SUPPORTING INFORMATION

Radical Transfer Hydrosilylation/Cyclization Using Silylated Cyclohexadienes

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Experimental

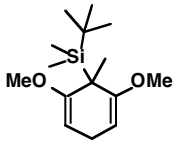
General. TLC: *Merck* silica gel *60* F_{254} plates; detection with UV or dipping into a soln. of $KMnO_4$ (1.5 g in 333 mL 1M NaOH) or a soln. of $Ce(SO_4)_2 \cdot H_2O$ (10 g), phosphormolybdic acid hydrate (25 g), conc. H_2SO_4 (60 mL), and H_2O (940 mL), followed by heating. FC: *Merck* or *Fluka* silica gel *60* (40 - 63 μm); at *ca.* 0.4 bar. GC: *Hewlett Packard 5890*, column: *Hewlett Packard HP-5* (30 m × 0.32 mm). M.p.: *Büchi 510* apparatus; uncorrected. I.R. spectra: *Perkin Elmer 782* or *Bruker IFS-200* spectrophotometer (*s* = strong, *m* = medium, *w* = weak, *br.* = broad signal). NMR Spectra: *Bruker AMX 500* (^{1}H 500 MHz, ^{13}C 125 MHz), *AMX 400* (^{1}H 400 MHz, ^{13}C 100 MHz), *Bruker AC 300* and *Varian Gemini 300* (^{1}H 300 MHz, ^{13}C 75 MHz); chemical shifts (δ) in ppm relative to $SiMe_4$ (= 0 ppm). Mass spectra: *VG Tribrid* or *Varian CH7* in *m*/*z* (% of basis peak). Elemental analyses were performed by the Microanalytical Laboratory of the Fachbereich Chemie der Philipps-Universität Marburg. Solvents were dried and purified by standard distillation techniques. All other commercially available reagents were used without further purification, unless otherwise noted. All operations were carried out under an Ar-atmosphere. All cyclization products were isolated as a mixture of diastereoisomers.

Abbreviations. AIBN: α,α'-azobis(isobutyronitrile); DMPSCl: dimethylphenylchlorosilane; HMPA: hexamethylphosphoramide; MTBE: *tert*-butyl methyl ether; TBDMSCl:

tert-butyldimethylchlorosilane; TBHN: di-*tert*-butyl hyponitrite[1]; TIPSCl: triisopropylchlorosilane; TMEDA: *N,N,N′,N′*-tetramethylethylendiamine; TMSCl: trimethylchlorosilane.

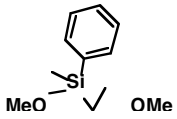
1,5-Dimethoxy-1,4-cyclohexadiene was prepared in 95% yield according to a literature procedure.[2]

3-*tert*-Butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene (6)



1,5-Dimethoxy-1,4-cyclohexadiene (21 g, 0.15 mol) was dissolved in THF (500 mL). The soln. was cooled to *ca.* –70 °C. After addition of *tert*-butyllithium (103 mL, 1.6 M in hexane, 0.165 mol) and stirring for 30 min, HMPA (31.5 mL, 0.18 mol) was added. The resulting red soln. was stirred for 10 min at –70 °C. A soln. of TBDMSCl (25 g, 0.17 mol) in THF (40 mL) was slowly added. The red color of the reaction mixture disappeared. The soln. was allowed to warm to *ca*. –50 °C over 30 min. After stirring for 60 min at –50 °C, butyllithium (110 mL, 1.52 M in hexane, 0.165 mol) was added. The soln. turned orange. After stirring for another 60 min (–50 °C), $(CH_3O)_2SO_2$ (14.8 mL, 0.18 mol) was added. The color of the reaction mixture disappeared. After 5 min, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. Pentane (300 mL) was added, followed by H_2O (100 mL). The phases were separated and the organic layer was additionally washed with H_2O (2 × 100 mL) and brine (100 mL). The organic layer was dried over $MgSO_4$. Removal of the solvent *in vacuo* yielded an oil which crystallized upon standing over night at 4 °C. Washing with methanol afforded after drying **6** (24 g, 0.11 mol, 71%) as white crystals. From the filtrate, the solvent was removed *in vacuo* to yield an oily residue, which was purified by FC (Et_2O / pentane 1 : 200): **6** (5 g, 0.02 mol, 14%). M.p. 32–33 °C. I.R. ($CHCl_3$): 2934*s*, 2855*s*, 1677*s*, 1643*w*, 1464*m*, 1344*m*, 1127*s*, 1076*m*, 977*w* cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.46 (*t*, *J* = 3.7 Hz, 2 H, CH); 3.45 (*s*, 6 H, OCH_3); 2.83–2.82 (*m*, 2 H, CH_2); 1.32 (*s*, 3 H, CH_3); 0.85 (*s*, 9 H, $C(CH_3)_3$); 0.00 (*s*, 6 H, $Si(CH_3)_2$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.9 (C); 88.4 (CH); 53.7 (CH_3); 35.7 (C); 27.3 (CH_3); 24.5 (CH_2); 19.8 (CH_3); 19.3 (C); –4.9 (CH_3). MS (EI): 268.2 (15, $[M]^+$), 253.1 (7, $[M–CH_3]^+$), 179.1 (4), 153.1 (29), 152.1 (55), 138.1 (9), 122.1 (21), 121.1 (12), 107.0 (19), 91.0 (11), 89.0 (20), 73.0 (100), 59.0 (16). Anal. calcd. for $C_{15}H_{28}O_2Si$ (268.47): C 67.11, H 10.51. Found: C 67.16, H 10.69.

