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Supporting Information

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Experimental Section.

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature, either at 400 MHz and 100 MHz respectively on an ARX 400 Bruker spectrometer or at 200 MHz and 50 MHz respectively on an AC200 Bruker spectrometer. Chemical shifts are reported in ppm referenced to the residual proton resonances of the solvents. ^{19}F NMR spectra were recorded at 367 MHz on an ARX 400 Bruker spectrometer.

^{2}H (deuterium) NMR spectra were obtained at room temperature at 46 MHz on an AC300 spectrometer with multinuclear capacity. For internal referencing deuterated chloroform (2.5% in volume : $\delta\ ^{2}H = 7.27$ ppm) was added to the $CHCl_3$ solution in 5 mm o. d. tubes. The spectra were recorded without lock through the lock coil of a QNP probehead. Infrared (IR) spectra were recorded with a Perkin Elmer 1420 spectrometer. Mass spectra (MS) were obtained on a GC-MS Hewlett-Packard HP 5971 apparatus and on a NERMAG R-30-10 apparatus. Melting points were obtained on a Reichert apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F 254. Silica gel Merck Geduran SI (40-63 μm) was used for column chromatography using Still's method.[1]
$[\alpha]^{20}_{D}$ were recorded on a Perkin-Elmer 241 polarimeter.

Solvents : THF was distilled from sodium-benzophenone ketyl. Benzene was distilled from calcium hydride. DMF was distilled under reduced pressure over calcium hydride.
Chromatography solvents: EE refers to ethyl ether, PE to petroleum ether, EA to ethyl acetate.

Tributyltin deuteride (isotopic purity > 95%) was purchased from Aldrich.

Preparation of starting materials :

Alcohol 2. A suspension of dried $CeCl_3$[2] (4.7 g, 19 mmol) and **1** (2.5 g, 15.8 mmol) under argon in THF (100 mL) was stirred at rt for 1.5 h. To a cold (-78°C) solution of 3,3-dimethyl-

1-butyne (2.15 g, 26 mmol) in THF (40 mL) was added *n*-BuLi (1.6 M hexanes, 11.9 mL, 19 mmol). After 1 h of stirring at -78 °C, this solution was cannulated into the first suspension cooled at -78 °C. After 3 h of stirring at this temperature, the mixture reaction was left to warm to rt. Ether was added and the organic layer was washed with saturated aqueous NH_4Cl, dried ($MgSO_4$), filtered (celite) and concentrated *in vacuo*. Flash chromatography (PE-EE, 80:20) gave pure **2**, 3.5 g (93 %) of yellowish oil which crystallises on standing, m.p. 105-106°C; $[\alpha]^{20}_D$ -54 (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.25, (d, J = 7.1 Hz, 3H), 1.34 (d, J = 7.1 Hz, 3H), 1.38 (s, 3H), 1.39 (s, 3H), 3.74 (q, J = 7.1 Hz, 1H), 3.96 (q, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 16.7, 23.1 (2C), 27.3 (3C), 30.8, 71.8, 71.9, 74.6, 76.7, 96.7, 100.9; IR (KBr) 3480, 2950, 2210, 1450, 1360, 1220, 1180, 1080, 1000, 870, 840 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.99; H, 10.10.

***meso* Alcohol.** Same procedure as before, on (2.0 g, 12.6 mmol) of the *meso* ketone.[3] Flash chromatography (PE-EE, 80:20) on silica gel gave 2.7 g (90 %) of white solid, m.p. 98-100°C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.29 (d, J = 6.0 Hz, 6H), 1.44 (s, 3H), 1.51 (s, 3H), 3.96 (q, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6 (2C), 19.3, 27.7, 30.2 (2C), 31.2 (3C), 68.3, 72.9 (2C), 76.0, 96.4, 99.4; IR (KBr) 3580, 2950, 2230, 1450, 1370, 1260, 1180, 1080, 1000, 750 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.78; H, 10.22.

Silyl ether 3. To a cold (0 °C), stirred solution of **2** (3.2 g, 13 mmol) and imidazole (1.4 g, 21 mmol) in DMF (10 mL) under argon, neat BMDMSCl (1.8 mL, 13 mmol) was slowly added. After stirring for 1 h at 0 °C, ether was added. The ethereal layer was washed with NH_4Cl and brine, dried over $MgSO_4$ and concentrated to dryness. Flash chromatography (PE-EE, 80:20) gave 4.9 g (95 %) of white solid, m.p. 35-36°C; $[\alpha]^{20}_D$ -36 (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.38 (s, 6H), 1.15 (d, J = 7.3 Hz, 3H), 1.27 (s, 9H), 1.28 (d, J = 7.3 Hz, 3H), 1.36 (s, 3H), 1.38 (s, 3H), 2.60 (m_{AB}, 2H), 3.20 (q, J = 7.3 Hz, 1H), 3.40 (q, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.8 (2C), 14.2, 16.6, 17.2, 24.0, 24.1, 27.4, 30.6 (3C), 72.6, 73.4, 77.2, 78.1, 97.9, 100.8; IR (KBr) 2960, 2220, 1450, 1370, 1220, 1100, 1040, 980, 840 cm^{-1}. UV $CHCl_3$, nm (log ε) 239 (2.15). Anal. Calcd for $C_{17}H_{31}BrO_3Si$: C, 52.16; H, 7.98. Found: C, 52.04; H, 8.01.

Silyl ether 9. Same procedure as before on (2.1 g, 8.7 mmol) of *meso* alcohol. Flash chromatography (PE-EE, 80:20) gave 3.1g (91%) of white solid, m.p. 29-31°C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.40 (s, 6H), 1.21 (s, 9H), 1.38 (s, 3H), 1.42 (d, J = 6.0 Hz, 6H), 1.43 (s, 3H), 2.63 (s, 2H), 3.84 (q, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CHCl_3$) δ 0.0 (2C), 17.0 (2C), 18.3, 19.5, 28.0, 30.5, 31.1 (3C), 70.6, 73.4 (2C), 79.1, 97.5, 98.8; IR (KBr) 2980, 2210, 1450, 1370, 1260, 1180, 1050, 850, 810 cm^{-1}. Anal. Calcd for $C_{17}H_{31}BrO_3Si$: C, 52.16; H, 7.98. Found: C, 52.19; H, 8.17.

