %**.

¹H NMR (400MHz, CDCl₃) δ 4.44 (br s, 2H), 4.40 (br s, 2H), 3.34 (s, 4H), 3.33 (s, 6H), 2.37 (s, 2H), 2.33 (s, 2H), 1.97 (t, *J* = 2.3 Hz, 1H), 1.84 (s, 3H), 1.07-1.02 (m, 14H). ¹³C NMR (100MHz,

CDCl_3) δ 81.4, 80.8 (2C), 80.6, 77.4, 73.6 (2C), 70.4, 59.3 (2C), 51.7 (2C), 41.8, 22.2, 21.9, 17.2 (4C), 12.2 (2C), 3.6. Anal. Calcd for $\text{C}_{22}\text{H}_{36}\text{O}_4\text{Si}$: C, 67.30; H, 9.24. Found: C, 67.19; H, 9.54.

Silaketal (5d): 1.62 g; **52%** (the reaction was carried out with 3.8 mmol)

^1H NMR (400MHz, CDCl_3) δ 7.79-7.71 (m, 4H), 7.45-7.38 (m, 6H), 5.11 (s, 1H), 4.44 (br s, 4H), 4.32 (t, $J = 1.2$ Hz, 1H), 2.37-2.22 (m, 10H), 1.82 (s, 3H), 1.70 (s, 3H), 1.66 (s, 3H), 1.10 (br s, 23H), 0.99 (t, $J = 6$ Hz, 3H), 0.92 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (100MHz, CDCl_3) δ 155.8, 139.4, 136.1 (2C), 135.9 (2C), 134.2, 134.0, 129.7, 129.6, 127.6 (2C), 127.3 (2C), 125.2, 124.8 (2C), 85.7, 83.8, 83.6, 82.4, 79.2, 78.2, 65.3, 51.8, 51.7, 31.7 (2C), 30.3, 27.0 (3C), 26.6 (2C), 21.9, 19.6, 19.4, 19.0, 18.1, 17.3 (4C), 12.2 (2C), 9.4 (3C), -4.1 (2C). IR (neat) 3000, 2940, 2320, 1590, 1050, 690 cm^{-1} . HRMS: Calcd. for $\text{C}_{50}\text{H}_{76}\text{O}_3\text{Si}_3$: 826.54 (MNH_4^+); Found 826.54.

But-2-ynyloxy-(2-isopropyl-5-methyl-cyclohexyloxy)-dimethyl-silane (6):

2.29 g; **81%**.

^1H NMR (400MHz, CDCl_3) δ 4.31 (m, 2H), 3.53 (m, 1H), 2.18 (m, 1H), 1.94 (m, 1H), 1.82 (m, 3H), 1.61 (m, 2H), 1.35 (m, 1H), 1.2-1.02 (m, 3H), 0.90-0.83 (m, 7H), 0.75 (d, $J = 5.8$ Hz, 3H), 0.16 (s, 6H). ^{13}C NMR (100MHz, CDCl_3) δ 81.0, 77.3, 72.6, 51.0, 49.9, 45.5, 34.5, 31.7, 25.4, 22.9, 22.3, 21.2, 15.9, 3.6, -2.1, -2.3. IR (neat) 2950, 2250, 1490, 1400, 1280, 1050 cm^{-1} .

Anal. Calcd for $\text{C}_{16}\text{H}_{30}\text{O}_2\text{Si}$: C, 68.03; H, 10.70. Found: C, 67.85; H, 10.84.

Preparation of of the Di-tert-butylsilaketal 8 and Silanol 9

To a solution of 1.50 g of 4-*tert*-butylphenol (10 mmol, 1 equiv) in 10 mL of CH₂Cl₂ were added 1.53 mL of triethylamine (11 mmol, 1.1 equiv), 122 mg of DMAP (1 mmol, 0.1 equiv) and 1.5 g of di-*tert*-butylchlorosilane (10 mmol, 1 equiv). The mixture was stirred at room temperature until completion of the reaction by TLC. This solution was then transferred under argon with filtration in another flask and NBS (1.96 g, 11 mmol, 1.1 equiv) was added slowly. The resulting mixture was stirred until completion of the reaction by TLC.