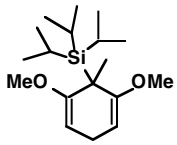
3-(Dimethylphenylsilyl)-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene (7)



1,5-Dimethoxy-1,4-cyclohexadiene (280 mg, 2 mmol) was dissolved in

THF (7 mL). The soln. was cooled to *ca.* –70 °C. After addition of *tert*-butyllithium (1.4 mL, 1.6 M in hexane, 2.2 mmol) and stirring for 30 min, HMPA (0.42 mL, 2.4 mmol) was added. The resulting red soln. was stirred for 10 min at –70 °C. A soln. of DMPSCl (0.37 mL, 2.2 mmol) in THF (2 mL) was slowly added. The red color of the reaction mixture disappeared. After stirring for 1 h at –70 °C, butyllithium (1.6 mL, 1.5 M in hexane, 2.4 mmol) was added. The mixture turned orange. After stirring for 1 h at –70 °C, $(CH_3O)_2SO_2$ (0.2 mL, 2.1 mmol) was added. The color of the reaction mixture disappeared. After 5 min, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. After addition of pentane and H_2O, the phases were separated. The organic layer was washed with H_2O and brine. The soln. was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by FC (Et_2O/pentane = 1 : 20) afforded **7** (427 mg, 74%) as a colorless oil. IR ($CHCl_3$): 3068*w*, 2998*m*, 2952*m*, 2903*m*, 2831*m*, 1677*s*, 1643*w*, 1451*m*, 1427*m*, 1346*m*, 1127*s*, 1076*w*, 979*w* cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.42–7.39 (*m*, 2 aromat. H); 7.29–7.20 (*m*, 3 aromat. H); 4.39 (*d*×*d*, J_1 = 4.6 Hz, J_2 = 2.7 Hz, 2 H, CH); 3.31 (*s*, 6 H, OCH_3); 2.62 (*d*×*t*, J_1 = 20.3 Hz, J_2 = 4.6 Hz, 1 H, CH_2); 2.42 (*d*×*t*, J_1 = 20.3 Hz, J_2 = 2.7 Hz, 1 H, CH_2); 1.28 (*s*, 3 H, CH_3); 0.26 (*s*, 6 H, $Si(CH_3)_2$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 157.5 (C); 138.6 (C); 134.1 (CH); 128.5 (CH); 126.9 (CH); 89.1 (CH); 53.8 (CH_3); 36.4 (C); 24.3 (CH_2); 17.1 (CH_3); –3.93 (CH_3). MS (EI): 288.2 (31, $[M]^+$); 271.1 (3); 195.1 (15); 180.1 (3); 163.0 (3); 152.1 (50); 135.0 (100); 122.0 (22); 107.0 (28); 91.0 (11); 77.0 (7). Anal. calcd. for $C_{17}H_{24}O_2Si$ (288.46): C 70.78, H 8.39. Found: C 70.73, H 8.24.