Radical cyclization products :

***Meso* 4a.** To a refluxing benzene solution (20 mL), under argon, of silyl ether **1** or **9** (196 mg, 0.5 mmol), AIBN (10 mg, 0.12 equiv.) was added a solution of Bu_3SnH (150 µL, 1.1 equiv.) and AIBN (20 mg, 0.24 equiv.) in benzene (7 mL). After completion of the reaction (4 h), the crude reaction mixture was evaporated, and then diluted with MeOH (10 mL). KF (150 mg, 5 equiv.) was added. After stirring for 2 h, evaporation, redilution in CH_2Cl_2 (2 x 10 mL) and filtration over celite, the crude product was purified by column chromatography (PE-EE, 90:10) to give 137 mg (88%) of colorless syrup; ^1H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 6H), 1.07 (d, J = 6.2 Hz, 6H), 1.19 (s, 9H), 1.44 (s, 3H), 1.53 (s, 3H), 1.75 (br s, 2H), 3.92 (q, J = 6.2 Hz, 2H), 6.18 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.6 (2C), 15.3 (2C), 19.0, 19.2, 29.6, 30.6 (3C), 33.2, 73.5 (2C), 82.5, 98.3, 131.0, 138.9; IR (film) 2870, 1450, 1380, 1260, 1190, 1110, 1020, 990, 890, 850, 830 cm^{-1}. Anal. Calcd for $C_{17}H_{32}O_3Si$: C, 65.33; H, 10.32. Found: C, 65.26; H, 10.37.

***Meso* 5a.** Same radical cyclization procedure as above from **3**. The reaction mixture was then treated with salt-free methyllithium (1.6 M hexanes, 1.6 mL, 5 equiv.) at 0°C. Stirring was maintained for 30 min. After dilution with ether, the organic phase was washed with a saturated NH_4Cl solution and brine, and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (PE-EE, 90:10) to give 141 mg (86 %) of white solid, m.p. 93°C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 9H), 1.11 (d, J = 6.8 Hz, 6H), 1.19 (s, 9H), 1.45 (s, 3H), 1.51 (s, 3H), 1.76 (s, 2H), 3.75 (q, J = 6.8 Hz, 2H), 5.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0 (3C), 15.6 (2C), 18.9, 21.0, 29.6, 31.7 (3C), 33.1, 73.2, 74.9 (2C), 98.5, 130.3, 135.8; IR (KBr) 3580, 2930, 1490, 1460, 1360, 1260, 1070, 870 cm^{-1}. Anal. Calcd for $C_{18}H_{36}O_3Si$: C, 65.80; H, 11.04. Found: C, 65.87; H, 10.98.

***Meso* 5aD.** Same procedure as for **5a**, using Bu_3SnD. Flash chromatography (PE-EE, 90:10) gave 140 mg (85 %) of white solid; $[\alpha]^{20}_D$ +0.93 (c 4.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 9H), 1.16 (s, 3H), 1.17 (d, J = 6.8 Hz, 3H), 1.18 (s, 9H), 1.45 (s, 3H), 1.51 (s, 3H), 1.60 (s, 2H), 3.70 (q, J = 6.8 Hz, 1H), 5.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0 (3C), 15.4, 15.5, 18.9, 20.9, 29.5, 31.7 (3C), 33.1, 74.4 (t, J = 20 Hz, CD), 74.9, 98.4, 130.2, 135.8; ^2H NMR (350 MHz, $CHCl_3$ + 2.5% $CDCl_3$) δ 3.70; IR (KBr) 3460, 2960, 1730, 1450, 1360, 1260, 1070, 850 cm^{-1}.

***Meso* 10.** Same procedure as for **5a** from **9**. Flash chromatography (PE-EE, 98:2) gave 82 mg (50 %) of pure oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9H), 0.98 (d, J = 6.0 Hz, 6H), 1.02 (s, 9H), 1.35 (s, 3H), 1.43 (s, 3H), 1.70 (s, 2H), 3.81 (q, J = 6.0 Hz, 2H), 4.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0 (3C), 14.4 (2C), 18.6, 19.4, 29.4, 30.8 (3C), 31.9, 72.9 (2C), 73.6, 97.9, 131.1, 136.5; IR (film) 3580, 2900, 1450, 1370, 1250, 1190, 1100, 850 cm^{-1}. Anal. Calcd for $C_{18}H_{36}O_3Si$: C, 65.80; H, 11.04. Found: C, 65.79; H, 11.20.

Meso **10D.** Same procedure as for **5aD** from **9**. Flash chromatography (PE-EE, 98:2) gave 84 mg (51 %) of pure oil; ^{1}H NMR (400 MHz, C_6D_6) δ 0.19 (s, 9H), 1.06 (s, 9H), 1.15 (d, *J* = 6.1 Hz, 3H), 1.16 (s, 3H), 1.21 (s, 3H), 1.32 (s, 3H), 1.86 (s, 2H), 3.86 (q, *J* = 6.1 Hz, 1H), 4.89 (s, 1H).

Alcohol 11. Same procedure as for **5a** from **9**. Flash chromatography (PE-EE, 98:2) gave 49 mg (30 %) of pure oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9H), 1.05 (s, 9H), 1.06 (d, *J* = 7.2 Hz, 3H), 1.09 (d, *J* = 7.2 Hz, 3H), 1.30 (s, 3H), 1.36 (s, 3H), 1.76 (s, 2H), 3.73 (q, *J* = 7.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 1H), 5.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0 (3C), 13.9, 17.2, 18.3, 24.1 (2C), 30.7 (3C), 32.0, 69.3, 75.9, 77.5, 99.1, 132.6, 135.1; IR (film) 3600, 3500, 2950, 1460, 1370, 1250, 1000, 850 cm^{-1}.

