CHAPITRE VII : Experimental section

VII.1. Instrumentation/procedure

Routine nuclear magnetic resonance (NMR) spectra were recorded on a VARIAN GEMINI-200 VXR-200 (^{1}H: 200 MHz and ^{13}C: 50 MHz), a BRUCKER AC-250 (^{1}H: 250 MHz and ^{13}C: 62.5 MHz), a VARIAN GEMINI-2000 (^{1}H: 300 MHz and ^{13}C: 75 MHz) and a BRUCKER AC-300 Avance II (^{1}H: 300 MHz and ^{13}C: 75 MHz). High field spectra were recorded on a BRUCKER AM-500 (^{1}H: 500 MHz and ^{13}C: 125 MHz). ^{1}H chemical shifts (δ_H) are reported in ppm and calibrated from $CHCl_3$. ^{13}C NMR spectra were also recorded using $CDCl_3$ as the internal standard.

Low resolution mass spectra were recorded using VARIAN MATT-44 and FINNIGAN MAT-TSQ 70 spectrometers.

Infra-red spectra (IR) were recorded, as thin films, on a PERKIN ELMER 681 spectrometer and a Shimadzu FTIR-8400S spectrometer and recorded in cm^{-1}.

Elemental analyses were carried out at the University of Stuttgart, Germany.

Thin layer chromatographies (TLC) were performed on TLC plastic sheets, Silica gel 60 F_{254} (MERCK and Aldrich). The plates were visualized using ultra-violet light (256 nm) and developed using

$KMnO_4$ and/or vanillin stain which were prepared according to the following procedures:

- **Potassium Permanganate:** This stain was prepared by dissolving
  3 g of $KMnO_4$ and 20 g of K_2CO_3 in 5 mL of 5% NaOH and 300 mL of water.
- **Vanillin:** This stain was prepared by dissolving 2 g of vanillin in 100 mL of EtOH containing 1 mL of conc. H_2SO_4. The plate was developed by heating.

Column chromatographies were performed using MERCK silica gel 60 (230-400 mesh) under pressure with the stated solvents.
All solvents were routinely distilled prior to use. Dry solvents were obtained by standard procedures according to D. D. Perrin and D. R. Perrin, *Purification of Laboratory Chemicals*. All compounds (Acros, Aldrich, Fluka, Lancaster and TCI) were used as received unless otherwise stated. All reactions were carried out under an atmosphere of argon in flame-dried apparatus with magnetic stirring, unless otherwise indicated.

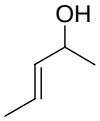
Structure determination

Structure determination of the tetrahydropyrannes was carried out with a help of 2D-COSY, 2D-HETCOR and 2D-HMQC.

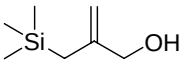
General remarks

- When the product was obtained as a mixture of two diastereoisomers, the signals for the minor isomer, if different from the major, are marked with '. *E.g.* .., 3.82-3.72 (1H, m, H-12), 3.72-3.63 (1H, m, H-12').
- When a CH_2 group, bearing two diastereotopic hydrogen atoms, is presented in the molecule, two different signals should be observed in ^{1}H-NMR spectra. To distinguish between them, the hydrogen atoms are described as *e.g.* H-1a and H-1b.

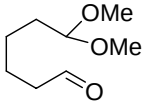
VII.2. List of compounds



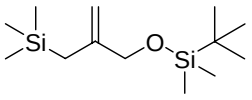
(*E*)-pent-3-en-2-ol p. 313



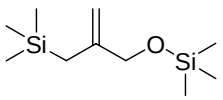
2-((trimethylsilyl)methyl) prop-2-en-1-ol p. 318



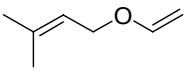
6,6-dimethoxyhexanal p. 314



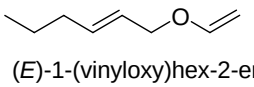
2-(*tert*butyldimethyl-silyloxy-methyl)-3-trimethylsilyl-propene p. 319



2-trimethylsilyl-3-trimethyl-silyloxy-propene p. 316

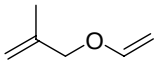


3-methyl-1-(vinyloxy)but-2-ene p. 321



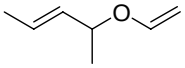
(*E*)-1-(vinyloxy)hex-2-ene

p. 322



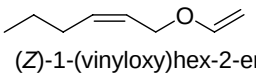
2-methyl-3-(vinyloxy)prop-1-ene

p. 323



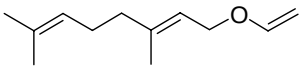
(*E*)-4-(vinyloxy)pent-2-ene

p. 325



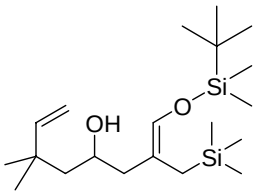
(*Z*)-1-(vinyloxy)hex-2-ene

p. 326



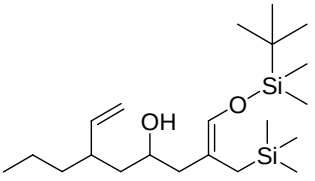
(*E*)-3,7-dimethyl-1-(vinyloxy) octa-2,6-diene

p. 328



(*Z*)-1-(*tert*butyldimethyl-silyloxy)-2-((trimethylsilyl)methyl)-6,6-dimethyl-octa-1,7-dien-4-ol

p. 329
p. 338



(*Z*)-1-(*tert*butyldimethyl-silyloxy)-2-((trimethylsilyl)methyl)-6-propyl-octa-1,7-dien-4-ol

p. 331
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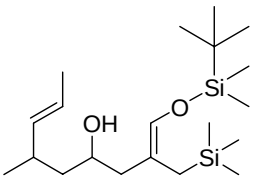
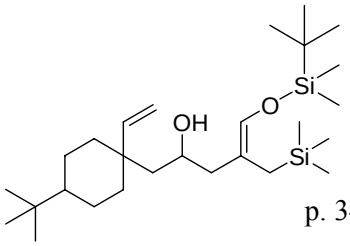
p. 341



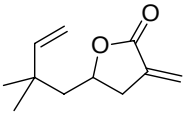
(1*Z,7E*)-1-(*tert*butyldimethyl-silyloxy)-2-((trimethylsilyl)methyl)-6-methylnona-1,7-dien-4-ol

p. 334
p. 340



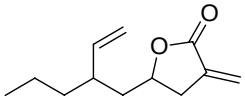
(Z)-5-(tertbutyldimethyl-silyloxy)-1-(4-tertbutyl-1-vinylcyclohexyl)-4-((trimethylsilyl)-methyl)-pent-4-en-2-ol

p. 342



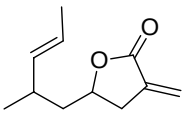
dihydro-5-(2,2-dimethyl-but-3-enyl)-3-methylene furan-2(3*H*)-one

p. 344



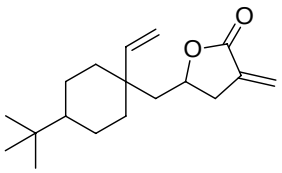
dihydro-3-methylene-5-(2-vinylpentyl)furan-2(3*H*)-one

p. 347

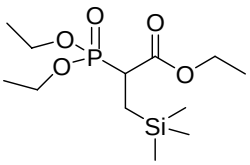


dihydro-3-methylene-5-((*E*)-2-methylpent-3-enyl) furan-2(3*H*)-one

p. 350


p. 352

5-((4-*tert*-butyl-1-vinylcyclohexyl) methyl)-dihydro-3-methylene-furan-2(3*H*)-one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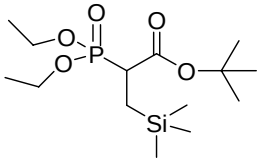
ethyl-1-((trimethylsilyl)methyl)-diethoxyphosphonoacétate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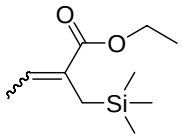
*tert*butyl-1-((trimethylsilyl) methyl)diethoxy-phosphonoacétate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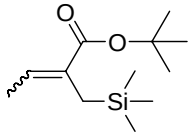
ethyl -2-((trimethylsilyl) methyl)but-2-enoate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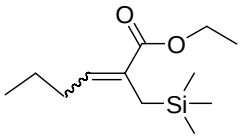
*tert*butyl-2-((trimethylsilyl) methyl)but-2-enoate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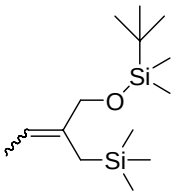
ethyl-2-((trimethylsilyl) methyl)hex-2-enoate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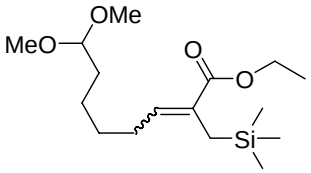
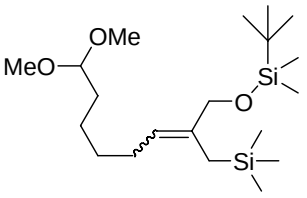
1-(*tert*butyldimethyl-silyloxy)-2-((trimethylsilyl)methyl)-but-2-ene


p. 366

ethyl-8,8-dimethoxy-2-((trimethylsilyl)methyl) oct-2-enoate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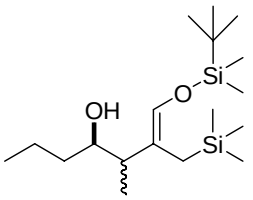
1-(*tert*butyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-8,8-dimethoxyoct-2-ene



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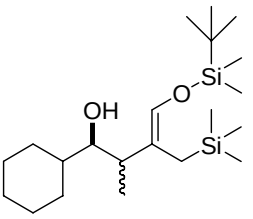
(*Z*)-1-(*tert*butyldimethyl-silyloxy)-2-((trimethylsilyl)methyl)-3-methyl-hept-1-en-4-ol



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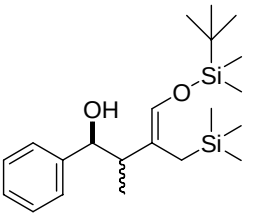

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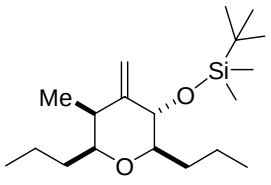

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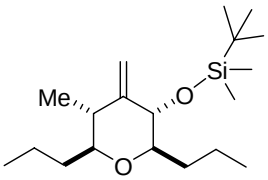
((2*R*,3*S*,5*S*,6*S*)-tetrahydro-5-methyl-4-methylene-2,6-dipropyl-2*H*-pyran-3-yloxy)(*tert*-butyl)dimethylsilane



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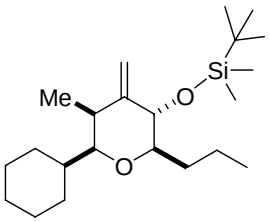

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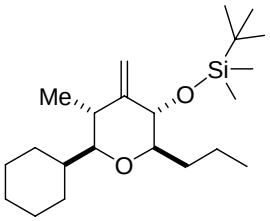
((2*R*,3*S*,5*S*,6*S*)-6-cyclohexyl-tetrahydro-5-methyl-4-methylene-2-propyl-2*H*-pyran-3-yloxy)(*tert*-butyl)dimethylsilane



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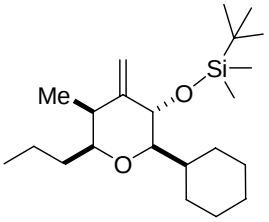
((2*R*,3*S*,5*R*,6*S*)-6-cyclohexyl-tetrahydro-5-methyl-4-methylene-2-propyl-2*H*-pyran-3-yloxy)(*tert*-butyl)dimethylsilane



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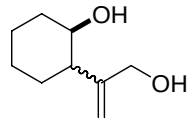

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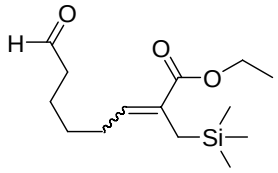
2-(1-hydroxyprop-2-en-2-yl) cyclohexanol



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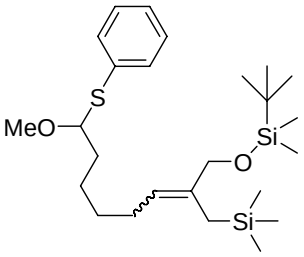
ethyl-7-formyl-2-((trimethylsilyl) methyl)hept-2-enoate



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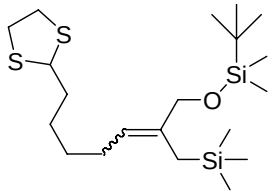
1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-8-methoxy-8-phenylthioxyoct-2-ene



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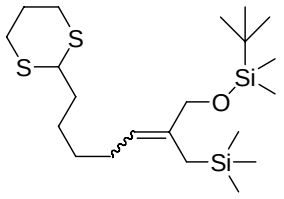

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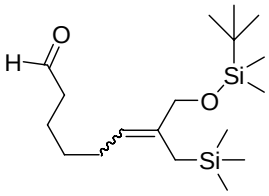

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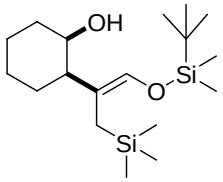
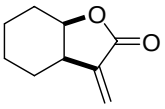


p. 403

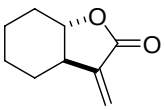
1-(*tert*butyldimethyl-silyloxy)-2-(2-hydroxy-cyclohexyl)-3-((trimethylsilyl)-prop-1-ene



p. 405

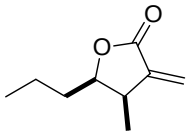
p. 408

syn-hexahydro-3-methylen benzofuran-2(3*H*)-one



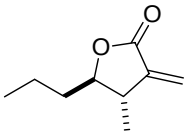
p. 407

anti-hexahydro-3-methylene-benzofuran-2(3*H*)-one



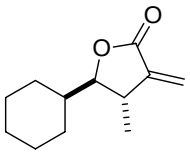
p. 409

syn-dihydro-4-methyl-3-methylene-5-propylfuran-2(3*H*)-one



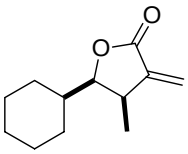
p. 411

anti-dihydro-4-methyl-3-methylene-5-propylfuran-2(3*H*)-one



p. 414

anti-5-cyclohexyl-dihydro-4-methyl-3-methylenefuran-2(3*H*)-one



p. 416

syn-5-cyclohexyl-dihydro-4-methyl-3-methylenefuran-2(3*H*)-one

VII.3. Synthesis of reactives:

VII.3.1. Synthesis of manganese dioxide

MnO_2 is freshly prepared before utilisation by the following reaction :

$$3\ MnSO_4 + 2\ KMnO_4 \xrightarrow{\Delta} 5\ MnO_2.2H_2O + 4\ NaOH + 8\ H_2O + K_2SO_4 + 2Na_2SO_4$$

The black solid formed is dried under vacuum at 120 °C for 24h. A fine black powder is then obtained with quantitative yield (35 g scale).

VII.3.2. Synthesis of thiophenyl chloride

$$\underset{\textbf{1047}}{PhSH} + \underset{\textbf{1048}}{SO_2Cl_2} \xrightarrow[\text{pentane}]{Et_3N\ \text{cat.}} \underset{\textbf{1049}}{PhSCl}$$

To a solution of thiophenol (17.5 ml, 168 mmol, 1 eq.) in 85 ml of pentane was added 60 µl of triethylamine (0.42 mmol, 0.25 mol%). The mixture was conscientiously kept under argon and cooled to 0 °C. SO_2Cl_2 (25 g, 185 mol, 1.1 eq.) was added dropwise in 45 min. at 0 °C. Then this cooled mixture was allowed to warm up to r.t. and was stirred for 1h. By distillation under vacuum, the volatiles were eliminated and 21.42 g of pure thiophenyl chloride were gathered (10 mm Hg, 83-86 °C).

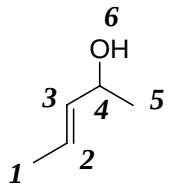
Isolated yield : 90 %

VII.4. Synthesis of pent-3-en-2-ol 744 :

751 **744**

To 75 ml of methyl-Grignard reagent (3M solution in ether, 0.225 mol, 1 eq) cooled at -10°C was added dropwise crotonaldehyde **751** (15.54 g, 0.222 mol, 1 eq.). This mixture was allowed to warm up to r.t. and was stirred for 3h. The resulting mixture was poured on 100ml of a saturated aqueous solution of NH_4Cl cooled at -10 °C and the aqueous layer was extracted with ether (3 x 100 ml). The combined extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo* at 0 °C. Distillation at normal pressure gave 14.73 g of pure allylic alcohol **744** (117-122°C).

Isolated yield : 76 %

	**Mol. Mass :** 86.13 g.mol^{-1} **Mol. Formula :** $C_5H_{10}O$ **R.N.** = [3899-34-1]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

5.65 (1H, dq, *J* = 15.3, 6.3 Hz, H-2), 5.53 (1H, ddd, *J* = 15.3, 6, 1.5 Hz, H-3), 4.31-4.19 (1H, m, H-4), 1.68 (3H, dd, *J* = 6.3, 1.2 Hz, H-1), 1.45-1.39 (1H, m, H-6), 1.25 (3H, d, *J* = 6.3 Hz, H-5).

^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm):

134.6 (C-3), 126.1 (C-2), 77.3 (C-4), 22.7 (C-5), 18.1 (C-1).

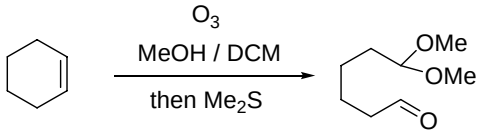
MS (EI, 70 eV) *m/z* (relative intensity, %):

87 ($MH^{+\bullet}$, 9), 72 ($M^{+\bullet}$-$CH_3^{\bullet}$, 48), 44 (100).

IR (film):

3362 [w] (O-H), 3126 [w] (=C-H), 3040-2850 [s] (C-H), 1681 [s] (C=C), 1462 [s], 1383 [m], 1301 [m], 1064 [s] (C-O), 982 [s], 921 [s] cm^{-1}.

VII.5. Synthesis of 6,6-dimethoxyhexanal 1009[291] :

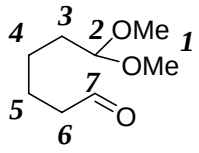


1008 **1009**

[291] Schreiber, S.L.; Claus, R.E. *Org. Synth.* **1986**, *64*, 150-156.

Through a solution of cyclohexene **1008** (15.4 g, 0.188 mol, 1 eq) in a mixture of 625 ml of dichloromethane P.A. and 125 ml of MeOH P.A. cooled at -78 °C bubbled a current of O_3 for 3h (until the solution became blue, O_2 bottle opened on 12-13 l/min. and ozonizer on position 3). The cooling bath was removed, *para*-toluenesulfonic acid (3.015 g, 17.51 mmol, 0.09 eq) was added and the solution was allowed to warm up to r.t. This mixture was stirred at r.t. for 1h30, anhydrous $NaHCO_3$ (5.543 g, 66 mmol, 0.35 eq) was added and the solution was stirred at r.t. for 15 min. Then dimethylsulfure (30 ml, 0.406 mol, excess) was added and the mixture was stirred at r.t. for 17h. Dichloromethane was evaporated *in vacuo* and 200 ml of water was added. The aqueous layer was extracted with CH_2Cl_2 (3 x 250 ml). The combined extracts were washed with 250 ml of water and the aqueous layer was extracted with 250 ml of CH_2Cl_2. The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Distillation of the residue at 2.7 mbars gave between 61 and 65 °C 22.62 g of pure aldehyde acetal **1009**.

Isolated yield : 75%

	**Mol. Mass :** 160.21 g.mol^{-1} **Mol. Formula :** $C_8H_{16}O_3$ **R.N.** = [55489-11-7]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

9.76 (1H, t, *J* = 1.8 Hz, H-7), 4.35 (1H, t, *J* = 6.6 Hz, H-2), 3.30 (6H, s, H-1), 2.44 (2H, td, *J* = 9, 1.8 Hz, H-6), 1.72-1.55 (4H, m, H-3 and H-5), 1.30-1.15 (2H, s, H-4).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

202.6 (+, C-7), 104.3 (+, C-2), 52.8 (+, C-1), 43.9 (-, C-6), 32.3 (-, C-3), 24.2 and 21.9 (-, C-4 and C-5).

MS (EI, 70 eV) *m/z* (relative intensity, %):

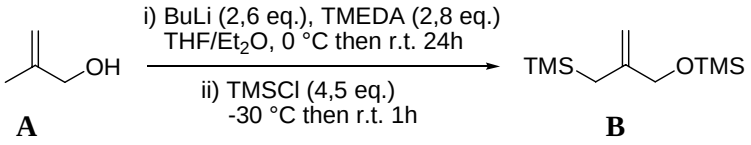
160 ($M^{+\bullet}$, 1), 143 (3), 129 ($M^{+\bullet}$-MeO$^{\bullet}$, 9), 97 (129-MeOH, 8), 75 ($(MeO)_2CH^+$, 100), 69 (14), 47 (19).

IR (film):

2945, 2868, 2830 [m] (C-H), 1722 [s] (large, C=O), 1462 [m], 1387 and 1365 [m], 1192 and 1167 [m], 1128, 1072 and 1051 [s] (C-O-C) cm^{-1}.

VII.6. Synthesis of allylsilane 379[299]

VII.6.1. 2-trimethylsilyl-3-trimethylsilyloxy-propene B



A **B**

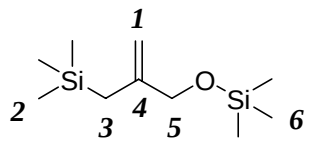
A 10 M solution of BuLi in hexane (100 ml, 1.0 mol, 2.8 eq.) was added over 45 minutes *via* cannula to a solution of TMEDA (140 ml) in anhydrous Et_2O (440 ml) cooled to 0 °C. After stirring for 15 minutes at this temperature, 2-methyl-2-propenol **A** (0.35 ml, 0.36 mol, 1 eq.) was added dropwise. A white precipitate appears and after a few minutes, the solution turned orange.

[299] Trost, B.M.; Chan, D.N.; Nanninga, M. *Org. Synth.* **1984**, *62*, 58-66.

The reaction mixture was then diluted with anhydrous THF (300 ml) and the temperature was raised to 20 °C. Vigorous mechanical stirring was continued for 24h. By this time, the colour of the solution turned to dark brown.

The reaction mixture was cooled at -30 °C and TMSCl (205 ml, 1.59 mol, 4.5 eq.) was added. The resulting milky white solution was allowed to warm to room temperature over a period of 30 minutes, diluted with Et_2O (200 ml) and poured into a separatory funnel. A saturated aqueous solution of $NaHCO_3$ (1 l) was added carefully to destroy the excess TMSCl. The ethereal layer was separated and washed with water (1 l), saturated aqueous $CuSO_4$ (2 x 1 l) and water again (0.8 l). The organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo*. Distillation of the residue under reduced pressure (bp 90-95 °C, 1.5 mm Hg) provided the title compound (37.1 g) as a colourless oil.

Isolated yield : 48 %

	**Mol. Mass :** 216.48 $g.mol^{-1}$ **Mol. Formula :** $C_{10}H_{24}OSi_2$ **R.N.** = [83378-96-5]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

4.88 (1H, s, H-1a), 4.60 (1H, s, H-1b), 3.93 (2H, s, H-5), 1.46 (2H, s, H-3), 0.10 (9H, s, H-6), 0.02 (9H, s, H-2).

^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm):

145.9 (C-4), 106.6 (C-1), 66.5 (C-5), 22.8 (C-3), -0.47 (C-6), -1.37 (C-2).

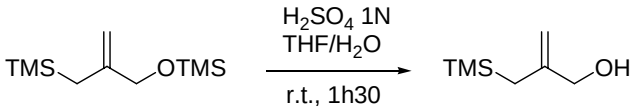
MS (EI, 70 eV) *m/z* (relative intensity, %):

216 ($M^{+\bullet}$, 2), 147 ($Me_3SiOSiMe_2^+$, 100), 133 ($Me_3SiOSiMeH^+$, 9), 113 (19), 73 (Me_3Si^+, 74).

IR (film):

2970-2850 [s] (C-H), 1647 [w] (C=C), 1254 [s] (C-Si), 1052 [s] (C-O), 847 [s] (C-Si) cm^{-1}.

VII.6.2. 2-trimethylsilylmethyl-prop-2-en-1-ol C

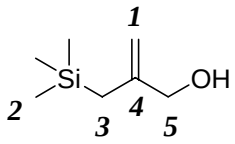


B **C**

A solution of silylether **B** (31.7 g, 0.17 mol, 1 eq.) and 1 N aqueous H_2SO_4 (70 ml, 35 mmol, 0.2 eq.) in THF (300 ml) was stirred at room temperature for 90 minutes. An aqueous solution of $CaCO_3$ was added portionwise until the effervescence stopped and complete neutralisation was observed.

Upon dilution with water (100 ml), the aqueous layer was separated and extracted by Et_2O (3 x 100 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Distillation of the residue under reduced pressure (bp 77-81 °C at 15 mm Hg) afforded the title compound (23.25 g) as a colourless oil.

Isolated yield : 93%

	**Mol. Mass :** 144.28 g.mol^{-1} **Mol. Formula :** $C_7H_{16}OSi$ **R.N.** = [81302-80-9]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

4.98 (1H, s, H-1a), 4.62 (1H, s, H-1b), 3.92 (2H, s, H-5), 2.14 (1H, bs, OH), 1.51 (2H, s, H-3), 0.02 (9H, s, H-2).

^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm):

146.9 (C-4), 106.7 (C-1), 67.0 (C-5), 23.3 (C-3), -1.37 (C-2).

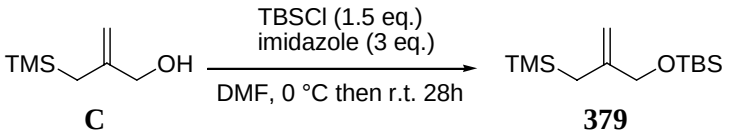
MS (EI, 70 eV) *m/z* (relative intensity, %):

144 ($M^{+\bullet}$, 8), 113 (27), 73 (Me_3Si^+, 100), 57 (34).

IR (film):

3490 [w] (O-H), 2970-2850 [s] (C-H), 1640 [w] (C=C), 1250 [s] (C-Si), 1050 [s] (C-O), 885 [s] (C-Si) cm^{-1}.

VII.6.3. 2-(tertbutyldimethyl-silyloxymethyl)-3-trimethylsilyl-propene 379

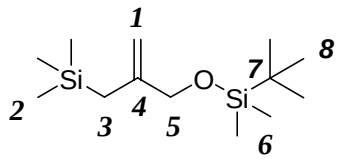


C **379**

To a cold (0 °C) mixture of TBSCl (36.43 g, 0.242 mol, 1.5 eq.) and imidazole (32.9 g, 0.483 mol, 3 eq.) in anhydrous DMF (100 ml) was added alcohol **C** (23.25 g, 0.161 mol, 1 eq.). The mixture was allowed to warm to room temperature and stirred for an additional 28h period.

The solution was then diluted with hexane (100 ml) and was washed twice with water (2 x 100 ml). The combined extracts were dried (K_2CO_3), filtered and concentrated *in vacuo*. Distillation of the residue under reduced pressure (bp 115-125 °C at 30 mm Hg) afforded allylsilane **379** as a colourless liquid (43.6 g, 81 % GC purity).

Isolated yield : 84%



Mol. Mass : 258.55 g.mol^{-1}
Mol. Formula : $C_{13}H_{30}OSi_2$
R.N. = [237749-52-9]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

4.90 (1H, s, H-1a), 4.60 (1H, s, H-1b), 3.95 (2H, s, H-5), 1.45 (2H, s, H-3), 0.88 (9H, s, H-8), 0.10 (6H, s, H-6), 0.00 (9H, s, H-2).

^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm):

147.9 (C-4), 108.9 (C-1), 68.8 (C-5), 28.0 (C-8), 24.7 (C-3), 20.2 (C-7), 0.66 (C-2), -5.28 (C-6).

MS (EI, 70 eV) *m/z* (relative intensity, %):

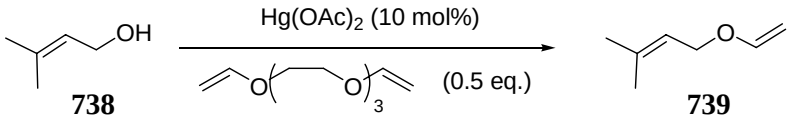
258 ($M^{+\bullet}$, 10), 201 (20), 147 ($Me_3SiOSiMe_2^+$, 100), 133 ($Me_3SiOSiMeH^+$, 22), 73 (Me_3Si^+, 92).

IR (film):

2970-2830 [s] (C-H), 1474 [m] (C=C), 1250 [s] (C-Si), 840 [s] (C-Si) cm^{-1}.

VII.7. Synthesis of allylvinylethers

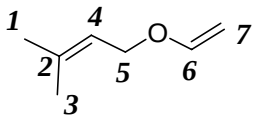
VII.7.1. 3-methyl-1-(vinyloxy)but-2-ene 739



738 **739**

In an oblong flask were introduced allylic alcohol **738** (1.737 g, 20.17 mmol, 1 eq.), triethyleneglycol-divinylether **722** (2.034 g, 10.06 mmol, 0.50 eq) and mercuric acetate (0.645 g, 2.02 mmol, 0.10 eq.). The flask was closed and the neat mixture was heated at 65 °C for 2h. The mixture was then cooled to r.t. and 2.5 ml of a saturated solution of $NaHCO_3$ was added dropwise. The organic layer was washed two times with 2.5 ml of a saturated solution of $NaHCO_3$, dried on Na_2SO_4 and filtrated on cotton wool. Horizontal distillation under vacuum (10 mm Hg, 50 °C) gave 0.694 g of pure allylvinylether **739**.