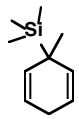
2,4-Dimethoxy-3-methyl-3-triisopropylsilyl-1,4-cyclohexadiene (8)



1,5-Dimethoxy-1,4-cyclohexadiene (4 g, 28 mmol) was dissolved in THF (100 mL). The soln. was cooled to *ca.* –70 °C. After addition of *tert*-butyllithium (20 mL, 1.6 M in hexane, 30 mmol) and stirring for 1 h, HMPA (6 mL, 33 mmol) was added. The resulting red soln. was stirred for 10 min at –70 °C. TIPSCl (6.68 mL, 30 mmol) was slowly added. The red color of the reaction mixture disappeared. After 5 min, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. Pentane was added, followed by H_2O. The phases were separated and the organic layer was additionally washed with H_2O (2×) and brine. The organic layer was dried over $MgSO_4$. Removal of the solvent *in vacuo* and distillation (140 °C at 0.2 mbar) afforded 2,4-dimethoxy-3-triisopropylsilyl-1,4-cyclohexadiene (7.4 g, 25 mmol, 89%) as a colorless oil. The crude product (3.6 g, 12.3 mmol) was dissolved in THF (50 mL). The soln. was cooled to *ca.* –40 °C. After addition of butyllithium (20 mL, 1.63 M in hexane, 30 mmol) and stirring for 2.5

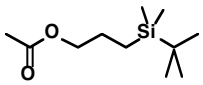
h at –40 to –30 °C, HMPA (5.4 mL, 30.8 mmol) was added. The resulting orange soln. was stirred for 15 min at –30 °C. $(CH_3O)_2SO_2$ (2.93 mL, 30.8 mmol) was added. The color of the reaction mixture disappeared. After 5 min, the cooling bath was removed and the soln. was allowed to warm to room temperature. Pentane was added, followed by H_2O. The phases were separated and the organic layer was additionally washed with H_2O (2×) and brine. The organic layer was dried over $MgSO_4$. Removal of the solvent *in vacuo* and purification by FC (pentane) afforded **8** (1.46 g, 47 mmol, 38%) as a colorless amorphous solid. I.R. ($CHCl_3$): 2947*s*, 2866*s*, 2831*s*, 1681*s*, 1642*m*, 1581*w*, 1465*s*, 1343*m*, 1128*s*, 980*m*, 882*m* cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.47 (*t*, *J* = 3.6 Hz, 2 H, CH); 3.47 (*s*, 6 H, OCH_3); 2.86–2.83 (*m*, 2 H, CH_2); 1.44 (*s*, 3 H, CH_3); 1.26–1.06 (*m*, 3 H, $CH(CH_3)_2$); 1.09 (*d*, *J* = 6.6 Hz, 18 H, $CH(CH_3)_2$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.3 (C); 88.4 (CH); 53.5 (CH_3); 24.9 (CH_2); 21.8 (CH); 19.6 (CH_3); 13.0 (CH). MS (EI): 310.3 (24, $[M]^+$), 294.2 (5, $[M–CH_3]^+$), 267.2 (12), 251.2 (16), 195.1 (10), 157.2 (41), 153.1 (20), 152.1 (100), 115.1 (47), 87.1 (11). Anal. calcd. for $C_{18}H_{34}O_2Si$ (310.55): C 69.62, H 11.03. Found: C 69.43, H 11.16.

3-Methyl-3-trimethylsilyl-1,4-cyclohexadiene (9)



1,4-Cyclohexadiene (0.93 mL, 10 mmol) was dissolved in THF (16 mL) and cooled to *ca.* –60 °C. *sec*-Butyllithium (8.5 mL 1.3 M in cyclohexane, 11 mmol) was added. The resulting yellow solution was treated with TMEDA (1.54 mL, 10 mmol). The reaction mixture was allowed to warm to –35 °C during a period of 2 h. After addition of TMSCl (1.39 mL, 11 mmol), the soln. was stirred for 1 h at room temperature. After cooling to –60 °C, *sec*-butyllithium (8.5 mL 1.3 M in cyclohexane, 11 mmol) was added. The mixture was allowed to warm to –40 to –35 °C . After stirring for 1.5 h at this temperature, $(CH_3O)_2SO_2$ (1.05 mL, 11 mmol) was added. After 5 min. the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. H_2O and ether was added. The organic layer was separated, washed with H_2O (2×) and brine and dried over $MgSO_4$. Removal of the solvent *in vacuo* and distillation (15 mbar, *ca.* 57 °C) afforded **9** (0.975 g, 5.9 mmol, 59%) as a colorless oil. I.R. ($CHCl_3$): 3008*m*, 2957*s*, 2863*m*, 2821*m*, 1662*w*, 1616*w*, 1461*m*, 1432*m*, 1404*w*, 1366*w*, 1333*w*, 1095*w*, 999*w*, 959*m*, 925*m* cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.58–5.54 (*m*, 2 H, CH_2–C*H*); 5.48–5.44 (*m*, 2 H, C–CH); 2.73–2.55 (*m*, 2 H, CH_2); 1.09 (*s*, 3 H, CCH_3); –0.01 (*s*, 9 H, $SiCH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 132.37 (CH); 120.80 (CH); 45.83 (C); 26.52 (CH_2); 22.61 (CH_3); –4.72 (CH_3). MS (EI): 166.2 (<1, $[M]^+$), 107.1 (2), 105.1 (2), 93.0 (1), 92.0 (3), 91.0 (2), 79.0 (3), 78.0 (2), 73.0 (21), 59.0 (2), 39.9 (3), 31.9 (29), 27.9 (100), 17.9 (5). Anal. calcd. for $C_{10}H_{18}Si$ (166.34): C 72.21, H 10.91. Found: C 71.97, H 10.90.