Finally the preceding solution was added, under argon, to a solution of 0.68 mL of allylic alcohol (10 mmol, 1 equiv), and 3.05 g of DMAP (25 mmol, 2.5 equiv) in 10 mL of DMF. The mixture was stirred at room temperature until completion of the reaction by TLC. The solution was diluted in Et₂O, washed with brine, dried over MgSO₄, filtered and concentrated. The crude oil was purified by flash chromatography (PE/EE 95/5) and furnished 2.09 g of silaketal **8** (60 %) as a colorless oil and 1.23g of silanol **9** (40%).

Allyloxy-di-*tert*-butyl-(4-*tert*-butylphenoxy)-silane (8) :

¹H NMR (400MHz, CDCl₃) δ 7.30 (m, 2H), 6.97 (m, 2H), 6.05 (m, 1H), 5.50 (d, *J* = 15.4 Hz, 1H), 5.25 (d, *J* = 8.8 Hz, 1H), 4.58 (m, 2H), 1.32 (s, 9H), 1.18 (s, 18H). ¹³C NMR (100MHz, CDCl₃) δ 153.4, 143.8, 137.0, 126.1 (2C), 119.1 (2C), 114.0, 65.0, 34.2, 31.7 (3C), 28.0 (6C), 21.6 (2C). IR (neat) 3300, 2950, 2100, 1600, 1500, 1440, 1250, 1065 cm⁻¹. Anal. Calcd for C₂₁H₃₆O₂Si: C, 72.35; H, 10.41. Found: C, 72.16; H, 10.48.

Di-*tert*-butyl-(4-*tert*butylphenoxy)silanol (9)

¹H NMR (400MHz, CDCl₃) δ 7.29 (m, 2H), 6.95 (m, 2H), 1.32 (s, 9H), 1.11 (s, 18H). ¹³C NMR (100MHz, CDCl₃) δ 153.3, 143.9, 126.2 (2C), 119.1 (2C), 34.1, 31.6 (3C), 27.5 (6C), 20.7 (2C).

IR (neat) 3450, 2980, 1215, 1080 cm^{-1} . HRMS Calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_2\text{Si}$: 308.22 (MH^+). Found: 308.23.

Preparation of the diisopropylsilylethers **15** :

1. Hex-1-ynyl-diisopropyl-silane (**12**)

To a cooled (-78°C) solution of 0.7 mL of hex-1-yne (6.0 mmol, 1 equiv) in 6 mL of THF was added dropwise 2.8 mL of *n*-BuLi (2.25 M in pentane, 6.35 mmol, 1.05 equiv). After being stirred 15 minutes at this temperature, 1.3 mL of chlorodiisopropylsilane (7.8 mmol, 1.2 equiv) was added and the reaction mixture was warmed to room temperature. The solution was then diluted in Et_2O , washed with saturated solution of NH_4Cl , brine, dried over MgSO_4 , filtered, concentrated *in vacuo* to give **12** as a colorless oil (**100%**).

^1H NMR (400MHz, CDCl_3) δ 3.68 (br s, 1H), 2.27 (t, $J = 7.7$ Hz, 2H), 1.61-1.42 (m, 4H), 1.07 (t, $J = 6.6$ Hz, 14H), 0.93 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100MHz, CDCl_3) δ 110.5, 77.7, 30.8, 21.9, 19.7, 18.6 (2C), 18.3 (4C), 13.6, 11.0. IR (neat) 2941, 2360, 2175, 2117, 1463, 800 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{Si}$: C, 73.38; H, 12.32. Found: C, 72.98; H, 12.60.

2. General procedure for the preparation of diisopropylsilylethers (**15**) :

To a solution of 357 mg of **12** (1.8 mmol, 1 equiv) in 8 mL of CH_2Cl_2 was added slowly 324 mg of NBS (1.8 mmol, 1 equiv). The mixture was stirred until completion of the reaction by TLC and then this solution was transferred into a solution of alcohol **14a-d** (1.6 mmol, 0.9 equiv), 0.25 mL of Et_3N (1.6 mmol, 1 equiv) and 22 mg of DMAP (0.1 equiv) in 8 mL of CH_2Cl_2 . After completion of the reaction by TLC, the mixture was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (PE/EE 95/5) and furnished the silylethers **15a-d** as colorless oils.

Hex-1-ynyl-diisopropyl-nona-2,8-diynyloxy-silane (15a) : 0.412 g; **78%**.