Alcohol 11D. Same procedure as for **5aD** from **9**. Flash chromatography (PE-EE, 98:2) gave 48 mg (29 %) of pure oil;^{1}H NMR (400 MHz, C_6D_6) δ 0.15 (s, 9H), 1.04 (s, 9H), 1.07 (s, 3H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.22 (s, 3H), 1.23 (s, 3H), 1.75 (m_{AB}, 2H), 4.16 (q, *J* = 6.6 Hz, 1H), 5.06 (s, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 75.4 (t, *J* = 20 Hz, CD).

Cyanide 4b. To a refluxing benzene solution (33 mL), under argon, of silyl ether **1** (196 mg, 0.5 mmol), AIBN (10 mg, 0.12 equiv.) and acrylonitrile (500 µL, 15 equiv.) was added a solution of Bu3SnH (150 µL, 1.1 equiv.) and AIBN (20 mg, 0.24 equiv.) in benzene (7 mL). Alternatively, silyl ether **1** (0.196 g, 0.5 mmol), AIBN (10 mg, 0.12 equiv.) and acrylonitrile (500 µL, 15 equiv.) were dissolved in dry benzene (10 mL) under argon. Tributyltinhydride (150 µL, 1.1 equiv.) was then added. The quartz probe of irradiation was sealed with a rubber septum and the mixture was irradiated (λ = 254 nm) for 8 h in a rayonet apparatus. A KF treatment as for **4a** was applied. Flash chromatography (PE-EE, 90:10) on silica gel gave 102 mg (56 %) of **4b** and 68 mg (35%) of **3**.

4b : colorless prisms, m.p. 60°C; $[\alpha]^{20}_D$ -44 (c 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.22 (s, 3H), 0.24 (s, 3H), 1.01 (s, 3H), 1.06, (d, *J* = 6.0 Hz, 3H), 1.18 (s, 9H), 1.40 (s, 3H), 1.52 (s, 3H), 1.65-1.78 (m, 2H), 2.09 (m, 1H), 2.37-2.48 (m, 3H), 4.17 (q, *J* = 6.0 Hz, 1H), 6.19 (t, *J* = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.2, 0.0, 11.6, 14.9, 17.9, 22.1, 23.4, 29.7 (3C), 30.3, 31.6, 32.5, 67.4, 78.6, 83.5, 97.8, 120.1, 131.9, 138.5; IR (KBr) 2920, 2220, 1460, 1370, 1250, 1050, 750 cm^{-1}. Anal. Calcd for $C_{20}H_{35}NO_3Si$: C, 65.71; H, 9.65; N, 3.83. Found: C, 65.83; H, 9.62; N, 3.92.

Sulfone 5c. To a refluxing benzene solution (20 mL), under argon, of silyl ether **1** (196 mg, 0.5 mmol), AIBN (10 mg, 0.12 equiv.) in presence of 1.26 g (15 equiv.) of vinylphenyl sulfone was added a solution of Bu3SnH (150 µL, 1.1 equiv.) and AIBN (20 mg, 0.24 equiv.) in benzene (7 mL)*via* a syringe-pump (2.10^{-4} mol h^{-1}). After completion of the addition (4 h), the crude reaction was refluxed for another 2 h period. After a KF treatment, a chromatography over a short pad of silica gel was run in order to remove most of the tin residues and of the viylphenylsulfone. At 0°C, the residue, dissolved in 3 mL of benzene, was then treated with salt-free methyllithium (1.6 M hexanes, 3.2 mL, 10 equiv.). Stirring was maintained for 30 min. After dilution with ether, the organic phase was washed with a saturated NH_4Cl solution

and brine, and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography (PE-EE, 50:50) on silica gel to give 89 mg (36 %) of **5c** as a yellow oil; $[\alpha]^{20}_D$ -28 (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 9H), 1.10 (d, *J* = 6.3 Hz, 3H), 1.12 (s, 9H), 1.15 (s, 3H), 1.37 (s, 6H), 1.60 (d, *J* = 14.2 Hz, 1H), 1.74 (d, *J* = 14.2 Hz, 1H), 2.08 (m, 1H), 2.33 (m, 1H), 3.23 (m, 2H), 3.99 (q, *J* = 6.3 Hz, 1H), 5.85 (s, 1H), 7.5-7.7 (m, 3H), 7.92 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.5 (3C), 16.0, 21.0, 23.9, 24.2, 29.2, 30.7, 31.5 (3C), 33.1, 52.7, 69.8, 75.9, 79.7, 98.6, 128.0 (2C), 129.3 (2C), 132.6, 133.7, 136.1, 139.3; IR (film) 3500, 2950, 1450, 1380, 1290, 1250, 1200, 1150, 1090, 850, 760 cm^{-1}. Anal. Calcd for $C_{26}H_{44}O_5SiS$: C, 62.86; H, 8.93. Found: C, 62.86; H, 8.94.

Acrylate 4d. A benzene solution (10 mL), under argon, of silyl ether **1** (196 mg, 0.5 mmol), AIBN (30 mg, 0.36 equiv.) in presence of 233 mg (1.2 equiv.) of stannyl acrylate **14** was refluxed for 13 h. After a KF treatment, flash chromatography (PE-EE, 90:10) on silica gel gave 66 mg (32 %) of **4d** as a pure oil; $[\alpha]^{20}_D$ -43 (c 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 3H), 0.20 (s, 3H), 1.05 (d, *J* = 6.0 Hz, 3H), 1.11 (s, 3H), 1.16 (s, 9H), 1.41 (s, 3H), 1.55 (s, 3H), 1.66-1.73 (m, 2H), 2.72-3.23 (m_{AB}, 2H), 2.37-2.48 (m, 2H), 3.72 (s, 3H), 4.27 (q, *J* = 6.2 Hz, 1H), 5.81 (d, *J* = 1.0 Hz, 1H), 6.16 (d, *J* = 1.0 Hz, 1H), 6.22 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.1, 0.0, 15.2, 18.3, 22.8, 24.3, 30.0 (3C), 30.8, 32.7, 36.6, 51.4, 67.9, 80.5, 84.1, 98.2, 125.6, 132.5, 138.3, 138.5, 168.7; IR (film) 2920, 1720, 1450, 1320, 1250, 1050, 750 cm^{-1}. Anal. Calcd for $C_{22}H_{38}O_5Si$: C, 64.35; H, 9.33. Found: C, 64.18; H, 9.53.