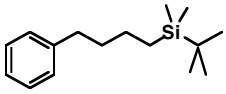
3-(*tert*-Butyldimethylsilyl)propyl acetate (10)



In a sealed tube, allyl acetate (100 mg, 1 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (400 mg, 1.5 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (4 mL) and stirred for 4.5 h at 90 °C. Removal of the solvent *in vacuo* and purification by FC (pentane / MTBE 20 : 1) afforded **10** (116 mg, 54 %) as a colorless oil. I.R. (nujol): 2953*s*, 2930*s*, 2885*m*, 2857*m*, 1744*s*, 1468*m*, 1363*m*, 1236*s*, 1048*m*, 835*m* cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.02 (*t*, *J* = 6.96 Hz, 2 H, OCH_2); 2.05 (*s*, 3 H, $COCH_3$); 1.67–1.56 (*m*, 2 H, CH_2–C*H*$_2$–CH_2); 0.87 (*s*, 9 H, $C(CH_3)_3$); 0.53–0.47 (*m*, 2 H, $SiCH_2$); –0.05 (*s*, 6 H, $Si(CH_3)_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.0 (C); 67.68 (CH_2); 26.92 (CH_3); 23.99 (CH_2); 21.42 (CH_3); 16.90 (C); 8.63 (CH_2); –6.01 (CH_3). M.S. (EI): 159.2 (14, $[M–C(CH_3)_3]^+$); 118.1 (8); 117.2 (92); 76.0 (7); 75.0 (100); 73.1 (13); 43.0 (14); 28.0 (5).

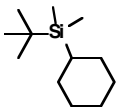
4-Phenylbutene was prepared according to a literature procedure.[3]

***tert*-Butyldimethyl-(4-phenylbutyl)-silane (11)**



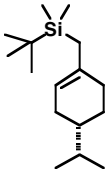
In a sealed tube, 4-phenylbutene (132 mg, 1 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (407 mg, 1.5 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (4 mL). After stirring for 4 h at 90 °C, additional AIBN (50 mg, 0.3 mmol) was added. The soln. was stirred for another 4 h at 90 °C. Removal of the solvent *in vacuo* and purification by FC (pentane) afforded **11** (136 mg, 55 %) as a colorless oil. I.R. (nujol): 2952*s*, 2927*s*, 2882*m*, 2855*s*, 1466*m*, 1251*s*, 830*s*, 803*m*, 746*m*, 698*s* cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.25–7.19 (*m*, 2 aromat. H); 7.15–7.14 (*m*, 3 aromat. H); 2.63–2.58 (*m*, 2 H, C_6H_5–C*H*$_2$); 1.69–1.59 (*m*, 2 H, CH_2); 1.41–1.30 (*m*, 2 H, CH_2); 0.86 (*s*, 9 H, $C(CH_3)_3$); 0.56–0.51 (*m*, 2 H, $Si(CH_2)$); –0.09 (*s*, 6 H, $Si(CH_3)_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 143.3 (C); 128.8 (CH); 128.6 (CH); 125.9 (CH); 36.1 (CH_2); 36.1 (CH_2); 27.0 (CH_3); 24.5 (CH_2); 17.0 (C); 12.7 (CH_2); –5.9 (CH_3). MS (EI): 233.2 (<1, $[M–CH_3]^+$); 192.1 (18); 191.2 (100, $[M–C(CH_3)_3)]^+$); 189.1 (18); 187.2 (9); 135.2 (8); 91.1 (12); 87.0 (21); 73.1 (40); 59.1 (65); 28.0 (13).