Isolated yield : 30%

	**Mol. Mass :** 112.13 g.mol^{-1} **Mol. Formula :** $C_7H_{12}O$ **R.N.** = [928-41-6]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.48 (1H, dd, *J* = 14.1, 6.9 Hz, H-6), 5.44-5.35 (1H, m, H-4), 4.21 (2H, d, *J* = 7.2 Hz, H-5), 4.20 (1H, dd, *J* = 14.4, 2.1 Hz, H-7*anti*), 4.00 (1H, dd, *J* = 6.6, 1.8 Hz, H-7*syn*), 1.77 (3H, s, H-1 or H-3), 1.70 (3H, s, H-1 or H-3).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

151.8 (-, C-6), 137.8 (+, C-2), 119.9 (-, C-4), 86.8 (+, C-7), 65.1 (+, C-5), 25.8 (-, C-1 and C-3).

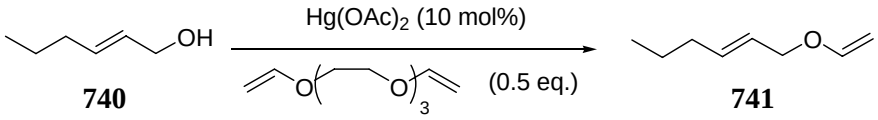
MS (EI, 70 eV) *m/z* (relative intensity, %):

113 ($MH^{+\bullet}$, 7), 112 ($M^{+\bullet}$, 3), 97 ($M^{+\bullet}$-$CH_3^{\bullet}$, 8), 85 (27), 69 ($M^{+\bullet}$-$OCH{:}CH_2^{\bullet}$, 100), 55 (13), 44 (6).

IR (film):

3132 [w] (=C-H), 3010-2840 [s] (C-H), 1760-1580 [s] (C=C), 1448 [m], 1380 [m], 1314 [m], 1194 [s] (C-O), 1051 [m] cm^{-1}.

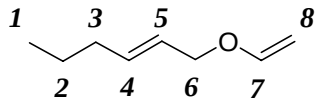
VII.7.2. (E)-1-(vinyloxy)hex-2-ene **741**



740 **741**

In an oblong flask were introduced allylic alcohol **740** (2.115 g, 20.27 mmol, 1 eq.), triethyleneglycol-divinylether **722** (2.007 g, 9.92 mmol, 0.49 eq) and mercuric acetate (0.788 g, 2.47 mmol, 0.12 eq.). The flask was closed and the neat mixture was heated at 65 °C for 2h. The mixture was then cooled to r.t. and 2.5 ml of a saturated solution of $NaHCO_3$ was added dropwise. The organic layer was washed two times with 2.5 ml of a saturated solution of $NaHCO_3$, dried on Na_2SO_4 and filtrated on cotton wool. Horizontal distillation under vacuum (10 mm Hg, 50 °C) gave 0.463 g of pure allylvinylether **741**.

Isolated yield : 18%

	**Mol. Mass :** 126.20 g.mol^{-1} **Mol. Formula :** $C_8H_{14}O$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.46 (1H, dd, *J* = 14.4, 6.6 Hz, H-7), 5.76 (1H, dt, *J* = 15.3, 6.6 Hz, H-4 or H-5), 5.60 (1H, dtt, *J* = 15.3, 6, 1.5 Hz, H-4 or H-5), 4.21 (1H, dd, *J* = 14.4, 1.8 Hz, H-8*anti*), 4.17 (2H, d, *J* = 6.6 Hz, H-6), 4.01 (1H, dd, *J* = 7.2, 2.1 Hz, H-8*syn*), 2.04 (2H, q, *J* = 7.2 Hz, H-3), 1.41 (2H, sext, *J* = 7.5 Hz, H-2), 0.90 (3H, t, *J* = 7.5 Hz, H-1).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

151.9 (-, C-7), 134.4 and 126.8 (-, C-4 and C-5), 87.2 (+, C-8), 66.2 (+, C-6), 34.6 (+, C-3), 22.5 (+, C-2), 13.9 (-, C-1).

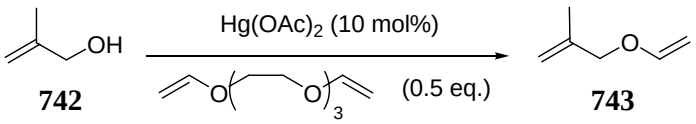
MS (EI, 70 eV) *m/z* (relative intensity, %):

127 ($MH^{+\bullet}$, 7), 126 ($M^{+\bullet}$, 3), 99 ($M^{+\bullet}$-$C_2H_3^{\bullet}$, 9), 83 ($M^{+\bullet}$-$OCH{:}CH_2^{\bullet}$, 100), 69 ($M^{+\bullet}$-$CH_2OCH{:}CH_2^{\bullet}$, 9), 55 (67), 44 (7).

IR (film):

3119 [w] (=C-H), 3040-2820 [s] (C-H), 1750-1570 [s] (C=C), 1459 [m], 1379 [m], 1320 [m], 1197 [s] (C-O), 970 [m], 814 [w] cm^{-1}.

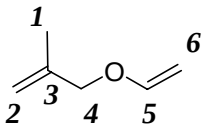
VII.7.3. 2-methyl-3-(vinyloxy)prop-1-ene 743



742 **743**

In an oblong flask were introduced allylic alcohol **742** (1.570 g, 21.33 mmol, 1 eq.), triethyleneglycol-divinylether **722** (2.010 g, 9.94 mmol, 0.47 eq) and mercuric acetate (0.786 g, 2.47 mmol, 0.12 eq.). The flask was closed and the neat mixture was heated at 65 °C for 4h. The mixture was then cooled to r.t. and 2.5 ml of a saturated solution of $NaHCO_3$ was added dropwise. The organic layer was washed two times with 2.5 ml of a saturated solution of $NaHCO_3$, dried on Na_2SO_4 and filtrated on cotton wool. Horizontal distillation under vacuum (10 mm Hg, 50 °C) gave 0.130 g of pure allylvinylether **743**.

Isolated yield : 7%

	**Mol. Mass :** 98.15 $g.mol^{-1}$ **Mol. Formula :** $C_6H_{10}O$ **R.N.** = [6552-32-5]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.46 (1H, dd, *J* = 14.4, 6.6 Hz, H-5), 5.00 (1H, s, H-2a), 4.94 (1H, s, H-2b), 4.23 (1H, dd, *J* = 14.1, 2.1 Hz, H-6*anti*), 4.13 (2H, s, H-4), 4.02 (1H, dd, *J* = 6.9, 2.1 Hz, H-6*syn*), 1.77 (3H, s, H-1).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

151.8 (-, C-5), 141.2 (+, C-3), 112.1 (+, C-2), 87.4 (+, C-6), 72.5 (+, C-4), 19.6 (-, C-1).

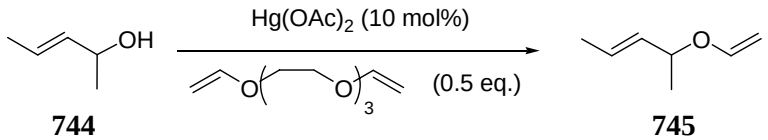
MS (EI, 70 eV) *m/z* (relative intensity, %):

99 ($MH^{+\bullet}$, 12), 85 (9), 55 ($M^{+\bullet}$-$OCH{:}CH_2^{\bullet}$, 91), 44 (100).

IR (film):

3081 [w] (=C-H), 3020-2860 [s] (C-H), 1750-1570 [s] (C=C), 1454 [m], 1199 [s] (C-O), 1150-1040 [s], 966 [m] cm^{-1}.

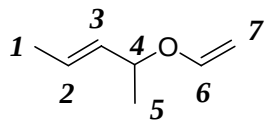
VII.7.4. (E)-4-(vinyloxy)pent-2-ene 745



744 **745**

In an oblong flask were introduced allylic alcohol **744** (1.382 g, 16.04 mmol, 1 eq.), triethyleneglycol-divinylether **722** (1.529 g, 7.56 mmol, 0.47 eq) and mercuric acetate (0.613 g, 1.92 mmol, 0.12 eq.). The flask was closed and the neat mixture was heated at 65 °C for 24h. The mixture was then cooled to r.t. and 2.5 ml of a saturated solution of $NaHCO_3$ was added dropwise. The organic layer was washed two times with 2.5 ml of a saturated solution of $NaHCO_3$, dried on Na_2SO_4 and filtrated on cotton wool. Horizontal distillation under vacuum (10 mm Hg, 50 °C) gave 0.312 g of pure allylvinylether **745**.

Isolated yield : 17%

	**Mol. Mass :** 112.13 $g.mol^{-1}$ **Mol. Formula :** $C_7H_{12}O$ **R.N.** = [100961-00-0]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.32 (1H, dd, *J* = 13.8, 6.9 Hz, H-6), 5.67 (1H, dq, *J* = 15.3, 6.3 Hz, H-2), 5.44 (1H, ddq, *J* = 15.3, 6.9, 1.5 Hz, H-3), 4.30 (1H, dd, *J* = 14.1, 1.2 Hz, H-

7*anti*), 4.27 (1H, quint, *J* = 6.6 Hz, H-4), 3.99 (1H, dd, *J* = 6.6, 1.5 Hz, H-7*syn*), 1.71 (3H, dd, *J* = 6, 1.2 Hz, H-1) 1.30 (3H, d, *J* = 6.3 Hz, H-5).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

150.7 (+, C-6), 132.5 and 127.8 (+, C-2 and C-3), 88.7 (-, C-7), 76.7 (+, C-4), 21.5 and 17.8 (+, C-1 and C-5).

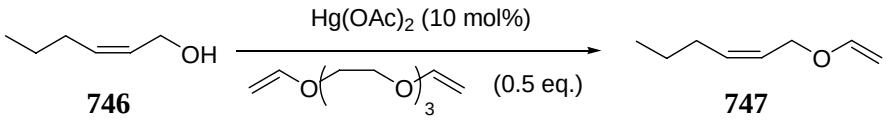
MS (EI, 70 eV) *m/z* (relative intensity, %):

112 ($M^{+\bullet}$, 2), 97 ($M^{+\bullet}$-$CH_3^\bullet$, 6), 85 ($M^{+\bullet}$-$C_2H_3^\bullet$, 5), 69 ($M^{+\bullet}$-$OCH{:}CH_2^\bullet$, 47), 44 (100).

IR (film):

3118 [w] (=C-H), 3050-2820 [s] (C-H), 1670-1590 [s] (C=C), 1450 [m], 1322 [m], 1194 [s] (C-O), 1080-1040 [s], 966 [s], 825 [w] cm^{-1}.

VII.7.5. (Z)-1-(vinyloxy)hex-2-ene 747

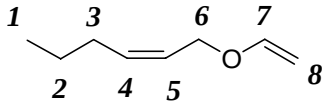


746 **747**

In an oblong flask were introduced allylic alcohol **746** (2.107 g, 19.98 mmol, 1 eq.), triethyleneglycol-divinylether **722** (2.006 g, 9.92 mmol, 0.50 eq) and mercuric acetate (0.786 g, 2.47 mmol, 0.12 eq.). The flask was closed and the neat mixture was heated at 65 °C for 3h. The mixture was then cooled to r.t. and 2.5 ml of a saturated solution of $NaHCO_3$ was added dropwise. The organic layer was washed two times with 2.5 ml of a saturated solution of $NaHCO_3$, dried on Na_2SO_4 and filtrated on cotton wool.

Horizontal distillation under vacuum (10 mm Hg, 50 °C) gave 0.513 g of pure allylvinylether **747**.

Isolated yield : 21%

	**Mol. Mass :** 126.20 g.mol^{-1} **Mol. Formula :** $C_8H_{14}O$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.48 (1H, dd, *J* = 14.4, 6.6 Hz, H-7), 5.61 (2H, m, H-4 and H-5), 4.28 (2H, d, *J* = 4.8 Hz, H-6), 4.17 (1H, dd, *J* = 14.4, 2.4 Hz, H-8*anti*), 4.02 (1H, dd, *J* = 6.9, 2.1 Hz, H-8*syn*), 2.06 (2H, q, *J* = 7.2 Hz, H-3), 1.41 (2H, sext, *J* = 7.2 Hz, H-2), 0.91 (3H, t, *J* = 7.2 Hz, H-1).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

151.8 (-, C-7), 134.2 and 125.1 (-, C-4 and C-5), 87.0 (+, C-8), 64.3 (+, C-6), 29.9 (+, C-3), 22.8 (+, C-2), 13.9 (-, C-1).

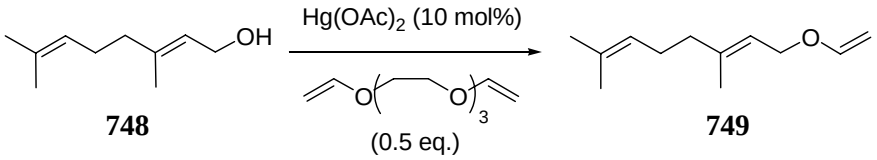
MS (EI, 70 eV) *m/z* (relative intensity, %):

127 ($MH^{+\bullet}$, 7), 126 ($M^{+\bullet}$, 5), 99 ($M^{+\bullet}$-$C_2H_3^{\bullet}$, 8), 83 ($M^{+\bullet}$-$OCH{:}CH_2^{\bullet}$, 100), 69 ($M^{+\bullet}$-$CH_2OCH{:}CH_2^{\bullet}$, 23), 55 (79), 44 (7).

IR (film):

3040-2840 [s] (C-H), 1750-1590 [s] (C=C), 1459 [m], 1380 [m], 1200-1080 [s] (C-O), 975 [m] cm^{-1}.

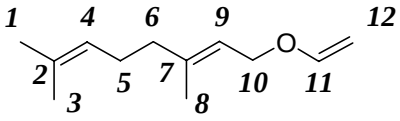
VII.7.6. (E)-3,7-dimethyl-1-(vinyloxy)octa-2,6-diene **749**



748 **749**

In an oblong flask were introduced allylic alcohol **748** (3.296 g, 21.37 mmol, 1 eq.), triethyleneglycol-divinylether **722** (2.049 g, 10.13 mmol, 0.47 eq) and mercuric acetate (0.793 g, 2.49 mmol, 0.12 eq.). The flask was closed and the neat mixture was heated at 65 °C for 3h. The mixture was then cooled to r.t. and 2.5 ml of a saturated solution of $NaHCO_3$ was added dropwise. The organic layer was washed two times with 2.5 ml of a saturated solution of $NaHCO_3$, dried on Na_2SO_4 and filtrated on cotton wool. Horizontal distillation under vacuum (10 mm Hg, 50 °C) gave 1.350 g of pure allylvinylether **749**.

Isolated yield : 37%

	**Mol. Mass :** 180.29 g.mol^{-1} **Mol. Formula :** $C_{12}H_{20}O$ **R.N.** = [17957-93-6]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.46 (1H, dd, *J* = 14.1, 6.6 Hz, H-11), 5.39 (1H, td, *J* = 6.6, 1.4 Hz, H-4 or H-9), 5.09 (1H, t, *J* = 6.3 Hz, H-4 or H-9), 4.24 (2H, d, *J* = 6.6 Hz, H-10), 4.21 (1H, dd, *J* = 14.4, 1.8 Hz, H-12*anti*), 4.01 (1H, dd, *J* = 6.6, 1.8 Hz, H-12*syn*), 2.17-2.01 (4H, m, H-5 and H-6), 1.69 (6H, s, H-1 and H-3), 1.60 (3H, s, H-8).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

151.9 (-, C-11), 141.2 and 131.9 (+, C-2 and C-7), 124.1 and 119.7 (-, C-4 and C-9), 86.9 (+, C-12), 65.3 (+, C-10), 39.8 and 26.7 (+, C-5 and C-6), 25.9 (-, C-8), 17.9 and 16.8 (-, C-1 and C-3).

MS (EI, 70 eV) *m/z* (relative intensity, %):

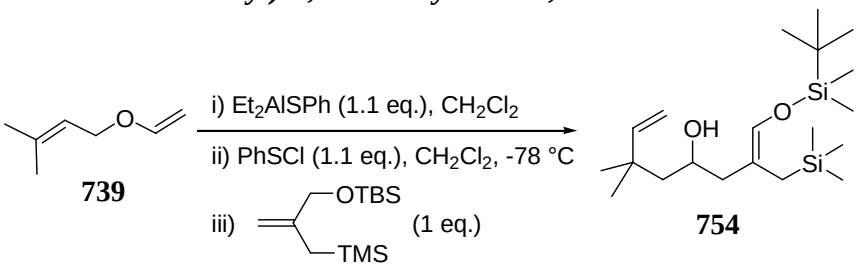
180 ($MH^{+\bullet}$, 1), 153 ($M^{+\bullet}$-$C_2H_3^{\bullet}$, 2), 137 ($M^{+\bullet}$-$OCH{:}CH_2^{\bullet}$, 10), 95 (9), 81 (33), 69 (100), 44 (3).

IR (film):

3118 [w] (=C-H), 3030-2810 [s] (C-H), 1760-1570 [s] (C=C), 1450 [m], 1378 [m], 1315 [m], 1195 [s] (C-O), 1050 [m], 987 [m], 813 [w] cm^{-1}.

VII.8. The "one-pot" Claisen-ene reactions

VII.8.1. (Z)-1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-6,6-dimethyl-octa-1,7-dien-4-ol 754

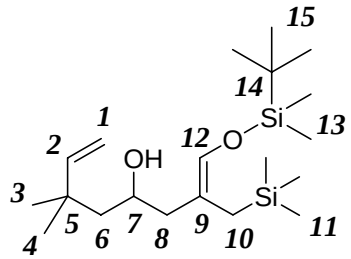


739 **379** **754**

To neat thiophenol (0.150 g, 1.35 mmol, 1.16 eq.) was added dropwise 1.35 ml of triethylaluminium (1M solution in hexanes, 1.35 mmol, 1.16 eq.). The mixture was stirred at 25 °C for 30 min. To a solution of

allylvinylether **739** (0.130 g, 1.16 mmol, 1 eq.) in 15 ml of CH_2Cl_2 was added dropwise the freshly prepared solution of Et_2AlSPh. This mixture was stirred at 25 °C for 30 min. and then cooled at -78 °C. To this cooled mixture was added dropwise and successively 0.193 g of PhSCl (1.33 mmol, 1.14 eq.) and 0.343 g of allylsilane **379** (86 % pur, 1.06 mmol, 0.91 eq.). The mixture was stirred at -78 °C for 2h, then 15 ml of a saturated aqueous solution of $NaHCO_3$ was added and the mixture was allowed to warm up to r.t.. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 0.195 g of pure ene adduct **754**.

Isolated yield : 51% (over three steps)



Mol. Mass : 370.72 $g.mol^{-1}$
Mol. Formula : $C_{20}H_{42}O_2Si_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.07 (1H, s, H-12), 5.90 (1H, dd, *J* = 17.1, 9.9 Hz, H-2), 4.97 (1H, dd, *J* = 17.4, 1.2 Hz, H-1*anti*), 4.95 (1H, dd, *J* = 10.5, 1.5 Hz, H-1*syn*), 3.75-3.65 (1H, m, H-7), 1.93 (1H, ddd, *J* = 13.8, 4.2, 0.9 Hz, H-8a), 1.83 (1H, dd, *J* = 13.8, 8.4 Hz, H-8b), 1.67 (1H, d, *J* = 13.5 Hz, H-10a), 1.48 (1H, dd, *J* = 14.1, 7.5 Hz, H-6a), 1.40 (1H, dd, *J* = 14.4, 3.3 Hz, H-6b), 1.26 (1H, d, *J* = 13.5 Hz, H-10b), 1.07 (3H, s, H-3 or H-4), 1.06 (3H, s, H-3 or H-4), 0.91 (9H, s, H-15), 0.10 (6H, s, H-13), 0.01 (9H, s, H-11).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

149.1 (+, C-2), 134.7 (+, C-12), 115.4 (-, C-9), 110.7 (-, C-1), 66.0 (+, C-7), 49.8 (-, C-6), 43.5 (-, C-8), 36.6 (-, C-5), 27.8 (+, C-15), 26.0 (+, C-3 and C-4), 18.4 (-, C-14), 17.5 (-, C-10), -0.40 (+, C-11), -4.93 (+, C-13).

MS (EI, 70 eV) *m/z* (relative intensity, %):

371 ($MH^{+\bullet}$, 1), 370 ($M^{+\bullet}$, 2), 355 ($M^{+\bullet}$-$CH_3^{\bullet}$, 2), 313 ($M^{+\bullet}$-C_2H_3-2*$CH_3^{\bullet}$, 10), 283 (7), 257 ($M^{+\bullet}$-CH_2:$CHC(CH_3)_2CH_2OH^{\bullet}$, 8), 233 (13), 218 (12), 185 ($M^{+\bullet}$-TBS-$TMS^{\bullet}$, 6), 147 ($Me_3SiOSiMe_2^{+}$, 18), 115 (TBS^{+}, 7), 95 (16), 75 (Me_2SiOH^{+}, 29), 73 (TMS^{+}, 100), 69 (52).

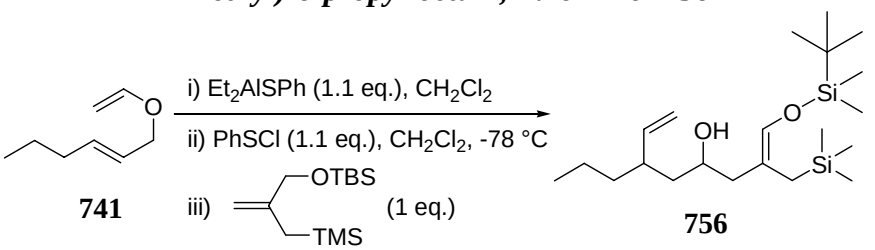
IR (film):

3397 [w] (O-H), 3082 [w] (=C-H), 2980-2830 [s] (C-H), 1662 and 1638 [m] (C=C), 1472 [m], 1412 [m], 1362 [m], 1249 [s] (C-O), 1166 [m] (C-Si), 1098 [w], 1003 [w], 838 [s] (C-Si) cm^{-1}.

Elemental Analysis:

($C_{20}H_{42}O_2Si_2$) *Calculated*: C, 64.80; H, 11.42% ; *found*: C, 65.26; H, 11.46 %.

VII.8.2. (Z)-1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-6-propyl-octa-1,7-dien-4-ol 756

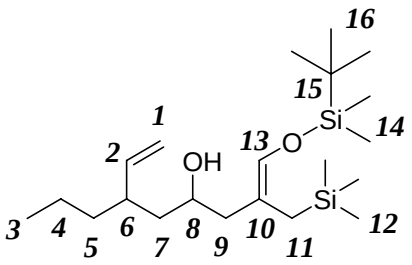


741 **379** **756**

To neat thiophenol (0.117 g, 1.06 mmol, 1.01 eq.) was added dropwise 1.05 ml of triethylaluminium (1M solution in hexanes, 1.05 mmol, 1.01 eq.). The mixture was stirred at 25 °C for 30 min. To a solution of allylvinylether **741** (0.131 g, 1.04 mmol, 1 eq.) in 15 ml of CH_2Cl_2 was added dropwise the freshly prepared solution of Et_2AlSPh. This mixture was stirred at 25 °C for 30 min. and then cooled at -78 °C. To this cooled mixture was added dropwise and successively 0.154 g of PhSCl (1.05 mmol, 1.01 eq.) and 0.287 g of allylsilane **379** (86 % pur, 0.96 mmol, 0.92 eq.). The mixture was stirred at -78 °C for 2h, then 15 ml of a saturated aqueous solution of $NaHCO_3$ was added and the mixture was allowed to warm up to r.t.. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 0.216 g of pure ene adduct **756**.

Isolated yield : 54% (over three steps)

Diastereoisomeric ratio : 3.5:1



Mol. Mass : 384.75 $g.mol^{-1}$
Mol. Formula : $C_{21}H_{44}O_2Si_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): major isomer

6.08 (1H, s, H-13), 5.51 (1H, ddd, *J* = 17.1, 10.5, 9 Hz, H-2), 5.07-4.98 (2H, m, H-1), 3.70-3.55 (1H, m, H-8), 2.38-2.24 (1H, m, H-6), 1.96 (1H, dd, *J* =

13.5, 3.6 Hz, H-9a), 1.81 (1H, dd, *J* = 13.8, 9 Hz, H-9b), 1.71 (1H, d, *J* = 13.2 Hz, H-11a), 1.56-1.16 (7H, m, H-4, H-5, H-7 and H-11b), 0.91 (9H, s, H-16), 0.89 (3H, t, *J* = 7.2 Hz, H-3), 0.10 (6H, s, H-14), 0.01 (9H, s, H-12).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): minor isomer

6.08 (1H, s, H-13), 5.62 (1H, dd, *J* = 17.1, 8.7 Hz, H-2), 5.03-4.94 (2H, m, H-1), 3.70-3.55 (1H, m, H-8), 2.38-2.24 (1H, m, H-6), 2.07 (1H, dd, *J* = 13.5, 2.4 Hz, H-9a), 1.78-1.69 (1H, m, H-9b), 1.71 (1H, d, *J* = 13.2 Hz, H-11a), 1.56-1.16 (7H, m, H-4, H-5, H-7 and H-11b), 0.91 (9H, s, H-16), 0.89 (3H, t, *J* = 7.2 Hz, H-3), 0.10 (6H, s, H-14), 0.01 (9H, s, H-12).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

143.2 (-, C-2), 134.5 (-, C-13), 114.9 (+, C-1), 114.3 (+, C-10), 66.2 (-, C-8), 42.7 (+, C-7), 40.9 (-, C-6), 38.3 (+, C-9), 26.0 (-, C-16), 20.4 (+, C-4 and C-5), 18.4 (+, C-15), 17.7 (+, C-11), 14.4 (-, C-3), -0.37 (-, C-12), -4.98 (-, C-14).

MS (EI, 70 eV) *m/z* (relative intensity, %):

385 ($MH^{+\bullet}$, 1), 384 ($M^{+\bullet}$, 4), 369 ($M^{+\bullet}$-$CH_3^{\bullet}$, 1), 257 (12), 218 (32), 199 ($M^{+\bullet}$-TBS-$TMS^{\bullet}$, 5), 185 (7), 147 ($Me_3SiOSiMe_2^{+}$, 14), 115 (TBS^{+}, 4), 109 (64), 75 (Me_2SiOH^{+}, 34), 73 (TMS^{+}, 100), 67 (16), 55 (18).

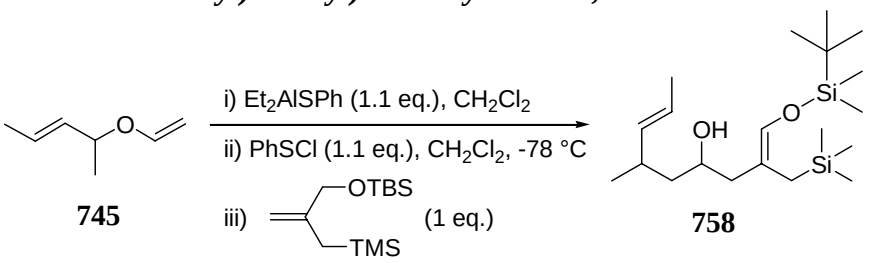
IR (film):

3423 [w] (O-H), 3075 [w] (=C-H), 2970-2840 [s] (C-H), 1660 [m] (C=C), 1472 [m], 1417 [m], 1362 [m], 1249 [s] (C-O), 1164 [s] (C-Si), 1101 [w], 875 [m], 838 [s] (C-Si) cm^{-1}.

Elemental Analysis:

($C_{21}H_{44}O_2Si_2$) *Calculated*: C, 65.56; H, 11.53 % ; *found*: C, 65.61; H, 11.34 %.

VII.8.3. (1Z,7E)-1-(tertbutyldimethyl-silyloxy)-2-((trimethyl-silyl)-methyl)-6-methyl-nona-1,7-dien-4-ol 758

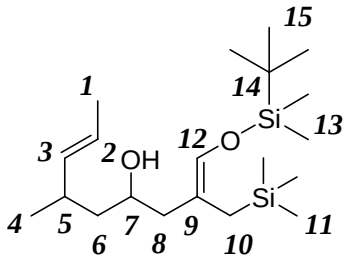


745 **379** **758**

To neat thiophenol (0.216 g, 1.95 mmol, 1.16 eq.) was added dropwise 1.95 ml of triethylaluminium (1M solution in hexanes, 1.95 mmol, 1.16 eq.). The mixture was stirred at 25 °C for 30 min. To a solution of allylvinylether **745** (0.188 g, 1.68 mmol, 1 eq.) in 20 ml of CH_2Cl_2 was added dropwise the freshly prepared solution of Et_2AlSPh. This mixture was stirred at 45 °C for 3h and then cooled at -78 °C. To this cooled mixture was added dropwise and successively 0.263 g of PhSCl (1.82 mmol, 1.08 eq.) and 0.528 g of allylsilane **379** (86 % pur, 1.82 mmol, 1.08 eq.). The mixture was stirred at -78 °C for 2h, then 20 ml of a saturated aqueous solution of $NaHCO_3$ was added and the mixture was allowed to warm up to r.t.. The aqueous layer was extracted with CH_2Cl_2 (3 x 25 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 0.313 g of pure ene adduct **758**.