The second fraction of the chromatography (colorless syrup) consisted in 41 mg (20 %) of the 2 : 1 mixture of diastereomeric **Cyclopropanes 15.** ^1H NMR (400 MHz, $CDCl_3$) δ 0.09, 0.22, 0.23, 0.25 (4s, 12H, m+M), 1.03-1.47 (m, 46H, +M), 2.45 (m, 2H, m+M), 2.55-2.86 (m, 4H, m+M), 3.73 (s, 3H, m), 3.75 (s, 3H, M), 4.83 (q, *J* = 6.8 Hz, 1H, M), 4.87 (q, *J* = 6.8 Hz, 1H, m), 5.54 (s, 1H, m), 5.56 (s, 1H, M), 6.13 (s, 1H, m), 6.15 (s, 1H, M); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0 (2C), 0.4 (2C), 2.0, 2.2, 13.6, 14.3, 23.0 (2C), 28.3 (2C), 28.2 (3C), 29.1 (3C), 30.39, 30.42, 30.5 (2C), 31.4, 34.3, 34.4, 47.0, 48.7, 51.78, 51.80, 66.2, 66.8, 96.9 (2C), 98.3 (2C), 98.7 (2C), 125.9, 126.3, 138.5, 139.8, 167.3, 167.6.

Acyclic derivative 16. Rearrangement of **15** in acidic medium (CDCl3 of a NMR tube) gave, after purification by flash chromatography (PE-EE, 75:25), **16** as a pure oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 9H), 1.96 (d, *J* = 7.1 Hz, 3H), 2.25 (s, 3H), 2.41 (s, 2H), 2.88 (d, *J* = 12.7 Hz, 1H), 3.83 (s, 3H), 5.13, 5.26, 5.51, 6.20 (4 x s, 4 x 1H), 6.58 (q, *J* = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7, 27.2, 28.3 (3C), 32.8, 34.8, 50.8, 51.8, 120.1, 126.7, 137.6, 140.0, 143.2, 149.2, 168.2, 199.8; IR (film) 2950, 1720, 1675, 1630, 1440, 1260, 1200, 1140 cm^{-1}; CIMS *m/z* (%) 296 (MNH_4^+, 85), 279 (MH^+, 100).

Allyl 5d. Silylether **1** (196 mg, 0.5 mmol) in presence of 901 mg (12 equiv.) of allylphenylsulfide were dissolved in dry benzene (10 mL). Hexabutyldistannane (380 µL, 1.5 equiv.) was added, and the solution was degassed with argon. The quartz probe of irradiation

was sealed with a rubber septum and the mixture was irradiated for 8 h in a rayonet apparatus. After completion of the reaction, the solvent was removed *in vacuo*. Flash chromatography (from PE 100 to PE-EE, 99.8:0.2) on silica gel gave by order of elution 108 mg (61 %) of **4e**, 30 mg (15%) of **3** and 34 mg (22%) of **4a**.

4e : colorless oil; $[\alpha]^{20}_D$ -33 (c 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 6H), 1.05 (s, 3H), 1.09 (d, *J* = 6.2 Hz, 3H), 1.20 (s, 9H), 1.44 (s, 3H), 1.53 (s, 3H), 1.75 (m_{AB}, *J* = 17.8 Hz, 2H), 2.41 (dd, *J* = 15.8, 8.2 Hz, 1H), 2.89 (dd, *J* = 15.8, 5.6 Hz, 1H), 4.26 (q, *J* = 6.2 Hz, 1H), 5.11 (m, 2H), 5.95 (m, 1H), 6.27 (t, *J* = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.6, 0.7, 15.6, 18.7, 23.6, 24.4, 30.4 (3C), 31.1, 33.1, 40.3, 68.0, 80.1, 84.2, 98.4, 117.3, 132.8, 135.9, 138.6; IR (film) 2960, 1460, 1180, 1170, 1250, 1200, 1070, 1050, 900, 890, 850, 810 cm^{-1}. Anal. Calcd for $C_{20}H_{36}O_3Si$: C, 68.13; H, 10.29. Found: C, 68.20; H, 10.21.

Synthesis of triol 18.

Cyanide 1-OH 17. Under argon, a mixture of **4b** (90 mg, 0.25 mmol), Bu_4NF/SiO_2 (0.74 g, 0.74 mmol) in DMF (3 mL) was stirred at 60 °C for 6 h. After this period, the crude reaction was diluted with water (20 mL) and extracted with ethyl acetate (3 x 10 mL). The organic layer was dried over $MgSO_4$ and concentrated to dryness. Flash chromatography of the crude product (PE-EE, 70:30, on silica gel) afforded 65 mg (85 %) of **17** as a colorless syrup; $[\alpha]^{20}_D$ -68 (c 2.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 3H), 1.04 (d, *J* = 6.3 Hz, 3H), 1.14 (s, 9H), 1.38 (s, 3H), 1.53 (s, 3H), 2.00 (s, 3H), 2.05-2.50 (m, 4H), 4.12 (q, *J* = 6.3 Hz, 1H), 5.54 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 14.9, 16.8, 22.7, 24.0, 30.7, 30.9 (3C), 32.1, 33.0, 68.2, 74.8, 78.2, 98.6, 120.7, 135.2, 136.6; IR (film) 3500, 2950, 2230, 1470, 1380, 1250, 1200, 1160, 1130, 1080, 1000, 740 cm^{-1}. Anal. Calcd for $C_{18}H_{31}NO_3$: C, 69.86; H, 10.10; N, 4.53. Found: C, 69.80; H, 10.00; N, 4.39.