***tert*-Butylcyclohexyldimethylsilane (12)**



In a sealed tube, cyclohexene (82 mg, 1 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (400 mg, 1.5 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (4 mL) and stirred for 15 h at 90 °C. Removal of the solvent *in vacuo* and purification by FC (pentane) afforded **12** (119 mg, 60 %) as a colorless oil. I.R. (nujol): 2955*s*, 2926*s*, 2852*s*, 1471*m*, 1446*m*, 1362*w*, 1254*m*, 1247*m*, 1097*w*, 888*w*, 850*m*, 827*m*, 799*m*, 765*m* cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.80–1.68 (*m*, 5 H, CH_2); 1.32–1.11 (*m*, 5 H, CH_2); 0.92 (*s*, 9 H, $C(CH_3)_3$); 0.81–0.73 (*m*, 1 H, Si(CH)); –0.08 (*s*, 6 H, $Si(CH_3)_2$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 28.92 (CH_2); 28.55 (CH_2); 27.55 (CH_3); 27.18 (CH_2); 24.22 (CH); 17.50 (C); –7.54 (CH_3). MS (EI): 198.4 (4, $[M]^+$); 142.5 (15); 141.4 (86); 113.3 (8); 99.2 (7); 81.3 (48); 74.2 (5); 73.2 (62); 60.2 (7); 59.2 (100); 28.0 (11).

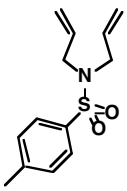
7-(*tert*-Butyldimethylsilyl)-Δ^1-*p*-menthene (13)



In a sealed tube, (1S)-(–)-β-pinene (136 mg, 1 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (400 mg, 1.5 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (4 mL) and stirred for 3 h at 90 °C. Removal of the solvent *in vacuo* and purification by FC (pentane) afforded **13** (177 mg, 70 %) as a colorless oil. I.R. (nujol): 2954*s*, 2928*s*, 2881*m*, 2856*m*, 1663*w*, 1468*m*, 1437*w*, 1386*w*, 1363*w*, 1250*m*, 1172*m*, 1149*w*, 1007*w*, 828*s*, 807*m*, 746*w* cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.23–5.18 (*m*, 1 H, C=CH); 2.02–0.82 (*m*, 16 H); 0.87 (*s*, 9 H, $C(CH_3)_3$); –0.05 (*s*, 3 H, CH_3); –0.06 (*s*, 3 H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 135.31 (C); 119.07 (CH); 40.15 (CH); 32.35 (CH); 31.97 (CH_2); 29.23 (CH_2); 26.78 (CH_2); 26.48 (CH_3); 23.15 (CH_2); 20.01 (CH_3); 19.74 (CH_3); 16.78 (C); –5.53 (CH_3); –5.89 (CH_3). MS (EI): 252.6 (9, $[M]^+$); 196.4 (15); 195.5 (97 $[M–C(CH_3)_3]^+$); 167.4 (11); 139.3 (8); 99.2 (10); 74.2 (8); 73.2 (100); 59.1 (16); 28.0 (14).

Diethyl bis-allyl malonate (14) was prepared according to a literature procedure.[4]

***N,N*-Diallyl toluenesulfonamide (16)**

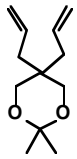


Allylamine (0.75 mL, 10 mmol) and triethylamine (1.53 mL, 11 mmol) were dissolved in CH_2Cl_2 (5 mL) and cooled to 0 °C. Toluene sulfonic acid chloride (2.10 g, 11 mmol) in CH_2Cl_2 (15 mL) was added dropwise. The solution was allowed to warm to room temperature and was stirred for 1 h. The reaction mixture was washed with sat. NH_4Cl-soln. and brine, dried over $MgSO_4$ and concentrated *in vacuo*. After purification by FC (pentane / MTBE 2 : 1), the obtained *N*-allyl toluenesulfonamide was dissolved in ethanol (5 mL). To the soln.,

powdered KOH (0.56 g, 10 mmol) was added. Allyl bromide (1.18 mL, 14 mmol) was added dropwise. The mixture was refluxed for 1 h. The same amount of allyl bromide was added and the mixture was refluxed for 2 h. The organic phase was separated from KOH and concentrated *in vacuo*. Purification by FC (pentane / MTBE 3 : 1) afforded **16** (1.86 g, 7.4 mmol, 74% over two steps) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[5]

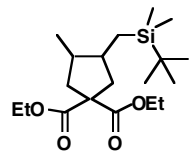
4,4-Bis(hydroxymethyl)-1,6-heptadiene (17) was prepared according to a literature procedure.[6]

5,5-Diallyl-2,2-dimethyl-1,3-dioxane (18)