Isolated yield : 50% (over three steps)

Diastereoisomeric ratio : 2:1



Mol. Mass : 370.72 g.mol^{-1}
Mol. Formula : $C_{20}H_{42}O_2Si_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): major isomer

6.08 (1H, s, H-12), 5.52-5.20 (2H, m, H-2 and H-3), 3.70-3.50 (1H, m, H-7), 2.42-2.32 (1H, m, H-5), 1.97 (1H, dd, *J* = 13.8, 4.2 Hz, H-8a), 1.79 (1H, dd, *J* = 13.8, 9 Hz, H-8b), 1.71 (1H, d, *J* = 13.2 Hz, H-10a), 1.66 (3H, dd, *J* = 6, 1.2 Hz, H-1), 1.52-1.15 (3H, m, H-6 and H-10b), 0.98 (3H, d, *J* = 6.6 Hz, H-4), 0.92 (9H, s, H-15), 0.10 (6H, s, H-13), 0.01 (9H, s, H-11).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): minor isomer

6.08 (1H, s, H-12), 5.52-5.08 (2H, m, H-2 and H-3), 3.70-3.50 (1H, m, H-7), 2.32-2.22 (1H, m, H-5), 2.03 (1H, dd, *J* = 14.1, 3.9 Hz, H-8a), 1.82-1.70 (1H, m, H-8b), 1.71 (1H, d, *J* = 13.2 Hz, H-10a), 1.64 (3H, dd, *J* = 5.4, 0.9 Hz, H-1), 1.52-1.15 (3H, m, H-6 and H-10b), 0.99 (3H, d, *J* = 6.6 Hz, H-4), 0.92 (9H, s, H-15), 0.10 (6H, s, H-13), 0.01 (9H, s, H-11).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

137.3, 134.6, 132.4, 129.3 and 123.9 (-, C-2, C-3 and C-12), 115.4 (+, C-9), 66.5 (-, C-7), 44.7 and 42.6 (+, C-6 and C-8), 34.1 (-, C-5), 25.9 (-, C-15),

21.9 and 18.1 (-, C-1 and C-4), 18.4 (+, C-14), 17.6 (+, C-10), -0.62 (-, C-11), -4.90 (-, C-13).

MS (EI, 70 eV) *m/z* (relative intensity, %):

370 ($M^{+\bullet}$, 1), 355 ($M^{+\bullet}$-$CH_3^{\bullet}$, 1), 250 (12), 218 (16), 185 ($M^{+\bullet}$-TBS-$TMS^{\bullet}$, 14), 150 (21), 109 (30), 95 ($CH_3CH{:}CHCH(CH_3)CH_2CH_2^+$, 23), 75 ($Me_2SiOH^+$, 75), 73 ($TMS^+$, 100), 69 (79), 55 (34).

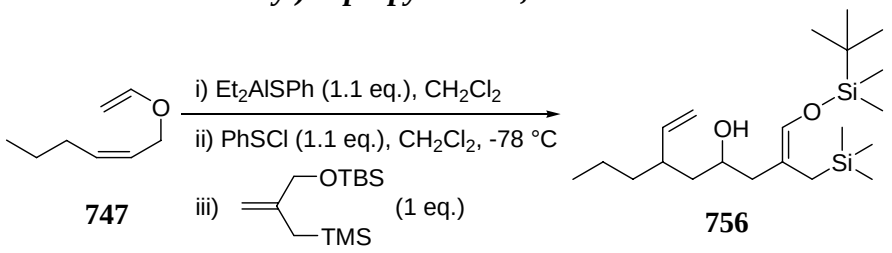
IR (film):

3450 [w] (O-H), 2980-2830 [s] (C-H), 1660 [m] (C=C), 1472 [m], 1407 [m], 1362 [w], 1249 [s] (C-O), 1163 [s] (C-Si), 1100 [m], 969 [w], 839 [s] (C-Si), 780 [m] cm^{-1}.

Elemental Analysis:

($C_{20}H_{42}O_2Si_2$) *Calculated*: C, 64.80; H, 11.42 % ; *found*: C, 64.94; H, 11.13 %.

VII.8.4. (Z)-1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-6-propyl-octa-1,7-dien-4-ol 756



747 **379** **756**

To neat thiophenol (0.139 g, 1.24 mmol, 1.11 eq.) was added dropwise 1.25 ml of triethylaluminium (1M solution in hexanes, 1.25 mmol, 1.12 eq.). The mixture was stirred at 25 °C for 30 min. To a solution of

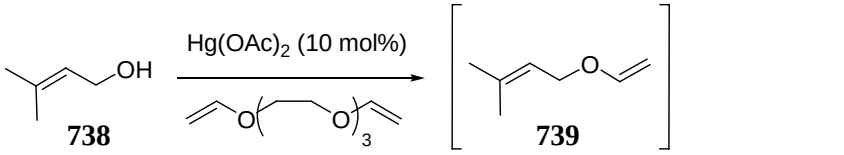
allylvinylether **747** (0.140 g, 1.11 mmol, 1 eq.) in 20 ml of CH_2Cl_2 was added dropwise the freshly prepared solution of Et_2AlSPh. This mixture was stirred at 45 °C for 3h and then cooled at -78 °C. To this cooled mixture was added dropwise and successively 0.182 g of PhSCl (1.26 mmol, 1.13 eq.) and 0.345 g of allylsilane **379** (86 % pur, 1.19 mmol, 1.07 eq.). The mixture was stirred at -78 °C for 2h, then 20 ml of a saturated aqueous solution of $NaHCO_3$ was added and the mixture was allowed to warm up to r.t.. The aqueous layer was extracted with CH_2Cl_2 (3 x 25 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 0.204 g of pure ene adduct **756**.

Isolated yield : 48% (over three steps)

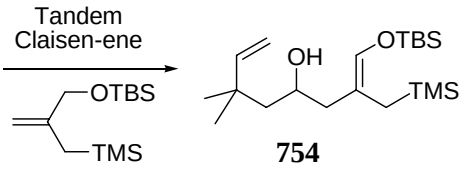
Analysis: *see* pg 332-334

VII.9. The "sequential" reactions

VII.9.1. (Z)-1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-6,6-dimethyl-octa-1,7-dien-4-ol 754



738 **722** (3 eq.) **739**



379 **754**

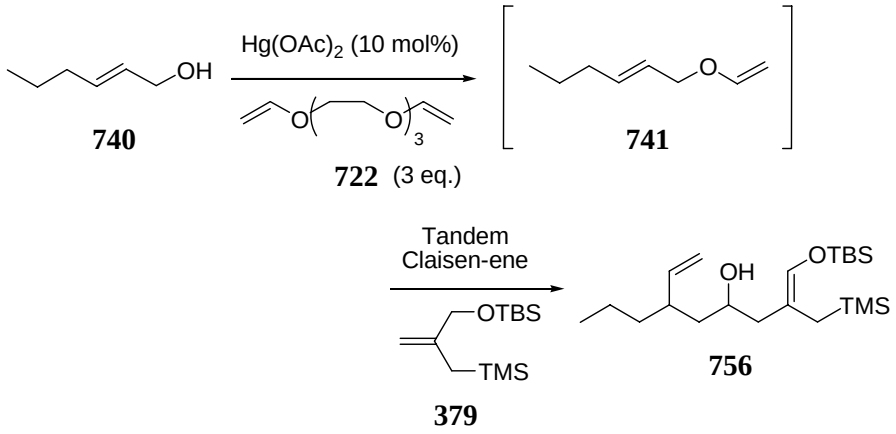
In an oblong flask were introduced allylic alcohol **738** (0.439 g, 5.10 mmol, 1 eq.), triethyleneglycol-divinylether **722** (3.029 g, 14.98 mmol, 2.94 eq.) and mercuric acetate (0.167 g, 0.53 mmol, 0.11 eq.). The flask was closed and the neat mixture was heated at 65 °C for 2h. Direct chromatography of this mixture over silica gel (eluted with CH_2Cl_2-pentane, 1:1) gave 54.70 g of diluted allylvinylether **739** directly used in the tandem Claisen-ene reaction (as below).

Using 0.620 g of thiophenol (5.60 mmol, 1.10 eq.), 5.60 ml of triethylaluminium (1M solution in hexanes, 5.60 mmol, 1.10 eq), 0.802 g of PhSCl (5.5 mmol, 1.08 eq.) and 1.621 g of allylsilane **379** (86 % pure, 5.40 mmol, 1.06 eq.). Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 0.843 g of pure ene adduct **754**.

Isolated yield : 45% (over four steps)

Analysis: *see* pg 330-331

VII.9.2. (Z)-1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-6-propyl-octa-1,7-dien-4-ol 756



740 **722** (3 eq.) **741**

379 **756**

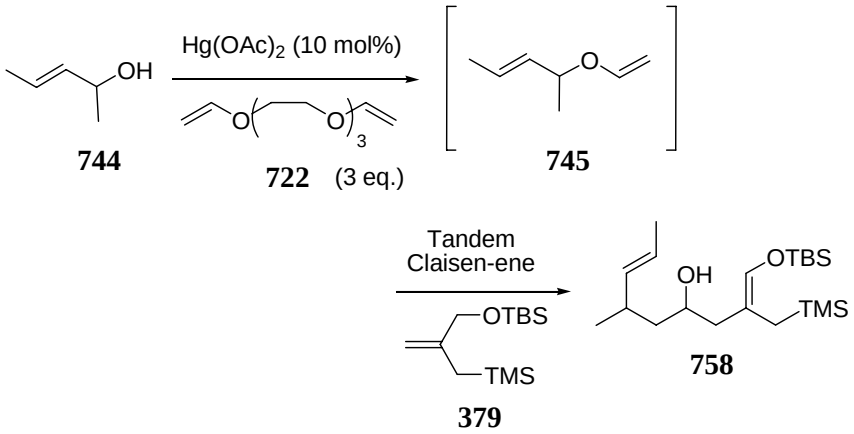
In an oblong flask were introduced allylic alcohol **740** (1.250 g, 12.48 mmol, 1 eq.), triethyleneglycol-divinylether **722** (7.575 g, 37.49 mmol, 3.00 eq.) and mercuric acetate (0.402 g, 1.26 mmol, 0.10 eq.). The flask was closed and the neat mixture was heated at 65 °C for 3h. Direct chromatography of this mixture over silica gel (eluted with CH_2Cl_2-pentane, 1:1) gave 154.28 g of diluted allylvinylether **741** directly used in the tandem Claisen-ene reaction (as below).

Using 1.387 g of thiophenol (12.51 mmol, 1 eq.), 12.50 ml of triethylaluminium (1M solution in hexanes, 12.50 mmol, 1 eq), 1.811 g of PhSCl (12.52 mmol, 1 eq.) and 3.549 g of allylsilane **379** (86 % pure, 11.99 mmol, 0.96 eq.). Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 1.483 g of pure ene adduct **756**.

Isolated yield : 33% (over four steps)

Analysis: *see* pg 332-334

VII.9.3. (1Z,7E)-1-(tertbutyldimethyl-silyloxy)-2-((trimethyl-silyl)-methyl)-6-methyl-nona-1,7-dien-4-ol **758**



744 **722** (3 eq.) **745** **379** **758**

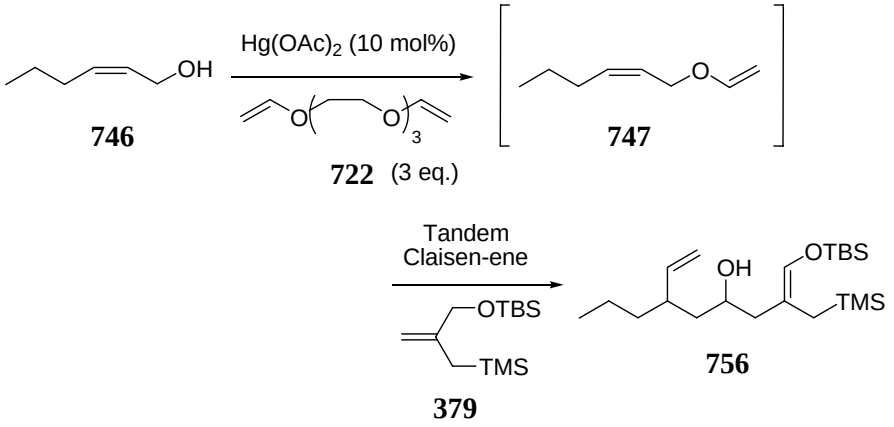
In an oblong flask were introduced allylic alcohol **744** (0.244 g, 2.83 mmol, 1 eq.), triethyleneglycol-divinylether **722** (1.743 g, 8.62 mmol, 3.04 eq.) and mercuric acetate (0.094 g, 0.29 mmol, 0.10 eq.). The flask was closed and the neat mixture was heated at 65 °C for 24h. Direct chromatography of this mixture over silica gel (eluted with CH_2Cl_2-pentane, 1:1) gave 36.17 g of diluted allylvinylether **745** directly used in the tandem Claisen-ene reaction (as below).

Using 0.367 g of thiophenol (3.31 mmol, 1.17 eq.), 3.30 ml of triethylaluminium (1M solution in hexanes, 3.30 mmol, 1.17 eq), 0.454 g of PhSCl (3.14 mmol, 1.11 eq.) and 0.922 g of allylsilane **379** (86 % pure, 3.17 mmol, 1.12 eq.). Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 0.302 g of pure ene adduct **758**.

Isolated yield : 29% (over four steps)

Analysis: *see* pg 335-336

VII.9.4. (Z)-1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-6-propyl-octa-1,7-dien-4-ol 756



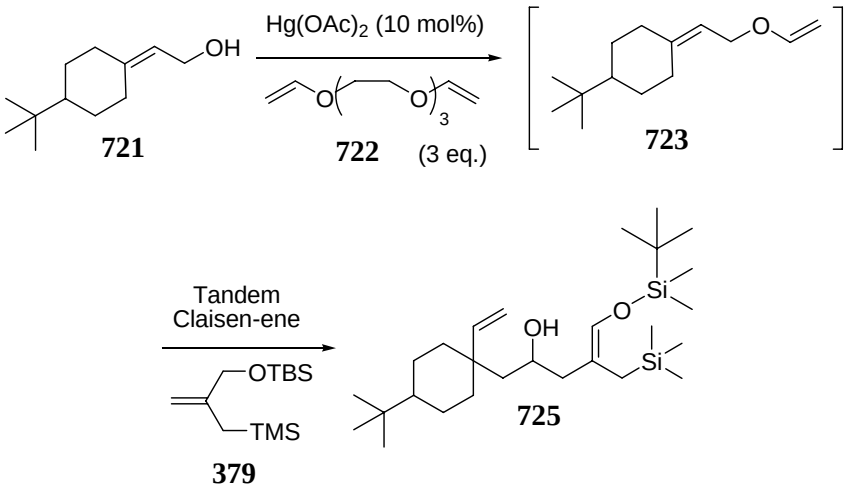
In an oblong flask were introduced allylic alcohol **746** (0.201 g, 2 mmol, 1 eq.), triethyleneglycol-divinylether **722** (1.205 g, 5.95 mmol, 2.98 eq.) and mercuric acetate (0.070 g, 0.22 mmol, 0.11 eq.). The flask was closed and the neat mixture was heated at 65 °C for 3h. Direct chromatography of this mixture over silica gel (eluted with CH_2Cl_2-pentane, 1:1) gave 23.27 g of diluted allylvinylether **747** directly used in the tandem Claisen-ene reaction (as below).

Using 0.234 g of thiophenol (2.11 mmol, 1.12 eq.), 2.10 ml of triethylaluminium (1M solution in hexanes, 2.10 mmol, 1.11 eq), 0.298 g of PhSCl (2.06 mmol, 1.09 eq.) and 0.538 g of allylsilane **379** (86 % pure, 1.79 mmol, 0.95 eq.). Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 0.222 g of pure ene adduct **756**.

Isolated yield : 32% (over four steps)

Analysis: *see* pg 332-334

VII.9.5. (Z)-5-(tertbutyldimethyl-silyloxy)-1-(4-tertbutyl-1-vinylcyclohexyl)-4-((trimethylsilyl)-methyl)-pent-4-en-2-ol 725



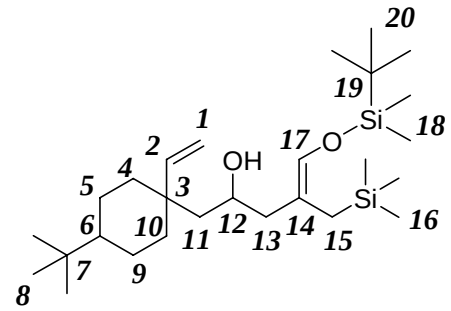
In an oblong flask were introduced allylic alcohol **721** (1.015 g, 5.57 mmol, 1 eq.), triethyleneglycol-divinylether **722** (3.329 g, 16.46 mmol, 2.96 eq.) and mercuric acetate (0.190 g, 0.60 mmol, 0.11 eq.). The flask was closed and the neat mixture was heated at 65 °C for 4h. Direct chromatography of this mixture over silica gel (eluted with CH_2Cl_2-pentane, 1:1) gave 56.13 g of diluted allylvinylether **723** directly used in the tandem Claisen-ene reaction (as below).

Using 0.677 g of thiophenol (6.10 mmol, 1.10 eq.), 6.10 ml of triethylaluminium (1M solution in hexanes, 6.10 mmol, 1.10 eq), 0.895 g of PhSCl (6.19 mmol, 1.11 eq.) and 1.659 g of allylsilane **379** (86 % pure, 5.58

mmol, 1 eq.). Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 1.192 g of pure ene adduct **725**.

Isolated yield : 46% (over four steps)

Diastereoisomeric ratio : 1:1



Mol. Mass : 466.90 g.mol^{-1}
Mol. Formula : $C_{27}H_{54}O_2Si_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.07 (1H, s, H-17), 6.04 (1H, s, H-17'), 5.87 (1H, dd, *J* = 17.7, 11.1 Hz, H-2), 5.66 (1H, dd, *J* = 17.7, 11.1 Hz, H-2'), 5.21 (1H, dd, *J* = 10.5, 0.9 Hz, H-1*syn*), 5.04 (1H, dd, *J* = 177, 0.9 Hz, H-1*anti*), 4.96 (1H, dd, *J* = 9.3, 0.9 Hz, H1*syn*'), 4.95 (1H, dd, *J* = 17.7, 0.9 Hz, H1*anti*'), 3.82-3.72 (1H, m, H-12), 3.72-3.63 (1H, m, H-12'), 1.97-1.72 (6H, m) and 1.72-1.44 (10H, m) and 1.44-1.02 (14H, m, H-4, H-5, H-6, H-9, H-10, H-11, H-13 and H-15), 0.90 (18H, s, H-20), 0.84 (9H, s, H-8), 0.80 (9H, s, H-8'), 0.09 (12H, s, H-18), 0.01 (18H, s, H-16).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

150.4 and 146.1 (-, C-2), 134.6 and 134.5 (-, C-17), 115.5 and 115.4 (+, C-14), 114.6 and 110.5 (+, C-1), 65.1 and 64.3 (-, C-12), 52.0 and 43.5 (+, C-11), 48.8 and 48.5 (-, C-6), 39.9 and 38.4 (+, C-7), 32.7 and 32.6 (+, C-13), 30.0 (+, C-3), 27.9 and 27.8 (-, C-8 or C-20), 26.1 and 26.0 (-, C-8 or C-20),

41.4, 37.3, 37.1, 35.9, 23.5, 23.4, 22.7 and 22.6 (+, C-4, C-5, C-9 and C-10), 18.4 (+, C-19), 17.6 and 17.4 (+, C-15), -0.30 and -0.38 (-, C-16), -4.88 and -4.95 (-, C-18).

MS (EI, 70 eV) *m/z* (relative intensity, %):

466 ($M^{+\bullet}$, 1), 451 ($M^{+\bullet}$-$CH_3^{\bullet}$, 16), 218 (36), 164 (47), 149 (70), 109 (100), 57 ($^tBu^+$, 43).

IR (film):

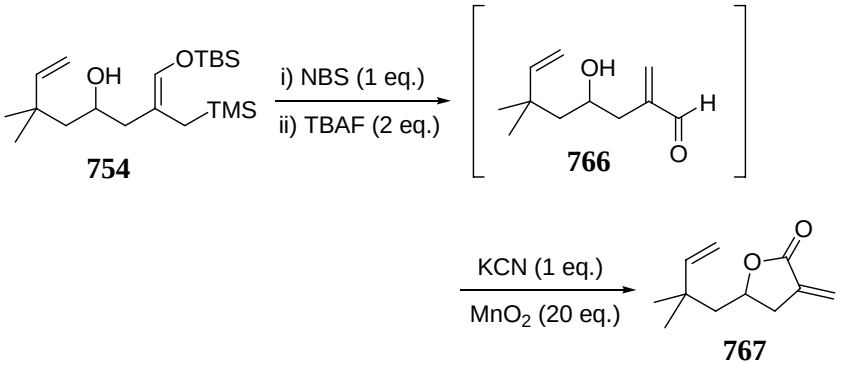
3563 [m] (O-H), 3064 [w] (=C-H), 2970-2800 [s] (C-H), 1656 [m] (C=C), 1468 [m], 1413 [m], 1365 [m], 1249 [s] (C-O), 1197 [s] (C-Si), 1113 [w], 838 [s] (C-Si) cm^{-1}.

HRMS (CI+, $M^{+\bullet}$):

($C_{27}H_{54}O_2Si_2$) *Calculated*: 466.3662 ; *found*: 466.3663.

VII.10. Synthesis of the α-methylene-γ-butyrolactones

VII.10.1. dihydro-5-(2,2-dimethylbut-3-enyl)-3-methylene-furan-2(3H)-one 767

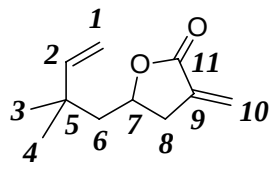


754 **766** **767**

To a solution of ene adduct **754** (0.900 g, 2.43 mmol, 1 eq.) in 30 ml of anhydrous THF was added N-bromosuccinimide (0.436 g, 2.45 mmol, 1.01 eq.). The mixture was stirred for 10 min. and the THF was eliminated *in vacuo*. The resulting white precipitate was filtered and washed with 25 ml of pentane. The pentane was removed under reduced pressure and this crude is directly dissolved in 30 ml of THF. To this mixture was added tetrabutylammonium fluoride (1 M solution in THF, 4.95 ml, 4.95 mmol, 2.03 eq.) and the resulting yellow solution was stirred for 5 min. The mixture was then diluted with 30 ml of Et_2O and transferred to a separatory funnel containing 50 ml of brine. After separation, the aqueous phase was extracted with ether (3 x 30 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude obtained was directly used in the subsequent oxidation step.

To a cold (0 °C) solution of crude enal **766** (0.443 g, 2.43 mmol, 1 eq.) in 30 ml of CH_3CN P.A. were successively added manganese dioxide (4.226 g, 48.61 mmol, 20 eq.) and potassium cyanide (0.158 g, 2.43 mmol, 1 eq.). The resulting black solution was stirred at room temperature for 15 h. The mixture was then filtered through silica gel and washed with 2 x 30 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.273 g of pure corresponding methylenelactone **767**.

Isolated yield : 63% (over three steps)

	**Mol. Mass :** 181.13 g.mol^{-1} **Mol. Formula :** $C_{11}H_{17}O_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.20 (1H, t, *J* = 2.7 Hz, H-10a), 5.81 (1H, dd, *J* = 17.7, 9.9 Hz, H-2), 5.60 (1H, t, *J* = 2.4 Hz, H-10b), 5.00 (1H, dd, *J* = 10.8, 0.9 Hz, H-1*syn*), 4.98 (1H, dd, *J* = 17.4, 0.9 Hz, H-1*anti*), 4.52 (1H, tdd, *J* = 7.5, 7.2, 4.5 Hz, H-7), 3.04 (1H, ddt, *J* = 17.1, 7.2, 2.4 Hz, H-8a), 2.54 (1H, ddt, *J* = 16.8, 7.2, 2.7 Hz, H-8b), 1.84 (1H, dd, *J* = 14.1, 7.2 Hz, H-6a), 1.60 (1H, dd, *J* = 14.4, 4.8 Hz, H-6b), 1.12 (3H, s, H-3 or H-4), 1.07 (3H, s, H-3 or H-4).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

170.4 (+, C-11), 147.4 (-, C-2), 135.1 (+, C-9), 121.7 (+, C-10), 111.7 (+, C-1), 75.7 (-, C-7), 49.2 (+, C-8), 36.3 (+, C-5), 35.8 (+, C-6), 28.5 and 26.5 (-, C-3 and C-4).

MS (EI, 70 eV) *m/z* (relative intensity, %):

181 ($MH^{+\bullet}$, 100), 163 ($M^{+\bullet}$-$CH{:}CH_2^{\bullet}$, 23), 135 ($M^{+\bullet}$-$CO_2^{\bullet}$-H, 46), 97 ($M^{+\bullet}$-$CH_2{:}CHC(CH_3)_2CH_2^{\bullet}$, 51), 95 (66), 69 ($C(O)C(CH_2)CH_2^{+}$, 81), 55 (15).

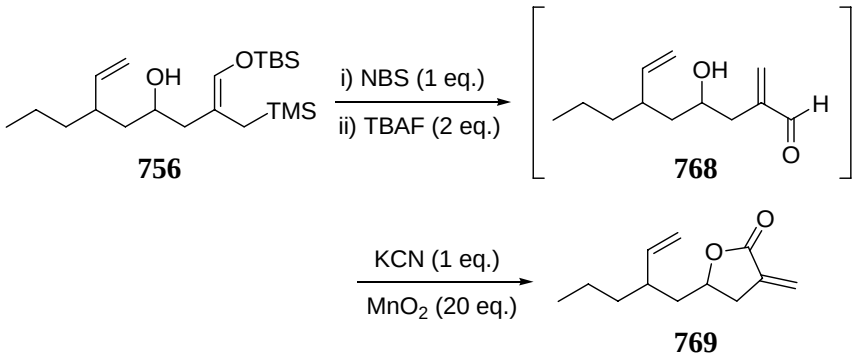
IR (film):

3084 [m] (=C-H), 2980-2850 [s] (C-H), 1763 [s] (C=O), 1666 and 1639 [m] (C=C), 1437, 1399 and 1352 [m], 1277 and 1252 [s] (C-O), 1124 [s], 995 and 913 [s] cm^{-1}.

HRMS ($MH^{+\bullet}$):

($C_{11}H_{17}O_2$) *Calculated*: 181.1228 ; *found*: 181.1226.

VII.10.2. dihydro-3-methylene-5-(2-vinylpentyl)furan-2(3H)-one 769



756 **768** **769**

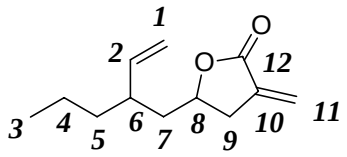
To a solution of ene adduct **756** (0.600 g, 1.56 mmol, 1 eq.) in 20 ml of anhydrous THF was added N-bromosuccinimide (0.280 g, 1.57 mmol, 1.01 eq.). The mixture was stirred for 10 min. and the THF was eliminated *in vacuo*. The resulting white precipitate was filtered and washed with 15 ml of pentane. The pentane was removed under reduced pressure and this crude is directly dissolved in 20 ml of THF. To this mixture was added tetrabutylammonium fluoride (1 M solution in THF, 3.1 ml, 3.1 mmol, 1.99 eq.) and the resulting yellow solution was stirred for 5 min. The mixture was then diluted with 20 ml of Et_2O and transferred to a separatory funnel containing 40 ml of brine. After separation, the aqueous phase was extracted with ether (3 x 20 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude obtained was directly used in the subsequent oxidation step.

To a cold (0 °C) solution of crude enal **768** (0.302 g, 1.56 mmol, 1 eq.) in 20 ml of CH_3CN P.A. were successively added manganese dioxide (2.732 g, 31.42 mmol, 20.1 eq.) and potassium cyanide (0.104 g, 1.59 mmol, 1.02 eq.). The resulting black solution was stirred at room temperature for 15

h. The mixture was then filtered through silica gel and washed with 2 x 20 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.185 g of pure corresponding methylenelactone **769**.