Triol 18. Under argon, a solution of **17** (60 mg, 0.19 mmol) in acetic acid (2 mL) and water (0.5 mL) was stirred at 60 °C for 2 h. After this period, the reaction mixture was diluted with water (10 mL) and extracted with dichloromethane (3 x 10 mL). The organic layer was dried over $MgSO_4$ and concentrated to dryness. Flash chromatography of crude (PE-EE, 50:50, on silica gel) gave 51 mg (99 %) of **18** as a white paste ; $[\alpha]^{20}_D$ -54 (c 1.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (s, 9H), 1.22 (s, 3H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.60 (ddd, *J* = 14.2, 10.2, 6.1 Hz, 1H), 1.85 (s, 3H), 1.91 (ddd, *J* = 14.2, 10.2, 5.6 Hz, 1H), 2.39 (ddd, *J* = 16.7, 10.2, 6.1 Hz, 1H), 2.53 (ddd, *J* = 16.7, 10.2, 5.6 Hz, 1H), 4.26 (q, *J* = 6.2 Hz, 1H), 5.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 15.7, 17.6, 20.8, 30.9 (3C), 32.5, 34.8, 69.7, 74.5, 82.5, 121.0, 134.8, 139.2; IR (film) 3600-3100, 2260 cm^{-1}. CIMS (*m/z*, %) 287 (MNH_4^+, 100), 270 (MH^+, 5), 252 (MH^+-H_2O, 2). Anal. Calcd for $C_{15}H_{27}NO_3$: C, 66.88; H, 10.10; N, 5.20. Found: C, 66.83; H, 10.22; N, 5.05.

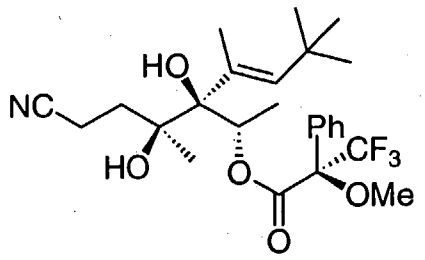
References :

1 Still, W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

2 Dimitrov, V.; Kostova, K.; Genov, M. *Tetrahedron Lett.* **1996**, *37*, 6787-6790.

3 Enders, D.; Jegelka, U.; Dücker, B. *Angew. Chem. Int. Ed.* **1993**, *32*, 423-425.

^{19}F NMR o f the *R*-Mosher ester of **18**.



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F1	7529.97 Hz
F2P	-310.000 ppm
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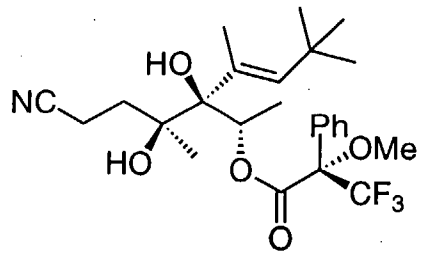
^{19}F NMR o f the *S*-Mosher ester of **18**.



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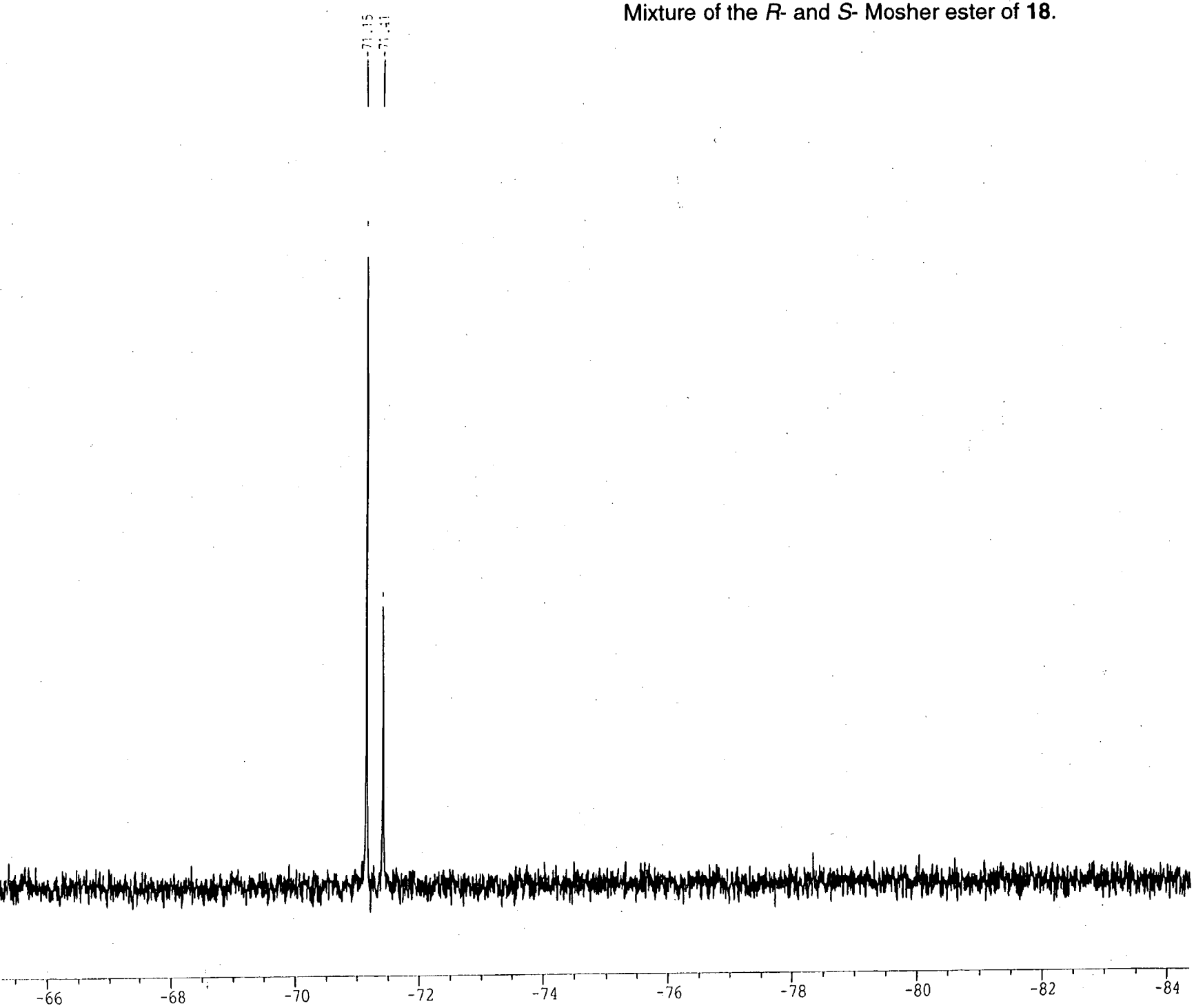
Mixture of the *R*- and *S*- Mosher ester of **18**.