^1H NMR (400MHz, CDCl_3) δ 4.43 (t, $J = 2.1$ Hz, 2H), 2.29 (t, $J = 6.8$ Hz, 2H), 2.27-2.22 (m, 4H), 1.96 (t, $J = 2.6$ Hz, 1H), 1.67-1.64 (m, 4H), 1.57-1.45 (m, 4H), 1.04 (m, 14H), 0.94 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100MHz, CDCl_3) δ 110.6, 85.0, 84.5, 79.3, 78.5, 68.8, 53.3, 31.0, 27.9 (2C), 22.2, 19.8, 18.7, 18.3, 17.4 (4C), 13.9 (2C), 13.4. IR (neat) 3311, 2942, 2865, 2172, 1464, 1083 cm^{-1} .

HRMS Calcd for $\text{C}_{21}\text{H}_{34}\text{OSi}$: 331.24 (MH^+). Found: 331.24.

Hex-1-ynyl-diisopropyl-octa-2,7-diynoxy-silane (15b) : 0.390 g; 77%.

^1H NMR (400MHz, CDCl_3) δ 4.41 (s, 2H), 2.36-2.26 (m, 6H), 1.95 (t, $J = 2.4$ Hz, 1H), 1.73 (quint, $J = 6.9$ Hz, 2H), 1.61 (m, 2H), 1.55-1.42 (m, 4H), 1.05 (se, 14H), 0.93 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100MHz, CDCl_3) δ 110.3, 84.0, 83.6, 79.4, 78.2, 68.8, 53.0, 30.7, 27.6, 21.9, 19.5, 17.9, 17.6, 17.2 (2C), 17.1 (2C), 13.6 (2C), 13.1. IR (neat) 3311, 2942, 2865, 2172, 1464, 1083 cm^{-1} .

Hex-1-ynyl-diisopropyl-(4-prop-2-ynyloxy-but-2-ynyloxy)-silane (15c):

0.392 g, 77%.

^1H NMR (400MHz, CDCl_3) δ 4.47 (t, $J = 1.8$ Hz, 2H), 4.30 (t, $J = 1.8$ Hz, 2H), 4.25 (t, $J = 2.3$ Hz, 2H), 2.44 (t, $J = 2.4$ Hz, 1H), 2.28(t, $J = 6.8$ Hz, 2H), 1.55-1.43 (m, 4H), 1.05 (br s, 14H), 0.90 (t, $J = 3.0$ Hz, 3H). ^{13}C NMR (100MHz, CDCl_3) δ 110.7, 85.7, 79.7, 79.0, 77.9, 75.9, 56.8,

56.3, 52.8, 30.7, 21.9, 19.5, 17.1 (2C), 16.9 (2C), 13.6 (2C), 13.1. IR (neat) 3309, 2957, 2865, 2171, 1464, 1131, 1074 cm^{-1} . HRMS Calcd for $\text{C}_{19}\text{H}_{30}\text{O}_2\text{Si}$: 319.20 (MH^+). Found: 319.20.

[4-(Hex-1-ynyl-diisopropyl-silanyloxy)-but-2-ynyl]-prop-2-ynyl- carbamic acid benzyl ester (15d): 0.527 g; **73 %**.

^1H NMR (400MHz, CDCl_3) δ 7.35-7.33 (m, 5H), 5.19 (s, 2H), 4.46 (s, 2H), 4.29 (br s, 4H), 2.31-2.26 (m, 3H), 1.55-1.45 (m, 4H), 1.06 (m, 14H), 0.92 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100MHz, CDCl_3) δ 155.1, 136.3, 128.6 (2C), 128.2, 128.0 (2C), 110.8, 79.1, 78.5, 77.9, 72.4, 72.3, 67.9 (2C), 52.8, 30.7 (2C), 21.9, 19.5, 17.1 (4C), 13.6 (2C), 13.1. IR (neat) 3310, 2940, 2865, 2170, 1710, 1237, 1085 cm^{-1} . HRMS Calcd for $\text{C}_{27}\text{H}_{37}\text{NO}_3\text{Si}$: 452.25 (MH^+). Found: 452.26.