Isolated yield : 59% (over three steps)

Diastereoisomeric ratio : 3.5:1

	**Mol. Mass :** 195.14 g.mol^{-1} **Mol. Formula :** $C_{12}H_{19}O_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): major isomer

6.21 (1H, t, *J* = 3 Hz, H-11a), 5.61 (1H, t, *J* = 2.7 Hz, H-11b), 5.48 (1H, ddd, *J* = 17.1, 10.2, 9.3 Hz, H-2), 5.08 (1H, ddd, *J* = 16.8, 2.1, 1.2 Hz, H-1*anti*), 5.06 (1H, dd, *J* = 9, 2.1 Hz, H-1*syn*), 4.61-4.50 (1H, m, H-8), 3.03 (1H, ddt, *J* = 16.8, 7.5, 2.7 Hz, H-9a), 2.54 (1H, ddt, *J* = 17.1, 6.6, 3.3 Hz, H-9b), 2.42-2.28 (1H, m, H-6), 1.74 (1H, ddd, *J* = 13.8, 10.2, 3.9 Hz, H-7a), 1.46 (1H, ddd, *J* = 14.4, 11.1, 3.3 Hz, H-7b), 1.41-1.18 (4H, m, H-4 and H-5), 0.90-0.84 (3H, m, H-3).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): minor isomer

6.21 (1H, t, *J* = 3 Hz, H-11a), 5.61 (1H, t, *J* = 2.7 Hz, H-11b), 5.63-5.52 (1H, m, H-2), 5.04-4.94 (2H, m, H-1), 4.61-4.50 (1H, m, H8), 3.03 (1H, ddt, *J* = 16.8, 7.5, 2.7 Hz, H-9a), 2.54 (1H, ddt, *J* = 17.1, 6.6, 3.3 Hz, H-9b), 2.20-2.06 (1H, m, H-6), 1.85 (1H, ddd, *J* = 14.1, 9, 6 Hz, H-7a), 1.58 (1H, ddd, *J*

= 13.8, 8.1, 57 Hz, H-7b), 1.41-1.18 (4H, m, H-4 and H-5), 0.92-0.86 (3H, m, H-3).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

170.4 (+, C-12), 141.9 and 141.7 (-, C-2), 135.1 and 135 (+, C-10), 121.9 (+, C-11), 116.2 and 115.3 (+, C-1), 75.9 (-, C-8), 42.4 and 41.4 (+, C-5, C-7 or C-9), 40.6 and 40.1 (-, C-6), 37.8 and 37.2 (+, C-5, C-7 or C-9), 34.4 and 33.7 (+, C-5, C-7 or C-9), 20.2 (+, C-4), 14.1 (-, C-3).

MS (EI, 70 eV) *m/z* (relative intensity, %):

195 ($MH^{+\bullet}$, 3), 179 ($M^{+\bullet}$-$CH_3^{\bullet}$, 2), 166 ($M^{+\bullet}$-C_2H_4, 4), 165 (9), 152 (7), 151 ($M^{+\bullet}$-$CH_3CH_2CH_2^{\bullet}$, 7), 149 ($M^{+\bullet}$-$CO_2^{\bullet}$-H, 8), 123 (151-C_2H_4, 11), 111 ($M^{+\bullet}$-CH_2:CHCH(Pr)$^{\bullet}$, 17), 109 (42), 97 ($M^{+\bullet}$-CH_2:CHCH(Pr)$CH_2^{\bullet}$, 100), 69 (C(O)C$(CH_2)CH_2^{+}$, 47), 67 (39), 55 (18).

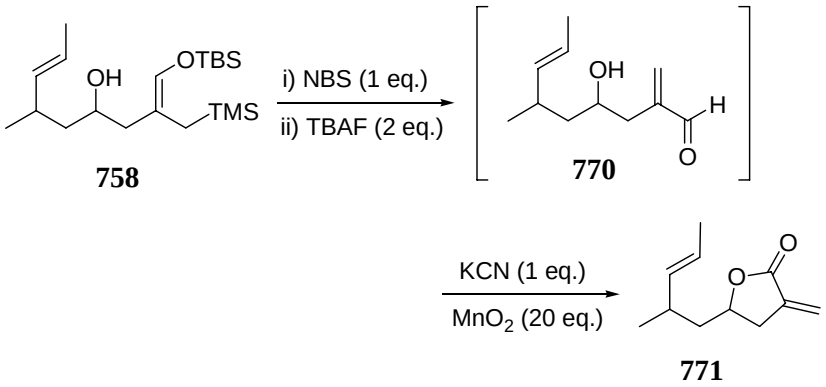
IR (film):

3076 [m] (=C-H), 2980-2820 [s] (C-H), 1764 [s] (C=O), 1666 and 1639 [m] (C=C), 1438, 1398 and 1352 [m], 1276 [s] (C-O), 1117 [s], 997 and 916 [m] cm^{-1}.

HRMS ($MH^{+\bullet}$):

($C_{12}H_{19}O_2$) *Calculated*: 195.1385 ; *found*: 195.1384.

VII.10.3. dihydro-3-methylene-5-((E)-2-methylpent-3-enyl)-furan-2(3H)-one 771



758 **770** **771**

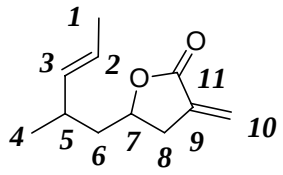
To a solution of ene adduct **758** (0.438 g, 1.18 mmol, 1 eq.) in 20 ml of anhydrous THF was added N-bromosuccinimide (0.216 g, 1.21 mmol, 1.03 eq.). The mixture was stirred for 10 min. and the THF was eliminated *in vacuo*. The resulting white precipitate was filtered and washed with 15 ml of pentane. The pentane was removed under reduced pressure and this crude is directly dissolved in 20 ml of THF. To this mixture was added tetrabutylammonium fluoride (1 M solution in THF, 2.4 ml, 2.4 mmol, 2.03 eq.) and the resulting yellow solution was stirred for 5 min. The mixture was then diluted with 20 ml of Et_2O and transferred to a separatory funnel containing 40 ml of brine. After separation, the aqueous phase was extracted with ether (3 x 20 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude obtained was directly used in the subsequent oxidation step.

To a cold (0 °C) solution of crude enal **770** (0.218 g, 1.18 mmol, 1 eq.) in 20 ml of CH_3CN P.A. were successively added manganese dioxide (2.102 g, 24.18 mmol, 20.5 eq.) and potassium cyanide (0.081 g, 1.24 mmol, 1.05 eq.). The resulting black solution was stirred at room temperature for 15

h. The mixture was then filtered through silica gel and washed with 2 x 20 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.109 g of pure corresponding methylenelactone **771**.

Isolated yield : 51% (over three steps)

Diastereoisomeric ratio : 2:1

	**Mol. Mass :** 181.13 g.mol^{-1} **Mol. Formula :** $C_{11}H_{17}O_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): major isomer

6.21 (1H, t, *J* = 2.7 Hz, H-10a), 5.60 (1H, t, *J* = 2.7 Hz, H-10b), 5.58-5.02 (2H, m, H-2 and H-3), 4.57-4.46 (1H, m, H-7), 3.03 (1H, ddt, *J* = 17.1, 7.8, 2.4 Hz, H-8a), 2.53 (1H, ddt, *J* = 17.1, 6, 3 Hz, H-8b), 2.48-2.34 (1H, m, H-5), 1.65 (3H, dd, *J* = 6.3, 1.8 Hz, H-1), 1.87-1.39 (2H, m, H-6), 1.00 (3H, d, *J* = 6.6 Hz, H-4).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): minor isomer

6.21 (1H, t, *J* = 2.7 Hz, H-10a), 5.60 (1H, t, *J* = 2.7 Hz, H-10b), 5.58-5.02 (2H, m, H-2 and H-3), 4.57-4.46 (1H, m, H-7), 3.03 (1H, ddt, *J* = 17.1, 7.8, 2.4 Hz, H-8a), 2.53 (1H, ddt, *J* = 17.1, 6, 3 Hz, H-8b), 2.36-2.21 (1H, m, H-5), 1.65 (3H, dd, *J* = 6.3, 1.8 Hz, H-1), 1.87-1.39 (2H, m, H-6), 1.00 (3H, d, *J* = 6.6 Hz, H-4).

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

170.5 (+, C-11), 136.1 and 135.7 (-, C-3), 135.1 (+, C-9), 125.3 and 124.6 (-, C-2), 121.9 (+, C-10), 76.3 and 76.1 (-, C-7), 44.3 and 43.5 (+, C-6), 34.3 (+, C-8), 34 and 33.3 (-, C-5), 21.7 (-, C-1), 18.1 (-, C-4).

MS (EI, 70 eV) *m/z* (relative intensity, %):

181 ($MH^{+\bullet}$, 4), 165 ($M^{+\bullet}$-$CH_3^{\bullet}$, 3), 163 ($M^{+\bullet}$-$CH{:}CH_2^{\bullet}$, 2), 137 (10), 135 ($M^{+\bullet}$-$CO_2^{\bullet}$-H, 28), 111 ($M^{+\bullet}$- $C(O)C(CH_2)CH_2^{\bullet}$, 11), 97 ($M^{+\bullet}$-$CH_3CH{:}CHCH(CH_3)CH_2^{\bullet}$, 49), 95 (45), 69 ($C(O)C(CH_2)CH_2^{+}$, 100), 67 (21), 55 (12).

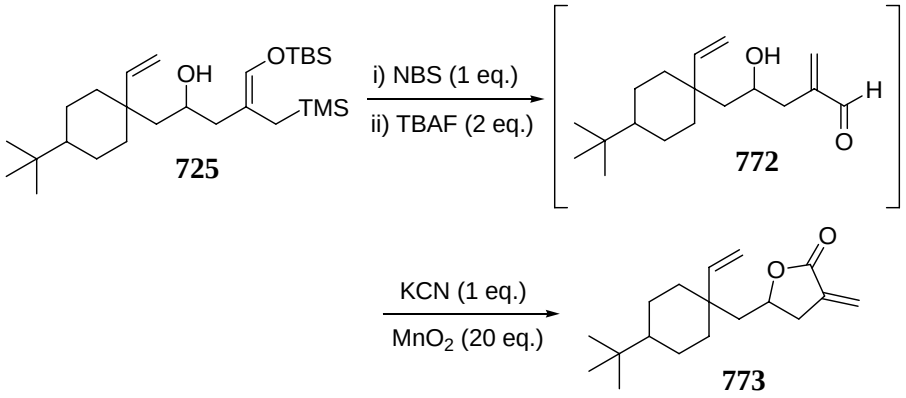
IR (film):

2980-2840 [s] (C-H), 1764 [s] (C=O), 1665 [m] (C=C), 1438, 1377 and 1353 [w], 1276 and 1249 [m] (C-O), 1117 [s], 971 [m] cm^{-1}.

HRMS ($MH^{+\bullet}$):

($C_{11}H_{17}O_2$) *Calculated*: 181.1228 ; *found*: 181.1234.

VII.10.4. 5-((4-tert-butyl-1-vinylcyclohexyl)methyl)-dihydro-3-methylenefuran-2(3H)-one 773

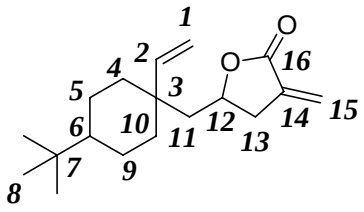


To a solution of ene adduct **725** (1.151 g, 2.46 mmol, 1 eq.) in 40 ml of anhydrous THF was added N-bromosuccinimide (0.439 g, 2.47 mmol, 1 eq.). The mixture was stirred for 10 min. and the THF was eliminated *in vacuo*. The resulting white precipitate was filtered and washed with 30 ml of pentane. The pentane was removed under reduced pressure and this crude is directly dissolved in 40 ml of THF. To this mixture was added tetrabutylammonium fluoride (1 M solution in THF, 4.95 ml, 4.95 mmol, 2.02 eq.) and the resulting yellow solution was stirred for 5 min. The mixture was then diluted with 40 ml of Et_2O and transferred to a separatory funnel containing 100 ml of brine. After separation, the aqueous phase was extracted with ether (3 x 50 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude obtained was directly used in the subsequent oxidation step.

To a cold (0 °C) solution of crude enal **772** (0.684 g, 2.46 mmol, 1 eq.) in 40 ml of CH_3CN P.A. were successively added manganese dioxide (4.284 g, 49.28 mmol, 20 eq.) and potassium cyanide (0.168 g, 2.58 mmol, 1.05 eq.). The resulting black solution was stirred at room temperature for 15 h. The mixture was then filtered through silica gel and washed with 2 x 50 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.474 g of pure corresponding methylenelactone **773**.

Isolated yield : 63% (over three steps)

Diastereoisomeric ratio : 1:1

	**Mol. Mass :** 276.42 g.mol^{-1} **Mol. Formula :** $C_{18}H_{28}O_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.19 (1H, t, *J* = 2.4 Hz, H-15a), 6.18 (1H, t, *J* = 2.4 Hz, H-15a'), 5.77 (1H, dd, *J* = 17.4, 10.8 Hz, H-2), 5.59 (1H, t, *J* = 2.4 Hz, H-15b), 5.58 (1H, t, *J* = 2.4 Hz, H-15b'), 5.57 (1H, dd, *J* = 17.4, 11.1 Hz, H-2'), 5.23 (1H, dd, *J* = 11.1, 1.5 Hz, H-1*syn*), 5.05 (1H, dd, *J* = 17.7, 1.2 Hz, H-1*anti*), 5.00 (1H, dd, *J* = 11.1, 1.5 Hz, H-1*syn*'), 4.96 (1H, dd, *J* = 17.7, 1.2 Hz, H-1*anti*'), 4.57 (1H, qd (dddd), *J* = 7.2, 4.8 Hz, H-12), 4.49 (1H, qd (dddd), *J* = 7.2, 4.8 Hz, H-12'), 3.01 (1H, ddt, *J* = 16.8, 7.2, 2.4 Hz, H-13a), 3.01 (1H, ddt, *J* = 16.5, 7.2, 2.1 Hz, H-13a'), 2.57 (1H, ddt, *J* = 16.8, 7.2, 2.7 Hz, H-13b), 2.51 (1H, ddt, *J* = 17.1, 7.2, 2.7 Hz, H-13b'), 2.17 (1H, dd, *J* = 15, 7.2 Hz), 2.05 (1H, dq, *J* = 13.5, 3 Hz), 1.93-1.84 (1H, m), 1.77-1.43 (5H, m), 1.73 (1H, dd, *J* = 14.4, 7.2 Hz, H-11a), 1.52 (1H, dd, *J* = 14.4, 4.5 Hz, H-11b), 1.34-1.06 (8H, m), 1.02-0.88 (2H, m), 0.85 (9H, s, H-8), 0.81 (9H, s, H-8').

^{13}C NMR (50 MHz, APT, $CDCl_3$) δ_C (ppm):

170.6 and 170.3 (+, C-16), 148.4 and 144.2 (-, C-2), 135.3 and 135.2 (+, C-14), 121.6 (+, C-15), 115.5 and 111.6 (+, C-1), 75.9 and 75.3 (-, C-12), 51.2 (+, C-3), 48.5 and 48.4 (-, C-6), 41.3, 38.3, 37.5, 36.0 and 34.0 (+, C-4, C-10, C-11 and C-13), 39.8 (+, C-7), 27.8 (-, C-8), 23.5, 23.2, 22.7 and 22.5 (+, C-5 and C-9).

MS (EI, 70 eV) *m/z* (relative intensity, %):

276 ($M^{+\bullet}$, 3), 191 (5), 165 ($^{t}BuCy(CH{:}CH_2)^{+}$, 7), 149 (6), 135 (7), 111 ($M^{+\bullet}$-$^{t}BuCy(CH{:}CH_2)^{\bullet}$, 12), 109 (27), 97 ($M^{+\bullet}$-$^{t}BuCy(CH{:}CH_2)CH_2^{\bullet}$, 100), 69 ($C(O)C(CH_2)CH_2^{+}$, 69), 67 (43), 57 ($^{t}Bu^{+}$, 15), 55 (26).

IR (film):

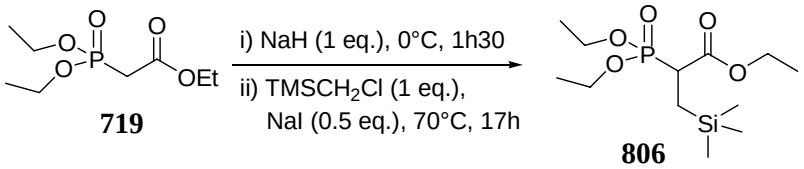
3080 [w] (=C-H), 2980-2840 [s] (C-H), 1768 [s] (C=O), 1666 and 1637 [m] (C=C), 1442, 1395 and 1365 [w], 1277 [m] (C-O), 1124 [s], 1033 [m], 997 [m] cm^{-1}.

Elemental Analysis:

($C_{18}H_{28}O_2$) *Calculated*: C, 78.21; H, 10.21 % ; *found*: C, 77.90; H, 10.20 %.

VII.11. Synthesis of the substituted allylsilanes

VII.11.1. ethyl-1-((trimethylsilyl)methyl)diethoxy-phosphonoacétate 806[253]

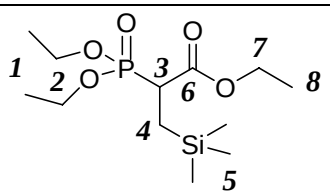


To a solution of triethylphosphonoacetate (45.70 g, 0.198 mol, 1 eq) in 500 ml of anhydrous dimethoxyethane cooled at 0 °C was added sodium hydride (60% w/w, 8.24 g, 0.206 mol, 1.04 eq.). This mixture was stirred for 1h30 at 0 °C and then the ice bath was removed. To this resulting yellow

[253] Henning, R.; Hoffmann, H.M.R. *Tetrahedron Lett.* **1982**, *23*, 2305-2308.

solution was added successively 25 g of chloromethyltrimethyl-silane (0.204 mol, 1.03 eq.) and 15.28 g of sodium iodide (0.102 mol, 0.52 eq.). This mixture was stirred at 70°C for 17h and was poured on 400 ml of water. The aqueous layer was extracted with ether (4 x 250 ml). The combined extracts were washed with 300 ml of a saturated aqueous solution of NaCl and dried ($MgSO_4$). After filtration, the crude was concentrated *in vacuo*. Distillation under reduce pressure (turbo pump, 10^{-5} mm Hg) gave 46.65 g of pure phosphonate **806** (74-93 °C).

Isolated yield : 75%



Mol. Mass : 310.39 g.mol^{-1}
Mol. Formula : $C_{12}H_{27}O_5PSi$
R.N. = [110481-61-3]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

4.23-4.06 (6H, m, H-2 and H-7), 2.94 (1H, ddd, *J* = 22.5, 12.6, 2.7 Hz, H-3), 1.32 (6H, t, *J* = 7.2 Hz, H-1), 1.28 (3H, t, *J* = 7.2 Hz, H-8), 1.34-1.18 (1H, m, H-4a), 1.03 (1H, td, *J* = 15, 2.4 Hz, H-4b), 0.00 (9H, s, H-5).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

170.0 (-, C-6), 63.0 and 62.8 (-, C-2), 61.5 (-, C-7), 42.0 and 40.3 (+, C-3), 16.7 and 16.5 (+, C-1), 14.3 (+, C-8), 13.4 and 13.3 (-, C-4), -1.48 (+, C-5).

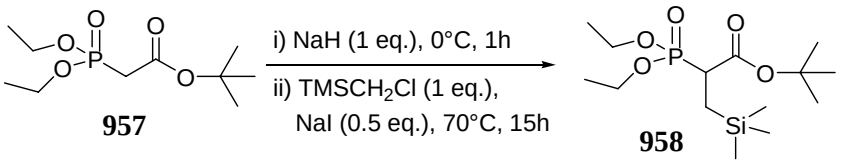
MS (EI, 70 eV) *m/z* (relative intensity, %):

311 ($MH^{+\bullet}$, 2), 310 ($M^{+\bullet}$, 1), 295 ($M^{+\bullet}$-$CH_3^{\bullet}$, 26), 237 (17), 210 (23), 165 (26), 148 (24), 147 ($Me_3SiOSiMe_2^+$, 100), 75 (Me_2SiOH^+, 27), 73 (TMS^+, 64), 55 (13), 45 (EtO^+, 13).

IR (film):

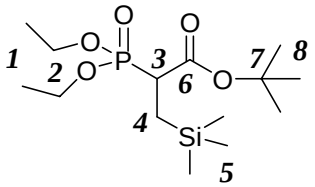
2982, 2955 and 2906 [m] (C-H), 1732 [s] (C=O), 1444 [m], 1392 [m], 1367 [m], 1321 [s], 1248 [s] (large, P=O and C-O), 1153 and 1130 [m] (C-Si), 1047, 1020 and 962 [s] (P-O), 847 [s] (C-Si), 787 [s], 760 [s], 735 [m] cm^{-1}.

VII.11.2. tertbutyl-1-((trimethylsilyl)methyl)diethoxy-phosphonoacétate **958**



To a solution of *tert*butyl-diethylphosphonate (1.75 g, 6.94 mmol, 1 eq) in 20 ml of anhydrous dimethoxyethane cooled at 0 °C was added sodium hydride (60% w/w, 0.281 g, 7.02 mmol, 1.01 eq.). This mixture was stirred for 1h at 0 °C and then the ice bath was removed. To this resulting yellow solution was added successively 0.862 g of chloromethyl-trimethylsilane (7.03 mmol, 1.01 eq.) and 0.526 g of sodium iodide (3.51 mmol, 0.51 eq.). This mixture was stirred at 70 °C for 15 h and was poured on 25 ml of water. The aqueous layer was extracted with ether (4 x 30 ml). The combined extracts were washed with 100 ml of a saturated aqueous solution of NaCl and dried ($MgSO_4$). After filtration, the crude was concentrated *in vacuo* and 1.630 g of pure phosphonate **958** is obtained.

Isolated yield : 71%

	**Mol. Mass :** 338.45 g.mol^{-1} **Mol. Formula :** $C_{14}H_{31}O_5PSi$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

4.16 (2H, q, *J* = 7.2 Hz, H-2a), 4.11 (2H, q, *J* = 7.2 Hz, H-2b), 2.85 (1H, ddd, *J* = 22.8, 12.6, 2.1 Hz, H-3), 1.46 (9H, s, H-8), 1.33 (3H, t, *J* = 7.2 Hz, H-1a), 1.32 (3H, t, *J* = 7.2 Hz, H-1b), 1.28-1.17 (1H, m, H-4a), 0.99 (1H, dt, *J* = 15.6, 1.8 Hz, H-4b), 0.01 (9H, s, H-5).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

169.0 (-, C-6), 81.7 (-, C-7), 62.9, 62.8, 62.7 and 62.6 (-, C-2), 42.8 and 41.2 (+, C-3), 28.1 (+, C-8), 16.8, 16.7, 16.6 and 16.5 (+, C-1), 13.1 and 13.0 (-, C-4), -1.23 (+, C-5).

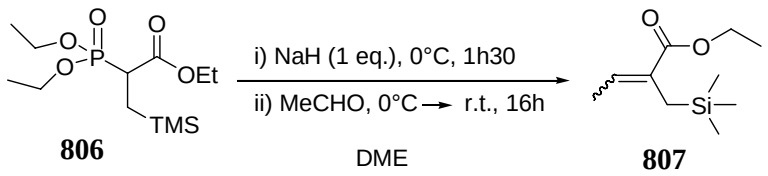
MS (EI, 70 eV) *m/z* (relative intensity, %):

339 ($MH^{+\bullet}$, 1), 338 ($M^{+\bullet}$, 2), 326 (24), 323 ($M^{+\bullet}$-$CH_3^{\bullet}$, 26), 282 (24), 267 (100), 237 (45), 210 (42), 197 (67), 179 (36), 165 (83), 137 (24), 84 (57), 73 (TMS^+, 76), 57 ($^t Bu^+$, 13), 49 (89).

IR (film):

2980, 2955, 2932 and 2908 [m] (C-H), 1730 [s] (C=O), 1479 and 1459 [w], 1392 [m], 1367 [m], 1325 [m], 1248 [s] (large, P=O and C-O), 1149 and 1130 [s] (C-Si), 1051, 1022 and 962 [s] (P-O), 844 [s] (C-Si) cm^{-1}.

VII.11.3. ethyl-2-((trimethylsilyl)methyl)but-2-enoate 807

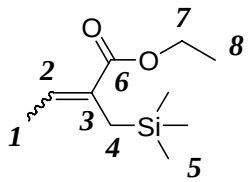


806 **807**

To a solution of phosphonate **806** (8.01 g, 25.8 mmol, 1 eq) in 90 ml of anhydrous dimethoxyethane cooled at 0 °C was added sodium hydride (60% w/w, 1.05 g, 26.34 mmol, 1.02 eq.). This mixture was stirred for 1h30 at 0 °C and to the resulting pale yellow solution was added in excess a solution of acetaldehyde in 10 ml of DME. The ice bath was removed and this mixture was stirred at r.t. for 16 h. The solution was poured on 300 ml of water. The aqueous layer was extracted with ether (4 x 100 ml). The combined extracts were washed with 300 ml of a diluted aqueous solution of NaCl and dried ($MgSO_4$). After filtration and concentration *in vacuo*, chromatography of the residue over neutralised silica gel (eluted with EtOAc-petroleum ether, 1:35) gave 3.448 g of pure α-β unsaturated ester **807**.

Isolated yield : 67%

Isomeric ratio : *Z-E* = 75-25[300]

	**Mol. Mass :** 200.35 g.mol^{-1} **Mol. Formula :** $C_{10}H_{20}O_2Si$ **R.N.** = mix *Z-E* [80361-24-6] pure *Z* [86547-57-1]

[300] Attributed by comparison with fully described product (with NOE effects), see : Hirose, Tomoyasu; Sunazuka, Toshiaki; Shirahata, Tatsuya; Yamamoto, Daisuke; Harigaya, Yoshihiro; Kuwajima, Isao; Omura, Satoshi. *Org. Lett.* **2002**, *4*, 501-503.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.70 (0.75H, q, *J* = 7.2 Hz, H-2*Z*), 5.76 (0.25H, q, *J* = 7.2 Hz, H-2*E*), 4.17 (0.5H, q, *J* = 7.2 Hz, H-7*E*), 4.15 (1.5H, q, *J* = 7.2 Hz, H-7*Z*), 1.93 (0.75H, d, *J* = 6.6 Hz, H-1*E*), 1.80 (2H, s, H-4), 1.71 (2.25H, d, *J* = 6.6 Hz, H-1*Z*), 1.29 (0.75H, t, *J* = 7.2 Hz, H-8*E*), 1.27 (2.25H, t, *J* = 7.2 Hz, H-8*Z*), -0.01 (6.75H, s, H-5*Z*), -0.03 (2.25H, s, H-5*E*).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

168.6 (-, C-6), 133.6 (+, C-2*E*), 133.2 (+, C-2*Z*), 131.5 (-, C-3*Z*), 130.5 (-, C-3*E*), 60.8 (-, C-7*Z*), 60.4 (-, C-7*E*), 24.5 (-, C-4*E*), 17.4 (-, C-4*Z*), 16.2 and 14.4 (+, C-8 or C-1), 15.3 and 14.8 (+, C-1 or C-8), -0.52 (+, C-5*Z*), -1.21 (+, C-5*E*).

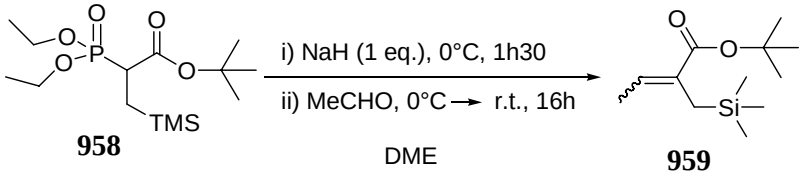
MS (EI, 70 eV) *m/z* (relative intensity, %):

200 ($M^{+\bullet}$, 11), 185 ($M^{+\bullet}$-$CH_3^{\bullet}$, 100), 157 (56), 155 ($M^{+\bullet}$-$EtO^{\bullet}$, 27), 141 (14), 82 (48), 75 (Me_2SiOH^+, 96), 73 (TMS^+, 79), 72 (73), 54 (51), 45 (EtO^+, 52).

IR (film):

2955, 2926 and 2906 [m] (C-H), 1707 [s] (large, C=C and C=O), 1639 [m] (C=C, *E* isomer), 1265 and 1247 [s] (C-O), 1172 and 1157 [s] (C-Si), 1047 [m] (=C-H), 849 [s] (C-Si), 742 [m] cm^{-1}.

VII.11.4. tertbutyl-2-((trimethylsilyl)methyl)but-2-enoate 959

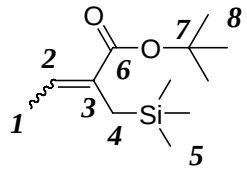


958 **959**

To a solution of phosphonate **958** (0.805 g, 2.38 mmol, 1 eq) in 10 ml of anhydrous dimethoxyethane cooled at 0 °C was added sodium hydride (60% w/w, 0.100 g, 2.50 mmol, 1.05 eq.). This mixture was stirred for 1h30 at 0 °C and to the resulting pale yellow solution was added in excess a solution of acetaldehyde in 2 ml of DME. The ice bath was removed and this mixture was stirred at r.t. for 16 h. The solution was poured on 30 ml of water. The aqueous layer was extracted with ether (4 x 15 ml). The combined extracts were washed with 30 ml of a diluted aqueous solution of NaCl and dried ($MgSO_4$). After filtration and concentration *in vacuo*, chromatography of the residue over neutralised silica gel (eluted with EtOAc-petroleum ether, 1:35) gave 0.188 g of pure α-β unsaturated ester **959**.

Isolated yield : 37%

Isomeric ratio : *Z*-*E* = 83-17[301]

	**Mol. Mass :** 228.40 g.mol^{-1} **Mol. Formula :** $C_{12}H_{24}O_2Si$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.62 (0.83H, q, *J* = 7.2 Hz, H-2*Z*), 5.68 (0.17H, q, *J* = 7.2 Hz, H-2*E*), 1.90 (0.51H, d, *J* = 7.2 Hz, H-1*E*), 1.78 (2H, s, H-4), 1.70 (2.49H, d, *J* = 6.9 Hz, H-1*Z*), 1.49 (1.53H, s, H-8*E*), 1.47 (7.47H, s, H-8*Z*), -0.00 (7.47H, s, H-5*Z*), -0.01 (1.53H, s, H-5*E*).