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D11 0.00020000 sec
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CPDPRG waltz16
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1D NMR plot parameters
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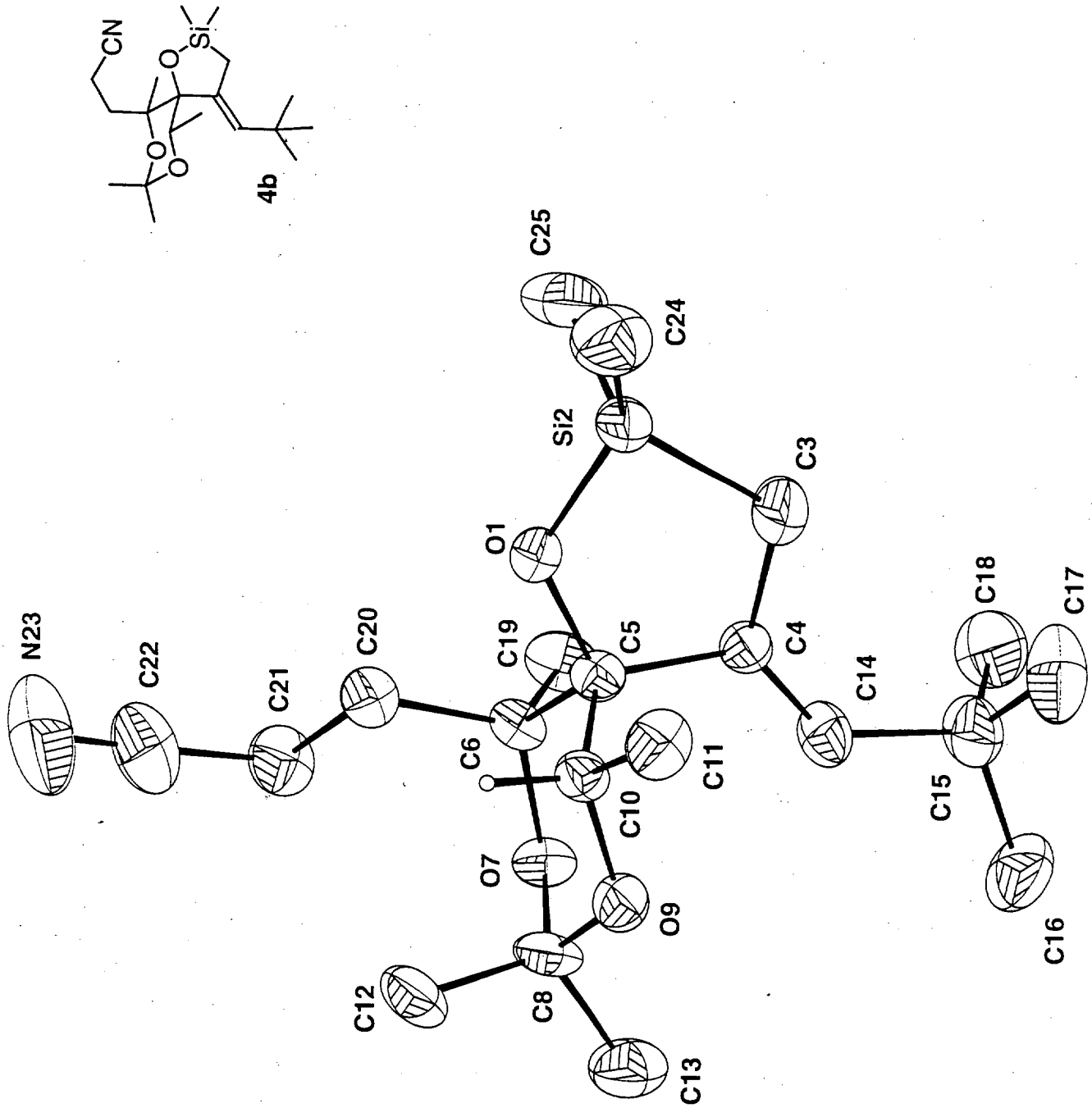
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Si
O
O
O
4b
C25
C24
Si2
C3
O1
C19
C5
C4
C20
C21
C22
N23
C6
C11
C10
C14
C18
C17
C15
O7
O9
C16
C12
C8
C13

CRYSTAL DATA for	$C_{20}H_{35}O_3NSi$
Fw	365.6
a (Å)	7.693(4)
b (Å)	9.571(3)
c (Å)	9.958(4)
α (°)	117.08(3)
β (°)	104.36(4)
γ (°)	104.39(3)
V (Å^3)	574.3(5)
Z	1
Crystal system	triclinic
Space group	P 1
Linear absorption coefficient μ (cm^{-1})	1.13
Density ρ (g.cm^{-3})	1.06
Diffractometer	CAD4 Enraf-Nonius
Radiation	MoKα (λ = 0.71069 Å)
Scan type	ω /2θ
Scan range (°)	0.8 + 0.345 tgθ
θ Limits (°)	1 - 25
Temperature of measurement	295K
Octants collected	0,9 ; -11,11 ; -11,11
Decay %	< 5
Nb of data collected	2180
Nb of unique data collected	2016 (R_{int} = 0.02)
Nb of unique data used for refinement	1073 $(Fo)^2 > 1.5\sigma(Fo)^2$
$R = \Sigma\|\|Fo\| - \|Fc\|\| / \Sigma\|Fo\|$	0.0795
$Rw^* = [\Sigma w(\|Fo\| - \|Fc\|)^2 / \Sigma w\|Fo\|^2]^{1/2}$	0.0758
S	1.22
Extinction parameter	none
Nb of variables	227
Δρmin (e.Å^{-3})	-0.32
Δρmax (e.Å^{-3})	0.43