3-[(Diisopropyl-prop-2-ynyloxy-silanyl)-ethynyl]-diisopropyl-silanyloxy}-propyne (18):

a- First step : preparation of 1,2-bis-(diisopropyl-silanyl)-ethyne (16):

To a cooled (0°C) solution of 29.2 mL of ethynyl Grignard (0.5M in THF, 14.6 mmol, 1.1 equiv) in 26 mL of THF was added dropwise a solution of 2.3 mL of chlorodiisopropylsilane (13.3 mmol, 1 equiv) in 9 mL of THF and the reaction mixture was warmed to room temperature. After being stirred 6 hours, the reaction mixture was cooled to 0°C and 9.7 mL of ethyl Grignard (1.5M in THF, 14.6 mmol, 1.1 equiv) was added dropwise. After being stirred 12 hours at room temperature, 2.3 mL of chlorodiisopropylsilane (13.3 mmol, 1 equiv) was added dropwise. The solution was then diluted in Et_2O , washed with saturated solution of NH_4Cl and brine, dried over MgSO_4 , filtered and concentrated *in vacuo* to give **16** as a colorless oil (2.66 g, **78%**).

^1H NMR (400MHz, CDCl_3) δ 3.72 (s, 2H), 1.11 (d, $J = 6.0\text{Hz}$, 28H). ^{13}C NMR (100MHz, CDCl_3) δ 95.8, 83.9, 18.5 (4C), 18.2 (4C), 10.8 (4C). IR (neat) 2945, 2866, 1462, 909, 788, 736 cm^{-1} .

HRMS Calcd for $C_{14}H_{30}Si_2$: 255.19 (MH^+). Found: 255.20.

b- Second step : preparation of the disilylether (18): 0.348 g; 60 %

The procedure is the same as for silylethers **15a-d**.

1H NMR (400MHz, $CDCl_3$) δ 4.48 (s, 4H), 2.42 (br s, 2H), 1.08 (br s, 28H). ^{13}C NMR (100MHz, $CDCl_3$) δ 110.2 (2C), 82.9 (2C), 73.22 (2C), 52.9 (2C), 17.1 (4C), 16.9 (4C), 12.9 (4C). IR (neat) 3310, 2950, 2100, 1460, 1100 cm^{-1} . HRMS Calcd for $C_{20}H_{34}O_2Si_2$: 363.21 (MH^+). Found: 363.21.

Preparation of silane (21)

1. Hex-1-ynyl-dimethyl-silane (19): 17.8 g, quantitative

The procedure is similar to the one described for **12**. The reaction was carried out with 100 mmol of 1-hexyne.

1H NMR (400MHz, $CDCl_3$) δ 4.08 (m, 1H), 2.20 (t, $J = 13.7$ Hz, 2H), 1.48-1.41 (m, 4H), 0.85 (t, $J = 13.3$ Hz, 3H), 0.18 (s, 3H), 0.16 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 109.0, 81.4, 30.5, 22.1, 19.9, 13.7, -2.7 (2C). IR (neat) 3310, 2950, 2100, 1460, 1100 cm^{-1} . IR (neat) 2940, 2360, 2175, 2115, 1460, 800 cm^{-1} .

2. Hex-1-ynyl-dimethyl-prop-2-ynyl-silane (21):

To a solution of **19** (7 g, 50 mmol, 1 equiv) in CH_2Cl_2 was added slowly NBS (8.9 g, 50 mmol, 1 equiv). The reaction was stirred and monitored by TLC until completion. The solvent was removed *in vacuo* and the crude residue is precipitated in pentane (40 mL) and filtered. To the resulting filtrate, propargyl Grignard (2M in Et_2O , 80 mmol, 1.6 equiv) was added at 0°C. After being warmed at room temperature, the mixture was stirred for an additionnal 1 h. The solution was diluted in Et_2O , washed with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated. Purification of the crude residue by flash chromatography (PE) afforded **21**: 7.12 g; **80%**.

^1H NMR (400MHz, CDCl_3) δ 2.20 (t, $J = 13.8$ Hz, 2H), 1.83 (t, $J = 5.9$ Hz, 1H), 1.59 (d, $J = 5.9$ Hz, 2H), 1.48-1.41 (m, 4H), 0.85 (t, $J = 13.8$ Hz, 3H), 0.23 (s, 6H). ^{13}C NMR (100MHz, CDCl_3) δ 109.3, 81.6, 81.5, 67.4, 30.6, 21.9, 19.6, 13.5, 6.9, -2.1 (2C). IR (neat) 3300, 2980, 2950, 2100, 1440, 1230 cm^{-1} . Anal. Calcd. for $\text{C}_{11}\text{H}_{18}\text{Si}$: C, 74.08; H, 10.17. Found: C, 73.94; H, 10.05.