[301] Attributed by analogy of the chemical shifts with **807**.

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

167.5 (-, C-6), 132.6 (-, C-3), 131.9 (+, C-2*Z*), 131.4 (+, C-2*E*), 80.0 (-, C-7), 30.0 (-, C-4*E*), 28.5 (+, C-8*E*), 28.4 (+, C-8*Z*), 17.0 (-, C-4*Z*), 15.0 (+, C-1*Z*), 14.4 (+, C-1*E*), -0.68 (+, C-5*Z*), -1.30 (+, C-5*E*).

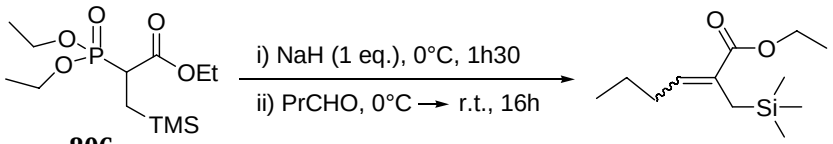
MS (EI, 70 eV) *m/z* (relative intensity, %):

230 ($MH^{+\bullet}$, 6), 229 ($M^{+\bullet}$, 16), 173 (17), 172 ($M^{+\bullet}$-^{t}Bu, 39), 157 ($M^{+\bullet}$-^{t}Bu - $CH_3^{\bullet}$, 100), 155 ($M^{+\bullet}$-^{t}BuO$^{\bullet}$, 33), 82 (41), 75 (Me_2SiOH^+, 26), 73 (TMS^+, 39), 57 ($^tBu^+$, 47), 54 (27).

IR (film):

2955, 2926 and 2854 [m] (C-H), 1703 [s] (large, C=O and C=C), 1639 [m] (C=C, *E* isomer), 1456 [w], 1366 [m], 1286 and 1249 [s] (C-O), 1151 and 1117 [m] (C-Si), 1026 and 986 [w] (=C-H), 849 [s] (C-Si), 742 [s] cm^{-1}.

VII.11.5. ethyl-2-((trimethylsilyl)methyl)hex-2-enoate **956**



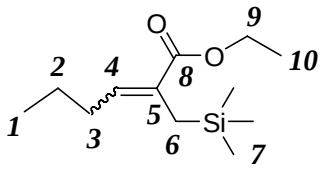
806 **956**

To a solution of phosphonate **806** (0.950 g, 3.06 mmol, 1 eq) in 15 ml of anhydrous dimethoxyethane cooled at 0 °C was added sodium hydride (60% w/w, 0.125 g, 3.12 mmol, 1.02 eq.). This mixture was stirred for 1h30 at 0 °C and to the resulting pale yellow solution was added 0.226 g of butyraldehyde (3.13 mmol, 1.02 eq.). The ice bath was removed and this mixture was stirred at r.t. for 16h. The solution was poured on 50 ml of

water. The aqueous layer was extracted with ether (4 x 20 ml). The combined extracts were washed with 50 ml of a diluted aqueous solution of NaCl and dried ($MgSO_4$). After filtration and concentration *in vacuo*, chromatography of the residue over neutralised silica gel (eluted with EtOAc-petroleum ether, 1:35) gave 0.503 g of pure α-β unsaturated ester **956**.

Isolated yield : 72%

Isomeric ratio : *Z*-*E* = 67-33[302]



Mol. Mass : 228.40 g.mol^{-1}
Mol. Formula : $C_{12}H_{24}O_2Si$
R.N. = pure *Z* [109481-86-9]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.60 (0.67H, q, *J* = 7.2 Hz, H-4*Z*), 5.66 (0.33H, q, *J* = 7.2 Hz, H-4*E*), 4.17 (2H, q, *J* = 7.2 Hz, H-9), 2.37 (0.66H, q, *J* = 7.2 Hz, H-3*E*), 2.06 (1.34H, q, *J* = 7.2 Hz, H-3*Z*), 1.80 (1.34H, s, H-6*Z*), 1.72 (0.66H, s, H-6*E*), 1.52-1.36 (2H, m, H-2), 1.30 (0.99H, t, *J* = 7.2 Hz, H-10*E*), 1.29 (2.01H, t, *J* = 7.2 Hz, H-10*Z*), 0.94 (2.01H, t, *J* = 7.5 Hz, H-1*Z*), 0.91 (0.99H, t, *J* = 7.5 Hz, H-1*E*), -0.01 (6.03H, s, H-7*Z*), -0.02 (2.97H, s, H-7*E*).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

168.5 (-, C-8), 139.0 (+, C-4*E*), 138.5 (+, C-4*Z*), 130.2 (-, C-5*Z*), 129.4 (-, C-5*E*), 60.5 (-, C-9*Z*), 60.2 (-, C-9*E*), 31.9 (-, C-3*E*), 31.3 (-, C-3*Z*), 24.3 and

[302] Attributed by analogy of the chemical shifts with **807**.

24.2 (-, C-2*E* and C-6*E*), 22.3 (-, C-2*Z*), 17.5 (-, C-6*Z*), 14.5, 14.2 and 14.1 (+, C-1 and C-10), -0.78 (+, C-7*Z*), -1.40 (+, C-7*E*).

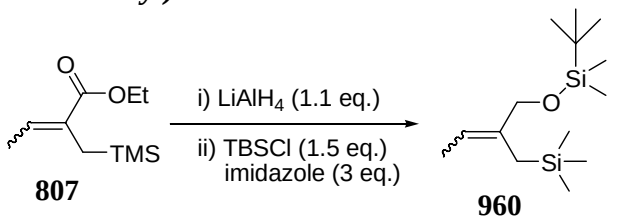
MS (EI, 70 eV) *m/z* (relative intensity, %):

229 ($MH^{+\bullet}$, 3), 228 ($M^{+\bullet}$, 13), 213 ($M^{+\bullet}$-$CH_3^{\bullet}$, 28), 186 (17), 185 ($M^{+\bullet}$-$CH_3CH_2CH_2^{\bullet}$, 98), 183 (20), 169 (16), 157 (18), 155 ($M^{+\bullet}$-Et -$CH_3CH_2CH_2^{\bullet}$, 6), 95 (26), 81 (39), 75 (Me_2SiOH^+, 51), 73 (TMS^+, 100), 67 (26), 45 (EtO^+, 30).

IR (film):

2957, 2933, 2903 and 2874 [m] (C-H), 1709 [s] (large, C=O and C=C), 1636 [m] (C=C, *E* isomer), 1464 and 1367 [m], 1279 and 1247 [s] (C-O), 1217 [m], 1159 [m] (C-Si), 1057 [s] (=C-H), 847 [s] (C-Si), 748 [m] cm^{-1}.

VII.11.6. 1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)but-2-ene 960



807

Z-E = 75-25

960

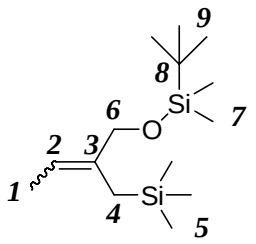
To a solution of α-β unsaturated ester **807** (3.10 g, 15.48 mmol, 1 eq) in 100 ml of anhydrous ether cooled at 0 °C was added lithium aluminium hydride (0.659 g, 17.36 mmol, 1.10 eq.). This mixture was stirred for 15 min. at 0°C, the ice bath was removed and this mixture was stirred at r.t. for 30 min. To this pale yellow solution was carefully added dropwise AcOEt (2 x 5 ml). After cooling again at 0°C, was successively added 10 ml

of water, 15 ml of a 15% w/w aqueous solution of NaOH and 10 ml of water. This mixture was stirred for 30 min. at 0 °C and the ice bath was removed. The aqueous layer was extracted with ether (3 x 100 ml). The combined extracts were dried ($MgSO_4$) and after filtration and concentration *in vacuo*, 2.274 g of crude alcohol was obtained.

To a solution of *tert*-butyldimethylsilylchloride (3.245 g, 21.55 mol, 1.5 eq) and imidazole (2.921 g, 42.88 mol, 3 eq) in 10 ml of anhydrous N,N-dimethylformamide cooled at 0 °C was added the crude alcohol (2.274 g, 14.36 mol, 1 eq.). The ice bath was removed and this mixture was stirred for 24h at r.t. To this solution was added 30 ml of hexane and the resulting mixture was washed with water (2 x 15 ml) and dried on K_2CO_3. After filtration and concentration *in vacuo*, 3.642 g of pure allylsilane **960** was obtained.

Isolated yield : 88%

Isomeric ratio : *Z*-*E* = 80-20



Mol. Mass : 272.58 g.mol^{-1}
Mol. Formula : $C_{14}H_{32}OSi_2$
R.N. = mix *Z*-*E* [113425-70-0]
pure *Z* [109481-86-9]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

5.38 (0.8H, q, *J* = 6.6 Hz, H-2*Z*), 5.10 (0.2H, q, *J* = 6.6 Hz, H-2*E*), 4.10 (0.4H, s, H-6*E*), 3.96 (1.6H, s, H-6*Z*), 1.61 (0.6H, d, *J* = 6.6 Hz, H-1*E*), 1.56 (2.4H, d, *J* = 6.9 Hz, H-1*Z*), 1.52 (2H, s, H-4), 0.91 (7.2H, s, H-9*Z*), 0.86

(1.8H, s, H-9*E*), 0.06 (6H, s, H-7), 0.02 (7.2H, s, H-5*Z*), -0.01 (1.8H, s, H-5*E*).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm): pure *Z*

137.2 (-, C-3), 115.7 (+, C-2), 68.4 (-, C-6), 26.2 (+, C-9), 18.6 (-, C-8), 18.2 (-, C-4), 13.8 (+, C-1), -0.42 (+, C-5), -5.08 (+, C-7).

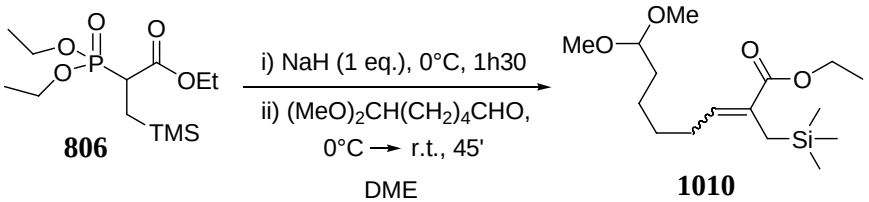
MS (EI, 70 eV) *m/z* (relative intensity, %):

272 ($M^{+\bullet}$, 2), 257 ($M^{+\bullet}$-$CH_3^{\bullet}$, 1), 215 ($M^{+\bullet}$-^{t}Bu$^{\bullet}$, 11), 148 (24), 147 ($Me_3SiOSiMe_2^+$, 100), 75 (Me_2SiOH^+, 19), 73 (TMS^+, 68), 57 (^{t}Bu$^+$, 6), 45 (11).

IR (film):

2955, 2930, 2887 and 2856 [s] (C-H), 1662 [w] (C=C), 1470 and 1464 [m], 1408 and 1362 [w], 1248 [s] (C-O), 1082 [m] (large, C-Si), 1005 [m] (=C-H), 833 and 773 [s] (C-Si) cm^{-1}.

VII.11.7. ethyl-8,8-dimethoxy-2-((trimethylsilyl)methyl)oct-2-enoate 1010

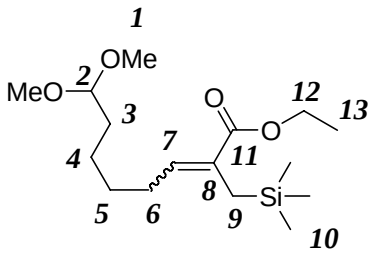


806 **1010**

To a solution of phosphonate **806** (10 g, 32.2 mmol, 1 eq) in 160 ml of anhydrous dimethoxyethane cooled at 0 °C was added sodium hydride (60% w/w, 1.322 g, 33 mmol, 1.05 eq.). This mixture was stirred for 1h30 at 0°C and to the resulting pale yellow solution was added the aldehyde-acetal **1009** (6.091 g, 32.3 mmol, 1 eq) in 10 ml of DME. This mixture was stirred at 0 °C for 45 min and the solution was poured on 300 ml of water. The aqueous layer was extracted with ether (4 x 200 ml). The combined extracts were washed with 300 ml of a diluted aqueous solution of NaCl and dried (Na_2SO_4). After filtration and concentration *in vacuo*, chromatography of the residue over neutralised silica gel (eluted with EtOAc-petroleum ether, 1:35 then 1:20) gave 6.782 g of pure α-β unsaturated ester-acetal **1010**.

Isolated yield : 66%

Isomeric ratio : *Z-E* = 64-36[303]

	**Mol. Mass :** 316.51 g.mol^{-1} **Mol. Formula :** $C_{16}H_{32}O_4Si$

Pics have been assigned with 2D-HMQC.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.58 (0.64H, t, *J* = 7.2 Hz, H-7*Z*), 5.64 (0.36H, t, *J* = 7.5 Hz, H-7*E*), 4.35 (0.64H, t, *J* = 5.7 Hz, H-2*Z*), 4.34 (0.36H, t, *J* = 5.4 Hz, H-2*E*), 4.16 (2H, q, *J* = 7.2 Hz, H-12), 3.31 (3.84H, s, H-1*Z*), 3.30 (2.16H, s, H-1*E*), 2.40

[303] Attributed by analogy of the chemical shifts with **807**.

(0.72H, q, *J* = 7.2 Hz, H-6*E*), 2.09 (1.28H, q, *J* = 7.2 Hz, H-6*Z*), 1.79 (1.28H, s, H-9*Z*), 1.72 (0.72H, s, H-9*E*), 1.66-1.55 (2H, m, H-3), 1.48-1.33 (4H, m, H-4 and H-5), 1.29 (1.08H, t, *J* = 7.2 Hz, H-13*E*), 1.28 (1.92H, t, *J* = 7.2 Hz, H-13*Z*), -0.01 (5.76H, s, H-10*Z*), -0.02 (3.24H, s, H-10*E*).

^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm):

168.5 (C-11), 138.8 (C-7*E*), 138.3 (C-7*Z*), 130.3 (C-8*Z*), 129.6 (C-8*E*), 104.6 (C-2), 60.5 (C-12*Z*), 60.2 (C-12*E*), 52.8 and 52.7 (C-1), 32.5 (C-3), 29.7 (C-6*E*), 29.2 (C-6*Z*), 28.8 and 24.6 (C-4 and C-5), 24.2 (C-9*E*), 17.4 (C-9*Z*), 14.4 (C-13), -0.91 (C-10*Z*), -1.52 (C-10*E*).

MS (EI, 70 eV) *m/z* (relative intensity, %):

316 ($M^{+\bullet}$, 2), 295 (27), 284 ($M^{+\bullet}$-MeOH, 5), 237 (13), 215 (19), 210 (18), 185 (18), 147 ($Me_3SiOSiMe_2^+$, 69), 75 ($(MeO)_2CH^+$, 48), 73 (TMS^+, 100), 68 (14), 45 (EtO^+, 20).

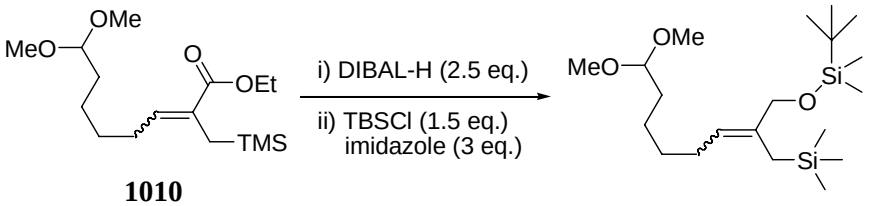
IR (film):

2980, 2945, 2905, 2860 and 2829 [m] (C-H), 1709 [s] (large, C=C and C=O), 1636 [m] (C=C, *E* isomer), 1461 and 1446 [m], 1367 [m], 1248 [s] (large, C-O), 1173 and 1126 [s] (C-Si), 1072 and 1051 [s] (C-O-C), 845 [s] (C-Si), 746 [s] cm^{-1}.

Elemental Analysis:

($C_{16}H_{32}O_4Si$) *Calculated*: C, 60.72; H, 10.19 % ; *found*: C, 60.77; H, 10.11 %.

VII.11.8. 1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-8,8-dimethoxyoct-2-ene **1013**



1010

Z-E = 64-36

1013

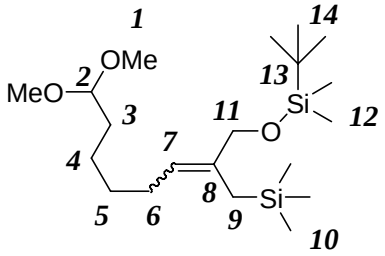
To a solution of α-β unsaturated ester-acetal **1010** (2.300 g, 7.27 mmol, 1 eq) in 175 ml of anhydrous dichloromethane cooled at -78°C was added dropwise di-*iso*butylaluminium hydride (1.5 M in toluene, 12 ml, 18 mmol, 2.48 eq.). This mixture was stirred for 15 min. at -78°C, the ice bath was removed and this mixture was stirred at r.t. for 30 min. To this pale yellow solution was carefully added dropwise AcOEt (2 x 5 ml). After cooling again at 0°C, was successively added 20 ml of water, 30 ml of a 15% w/w aqueous solution of NaOH and 20 ml of water. This mixture was stirred for 30 min. at 0 °C and the ice bath was removed. The aqueous layer was extracted with dichloromethane (3 x 150 ml). The combined extracts were dried (Na_2SO_4) and after filtration and concentration *in vacuo*, 2.137 g of crude alcohol was obtained.

To a solution of *tert*-butyldimethylsilylchloride (1.756 g, 11.72 mol, 1.53 eq) and imidazole (1.589 g, 23.33 mol, 3 eq) in 45 ml of anhydrous N,N-dimethylformamide cooled at 0°C was added the crude alcohol (2.137 g, 7.27 mol, 1 eq.). The ice bath was removed and this mixture was stirred for 24 h at r.t. To this solution was added 150 ml of hexane and the resulting mixture was washed with water (2 x 75 ml) and dried on K_2CO_3. After

filtration and concentration *in vacuo*, 2.614 g of pure allylsilane-acetal **1013** was obtained.

Isolated yield : 88%

Isomeric ratio : *Z*-*E* = 70-30



Mol. Mass : 388.73 g.mol^{-1}
Mol. Formula : $C_{20}H_{44}O_3Si_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

5.26 (0.7H, t, *J* = 6.9 Hz, H-7*Z*), 5.02 (0.3H, t, *J* = 7.2 Hz, H-7*E*), 4.35 (0.7H, t, *J* = 5.7 Hz, H-2*Z*), 4.34 (0.3H, t, *J* = 5.7 Hz, H-2*E*), 4.07 (0.6H, s, H-11*E*), 3.95 (1.4H, s, H-11*Z*), 3.31 (6H, s, H-1), 2.06-1.95 (0.6H, m, H-6*E*), 2.00-1.91 (1.4H, m, H-6*Z*), 1.63-1.55 (2H, m, H-3), 1.57 (0.6H, s, H-9*E*), 1.49 (1.4H, s, H-9*Z*), 1.39-1.28 (4H, m, H-4 and H-5), 0.90 (9H, s, H-14), 0.05 (6H, s, H-12), 0.01 (6.3H, s, H-10*Z*), -0.01 (2.7H, s, H-10*E*).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

136.2 (-, C-8), 124.4 (+, C-7*E*), 121.4 (+, C-7*Z*), 104.6 (+, C-2), 68.3 (-, C-11*Z*), 61.8 (-, C-11*E*), 52.8 (+, C-1), 32.7 (-, C-3), 30.5 (-, C-4*E* or C-5*E*), 29.9 (-, C-4*Z* or C-5*Z*), 28.2 (-, C-6*Z*), 27.8 (-, C-6*E*), 26.3 (+, C-14), 24.8 (-, C-4*Z* or C-5*Z*), 24.6 (-, C-4*E* or C-5*E*), 24.1 (-, C-9*E*), 18.7 (-, C-9*Z*), 18.6 (+, C-13), -0.31 (+, C-10), -4.92 (+, C-12).

MS (EI, 70 eV) *m/z* (relative intensity, %):

389 ($M^{+\bullet}$, 1), 357 ($M^{+\bullet}$-MeOH, 3), 263 (15), 221 (27), 189 (26), 147 ($Me_3SiOSiMe_2^+$, 100), 75 ($(MeO)_2CH^+$, 28), 73 (TMS^+, 41), 57 ($^tBu^+$, 7).

IR (film):

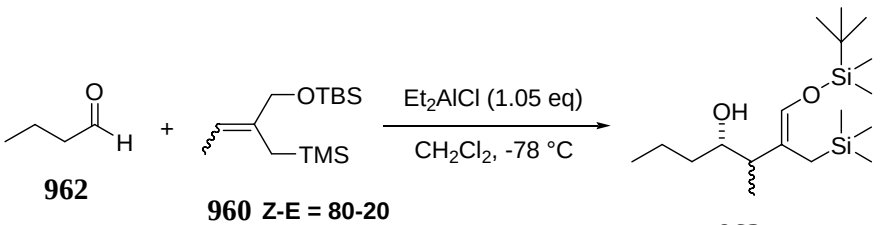
2951, 2930, 2895, 2856 and 2829 [s] (C-H), 1715 and 1655 [w] (C=C), 1482 and 1462 [m], 1387 and 1362 [m], 1248 [s] (large, C-O), 1126 [s] (C-Si), 1072 and 1053 [s] (C-O-C), 845 [s] (C-Si), 746 [m] cm^{-1}.

Elemental Analysis:

($C_{20}H_{44}O_3Si_2$) *Calculated*: C, 61.80; H, 11.41 % ; *found*: C, 61.78; H, 10.32 %.

VII.12. Synthesis of the ene adducts

VII.12.1. (Z)-1-(tertbutyldimethyl-silyloxy)-2-((trimethyl-silyl)methyl)-3-methylhept-1-en-4-ol 963



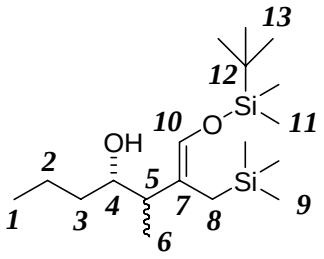
962 **960** **Z-E = 80-20** **963**

To a solution of Me-allylsilane **960** (95% pure, 0.412 g, 1.43 mmol, 1 eq) and butyraldehyde (0.105 g, 1.46 mmol, 1.02 eq) in 15 ml of anhydrous dichloromethane cooled at -78°C was added dropwise diethylaluminium chloride (1 M in CH_2Cl_2, 1.5 ml, 1.5 mmol, 1.05 eq.). This mixture was stirred for 1h50 at -78°C. 15 ml of a saturated aqueous solution

of $NaHCO_3$ was added and the mixture was allowed to warm up to r.t.. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with Ether-petroleum ether, 1:8) gave 0.334 g of pure ene adduct **963**.

Isolated yield : 65%

Diastereoisomeric ratio : 80:20



Mol. Mass : 344.68 $g.mol^{-1}$
Mol. Formula : $C_{18}H_{40}O_2Si_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): major isomer *SYN*

6.07 (1H, s, H-10), 3.56 (1H, dt, *J* = 7.5, 3.9 Hz, H-4), 1.99 (1H, dq, *J* = 6.6, 3.3 Hz, H-5), 1.80 (1H, d, *J* = 13.5 Hz, H-8a), 1.53-1.24 (4H, m, H-2 and H-3), 1.14 (1H, d, *J* = 12.9 Hz, H-8b), 0.96 (3H, d, *J* = 6.6 Hz, H-6), 0.95 (3H, t, *J* = 7.2 Hz, H-1), 0.92 (9H, s, H-13), 0.10 (6H, s, H-11), 0.01 (9H, s, H-9).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): minor isomer *ANTI*

6.13 (1H, s, H-10), 3.55 (1H, td, *J* = 8.7, 1.8 Hz, H-4), 1.92 (1H, quint (dq), *J* = 7.2 Hz, H-5), 1.61-1.19 (4H, m, H-2 and H-3), 1.48 (1H, d, *J* = 13.5 Hz, H-8a), 1.40 (1H, d, *J* = 13.8 Hz, H-8b), 0.96 (3H, d, *J* = 7.2 Hz, H-6), 0.92 (9H, s, H-13), 0.91 (3H, t, *J* = 6.6 Hz, H-1), 0.11 (6H, s, H-11), 0.03 (9H, s, H-9).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

133.5 (+, C-10), 121.6 (-, C-7), 71.2 (+, C-4), 42.6 (+, C-5), 36.6 (-, C-3), 25.9 (+, C-13), 19.9 (-, C-2), 18.2 (-, C-8), 17.9 (-, C-12), 14.4 (+, C-1), 12.1 (+, C-6), -0.35 (+, C-9), -4.98 (+, C-11).

MS (EI, 70 eV) *m/z* (relative intensity, %):

345 ($MH^{+\bullet}$, 3), 344 ($M^{+\bullet}$, 10), 272 ($MH^{+\bullet}$-$TMS^{\bullet}$, 26), 271 ($M^{+\bullet}$-$TMS^{\bullet}$, 100), 199 (272-$PrCHOH^{\bullet}$, 26), 147 ($Me_3SiOSiMe_2^+$, 13), 145 (19), 141 (13), 115 (TBS^+, 4), 75 (Me_2SiOH^+, 21), 73 (TMS^+, 86), 55 (8), 45 (9).

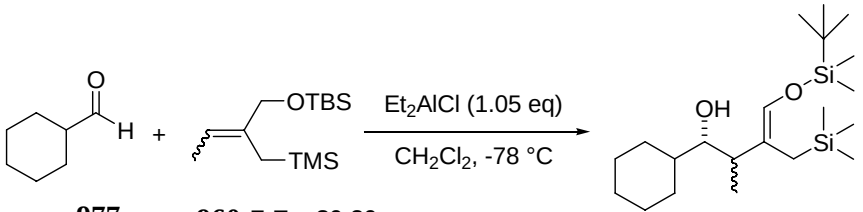
IR (film):

3375 [w] (O-H), 2970-2840 [m] (C-H), 1655 [m] (C=C), 1464 [m], 1408 [m], 1362 [m], 1248 [s] (C-O), 1163 [s] (C-Si), 1080 [w], 993 [m], 835 and 777 [s] (C-Si) cm^{-1}.

Elemental Analysis:

($C_{18}H_{40}O_2Si_2$) *Calculated*: C, 62.73; H, 11.70 % ; *found*: C, 62.94; H, 11.59 %.

VII.12.2. (Z)-1-(tertbutyldimethyl-silyloxy)-2((trimethylsilyl)-methyl)-3-methyl-4-cyclohexylbut-1-en-4-ol 978

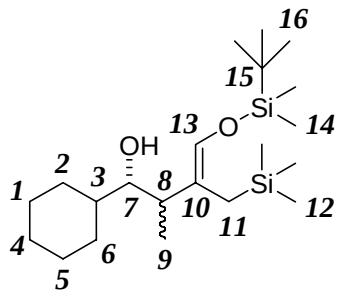


977 **960** **Z-E = 80-20** **978**

To a solution of Me-allylsilane **960** (95% pure, 0.437 g, 1.52 mmol, 1 eq) and cyclohexanecarboxaldehyde (0.176 g, 1.57 mmol, 1.03 eq) in 15 ml of anhydrous dichloromethane cooled at -78°C was added dropwise diethylaluminium chloride (1 M in CH_2Cl_2, 1.65 ml, 1.65 mmol, 1.08 eq.). This mixture was stirred for 2h30 at -78°C. 15 ml of a saturated aqueous solution of $NaHCO_3$ was added and the mixture was allowed to warm up to r.t. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:100 then 1:30) gave 0.111 g of Z-allylsilane **960** recovered and 0.284 g of pure ene adduct **978**.

Isolated yield : 49%
27% Z-allylsilane **960** recovered

Diastereoisomeric ratio : 70:30



Mol. Mass : 384.75 g.mol^{-1}
Mol. Formula : $C_{21}H_{44}O_2Si_2$

Pics have been assigned with 2D-HMQC.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): major isomer *SYN*

6.07 (1H, s, H-13), 3.21 (1H, dd, *J* = 8.1, 3 Hz, H-7), 2.20 (1H, qd, *J* = 6.6, 3.3 Hz, H-8), 1.83 (1H, d, *J* = 13.5 Hz, H-11a), 1.45-1.28 (1H, m, H-3), 2.12-2.02 (1H, m), 1.82-1.53 (5H, m) and 1.31-1.09 (4H, m, H-1, H-2 and

H-4 to H-6), 1.08 (1H, d, *J* = 13.5 Hz, H-11b), 0.92 (3H, d, *J* = 7.2 Hz, H-9), 0.91 (9H, s, H-16), 0.10 (6H, s, H-14), 0.01 (9H, s, H-12).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): minor isomer *ANTI*

6.13 (1H, s, H-13), 3.16 (1H, d, *J* = 9.6 Hz, H-7), 2.07 (1H, dq, *J* = 9.3, 6.9 Hz, H-8), 1.52 (1H, d, *J* = 13.2 Hz, H-11a), 1.35 (1H, d, *J* = 13.5 Hz, H-11b), 1.82-1.53 (5H, m), 1.48-1.37 (2H, m) and 1.29-1.10 (4H, m, H-1 to H-6), 0.93 (3H, d, *J* = 7.2 Hz, H-9), 0.92 (9H, s, H-16), 0.12 (6H, s, H-14), 0.04 (9H, s, H-12).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

133.7 (+, C-13), 121.6 (-, C-10), 74.9 (+, C-7), 39.9 (+, C-3), 39.1 (+, C-8), 30.2 and 29.0 (-, C-2 and C-6), 26.7, 26.3 and 26.1 (-, C-1, C-4 and C-5), 25.9 (+, C-16), 18.3 (-, C-15), 17.9 (-, C-11), 11.3 (+, C-9), -0.39 (+, C-12), -4.95 and -5.14 (+, C-14).