* $w = w'[1-((|\|Fo|-|Fc|\|)/6.\sigma(Fo))^2]^2$ with $w'=1/\Sigma r\ A_r T_r(X)$ with 3 coefficients 5.36, -1.08 and 4.15 for a Chebyshev Series, for which X is $F_c/F_c(max)$

Table 1: Fractional parameters for $C_{20}H_{35}O_3NSi$

Atom	x/a	y/b	z/c	U(eq)
O(1)	0.1191(8)	0.9068(7)	0.4345(7)	0.0471
Si(2)	0.1465(5)	0.8784(4)	0.5856(4)	0.0640
C(3)	0.384(2)	1.068(2)	0.728(2)	0.0923
C(4)	0.419(1)	1.162(1)	0.649(1)	0.0505
C(5)	0.261(1)	1.063(1)	0.468(1)	0.0494
C(6)	0.142(1)	1.163(1)	0.433(1)	0.0423
O(7)	0.2581(9)	1.2863(7)	0.4092(8)	0.0531
C(8)	0.366(2)	1.242(1)	0.311(1)	0.0582
O(9)	0.4663(9)	1.1510(8)	0.3479(7)	0.0596
C(10)	0.350(1)	1.006(1)	0.341(1)	0.0499
C(11)	0.477(2)	0.916(1)	0.365(1)	0.0720
C(12)	0.240(2)	1.143(2)	0.127(1)	0.0767
C(13)	0.520(2)	1.413(2)	0.369(2)	0.0873
C(14)	0.557(2)	1.313(1)	0.717(1)	0.0630
C(15)	0.732(2)	1.435(1)	0.890(1)	0.0782
C(16)	0.876(2)	1.577(2)	0.890(2)	0.1005
C(17)	0.848(2)	1.343(2)	0.939(2)	0.1151
C(18)	0.653(2)	1.519(2)	1.018(2)	0.1036
C(19)	0.106(2)	1.277(1)	0.582(1)	0.0650
C(20)	-0.056(1)	1.034(1)	0.281(1)	0.0553
C(21)	-0.167(2)	1.123(1)	0.223(1)	0.0721
C(22)	-0.336(2)	0.995(2)	0.066(2)	0.0897
N(23)	-0.469(3)	0.892(2)	-0.056(2)	0.1510
C(24)	0.139(2)	0.665(2)	0.520(2)	0.1049
C(25)	-0.059(2)	0.882(2)	0.649(2)	0.0943

Table 2: Anisotropic thermal parameters for $C_{20}H_{35}O_3NSi$

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
O(1)	0.045(3)	0.044(3)	0.054(4)	0.022(3)	0.024(3)	0.023(3)
Si(2)	0.068(2)	0.060(2)	0.063(2)	0.039(2)	0.015(2)	0.015(1)
C(3)	0.089(9)	0.10(1)	0.078(9)	0.055(8)	-0.013(7)	-0.017(8)
C(4)	0.056(5)	0.042(5)	0.049(6)	0.026(5)	0.016(5)	0.013(5)
C(5)	0.061(6)	0.039(5)	0.055(6)	0.026(4)	0.026(5)	0.024(5)
C(6)	0.062(6)	0.051(5)	0.049(5)	0.032(4)	0.035(5)	0.039(5)
O(7)	0.067(4)	0.053(4)	0.071(4)	0.040(3)	0.043(4)	0.034(3)
C(8)	0.075(7)	0.089(8)	0.079(8)	0.067(7)	0.050(7)	0.041(7)
O(9)	0.053(4)	0.070(4)	0.058(4)	0.035(3)	0.023(3)	0.027(3)
C(10)	0.051(5)	0.062(6)	0.050(6)	0.032(5)	0.027(5)	0.030(5)
C(11)	0.068(7)	0.074(7)	0.097(8)	0.049(6)	0.035(6)	0.043(6)
C(12)	0.091(8)	0.13(1)	0.075(8)	0.073(8)	0.048(7)	0.063(8)
C(13)	0.095(9)	0.094(9)	0.12(1)	0.078(8)	0.056(9)	0.043(8)
C(14)	0.083(7)	0.055(6)	0.042(6)	0.019(5)	0.020(5)	0.023(6)
C(15)	0.089(8)	0.071(7)	0.048(6)	0.019(6)	0.011(6)	0.016(7)
C(16)	0.083(9)	0.087(9)	0.087(9)	0.023(7)	0.018(8)	-0.006(7)
C(17)	0.10(1)	0.11(1)	0.10(1)	0.034(9)	-0.013(8)	0.031(9)
C(18)	0.13(1)	0.096(9)	0.060(7)	0.018(6)	0.029(8)	0.010(8)
C(19)	0.099(8)	0.067(6)	0.081(7)	0.040(6)	0.063(7)	0.053(6)
C(20)	0.056(6)	0.063(6)	0.059(6)	0.032(5)	0.027(5)	0.036(5)
C(21)	0.064(7)	0.098(8)	0.087(8)	0.057(7)	0.031(7)	0.051(7)
C(22)	0.11(1)	0.14(1)	0.11(1)	0.08(1)	0.04(1)	0.09(1)
N(23)	0.15(1)	0.18(2)	0.13(1)	0.08(1)	-0.01(1)	0.07(1)
C(24)	0.11(1)	0.12(1)	0.15(1)	0.09(1)	0.06(1)	0.062(9)
C(25)	0.14(1)	0.097(9)	0.11(1)	0.073(8)	0.07(1)	0.045(9)