MS (EI, 70 eV) *m/z* (relative intensity, %):

385 ($M^{+\bullet}$, 1), 356 (3), 271 ($M^{+\bullet}$-TBS$^{\bullet}$, 14), 149 (14), 147 ($Me_3SiOSiMe_2^+$, 53), 83 (23), 75 (Me_2SiOH^+, 100), 73 (TMS^+, 94), 57 ($^tBu^+$, 17), 55 (25).

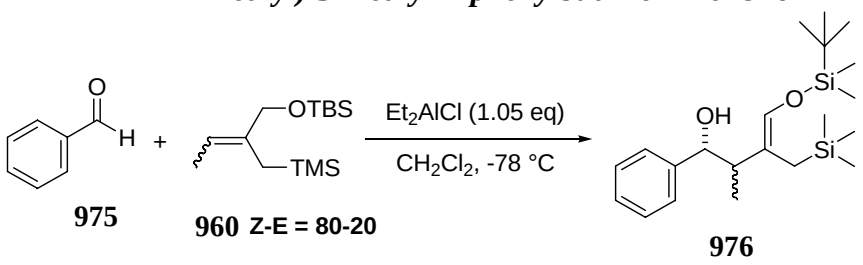
IR (film):

3506 [w] (O-H), 2970-2830 [s] (C-H), 1655 [m] (C=C), 1469 and 1450 [m], 1408 [m], 1362 [m], 1248 [s] (C-O), 1163 [s] (C-Si), 1105 and 1074 [w], 1005 and 976 [m], 835 and 779 [s] (C-Si) cm^{-1}.

Elemental Analysis:

($C_{21}H_{44}O_2Si_2$) *Calculated*: C, 65.56; H, 11.53 % ; *found*: C, 65.83; H, 11.43 %.

VII.12.3. (Z)-1-(tertbutyldimethyl-silyloxy)-2((trimethylsilyl)-methyl)-3-methyl-4-phenylbut-1-en-4-ol **976**

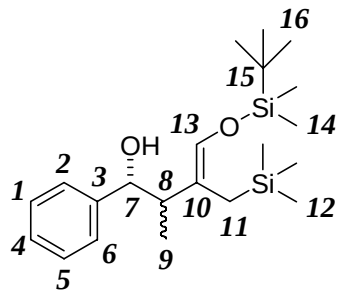


975 **960** **Z-E = 80-20** **976**

To a solution of Me-allylsilane **960** (95% pure, 0.432 g, 1.51 mmol, 1 eq) and benzaldehyde (0.164 g, 1.54 mmol, 1.02 eq) in 15 ml of anhydrous dichloromethane cooled at -78°C was added dropwise diethylaluminium chloride (1 M in CH_2Cl_2, 1.65 ml, 1.65 mmol, 1.09 eq.). This mixture was stirred for 2h30 at -78°C. 15 ml of a saturated aqueous solution of $NaHCO_3$ was added and the mixture was allowed to warm up to r.t.. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:100 then 1:30) gave 0.122 g of Z-allylsilane **960** recovered and 0.215 g of pure ene adduct **976**.

Isolated yield : 35%
30% Z-allylsilane **960** recovered

Diastereoisomeric ratio : 65:35 (*syn* : *anti* but inseparable)

	**Mol. Mass :** 378.70 g.mol^{-1} **Mol. Formula :** $C_{21}H_{38}O_2Si_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

7.36-7.30 (5H, m, H-Ph), 6.24 (0.35H, s, H-13*anti*), 6.11 (0.65H, s, H-13*syn*), 4.76 (0.65H, d, *J* = 4.2 Hz, H-7*syn*), 4.31 (0.35H, d, *J* = 9 Hz, H-7*anti*), 2.32 (0.65H, qd, *J* = 6.6, 3.3 Hz, H-8*syn*), 2.20 (0.35H, dq, *J* = 8.4, 7.2 Hz, H-8*anti*), 1.86 (0.65H, d, *J* = 13.8 Hz, H-11a *syn*), 1.56 (0.35H, d, *J* = 14.4 Hz, H-11a *anti*), 1.43 (0.35H, d, *J* = 13.8 Hz, H-11b *anti*), 1.21 (0.65H, d, *J* = 13.5 Hz, H-11b *syn*), 0.94 (3.15H, s, H-16*anti*), 0.91 (5.85H, s, H-16*syn*), 0.85 (1.95H, d, *J* = 7.2 Hz, H-9*syn*), 0.78 (1.05H, d, *J* = 7.2 Hz, H-9*anti*), 0.16 and 0.15 (2.1H, 2s, H-14*anti*), 0.10 and 0.09 (3.9H, 2s, H-14*syn*), 0.07 (3.15H, s, H-12*syn*), 0.04 (5.85H, s, H-12*anti*).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

143.2 (-, C3*syn*), 142.7 (-, C3*anti*), 135.0 (+, C-13*anti*), 134.2 (+, C-13*syn*), 128.3, 128.2, 127.7, 127.3, 126.9, 126.0 and 125.7 (+, C-1, C-2 and C-4 to C-6), 120.8 (-, C-10*syn*), 119.8 (-, C-10*anti*), 76.1 (+, C-7*anti*), 73.6 (+, C-7*syn*), 46.4 (+, C-8*anti*), 45.2 (+, C-8*syn*), 25.9 (+, C-16), 18.3 (-, C-11*syn*), 18.2 (-, C-15), 16.4 (+, C-9*anti*), 15.6 (-, C-11*anti*), 12.0 (+, C-9*syn*), 0.01 and -0.30 (+, C-12), -4.94, -5.02 and -5.07 (+, C-14).

MS (EI, 70 eV) *m/z* (relative intensity, %):

379 ($M^{+\bullet}$, 1), 357 (5), 271 ($M^{+\bullet}$-$PhCHOH^{\bullet}$, 16), 221 (12), 147 ($Me_3SiOSiMe_2^+$, 66), 106 ($PhCHO^{\bullet}$, 34), 105 ($PhCO^+$, 43), 93 (28), 77 (Ph^+, 33), 75 (Me_2SiOH^+, 84), 73 (TMS^+, 100), 57 ($^tBu^+$, 14), 51 (14).

IR (film):

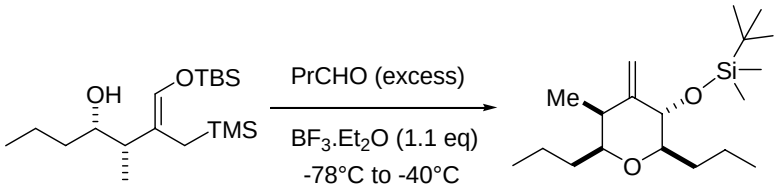
3435 [w] (O-H), 3063 and 3030 [w] (=C-H), 2970-2830 [s] (C-H), 1659 [m] (large, C=C), 1472 and 1454 [m], 1391 [m], 1362 [m], 1248 [s] (C-O), 1165 [s] (C-Si), 1005 [s] (large, =C-H in plane), 874, 827, 779 and 761 [s] (C-Si and =C-H out of plane) cm^{-1}.

Elemental Analysis:

($C_{21}H_{38}O_2Si_2$) *Calculated*: C, 66.61; H, 10.11 % ; *found*: C, 66.82; H, 10.06 %.

VII.13. Synthesis of the tetrahydropyrans

VII.13.1. ((2R,3S,5S,6S)-tetrahydro-5-methyl-4-methylene-2,6-dipropyl-2H-pyran-3-yloxy)(tert-butyl)dimethyl-silane 968

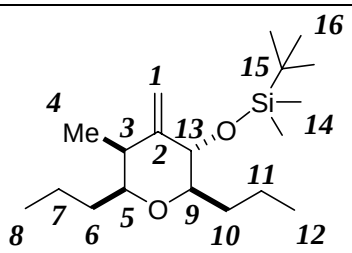


963 ***Syn*** **968**

To a solution of ene adduct **963** *syn* (0.209 g, 0.61 mmol, 1 eq) and butyraldehyde (0.048 g, 0.66 mmol, 1.1 eq) in 10 ml of anhydrous

dichloromethane cooled at -78 °C was added dropwise freshly distilled etherate trifluoroborane (0.096 g, 0.68 mmol, 1.11 eq.). This mixture was stirred for 1h30 at -78 °C and then slowly warmed up to -40 °C. 15 ml of a saturated aqueous solution of $NaHCO_3$ and 10 ml of dichloromethane was added and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:200) gave 0.185 g of pure *syn* tetrahydropyrane **968**.

Isolated yield : 94%



Mol. Mass : 326.59 g.mol^{-1}
Mol. Formula : $C_{19}H_{38}O_2Si$

Pics have been assigned with 2D-COSY and 2D-HETCOR (old Varian 300MHz NMR).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

4.91 (1H, t, *J* = 2.1 Hz, H-1a), 4.79 (1H, t, *J* = 1.8 Hz, H-1b), 3.88 (1H, dt, *J* = 9, 1.8 Hz, H-13), 3.36 (1H, ddd, *J* = 8.7, 7.5, 2.4 Hz, H-5), 2.97 (1H, td (ddd), *J* = 9.3, 2.4 Hz, H-9), 2.45 (1H, qd, *J* = 7.2, 2.4 Hz, H-3), 1.82-1.69 (1H, m), 1.63-1.41 (3H, m) and 1.41-1.20 (4H, m, C-6, C-7, C-10 and C-11), 1.03 (3H, d, *J* = 7.2 Hz, H-4), 0.94 (9H, s, H-16), 0.91 (3H, t, *J* = 6.9 Hz, H-8 or H-12), 0.90 (3H, t, *J* = 6.9 Hz, H-8 or H-12), 0.08 and 0.04 (6H, 2s, H-14).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

153.7 (-, C-2), 105.1 (-, C-1), 83.8 (+, C-9), 80.9 (+, C-5), 72.0 (+, C-13), 44.1 (+, C-3), 35.1 and 34.7 (-, C-6 and C-10), 26.2 (+, C-16), 19.7 and 19.2 (-, C-7 and C-11), 18.5 (-, C-15), 14.4 and 14.3 (+, C-8 and C-12), 13.4 (+, C-4), -4.09 and -4.44 (+, C-14).

MS (EI, 70 eV) *m/z* (relative intensity, %):

327 ($MH^{+\bullet}$, 9), 326 ($M^{+\bullet}$, 36), 269 ($M^{+\bullet}$-^{t}Bu$^\bullet$, 53), 254 (269 –$CH_3^\bullet$, 42), 239 (254-$CH_3^\bullet$, 28), 197 (100), 147 ($Me_3SiOSiMe_2^+$, 13), 141 (22), 75 (Me_2SiOH^+, 90), 73 (80), 57 (^{t}Bu, 23), 55 (19).

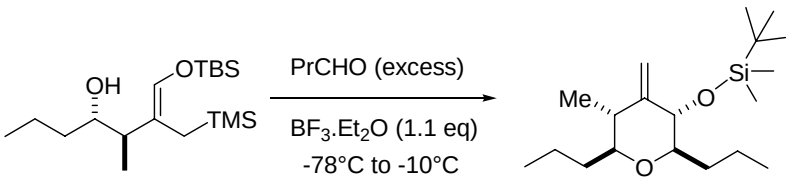
IR (film):

3095 [w] (=C-H), 2970-2830 [s] (C-H), 1653 and 1626 [w] (C=C), 1462 [m], 1388 [w], 1377 [w], 1252 [s] (C-O), 1113 [s] (large, C-Si and C-O-C), 1018 [w] (=C-H), 899 and 872 [s] (C-Si), 837 and 775 [s] cm^{-1}.

Elemental Analysis:

($C_{19}H_{38}O_2Si$) *Calculated*: C, 69.88; H, 11.73 % ; *found*: C, 69.72; H, 11.72 %.

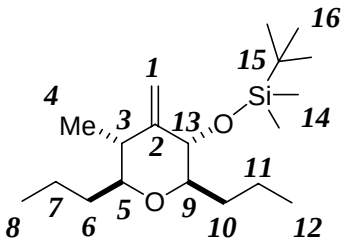
VII.13.2. ((2R,3S,5R,6S)-tetrahydro-5-methyl-4-methylene-2,6-dipropyl-2H-pyran-3-yloxy)(tert-butyl)dimethyl-silane 969



963 ***Anti*** **969**

To a solution of ene adduct **963** *anti* (0.050 g, 0.14 mmol, 1 eq) and butyraldehyde (0.017 g, 0.23 mmol, 1.6 eq) in 5 ml of anhydrous dichloromethane cooled at -78 °C was added dropwise freshly distilled etherate trifluoroborane (0.023 g, 0.16 mmol, 1.1 eq.). This mixture was stirred for 1h30 at -78 °C and then slowly warmed up to -10°C. 10 ml of a saturated aqueous solution of $NaHCO_3$ and 5 ml of dichloromethane was added and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:200) gave 0.038 g of pure *anti* tetrahydropyrane **969**.

Isolated yield : 78%



Mol. Mass : 326.59 $g.mol^{-1}$
Mol. Formula : $C_{19}H_{38}O_2Si$

Pics have been assigned with 2D-COSY and 2D-HETCOR (old Varian 300MHz NMR).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

5.09 (1H, t, *J* = 1.5 Hz, H-1a), 4.76 (1H, t, *J* = 1.8 Hz, H-1b), 3.68 (1H, d, *J* = 8.7 Hz, H-13), 2.98 (1H, td (ddd), *J* = 9.3, 2.4 Hz, H-9), 2.83 (1H, td (ddd), *J* = 9.3, 2.1 Hz, H-5), 1.99 (1H, dq, *J* = 9, 7.2 Hz, H-3), 1.85-1.71 (1H, m), 1.68-1.46 (3H, m) and 1.46-1.19 (4H, m, C-6, C-7, C-10 and C-11),

1.00 (3H, d, *J* = 6 Hz, H-4), 0.94 (9H, s, H-16), 0.90 (6H, bt, *J* = 7.2 Hz, H-8 and H-12), 0.07 and 0.02 (6H, 2s, H-14).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

153.1 (-, C-2), 103.3 (-, C-1), 83.6 and 83.5 (+, C-5 and C-9), 75.8 (+, C-13), 42.4 (+, C-3), 36.3 and 35.5 (-, C-6 and C-10), 26.4 (+, C-16), 19.4 and 19.3 (-, C-7 and C-11), 18.8 (-, C-15), 14.5 (+, C-8 and C-12), 13.5 (+, C-4), -3.76 and -4.20 (+, C-14).

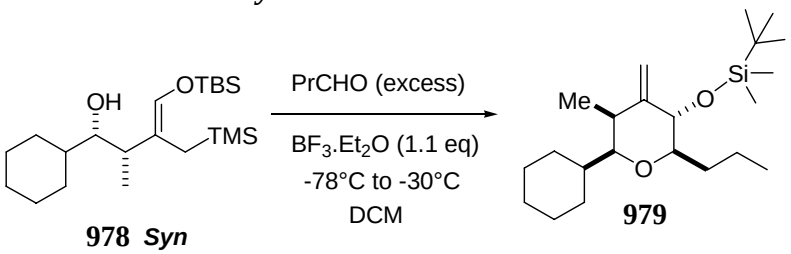
MS (EI, 70 eV) *m/z* (relative intensity, %):

327 ($MH^{+\bullet}$, 9), 326 ($M^{+\bullet}$, 36), 269 ($M^{+\bullet}$-^{t}Bu$^\bullet$, 53), 254 (269 –$CH_3^\bullet$, 42), 239 (254-$CH_3^\bullet$, 28), 197 (100), 147 ($Me_3SiOSiMe_2^+$, 13), 141 (22), 75 (Me_2SiOH^+, 90), 73 (80), 57 (^{t}Bu, 23), 55 (19).

IR (film):

3095 [w] (=C-H), 2970-2830 [s] (C-H), 1653 and 1626 [w] (C=C), 1462 [m], 1388 [w], 1377 [w], 1252 [s] (C-O), 1113 [s] (large, C-Si and C-O-C), 1018 [w] (=C-H), 899 and 872 [s] (C-Si), 837 and 775 [s] cm^{-1}.

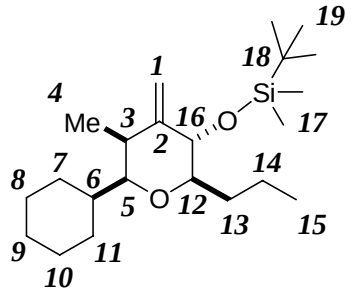
VII.13.3. ((2R,3S,5S,6S)-6-cyclohexyl-tetrahydro-5-methyl-4-methylene-2-propyl-2H-pyran-3-yloxy)(tert-butyl)-dimethylsilane 979



978 ***Syn*** **979**

To a solution of ene adduct **978** *syn* (0.204 g, 0.53 mmol, 1 eq) and butyraldehyde (0.048 g, 0.66 mmol, 1.25 eq) in 10 ml of anhydrous dichloromethane cooled at -78 °C was added dropwise freshly distilled etherate trifluoroborane (0.085 g, 0.60 mmol, 1.13 eq.). This mixture was stirred for 1h30 at -78 °C and then slowly warmed up to -30 °C. 15 ml of a saturated aqueous solution of $NaHCO_3$ and 10 ml of dichloromethane was added and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:100) gave 0.164 g of pure *syn* tetrahydropyrane **979**.

Isolated yield : 85%



Mol. Mass : 366.66 $g.mol^{-1}$
Mol. Formula : $C_{22}H_{42}O_2Si$

Pics have been assigned with 2D-COSY and 2D-HETCOR (old Varian 300MHz NMR).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

4.90 (1H, t, *J* = 2.1 Hz, H-1a), 4.79 (1H, t, *J* = 1.8 Hz, H-1b), 3.90 (1H, d, *J* = 9.3 Hz, H-16), 2.95 (1H, dd, *J* = 10.2, 2.4 Hz, H-5), 2.93 (1H, td (ddd), *J* = 9.9, 2.4 Hz, H-12), 2.60 (1H, qd, *J* = 7.2, 1.8 Hz, H-3), 2.17-2.06 (1H, m), 1.82-1.50 (7H, m), 1.47-1.28 (3H, m) and 1.28-1.08 (4H, m, C-6 to C-11 and

C-13, C-14), 1.02 (3H, d, *J* = 7.2 Hz, H-4), 0.94 (9H, s, H-19), 0.90 (3H, t, *J* = 7.2 Hz, H-15), 0.07 and 0.03 (6H, 2s, H-17).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

153.7 (-, C-2), 105.1 (-, C-1), 85.7 (+, C-5), 83.8 (+, C-12), 72.3 (+, C-16), 41.5 (+, C-3), 39.0 (+, C-6), 35.2 (-, C-13), 30.6, 28.6, 26.8, 26.3 and 26.0 (-, C-7 to C-11), 26.2 (+, C-19), 19.2 (-, C-14), 18.6 (-, C-18), 14.2 (+, C-4), 13.3 (+, C-15), -4.09 and -4.41 (+, C-17).

MS (EI, 70 eV) *m/z* (relative intensity, %):

367 ($MH^{+\bullet}$, 2), 366 ($M^{+\bullet}$, 7), 344 (10), 309 ($M^{+\bullet}$-^{t}Bu$^\bullet$, 10), 272 (34), 271 (100), 254 (12), 199 (15), 145 (6), 75 (Me_2SiOH^+, 14), 73 (42), 57 (^{t}Bu$^+$, 8), 55 (7).

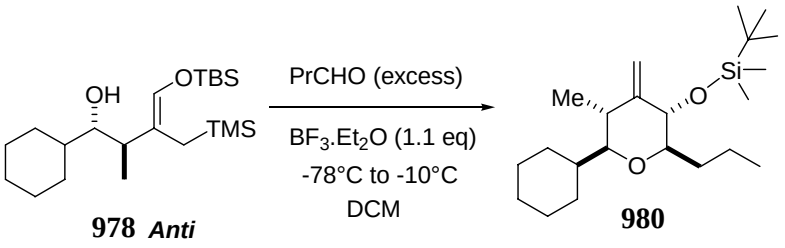
IR (film):

3095 [w] (=C-H), 2970-2830 [s] (C-H), 1651 and 1626 [w] (C=C), 1466 and 1450 [m], 1388 [w], 1373 [w], 1315 [w], 1252 [s] (C-O), 1113 [s] (large, C-Si and C-O-C), 1022 [w] (=C-H), 897 and 876 [s] (C-Si), 835 and 775 [s] cm^{-1}.

Elemental Analysis:

($C_{22}H_{42}O_2Si$) *Calculated*: C, 72.07; H, 11.55 % ; *found*: C, 72.06; H, 11.54 %.

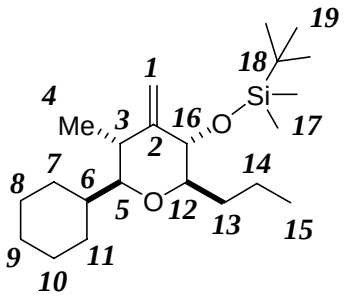
VII.13.4. ((2R,3S,5R,6S)-6-cyclohexyl-tetrahydro-5-methyl-4-methylene-2-propyl-2H-pyran-3-yloxy)(tert-butyl) dimethylsilane **980**



978 ***Anti*** **980**

To a solution of ene adduct **978** *anti* (0.098 g, 0.25 mmol, 1 eq) and butyraldehyde (0.024 g, 0.33 mmol, 1.3 eq) in 4 ml of anhydrous dichloromethane cooled at -78 °C was added dropwise freshly distilled etherate trifluoroborane (0.040 g, 0.28 mmol, 1.13 eq.). This mixture was stirred for 1h30 at -78 °C and then slowly warmed up to -10 °C. 8 ml of a saturated aqueous solution of $NaHCO_3$ and 5 ml of dichloromethane was added and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:100) gave 0.050 g of pure *anti* tetrahydropyrane **980**.

Isolated yield : 54%

	**Mol. Mass :** 366.66 $g.mol^{-1}$ **Mol. Formula :** $C_{22}H_{42}O_2Si$

Pics have been assigned with 2D-COSY and 2D-HETCOR (old Varian 300MHz NMR).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

5.07 (1H, t, *J* = 1.5 Hz, H-1a), 4.74 (1H, t, *J* = 1.5 Hz, H-1b), 3.60 (1H, d, *J* = 9.6 Hz, H-16), 2.92 (1H, td (ddd), *J* = 9, 2.7 Hz, H-12), 2.67 (1H, d, *J* = 9.6 Hz, H-5), 2.22-2.10 (1H, m, H-3), 1.83-1.69 (3H, m), 1.68-1.58 (2H, m), 1.58-1.29 (6H, m) and 1.29-1.11 (4H, m, C-6 to C-11 and C-13, C-14), 1.0(-0.82 (6H, m, H-4 and H-15), 0.94 (9H, s, H-19), 0.08 and 0.03 (6H, 2s, H-17).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

153.6 (-, C-2), 102.8 (-, C-1), 87.5 (+, C-5), 83.4 (+, C-12), 75.6 (+, C-16), 39.7 (+, C-6), 38.3 (+, C-3), 35.3 (-, C-13), 31.1, 27.3, 27.0, 26.9 and 25.0 (-, C-7 to C-11), 19.0 (+, C-19), 18.6 (-, C-14), 18.6 (-, C-18), 14.4 (+, C-4), 12.9 (+, C-15), -3.92 and -4.31 (+, C-17).

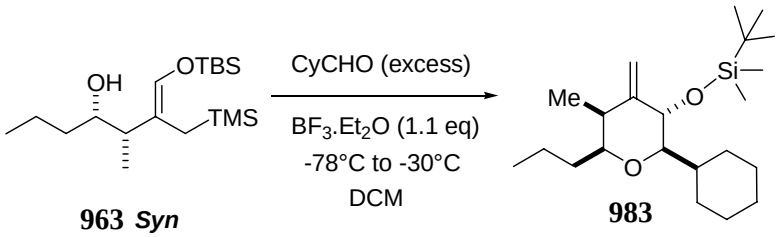
MS (EI, 70 eV) *m/z* (relative intensity, %):

367 ($MH^{+\bullet}$, 2), 366 ($M^{+\bullet}$, 7), 344 (10), 309 ($M^{+\bullet}$-$^{t}Bu^{\bullet}$, 10), 272 (34), 271 (100), 254 (12), 199 (15), 145 (6), 75 (Me_2SiOH^{+}, 14), 73 (42), 57 ($^{t}Bu^{+}$, 8), 55 (7).

IR (film):

3095 [w] (=C-H), 2970-2830 [s] (C-H), 1651 and 1626 [w] (C=C), 1466 and 1450 [m], 1388 [w], 1373 [w], 1315 [w], 1252 [s] (C-O), 1113 [s] (large, C-Si and C-O-C), 1022 [w] (=C-H), 897 and 876 [s] (C-Si), 835 and 775 [s] cm^{-1}.

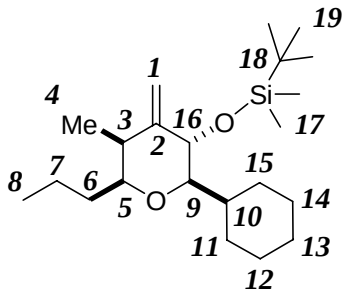
VII.13.5. ((2R,3S,5S,6S)-2-cyclohexyl-tetrahydro-5-methyl-4-methylene-6-propyl-2H-pyran-3-yloxy)(tert-butyl) dimethylsilane **983**



963 ***Syn*** **983**

To a solution of ene adduct **963** *syn* (0.182 g, 0.53 mmol, 1 eq) and cyclohexanecarboxaldehyde (0.085 g, 0.76 mmol, 1.40 eq) in 6 ml of anhydrous dichloromethane cooled at -78 °C was added dropwise freshly distilled etherate trifluoroborane (0.086 g, 0.60 mmol, 1.14 eq.). This mixture was stirred for 1h at -78 °C and then slowly warmed up to -30 °C. 10 ml of a saturated aqueous solution of $NaHCO_3$ and 10 ml of dichloromethane was added and the aqueous layer was extracted with CH_2Cl_2 (3 x 15 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:200 then 1:100) gave 0.144 g of pure *syn* tetrahydropyrane **983**.

Isolated yield : 75%

	**Mol. Mass :** 366.66 g.mol^{-1} **Mol. Formula :** $C_{22}H_{42}O_2Si$

Pics have been assigned with 2D-HMQC.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

4.89 (1H, bs, H-1a), 4.79 (1H, bs, H-1b), 4.11 (1H, d, *J* = 9.6 Hz, H-16), 3.28 (1H, m, H-5), 2.80 (1H, d, *J* = 9.6 Hz, H-9), 2.40 (1H, q, *J* = 6.3 Hz, H-3), 1.81-1.53 (5H, m), 1.54-1.38 (3H, m), 1.38-1.09 (7H, m,C-6, C-7 and C-10 to C-15), 0.97 (3H, d, *J* = 7.2 Hz, H-4), 0.94 (9H, s, H-19), 0.90 (3H, t, *J* = 7.5 Hz, H-8), 0.07 and 0.04 (6H, 2s, H-17).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

154.7 (-, C-2), 105.0 (-, C-1), 87.8 (+, C-9), 80.6 (+, C-5), 68.0 (+,C-16), 44.2 (+, C-3), 37.7 (+, C-10), 34.6 (-, C-6), 31.5, 27.3, 26.8, 26.5 and 25.2 (-, C-11 to C-15), 26.2 (+, C-19), 19.6 (-, C-7), 18.5 (-, C-18), 14.3 and 12.9 (+, C-4 and C-8), -3.99 and -4.69 (+, C-17).

MS (EI, 70 eV) *m/z* (relative intensity, %):

367 ($MH^{+\bullet}$, 2), 366 ($M^{+\bullet}$, 7), 309 ($M^{+\bullet}$-$^{t}Bu^{\bullet}$, 4), 237 (10), 205 (5), 86 (67), 84 ($Cy^{+\bullet}$, 100), 75 (Me_2SiOH^{+}, 7), 73 (6), 51 (32), 49 (91).

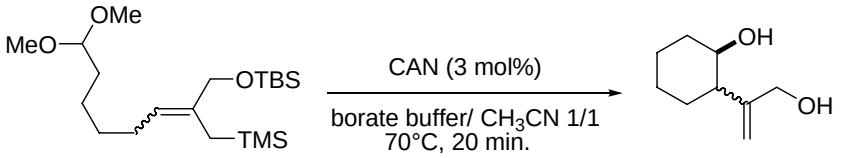
IR (film):

3087 [w] (=C-H), 2970-2830 [s] (C-H), 1651 and 1626 [w] (C=C), 1471 and 1450 [m], 1389 [w], 1362 [w], 1252 [s] (C-O), 1117 [s] (large, C-Si and C-O-C), 1005 [w] (=C-H), 895 and 874 [s] (C-Si), 835 and 773 [s] cm^{-1}.

Elemental Analysis:

($C_{22}H_{42}O_2Si$) *Calculated*: C, 72.07; H, 11.55 % ; *found*: C, 72.53; H, 11.53 %.

VII.14. 2-(1-hydroxyprop-2-en-2-yl)cyclohexanol 1014

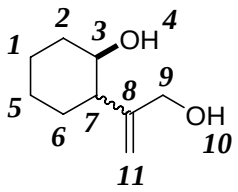


1013 **Z-E = 70-30** **1014**

To a solution of allylsilane-acetal **1013** (1.095 g, 2.8 mmol, 1 eq) in a mixture 1:1 of borate buffer and acetonitrile (2 x 10 ml) warmed up at 70 °C was added Cerium-Ammoniun Nitrate (0.059 g, 0.1 mmol, 0.04 eq.). This mixture was stirred for 20 min. at 70 °C and 5 ml of a saturated aqueous solution of $NaHCO_3$ was added. The aqueous layer was extracted with ethyl acetate (3 x 20 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with Ether-petroleum ether, 1:3) gave 0.365 g of pure diol **1014**.

Isolated yield : 83%

Isomeric ratio : *Z-E* = 75-25

	**Mol. Mass :** 156.22 g.mol^{-1} **Mol. Formula :** $C_{21}H_{38}O_2Si_2$ **R.N.** = mix [91240-67-4] anti [3727-49-9] syn [3727-55-7]

^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm): major isomer *SYN*

5.17 (1H, s, H-11a), 4.98 (1H, s, H-11b), 4.12 (1H, d, *J* = 13.1 Hz, H-9a), 4.04 (1H, d, *J* = 13 Hz, H-9b), 3.94 (1H, bs, H-3), 2.66 (2H, m, H-4 and H-10), 2.28-2.18 (1H, m) and 1.96-1.22 (8H, m, H-1, H-2 and H-5 to H-7).

^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm): minor isomer *ANTI*

5.20 (1H, s, H-11a), 5.05 (1H, s, H-11b), 4.15 (1H, d, *J* = 12.8 Hz, H-9a), 4.08 (1H, d, *J* = 13 Hz, H-9b), 3.48 (1H, td, *J* = 10.5, 4.2 Hz, H-3), 2.34 (2H, bs, H-4 and H-10), 2.10-1.92 (2H, m), 1.86-1.56 (3H, m) and 1.41-1.15 (4H, m, H-1, H-2 and H-5 to H-7).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

150.9 (-, C-8), 113.4 (-, C-11*syn*), 112.7 (-, C-11*anti*), 73.8 (+, C-9*anti*), 68.1 (+, C-9*syn*), 65.8 (-, C-3*anti*), 65.0 (-, C-3*syn*), 50.7 (+, C-7*anti*), 46.6 (+, C-7*syn*), 35.1 (-, C-2*anti*), 32.9 (-, C-2*syn*), 32.0, 26.2, 26.0, 25.1, 24.3 and 19.8 (C-1, C-5 and C-6).

MS (EI, 70 eV) *m/z* (relative intensity, %):

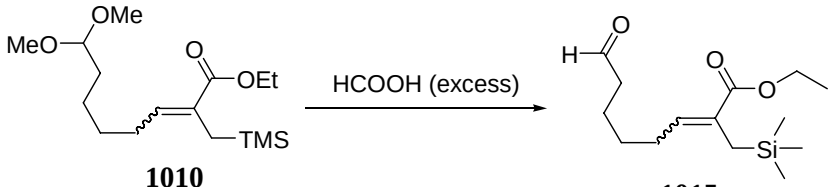
156 ($M^{+\bullet}$, 1), 138 ($M^{+\bullet}$-H_2O, 19), 109 (44), 94 (91), 82 (81), 79 (100), 67 (63), 55 (*52*).

IR (film):

3415 [large] (O-H), 2930-2840 [s] (C-H), 1649 [m] (C=C), 1450 [s], 1038 [m], 891 [m].

VII.15. Deprotections of the masked aldehydes

VII.15.1. ethyl-7-formyl-2-((trimethylsilyl)methyl)hept-2-enoate 1015[294]



1010
Z-E = 64-36

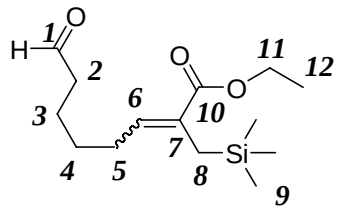
1015

To α,β-unsaturated ester-acetal **1010** (0.321 g, 1.01 mmol, 1 eq) was added formic acid (90% pure, 1.5 g, 29.3 mmol, 29 eq.). This mixture was stirred for 10 min. at 5 ml of water was added. The aqueous layer was extracted with ether (3 x 10 ml). The combined extracts were washed with 30 ml of water and dried (Na_2SO_4). After filtration and concentration *in vacuo*, chromatography of the residue over neutralised silica gel (eluted with Ether-petroleum ether, 1:10) gave 0.212 g of pure aldehyde ester **1015**.

Isolated yield : 77%

Isomeric ratio : *Z-E* = 72-28

[294] Gorgues, A. *Bull. Soc. Chim. Fr.* **1974**, 529-530.



Mol. Mass : 270.44 g.mol^{-1}
Mol. Formula : $C_{14}H_{26}O_3Si$
R.N. = *Z* [111191-51-6]
E [148730-95-4]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

9.75 (1H, t, *J* = 1.8 Hz, H-1), 6.55 (0.72H, t, *J* = 7.2 Hz, H-6*Z*), 5.62 (0.28H, t, *J* = 7.5 Hz, H-6*E*), 4.15 (1H, q, *J* = 7.2 Hz, H-11), 2.48-2.35 (2.28H, m, H-2 and H-5*E*), 2.10 (0.72H, q, *J* = 7.5 Hz, H-5*Z*), 1.78 (1.44H, s, H-8*Z*), 1.71 (0.56H, s, H-8*E*), 1.70-1.56 (2H, m) and 1.52-1.38 (2H, m, C-3 and C-4), 1.28 (2.16H, t, *J* = 7.2 Hz, H-12*Z*), 1.27 (0.84H, t, *J* = 7.2 Hz, H-12*E*), -0.02 (6.48H, s, H-9*Z*), -0.04 (2.52H, s, H-9*E*).

^{13}C NMR (75 MHz, APT, $CDCl_3$) δ_C (ppm):

202.7 (+, C-1*E*), 202.3 (+, C-1*Z*), 168.3 (-, C-10), 138.1 (C-7*E*), 137.5 (C-7*Z*), 130.7 (C-6*Z*), 130.0 (C-6*E*), 60.7 (C-11*Z*), 60.3 (C-11*E*), 44.0 (C-2*Z*), 43.9 (C-2*E*), 29.5, 29.4, 29.0 and 28.6 (C-3 and C-5), 24.3, 22.1, 22.0 and 17.6 (C-4 and C-8), -0.78 (C-9*Z*), -1.38 (C-9*E*).

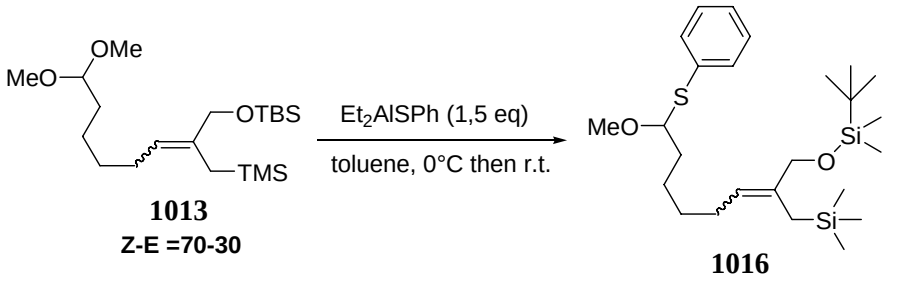
MS (EI, 70 eV) *m/z* (relative intensity, %):

270 ($M^{+\bullet}$, 1), 213 (8), 185 (33), 172 (35), 157 (49), 155 (28), 82 (54), 75 (Me_2SiOH^+, 47), 73 (TMS^+, 100), 57 ($CHOCH_2CH_2^+$, 51), 45 (EtO^+, 28).

IR (film):

2990-2860 [m] (C-H), 1713 [s] (large, C=O), 1616 [m] (large, C=C), 1421 [m], 1367 [m], 1247 [s] (large, C-O), 1173 [s] (C-Si), 895 and 854 [s] (C-Si) cm^{-1}.

VII.15.2. 1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-8-methoxy-8-phenylthioxyoct-2-ene **1016**[295]



1013
Z-E =70-30

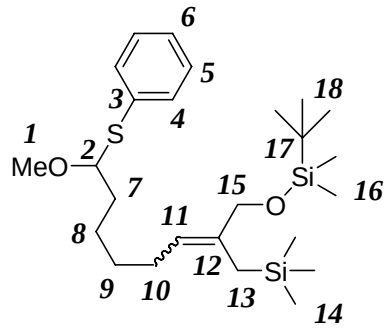
1016

To neat thiophenol (0.515 g, 4.64 mmol, 1.49 eq.) was added dropwise 4.65 ml of triethylaluminium (1M solution in hexanes, 4.65 mmol, 1.5 eq.). The mixture was stirred at 25 °C for 30 min. To a solution of allylsilane acetal **1013** (1.2 g, 3.09 mmol, 1 eq) in 50 ml of toluene cooled at 0 °C was added dropwise the freshly prepared solution of Et_2AlSPh. This mixture was stirred at 0 °C for 30 min. and was allowed to warm up to r.t. The solution was stirred at r.t. for 15 h and 50 ml of a saturated aqueous solution of $NaHCO_3$ was added. The aqueous layer was extracted with ether (3 x 100 ml). The combined extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Chromatography of the residue over neutralised silica gel (eluted with Ether-petroleum ether, 1:70) gave 1.035 mg of pure allylsilane *O*,*S*-acetal **1016**.

Isolated yield : 72%

Isomeric ratio : *Z-E* = 75-25

[295] Masaki, Y.; Serizawa, Y.; Kaji, K. *Chem. Lett.* **1985**, 1933-1936.

	**Mol. Mass :** 466.87 g.mol^{-1} **Mol. Formula :** $C_{25}H_{46}O_2SSi$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

7.49-7.43 (2H, m) and 7.32-7.23 (3H, m, H-4 to H-6), 5.24 (0.75H, t, *J* = 7.2 Hz, H-11*Z*), 4.99 (0.25H, t, *J* = 7.2 Hz, H-11*E*), 4.60 (1H, t, *J* = 6.9 Hz, H-2), 4.05 (0.5H, s, H-15*E*), 3.93 (1.5H, s, H-15*Z*), 3.46 (3H, s, H-1), 1.98 (0.5H, q, *J* = 7.2 Hz, H-10*E*), 1.92 (1.5H, q, *J* = 7.2 Hz, H-10*Z*), 1.81-1.63 (2H, m, H-7), 1.56 (0.5H, s, H-13*E*), 1.47 (1.5H, s, H-13*Z*), 1.52-1.40 (2H, m) and 1.37-1.24 (2H, m, H-8 and H-9), 0.90 (9H, s, H-18), 0.04 (6H, s, H-16), 0.00 (6.75H, s, H-14*Z*), -0.02 (2.25H, s, H-14*E*).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

136.7 (-, C-12*E*), 136.3 (-, C-12*Z*), 133.8, 133.7, 129.2 and 128.9 (+, C4 and C-5), 133.5 (-, C-3), 127.6 (+, C-6), 124.4 (+, C-11*E*), 121.4 (+, C-11*Z*), 91.1 (+, C-2), 68.3 (-, C-15*Z*), 61.8 (-, C-15*E*), 55.5 (+, C-1), 35.8 (-, C-7), 30.0 (-, C-8*E* or C-9*E*), 29.5 (-, C-8*Z* or C-9*Z*), 28.0 (-, C-10*Z*), 27.7 (-, C-10*E*), 26.3 (-, C-8*Z* or C-9*Z*), 26.1 (-, C-8*E* or C-9*E*), 26.2 (+, C-18), 24.0 (-, C-13*E*), 18.6 (-, C-13*Z* and C-17), -0.42 (+, C-14*Z*), -1.00 (+, C-14*E*), -4.83 and -5.04 (+, C-16).

MS (APCI, 70 eV) *m/z* (relative intensity, %):

467 (M+1, 1), 436 (36), 435 ($M^{+\bullet}$-$MeO^{\bullet}$, 100), 357 ($M^{+\bullet}$-$PhS^{\bullet}$, 3), 325 (357-MeOH, 51), 303 (435-TBSOH, 22), 253 (8), 231 (11), 191 (6), 121 (12), 93 (10), 73 (TMS^{+}, 8).

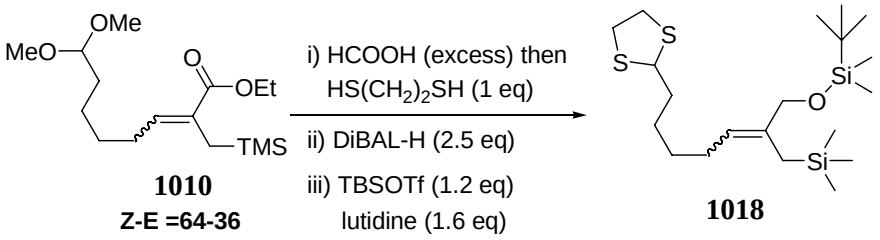
IR (film):

3074 and 3050 [w] (=C-H), 2951, 2928, 2896, 2856 and 2822 [s] (C-H), 1656 and 1583 [w] (C=C), 1472, 1462 and 1439 [m], 1360 [m], 1248 [s] (large, C-O), 1105, 1082 and 1067 [s] (C-Si), 1026 and 1005 [m] (=C-H in plane), 835 [s] (C-Si), 773, 744 and 717 [m] (=C-H out of plane) cm^{-1}.

Elemental Analysis:

($C_{25}H_{46}O_2SSi_2$) *Calculated*: C, 64.32; H, 9.93; S, 6.87 % ; *found*: C, 64.44; H, 9.81; S, 6.82 %.

VII.15.3. 1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-8-dithiolane-oct-2-ene **1018**



1010
Z-E =64-36

1018

To α,β-unsaturated ester-acetal **1010** (1.511 g, 4.77 mmol, 1 eq) was added formic acid (90% pure, 7.6 g, 0.165 mol, 35 eq.). This mixture was stirred for 20 min. at r.t. and pure ethanedithiol (0.478, 5.08 mmol, 1.06 eq) was added. The resulting turbid white solution was stirred at r.t. for 10 min. and 15 ml of water was added. The aqueous layer was extracted with

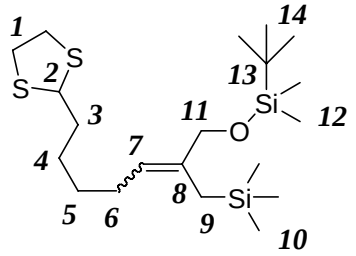
dichloromethane (3 x 20 ml). The combined extracts were washed with 50 ml of water and dried (Na_2SO_4). After filtration and concentration *in vacuo*, 1.820 g of crude dithiolane-ester was obtained.

To a solution of this crude in 120 ml of anhydrous dichloromethane cooled at -78 °C was added dropwise di-*iso*butylaluminium hydride (1.0 M in toluene, 12 ml, 12 mmol, 2.51 eq.). This mixture was stirred for 15 min. at -78 °C, the ice bath was removed and this mixture was stirred at r.t. for 30 min. To this pale yellow solution was carefully added dropwise AcOEt (2 x 5 ml). After cooling again at 0 °C, was successively added 15 ml of water, 20 ml of a 15% w/w aqueous solution of NaOH and 15 ml of water. This mixture was stirred for 30 min. at 0 °C and the ice bath was removed. The aqueous layer was extracted with dichloromethane (3 x 150 ml). The combined extracts were dried (Na_2SO_4) and after filtration and concentration *in vacuo*, 2.137 g of crude dithiolane-alcohol was obtained.

To a solution of this crude and 2,6-lutidine (0.781 g, 7.29 mmol, 1.53 eq) in 40 ml of anhydrous dichloromethane cooled at 0 °C was added dropwise *tert*-butyldimethylsilyl triflate (1.460 g, 5.52 mmol, 1.16 eq.). After 30 min. at 0 °C, the ice bath was removed and the mixture was allowed to warm up to r.t. To this solution was added 100 ml of a saturated aqueous solution of $NaHCO_3$ and the aqueous layer was extracted with dichloromethane (3 x 100 ml). The combined extracts were successively washed with 200 ml of water, 200 ml of brine, 300 ml of a saturated aqueous solution of $CuSO_4$, 200 ml of water and 200 ml of brine. After filtration and concentration *in vacuo*, 1.888 g of dithiolane-allylsilane **1018** was obtained.

Isolated yield : 85% (90% pure)

Isomeric ratio : *Z*-*E* = 75-25

	**Mol. Mass :** 418.87 g.mol^{-1} **Mol. Formula :** $C_{20}H_{42}OS_2Si_2$

Pics have been assigned with 2D-HMQC.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

5.26 (0.75H, t, *J* = 7.2 Hz, H-7*Z*), 5.02 (0.25H, t, *J* = 7.5 Hz, H-7*E*), 4.46 (1H, td, *J* = 6.9, 2.1 Hz, H-2), 4.07 (0.5H, s, H-11*E*), 3.96 (1.5H, s, H-11*Z*), 3.30-3.15 (4H, m, H-1), 2.02 (0.5H, q, *J* = 7.2 Hz, H-6*E*), 1.95 (1.5H, q, *J* = 7.2 Hz, H-6*Z*), 1.87-1.77 (2H, m, H-3), 1.57 (0.5H, s, H-9*E*), 1.49 (1.5H, s, H-9*Z*), 1.52-1.31 (4H, m, H-4 and H-5), 0.91 (9H, s, H-14), 0.05 (6H, s, H-12), 0.01 (6.75H, s, H-10*Z*), -0.01 (2.25H, s, H-10*E*).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

136.3 (-, C-8), 124.3 (+, C-7*E*), 121.3 (+, C-7*Z*), 68.2 (-, C-11*Z*), 61.8 (-, C-11*E*), 53.9 (+, C-2), 39.6 (-, C-3), 38.5 (-, C-14), 30.1 (-, C-4*E* or C-5*E*), 29.8 (-, C-4*Z* or C-5*Z*), 29.4 (-, C-4*Z* or C-5*Z*), 29.1 (-, C-4*E* or C-5*E*), 28.0 (-, C-6*Z*), 27.6 (-, C-6*E*), 26.2 (+, C-14), 24.0 (-, C-9*E*), 18.6 (-, C-9*Z* and C-13), -0.43 (+, C-10*Z*), -1.00 (+, C-10*E*), -5.04 (+, C-12).

MS (APCI, 70 eV) *m/z* (relative intensity, %):

420 (M+1, 10), 419 ($M^{+\bullet}$, 46), 345 (21), 316 (28), 314 (M+1-$(CH_2S)_2CH_2$, 32), 287 (100), 215 (33), 149 (36), 131 ($TBSO^+$, 33), 105 ($(CH_2S)_2CH^+$, 59), 91 (39), 73 (TMS^+, 84).

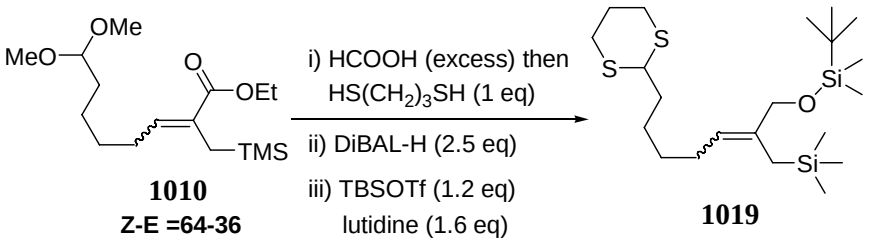
IR (film):

2953, 2928, 2897, 2854 [m] (C-H), 1709 and 1655 [w] (C=C), 1486 and 1462 [m], 1360 [m], 1248 [s] (large, C-O), 1119, 1086 and 1059 [s] (C-Si), 835 [s] (C-Si), 775 [m] (C-S) cm^{-1}.

Elemental Analysis:

($C_{20}H_{42}OS_2Si_2$) *Calculated*: C, 57.35; H, 10.11; S, 15.31 % ; *found*: C, 57.74; H, 10.05; S, 15.08 %.

VII.15.4. 1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-8-dithiane-oct-2-ene **1019**



1010
Z-E =64-36

1019

To α,β-unsaturated ester-acetal **1010** (1.248 g, 3.94 mmol, 1 eq) was added formic acid (90% pure, 6.24 g, 0.136 mol, 34.4 eq.). This mixture was stirred for 20 min. at r.t. and pure propanedithiol (0.436, 4.03 mmol, 1.2 eq) was added. The resulting turbid white solution was stirred at r.t. for 10 min. and 15 ml of water was added. The aqueous layer was extracted with dichloromethane (3 x 20 ml). The combined extracts were washed with 50 ml of water and dried (Na_2SO_4). After filtration and concentration *in vacuo*, 1.437 g of crude dithiane-ester was obtained.

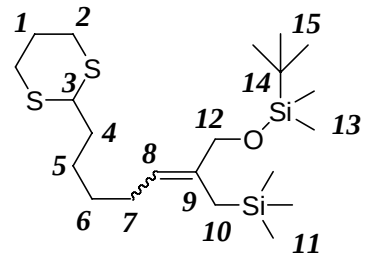
To a solution of this crude in 80 ml of anhydrous dichloromethane cooled at -78 °C was added dropwise di-*iso*butylaluminium hydride (1.5 M

in toluene, 6.8 ml, 10.2 mmol, 2.59 eq.). This mixture was stirred for 15 min. at -78 °C, the ice bath was removed and this mixture was stirred at r.t. for 30 min. To this pale yellow solution was carefully added dropwise AcOEt (2 x 5 ml). After cooling again at 0 °C, was successively added 15 ml of water, 20 ml of a 15% w/w aqueous solution of NaOH and 15 ml of water. This mixture was stirred for 30 min. at 0 °C and the ice bath was removed. The aqueous layer was extracted with dichloromethane (3 x 150 ml). The combined extracts were dried (Na_2SO_4) and after filtration and concentration *in vacuo*, 1.126 g of crude dithiane-alcohol was obtained.

To a solution of this crude and 2,6-lutidine (0.652 g, 6.09 mmol, 1.54 eq) in 35 ml of anhydrous dichloromethane cooled at 0 °C was added dropwise *tert*-butyldimethylsilyl triflate (1.168 g, 4.42 mmol, 1.12 eq.). After 30 min. at 0 °C, the ice bath was removed and the mixture was allowed to warm up to r.t. To this solution was added 100 ml of a saturated aqueous solution of $NaHCO_3$ and the aqueous layer was extracted with dichloromethane (3 x 100 ml). The combined extracts were successively washed with 200 ml of water, 200 ml of brine, 300 ml of a saturated aqueous solution of $CuSO_4$, 200 ml of water and 200 ml of brine. After filtration and concentration *in vacuo*, 1.305 g of dithiolane-allylsilane **1019** was obtained.

Isolated yield : 74% (95% pure)

Isomeric ratio : *Z*-*E* = 75-25

	**Mol. Mass :** 432.90 g.mol^{-1} **Mol. Formula :** $C_{21}H_{44}OS_2Si_2$

Pics have been assigned with 2D-HMQC.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

5.26 (0.75H, t, *J* = 7.2 Hz, H-8*Z*), 5.02 (0.25H, t, *J* = 7.2 Hz, H-8*E*), 4.07 (0.5H, s, H-12*E*), 4.04 (0.75H, t, *J* = 6.9 Hz, H-3*Z*), 4.03 (0.25H, t, *J* = 6.9 Hz, H-3*E*), 3.95 (1.5H, s, H-12*Z*), 2.98-2.73 (4H, m, H-2), 2.17-1.82 (3H, m, H-1 and H-7), 1.82-1.69 (2H, m, H-4), 1.57 (0.5H, s, H-10*E*), 1.61-1.47 (2H, m H-5), 1.49 (1.5H, s, H-10*Z*), 1.44-1.28 (2H, m, H-6), 0.91 (9H, s, H-15), 0.05 (6H, s, H-13), 0.01 (6.75H, s, H-11*Z*), -0.01 (2.25H, s, H-11*E*).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

136.3 (-, C-9), 124.3 (+, C-8*E*), 121.3 (+, C-8*Z*), 68.2 (-, C-12*Z*), 61.8 (-, C-12*E*), 47.7 (+, C-3), 35.5 (-, C-4), 30.6 (-, C-2), 30.1 (-, C-5*E* or C-6*E*), 29.5 (-, C-5*Z* or C-6*Z*), 28.0 (-, C-7*Z*), 27.5 (-, C-7*E*), 26.7(-, C-5*Z* or C-6*Z*), 26.5 (-, C-5*E* or C-6*E*), 26.2 (-, C-1), 26.1 (+, C-15), 24.0 (-, C-10*E*), 18.6 (-, C-10*Z* and C-14), -0.44 (+, C-11*Z*), -1.03 (+, C-11*E*), -5.05 (+, C-13).

MS (APCI, 70 eV) *m/z* (relative intensity, %):

434 (M+1, 5), 433 ($M^{+\bullet}$, 15), 361 (M+1-$Me_3Si^{\bullet}$, 18), 301 (M+1-$(CH_2S)_2CHCH_2^{\bullet}$, 100), 229 (16), 147 ($Me_3SiOSiMe_2^{+}$, 7), 121 (9), 105 ($(CH_2S)_2CH^{+}$, 9), 92 (8), 73 ($TMS^{+}$, 17).

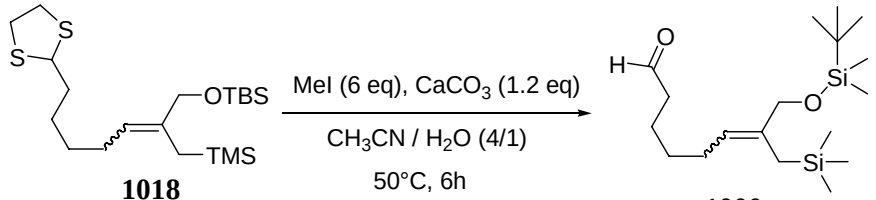
IR (film):

2951, 2928, 2897, 2854 [m] (C-H), 1659 and 1632 [w] (C=C), 1462 and 1421 [m], 1360 [m], 1248 [s] (large, C-O), 1086 and 1063 [m] (C-Si), 835 [s] (C-Si), 775 [m] (C-S) cm^{-1}.

Elemental Analysis:

($C_{21}H_{44}OS_2Si_2$) *Calculated*: C, 58.27; H, 10.25; S, 14.81 % ; *found*: C, 58.49; H, 10.21; S, 14.78 %.

VII.15.5. 1-(tertbutyldimethyl-silyloxy)-2-((trimethylsilyl)-methyl)-7-formyl-hept-2-ene **1000**



1018

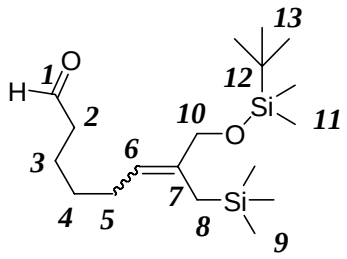
Z-E =75-25

1000

In an oblong flask was introduced allylsilane dithiolane **1018** (0.521 g, 1.25 mmol, 1 eq.), calcium carbonate (0.155 g, 1.55 mmol, 1.24 eq), 2 ml of acetonitrile P.A. and 0.5 ml of water. To this mixture was added dropwise methyliodide (1.027 g, 7.24 mmol, 5.79 eq), the flask was closed and the solution was heated at 50 °C for 6h. The mixture was then cooled to r.t. and filtered over a pad of neutralised silica gel. Chromatography of the residue over neutralised silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 0.271 g of pure allylsilane aldehyde **1000**.

Isolated yield : 65%

Isomeric ratio : *Z*-*E* = 75-25



Mol. Mass : 343.67 g.mol^{-1}
Mol. Formula : $C_{18}H_{38}O_2Si_2$

Pics have been assigned with 2D-HMQC.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

9.76 (1H, t, *J* = 1.8 Hz, H-1), 5.26 (0.75H, t, *J* = 6.9 Hz, H-6*Z*), 5.01 (0.25H, t, *J* = 7.5 Hz, H-6*E*), 4.07 (0.5H, s, H-10*E*), 3.95 (1.5H, s, H-10*Z*), 2.42 (2H, t, *J* = 7.8 Hz, H-2), 2.04 (0.5H, q, *J* = 7.2 Hz, H-5*E*), 1.98 (1.5H, q, *J* = 7.2 Hz, H-5*Z*), 1.71-1.55 (2H, m, H-3), 1.57 (0.5H, s, H-8*E*), 1.48 (1.5H, s, H-8*Z*), 1.45-1.31 (2H, m, H-4), 0.90 (9H, s, H-13), 0.05 (6H, s, H-11), 0.01 (6.75H, s, H-9*Z*), -0.01 (2.25H, s, H-9*E*).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

202.9 (+, C-1*Z*), 202.8 (+, C-1*E*), 136.7 (-, C-7), 123.9 (+, C-6*E*), 120.7 (+, C-6*Z*), 68.2 (-, C-10*Z*), 61.8 (-, C-10*E*), 44.0 (-, C-2), 30.0 (-, C-3*E*), 29.4 (-, C-3*Z*), 27.9 (-, C-5*Z*), 27.5 (-, C-5*E*), 26.1 (+, C-13), 24.1 (-, C-8*E*), 22.1 (-, C-4*Z*), 21.8 (-, C-4*E*), 18.7 (-, C-8*Z* and C-12), -0.45 (+, C-9*Z*), -1.04 (+, C-9*E*), -5.07 (+, C-11).