Table 3: Interatomic distances (Å) for $C_{20}H_{35}O_3NSi$

O(1)	- Si(2)	1.620(6)	O(1)	- C(5)	1.45(1)
Si(2)	- C(3)	1.84(1)	Si(2)	- C(24)	1.82(1)
Si(2)	- C(25)	1.84(2)	C(3)	- C(4)	1.47(1)
C(4)	- C(5)	1.55(1)	C(4)	- C(14)	1.29(1)
C(5)	- C(6)	1.58(1)	C(5)	- C(10)	1.53(1)
C(6)	- O(7)	1.44(1)	C(6)	- C(19)	1.53(1)
C(6)	- C(20)	1.53(1)	O(7)	- C(8)	1.42(1)
C(8)	- O(9)	1.40(1)	C(8)	- C(12)	1.51(2)
C(8)	- C(13)	1.50(2)	O(9)	- C(10)	1.41(1)
C(10)	- C(11)	1.51(1)	C(14)	- C(15)	1.54(1)
C(15)	- C(16)	1.53(2)	C(15)	- C(17)	1.54(2)
C(15)	- C(18)	1.54(2)	C(20)	- C(21)	1.54(1)
C(21)	- C(22)	1.45(2)	C(22)	- N(23)	1.13(2)

Table 5: Hydrogen atoms fractional parameters for $C_{20}H_{35}O_3NSi$

Atom	x/a	y/b	z/c	U(iso)
H(31)	0.3840	1.1349	0.8360	0.116(8)
H(32)	0.4911	1.0211	0.7401	0.116(8)
H(101)	0.2446	0.9262	0.2252	0.116(8)
H(111)	0.5277	0.8811	0.2828	0.116(8)
H(112)	0.5832	0.9932	0.4814	0.116(8)
H(113)	0.3885	0.8089	0.3574	0.116(8)
H(121)	0.3174	1.1182	0.0636	0.116(8)
H(122)	0.1745	1.2171	0.1060	0.116(8)
H(123)	0.1314	1.0357	0.0956	0.116(8)
H(131)	0.6052	1.3961	0.3073	0.116(8)
H(132)	0.4576	1.4876	0.3552	0.116(8)
H(133)	0.6059	1.4718	0.4914	0.116(8)
H(141)	0.5453	1.3614	0.6459	0.116(8)
H(161)	0.9933	1.6525	0.9988	0.116(8)
H(162)	0.8084	1.6434	0.8667	0.116(8)
H(163)	0.9229	1.5219	0.7995	0.116(8)
H(171)	0.9624	1.4319	1.0501	0.116(8)
H(172)	0.9023	1.2911	0.8549	0.116(8)
H(173)	0.7608	1.2534	0.9436	0.116(8)
H(181)	0.7677	1.5950	1.1310	0.116(8)
H(182)	0.5901	1.5840	0.9913	0.116(8)
H(183)	0.5578	1.4236	1.0161	0.116(8)
H(191)	0.0304	1.3378	0.5550	0.116(8)
H(192)	0.2361	1.3636	0.6803	0.116(8)
H(193)	0.0289	1.2027	0.6124	0.116(8)
H(201)	-0.1435	0.9654	0.3095	0.116(8)
H(202)	-0.0320	0.9525	0.1873	0.116(8)
H(211)	-0.2129	1.1874	0.3043	0.116(8)
H(212)	-0.0749	1.2038	0.2066	0.116(8)
H(241)	0.0015	0.5762	0.4428	0.116(8)
H(242)	0.1866	0.6605	0.6194	0.116(8)
H(243)	0.2280	0.6449	0.4611	0.116(8)
H(251)	-0.1777	0.7764	0.5634	0.116(8)
H(252)	-0.0778	0.9872	0.6663	0.116(8)
H(253)	-0.0181	0.8901	0.7572	0.116(8)

Table 4: Bond angles (°) for $C_{20}H_{35}O_3NSi$

Si(2) - O(1) - C(5)	117.6(5)	O(1) - Si(2) - C(3)	94.5(4)
O(1) - Si(2) - C(24)	110.6(5)	C(3) - Si(2) - C(24)	118.6(7)
O(1) - Si(2) - C(25)	111.7(5)	C(3) - Si(2) - C(25)	116.5(7)
C(24) - Si(2) - C(25)	104.7(6)	Si(2) - C(3) - C(4)	107.5(7)
C(3) - C(4) - C(5)	112.0(8)	C(3) - C(4) - C(14)	126.4(9)
C(5) - C(4) - C(14)	121.6(8)	O(1) - C(5) - C(4)	107.8(7)
O(1) - C(5) - C(6)	106.9(7)	C(4) - C(5) - C(6)	114.7(7)
O(1) - C(5) - C(10)	106.8(6)	C(4) - C(5) - C(10)	112.2(7)
C(6) - C(5) - C(10)	108.0(7)	C(5) - C(6) - O(7)	109.9(7)
C(5) - C(6) - C(19)	112.6(7)	O(7) - C(6) - C(19)	103.1(7)
C(5) - C(6) - C(20)	109.4(7)	O(7) - C(6) - C(20)	111.7(7)
C(19) - C(6) - C(20)	110.1(7)	C(6) - O(7) - C(8)	121.2(6)
O(7) - C(8) - O(9)	111.0(7)	O(7) - C(8) - C(12)	113.0(9)
O(9) - C(8) - C(12)	111.0(9)	O(7) - C(8) - C(13)	104.1(9)
O(9) - C(8) - C(13)	107.1(9)	C(12) - C(8) - C(13)	110.3(9)
C(8) - O(9) - C(10)	115.6(7)	C(5) - C(10) - O(9)	110.3(7)
C(5) - C(10) - C(11)	114.1(7)	O(9) - C(10) - C(11)	107.6(7)
C(4) - C(14) - C(15)	131.6(9)	C(14) - C(15) - C(16)	108.7(10)
C(14) - C(15) - C(17)	113.5(10)	C(16) - C(15) - C(17)	107.9(12)
C(14) - C(15) - C(18)	108.4(11)	C(16) - C(15) - C(18)	108.3(11)
C(17) - C(15) - C(18)	110.0(12)	C(6) - C(20) - C(21)	112.6(8)
C(20) - C(21) - C(22)	109.5(10)	C(21) - C(22) - N(23)	178.4(18)