MS (EI, 70 eV) *m/z* (relative intensity, %):

342 ($M^{+\bullet}$, 1), 326 ($M^{+\bullet}$-$CH_3^\bullet$, 13), 269 ($M^{+\bullet}$-$TMS^\bullet$, 16), 314 ($M^{+\bullet}$-$TMSCH_3$, 15), 197 ($M^{+\bullet}$-$TBSOCH_2^\bullet$, 21), 147 ($Me_3SiOSiMe_2^+$, 14), 86 (53), 84 (100), 75 (Me_2SiOH^+, 77), 73 (TMS^+, 78), 57 ($^tBu^+$, 18), 51 (29), 49 (88).

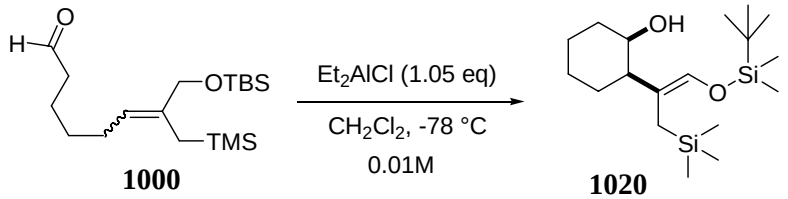
IR (film):

2953, 2928, 2895, 2856 [s] (C-H), 1728 [s] (large, C=O), 1655 [w] (large, C=C), 1486 and 1462 [m], 1410, 1389 and 1361 [m], 1248 [s] (large, C-O), 1086 and 1070 [s] (C-Si), 835 and 773 [s] (C-Si) cm^{-1}.

Elemental Analysis:

($C_{18}H_{38}O_2Si_2$) *Calculated*: C, 63.09; H, 11.18 % ; *found*: C, 62.42; H, 11.04 %.

VII.16. 1-(tertbutyldimethyl-silyloxy)-2-(2-hydroxy-cyclohexyl)-3-((trimethylsilyl)-prop-1-ene 1020

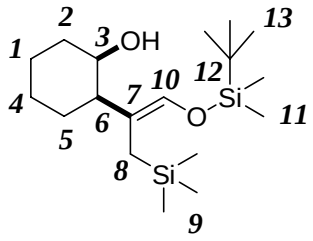


1000
Z-E =75-25

1020

To a solution of allylsilane aldehyde **1000** (0.147 g, 0.43 mmol, 1 eq) in 50 ml of anhydrous dichloromethane cooled at -78 °C was added dropwise diethylaluminium chloride (1 M in CH_2Cl_2, 0.45 ml, 0.45 mmol, 1.05 eq.). This mixture was stirred for 15 min. at -78 °C. 25 ml of a saturated aqueous solution of $NaHCO_3$ was added and the mixture was allowed to warm up to r.t. The aqueous layer was extracted with CH_2Cl_2 (3 x 30 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:40) gave 0.070 g of pure *syn* cyclic ene adduct **1020**.

Isolated yield : 47%

	**Mol. Mass :** 343.67 g.mol^{-1} **Mol. Formula :** $C_{18}H_{38}O_2Si_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.04 (1H, s, H-10), 3.87 (1H, bs, H-3), 1.91 (1H, d, *J* = 13.5 Hz, H-8a), 2.04-1.85 (2H, m), 1.79-1.68 (1H, m), 1.64-1.31 (5H, m), and 1.30-1.15 (1H, m, H-1, H-2 and H-4 to H-6), 1.06 (1H, d, *J* = 13.5 Hz, H-8b), 0.91 (9H, s, H-13), 0.11 (6H, s, H-11), 0.00 (9H, s, H-9).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

133.5 (+, C-10), 121.1 (-, C-7), 65.4 (+, C-3), 46.7 (+, C-6), 31.9, 26.8, 24.0 and 20.0 (-, C-1, C-2, C-4 and C-5), 25.8 (+, C-13), 18.2 (-, C-12), 17.9 (-, C-8), -0.46 (+, C-9), -4.91 (+, C-11).

MS (EI, 70 eV) *m/z* (relative intensity, %):

344 ($M^{+\bullet}$, 3), 229 ($M^{+\bullet}$-TBS$^\bullet$, 22), 147 ($Me_3SiOSiMe_2^+$, 69), 108 (15), 75 (Me_2SiOH^+, 100), 73 (TMS^+, 87), 57 ($^tBu^+$, 13), 55 (28).

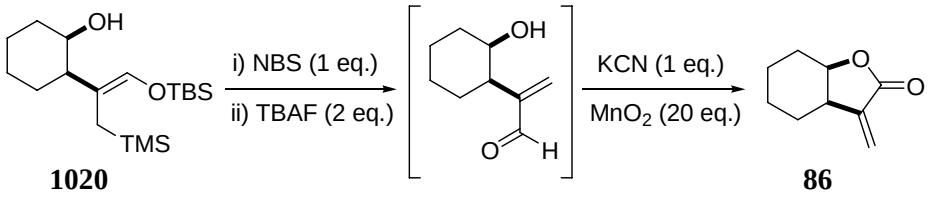
IR (film):

3403 [w] (O-H), 2960-2830 [m] (C-H), 1659 [m] (C=C), 1465 [m], 1423 [m], 1370 [m], 1249 [s] (C-O), 1167 [s] (C-Si), 1071 [w], 991 [m], 839 and 767 [s] (C-Si) cm^{-1}.

Elemental Analysis: in progress

VII.17. Synthesis of the α-methylene-γ-butyrolactones

VII.17.1. syn-hexahydro-3-methylene-benzofuran-2(3H)-one **86**

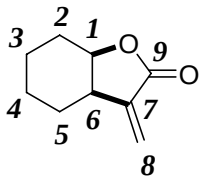


1020 **86**

To a solution of ene adduct **1020** (0.202 g, 0.59 mmol, 1 eq.) in 7 ml of anhydrous THF was added N-bromosuccinimide (0.108 g, 0.60 mmol, 1.01 eq.). The mixture was stirred for 10 min. and the THF was eliminated *in vacuo*. The resulting white precipitate was filtered and washed with 7 ml of pentane. The pentane was removed under reduced pressure and this crude is directly dissolved in 7 ml of THF. To this mixture was added tetrabutylammonium fluoride (1 M solution in THF, 1.3 ml, 1.3 mmol, 2.2 eq.) and the resulting yellow solution was stirred for 5 min. The mixture was then diluted with 10 ml of Et_2O and transferred to a separatory funnel containing 20 ml of brine. After separation, the aqueous phase was extracted with ether (3 x 10 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude obtained was directly used in the subsequent oxidation step.

To a cold (0 °C) solution of crude enal in 7 ml of CH_3CN P.A. were successively added manganese dioxide (1.022 g, 11.75 mmol, 19.9 eq.) and potassium cyanide (0.040 g, 0.61 mmol, 1.04 eq.). The resulting black solution was stirred at room temperature for 24 h. The mixture was then filtered through silica gel and washed with 2 x 10 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.052 g of pure *syn* bicyclic 6,5 α-methylene-γ-lactone **86**.

Isolated yield : 58% (over three steps)

	**Mol. Mass :** 152.20 g.mol^{-1} **Mol. Formula :** $C_9H_{12}O_2$ **R.N.** = (R,R) [38602-11-8] (S,S) [16822-06-3] (S,R) [3727-53-5]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.17 (1H, s, H-8a), 5.50 (1H, s, H-8b), 4.53 (1H, q (ddd), *J* = 10 Hz, H-1), 3.01 (1H, m, H-6), 1.95-1.82 (1H, m), 1.82-1.47 (4H, m) and 1.47-1.29 (3H, m, H-2 to H-5).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

170.9 (+, C-9), 139.8 (+, C-7), 119.6 (+, C-8), 76.8 (-, C-1), 39.4 (-, C-6), 28.7, 26.1, 21.0 and 20.4 (+, C-2 to C-5).

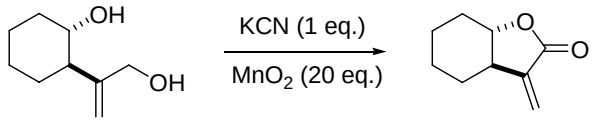
MS (APCI, 70 eV) *m/z* (relative intensity, %):

154 (21), 153 (M+1, 100), 149 (14), 135 (41), 117 (14), 107 ($M^{+\bullet}$-$CO_2H^{\bullet}$, 91), 79 (8).

IR (film):

3078 [m] (=C-H), 2960-2840 [s] (C-H), 1759 [s] (C=O), 1668 [m] (C=C), 1450, 1402 and 1362 [m], 1311 [m], 1263 and 1232 [s] (C-O), 1161, 1126 and 1097 [s], 1012, 978 and 964 [s] cm^{-1}.

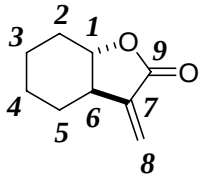
VII.17.2. anti-hexahydro-3-methylene-benzofuran-2(3H)-one **75**



1014 ***Anti*** **75**

To a solution of diol *anti* **1014** (0.030 g, 0.19 mmol, 1 eq.) in 3 ml of CH_3CN P.A. were successively added manganese dioxide (0.333 g, 3.83 mmol, 20.1 eq.) and potassium cyanide (0.015 g, 0.23 mmol, 1.20 eq.). The resulting black solution was stirred at room temperature for 24 h. The mixture was then filtered through silica gel and washed with 2 x 10 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.022 g of pure *anti* bicyclic 6,5 α-methylene-γ-lactone **75**.

Isolated yield : 76% (over three steps)

	**Mol. Mass :** 152.20 $g.mol^{-1}$ **Mol. Formula :** $C_9H_{12}O_2$ **R.N.** = (R,R) [38602-11-8] (S,S) [16822-06-3] (S,R) [3727-53-5]

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.07 (1H, s, H-8a), 5.39 (1H, s, H-8b), 3.72 (1H, td (ddd), *J* = 11, 3.7 Hz, H-1), 2.50-5.34 (1H, m, H-6), 2.32-2.22 (1H, m), 2.19-2.08 (1H, m), 2.02-1.92 (1H, m), 1.90-1.81 (1H, m), 1.71-1.54 (1H, m) and 1.50-1.28 (3H, m, H-2 to H-5).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

171.2 (+, C-9), 139.6 (+, C-7), 119.5 (+, C-8), 76.8 (-, C-1), 39.9 (-, C-6), 28.4, 26.2, 21.3 and 20.4 (+, C-2 to C-5).

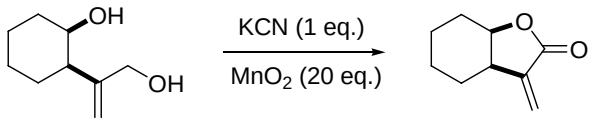
MS (APCI, 70 eV) *m/z* (relative intensity, %):

154 (18), 153 (M+1, 100), 149 (9), 135 (45), 107 ($M^{+\bullet}$-$CO_2H^{\bullet}$, 83), 79 (15).

IR (film):

3083 [m] (=C-H), 2960-2840 [s] (C-H), 1761 [s] (C=O), 1666 [m] (C=C), 1448, 1407 and 1369 [m], 1267 and 1230 [s] (C-O), 1166, 1129 and 1095 [s], 983 and 966 [s] cm^{-1}.

VII.17.3. syn-hexahydro-3-methylene-benzofuran-2(3H)-one **86**



1014 *Syn* **86**

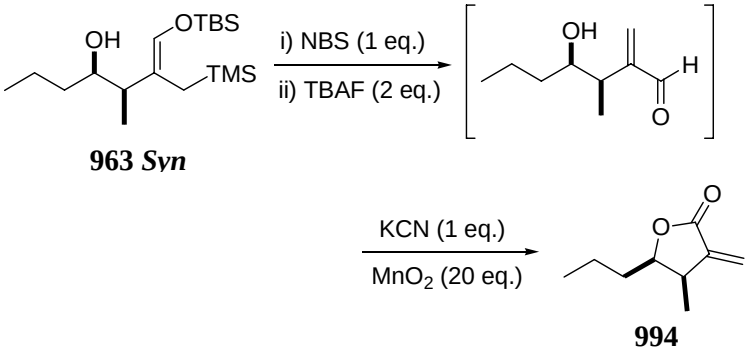
To a solution of diol *syn* **1014** (0.065 g, 0.42 mmol, 1 eq.) in 6 ml of CH_3CN P.A. were successively added manganese dioxide (0.765 g, 8.80 mmol, 20.9 eq.) and potassium cyanide (0.029 g, 0.44 mmol, 1.07 eq.). The

resulting black solution was stirred at room temperature for 24 h. The mixture was then filtered through silica gel and washed with 2 x 10 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.046 g of pure *syn* bicyclic 6,5 α-methylene-γ-lactone **86**.

Isolated yield : 71% (over three steps)

Analysis: *see* pg 406-407

VII.17.4. syn-dihydro-4-methyl-3-methylene-5-propylfuran-2(3H)-one **994**

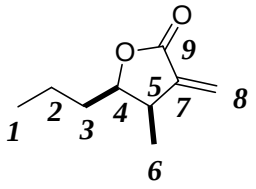


To a solution of ene adduct *syn* **963** (0.400 g, 1.16 mmol, 1 eq.) in 15 ml of anhydrous THF was added N-bromosuccinimide (0.218 g, 1.22 mmol, 1.05 eq.). The mixture was stirred for 10 min. and the THF was eliminated *in vacuo*. The resulting white precipitate was filtered and washed with 15 ml of pentane. The pentane was removed under reduced pressure and this crude is directly dissolved in 15 ml of THF. To this mixture was added tetrabutylammonium fluoride (1 M solution in THF, 2.4 ml, 2.4 mmol, 2.07 eq.) and the resulting yellow solution was stirred for 5 min. The

mixture was then diluted with 30 ml of Et_2O and transferred to a separatory funnel containing 50 ml of brine. After separation, the aqueous phase was extracted with ether (3 x 30 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude obtained was directly used in the subsequent oxidation step.

To a cold (0 °C) solution of crude enal in 15 ml of CH_3CN P.A. were successively added manganese dioxide (1.975 g, 22.71 mmol, 19.6 eq.) and potassium cyanide (0.076 g, 1.17 mmol, 1 eq.). The resulting black solution was stirred at room temperature for 24 h. The mixture was then filtered through silica gel and washed with 2 x 25 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.119 g of pure *syn* α-methylene-γ-lactone Pr Me **994**.

Isolated yield : 63 % (over three steps)

	**Mol. Mass :** 154.21 g.mol^{-1} **Mol. Formula :** $C_9H_{14}O_2$

Pics have been assigned with 2D-HMQC.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.19 (1H, d, *J* = 2.4 Hz, H-8a), 5.52 (1H, s, *J* = 2.4 Hz, H-8b), 4.54 (1H, m, H-4), 3.15 (1H, quint(t), *J* = 7.1, 2.7 Hz, H-5), 1.67-1.32 (4H, m, H-2 and H-3), 1.15 (3H, d, *J* = 7.1 Hz, H-6) and 0.95 (3H, t, *J* = 7.6 Hz, H-1).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

170.6 (-, C-9), 141.0 (-, C-7), 120.5 (-, C-8), 81.1 (+, C-4), 37.6 (+, C-5), 32.7 (-, C-3), 18.9 (-, C-2), 13.9 (+, C-1 and C-6).

MS (EI, 70 eV) *m/z* (relative intensity, %):

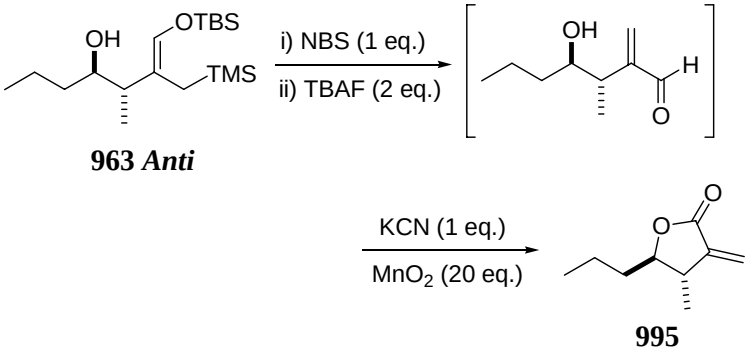
155 ($MH^{+\bullet}$, 12), 154 ($M^{+\bullet}$, 7), 139 ($M^{+\bullet}$-$CH_3^{\bullet}$, 3), 111 ($M^{+\bullet}$-$Pr^{\bullet}$, 26), 83 (32), 82 ($M^{+\bullet}$-PrCHO, 100), 54 (100), 53 (21), 43 (Pr^+, 3).

IR (film):

3086 [m] (=C-H), 2980-2840 [s] (C-H), 1759 [s] (C=O), 1664 [m] (C=C), 1458, 1398 and 1333 [m], 1267 and 1248 [s] (C-O), 1169, 1128 and 1105 [m], 960 [m], 815 [w] cm^{-1}.

HRMS : in progress

VII.17.5. anti-dihydro-4-methyl-3-methylene-5-propylfuran-2(3H)-one 995



963 ***Anti***

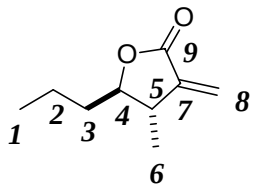
995

To a solution of ene adduct *anti* **963** (0.400 g, 1.16 mmol, 1 eq.) in 15 ml of anhydrous THF was added N-bromosuccinimide (0.209 g, 1.17 mmol, 1.01 eq.). The mixture was stirred for 10 min. and the THF was

eliminated *in vacuo*. The resulting white precipitate was filtered and washed with 15 ml of pentane. The pentane was removed under reduced pressure and this crude is directly dissolved in 15 ml of THF. To this mixture was added tetrabutylammonium fluoride (1 M solution in THF, 2.6 ml, 2.6 mmol, 2.24 eq.) and the resulting yellow solution was stirred for 5 min. The mixture was then diluted with 30 ml of Et_2O and transferred to a separatory funnel containing 50 ml of brine. After separation, the aqueous phase was extracted with ether (3 x 30 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude obtained was directly used in the subsequent oxidation step.

To a cold (0 °C) solution of crude enal in 15 ml of CH_3CN P.A. were successively added manganese dioxide (2.020 g, 23.23 mmol, 20.0 eq.) and potassium cyanide (0.079 g, 1.22 mmol, 1.05 eq.). The resulting black solution was stirred at room temperature for 24 h. The mixture was then filtered through silica gel and washed with 2 x 25 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.110 g of pure *anti* α-methylene-γ-lactone Pr Me **995**.

Isolated yield : 58 % (over three steps)

	**Mol. Mass :** 154.21 $g.mol^{-1}$ **Mol. Formula :** $C_9H_{14}O_2$

Pics have been assigned with 2D-HMQC.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.24 (1H, d, *J* = 3.1 Hz, H-8a), 5.55 (1H, s, *J* = 2.9 Hz, H-8b), 4.02 (1H, q (dt), *J* = 6.2 Hz, H-4), 2.69 (1H, m, H-5), 1.73-1.38 (4H, m, H-2 and H-3), 1.26 (3H, d, *J* = 6.8 Hz, H-6) and 0.99 (3H, t, *J* = 7.3 Hz, H-1).

^{13}C NMR (75 MHz, DEPT_Q, $CDCl_3$) δ_C (ppm):

170.7 (-, C-9), 141.4 (-, C-7), 121.1 (-, C-8), 85.2(+, C-4), 40.35 and 37.3 (+, C-5 and C-3), 19.0, 17.4 and 14.2 (-, C-1, C-2 and C-6).

MS (EI, 70 eV) *m/z* (relative intensity, %):

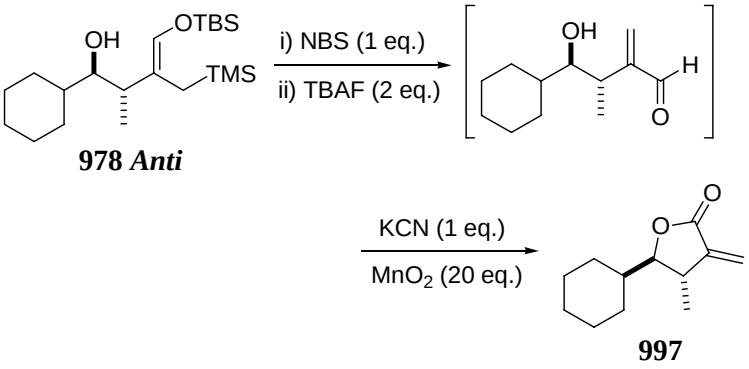
155 ($MH^{+\bullet}$, 14), 154 ($M^{+\bullet}$, 7), 111 ($M^{+\bullet}$-$Pr^{\bullet}$, 19), 83 (12), 82 ($M^{+\bullet}$-PrCHO, 83), 55 (28), 54 (100), 43 (Pr^{+}, 3).

IR (film):

3089 [m] (=C-H), 2980-2840 [s] (C-H), 1759 [s] (C=O), 1664 [m] (C=C), 1460, 1404 and 1319 [m], 1249 [s] (C-O), 1153, 1122 and 1097 [m], 966 and 941 [m], 814 [m] cm^{-1}.

HRMS: in progress

VII.17.6. anti-5-cyclohexyl-dihydro-4-methyl-3-methylene-furan-2(3H)-one **997**



978 ***Anti***

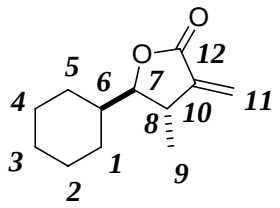
997

To a solution of ene adduct *anti* **978** (0.320 g, 0.83 mmol, 1 eq.) in 15 ml of anhydrous THF was added N-bromosuccinimide (0.148 g, 0.83 mmol, 1 eq.). The mixture was stirred for 10 min. and the THF was eliminated *in vacuo*. The resulting white precipitate was filtered and washed with 15 ml of pentane. The pentane was removed under reduced pressure and this crude is directly dissolved in 15 ml of THF. To this mixture was added tetrabutylammonium fluoride (1 M solution in THF, 1.8 ml, 1.8 mmol, 2.2 eq.) and the resulting yellow solution was stirred for 5 min. The mixture was then diluted with 30 ml of Et_2O and transferred to a separatory funnel containing 50 ml of brine. After separation, the aqueous phase was extracted with ether (3 x 30 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude obtained was directly used in the subsequent oxidation step.

To a cold (0 °C) solution of crude enal in 15 ml of CH_3CN P.A. were successively added manganese dioxide (1.445 g, 16.62 mmol, 20.0 eq.) and potassium cyanide (0.057 g, 0.87 mmol, 1.05 eq.). The resulting black solution was stirred at room temperature for 24 h.

The mixture was then filtered through silica gel and washed with 2 x 25 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.040 g of pure *anti* α-methylene-γ-lactone Cy Me **997**.

Isolated yield : 25 % (over three steps)

	**Mol. Mass :** 154.21 g.mol^{-1} **Mol. Formula :** $C_{12}H_{18}O_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.22 (1H, d, *J* = 3 Hz, H-11a), 5.54 (1H, s, *J* = 2.8 Hz, H-11b), 3.82 (1H, t (dd), *J* = 6 Hz, H-7), 2.84 (1H, m, H-8), 1.90-1.62 (5H, m), 1.60-1.48 (1H, m) and 1.32-0.98 (5H, m, H-1 to H-6), 1.24 (3H, d, *J* = 6.9 Hz, H-9).

^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm):

170.7 (C-12), 141.5 (C-10), 121.4 (C-11), 89.4 (C-7), 42.6 and 37.0 (C-6 and C-8), 28.8, 28.1, 26.5, 26.2 and 26.0 (C-1 to C-5), 15.6 (C-9).

MS (EI, 70 eV) *m/z* (relative intensity, %):

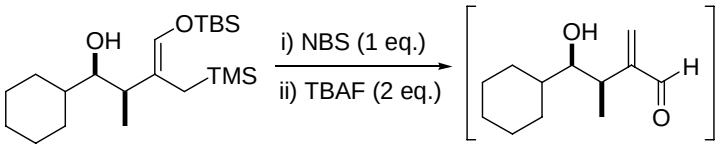
195 ($MH^{+\bullet}$, 6), 194 ($M^{+\bullet}$, 11), 179 ($M^{+\bullet}$-$CH_3^{\bullet}$, 4), 165 (9), 111 ($M^{+\bullet}$-$Cy^{\bullet}$, 21), 83 (32), 82 ($M^{+\bullet}$-CyCHO, 87), 55 (53), 54 (100).

IR (film):

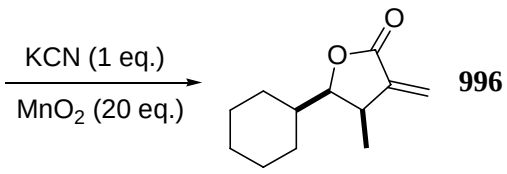
3087 [m] (=C-H), 2970-2820 [s] (C-H), 1758 [s] (C=O), 1661 [m] (C=C), 1462 and 1336 [m], 1262 and 1249 [s] (C-O), 1154, 1110 and 1083 [m], 986 and 968 [m], 813 [m] cm^{-1}.

HRMS: in progress

VII.17.7. syn-5-cyclohexyl-dihydro-4-methyl-3-methylene-furan-2(3H)-one **996**



978 ***Syn***



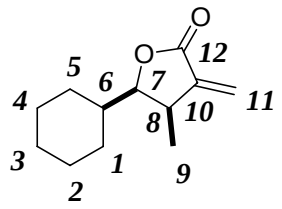
996

To a solution of ene adduct *syn* **978** (0.570 g, 1.48 mmol, 1 eq.) in 15 ml of anhydrous THF was added N-bromosuccinimide (0.264 g, 1.48 mmol, 1 eq.). The mixture was stirred for 10 min. and the THF was eliminated *in vacuo*. The resulting white precipitate was filtered and washed with 15 ml of pentane. The pentane was removed under reduced pressure and this crude is directly dissolved in 15 ml of THF. To this mixture was added tetrabutylammonium fluoride (1 M solution in THF, 3.3 ml, 3.3 mmol, 2.2 eq.) and the resulting yellow solution was stirred for 5 min. The mixture was then diluted with 30 ml of Et_2O and transferred to a separatory funnel containing 50 ml of brine. After separation, the aqueous phase was

extracted with ether (3 x 30 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude obtained was directly used in the subsequent oxidation step.

To a cold (0 °C) solution of crude enal in 15 ml of CH_3CN P.A. were successively added manganese dioxide (2.574 g, 29.61 mmol, 20.0 eq.) and potassium cyanide (0.102 g, 1.57 mmol, 1.06 eq.). The resulting black solution was stirred at room temperature for 24 h. The mixture was then filtered through silica gel and washed with 2 x 25 ml of DCM. The crude was concentrated *in vacuo* and chromatography of the residue over silica gel (eluted with EtOAc-petroleum ether, 1:14) gave 0.083 g of pure *syn* α-methylene-γ-lactone Cy Me **996**.

Isolated yield : 29 % (over three steps)



Mol. Mass : 154.21 $g.mol^{-1}$
Mol. Formula : $C_{12}H_{18}O_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm):

6.12 (1H, d, *J* = 2.1 Hz, H-11a), 5.50 (1H, s, *J* = 1.9 Hz, H-11b), 4.11 (1H, t (dd), *J* = 7 Hz, H-7), 3.10 (1H, m, H-8), 1.92-1.53 (6H, m) and 1.40-0.87 (5H, m, H-1 to H-6), 1.15 (3H, d, *J* = 7.1 Hz, H-9).

^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm):

170.1 (C-12), 142.4 (C-10), 120.0 (C-11), 85.2 (C-7), 38.4 and 37.6 (C-6 and C-8), 29.5, 29.0, 26.5, 26.0 and 25.7 (C-1 to C-5), 14.8 (C-9).

MS (EI, 70 eV) *m/z* (relative intensity, %):

195 ($MH^{+\bullet}$, 3), 194 ($M^{+\bullet}$, 18), 179 ($M^{+\bullet}$-$CH_3^{\bullet}$, 2), 165 (6), 111 ($M^{+\bullet}$-$Cy^{\bullet}$, 27), 83 (18), 82 ($M^{+\bullet}$-CyCHO, 100), 55 (43), 54 (74).

IR (film):

3083 [m] (=C-H), 2960-2820 [s] (C-H), 1759 [s] (C=O), 1666 [m] (C=C), 1450 and 1329 [m], 1267 and 1248 [s] (C-O), 1149, 1121 and 1090 [m], 981 and 960 [m], 815 [m] cm^{-1}.

Elemental Analysis:

($C_{12}H_{18}O_2$) *Calculated*: C, 74.19; H, 9.34 % ; *found*: C, 74.20; H, 9.23 %.