4,4-Bis(hydroxymethyl)-1,6-heptadiene **17** (625 mg, 4 mmol) and triethyl orthoformiate (1.64 mL, 16 mmol) were dissolved in acetone (4 mL). A catalytic amount of conc. sulfuric acid was added. After refluxing for 4 h, the mixture was washed with sat. $NaHCO_3$ and brine. The organic phase was separated, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by FC (pentane / MTBE 20 : 1) afforded **18** as a yellowish oil (606 mg, 77%). I.R. (nujol): 3076*m*, 2993*s*, 2939*m*, 2916*m*, 2860*s*, 1638*m*, 1266*m*, 1232*m*, 1199*s*, 1155*m*, 1104*s*, 1036*m*, 916*m*, 830*m* cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.86–5.72 (*m*, 2 H, C*H*=CH_2); 5.13–5.08 (*m*, 4 H, CH=CH_2); 3.58 (*s*, 4 H, OCH_3); 2.14 (*d*, J = 7.6 Hz, 4 H, CH_2–CH=CH_2); 1.41 (*s*, 6 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 133.54 (CH_2); 118.76 (CH); 98.38 (C); 67.61 (CH_2); 37.09 (CH_2); 35.90 (C); 24.22 (CH_3). MS (EI): 181.2 (100, $[M–CH_3]^+$); 123.1 (6); 93.1 (81); 80.1 (18); 79.1 (58); 67.1 (44); 59.1 (30); 55.1 (21); 43.0 (76); 41.1 (35); 28.0 (25).

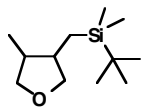
Diethyl 3-[(*tert*-butyldimethylsilyl)methyl]-4-methyl-cyclopentane-1,1-dicarboxylate (19)



In a sealed tube, diethyl bis-allyl malonate **14** (242 mg, 1 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (400 mg, 1.5 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (4 mL) and heated to 90 °C for 4 h. Removal of the solvent *in vacuo* and purification by FC (pentane/ MTBE 30 : 1) afforded **19** (286 mg, 0.80 mmol, 80 %) as a colorless oil. The diastereoisomeric ratio was determined by GC on the crude reaction mixture: dr (*cis : trans*) 4.3 : 1. I.R. (nujol): 2954*s*, 2930*s*, 2857*s*, 1732*s*, 1255*s*, 1201*m*, 1179*m*, 1150*m*, 1099*m*, 828*s*, 810*m* cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): *cis*-**19**: δ = 4.19–4.11 (*m*, 4 H, C$H_2$$CH_3$); 2.38–2.33 (*m*, 2 H, CH_2/CH); 2.10–2.01 (*m*, 3 H, CH_2/CH); 1.87 (*d*×*d*, 1 H, J_1 = 13.4 Hz, J_2 = 9.8 Hz, CH_2); 1.23 (*t*, 6 H, J = 7.1 Hz, CH_2C*H*$_3$); 0.85 (*s*, 9 H, $C(CH_3)_3$); 0.82 (*d*,

3 H, J = 6.6 Hz, CH–CH_3); 0.61 (*d*×*d*, 1 H, J_1 = 14.7 Hz, J_2 = 4.5 Hz, Si(CH_2)); 0.42 (*d*×*d*, 1 H, J_1 = 14.7 Hz, J_2 = 9.3 Hz, Si(CH_2)); –0.04 (2×*s*, 6 H, Si(CH_3)). *trans*-**19**: δ = 4.19–4.11 (*m*, 4 H, C$H_2$$CH_3$); 2.56 (*d*×*d*, 1 H, J_1 = 13.5 Hz, J_2 = 6.9 Hz, CH_2); 2.49 (*d*×*d*, 1 H, J_1 = 13.4 Hz, J_2 = 7.0 Hz, CH_2); 1.69–1.62 (*m*, 2 H, CH_2/CH); 1.48–1.35 (*m*, 2 H, CH_2/CH); 1.23 (*t*, 6 H, J = 7.1 Hz, CH_2CH_3); 0.95 (*d*, 3 H, J = 6.3 Hz, CH–CH_3); 0.85 (*s*, 9 H, C(CH_3)$_3$); 0.93–0.85 (*m*, 1 H, Si(CH_2); 0.23 (*d*×*d*, 1 H, J_1 = 14.5 Hz, J_2 = 11.1 Hz, Si(CH_2)); –0.04 (2×*s*, 6 H, Si(CH_3)). ^{13}C-NMR (133 MHz, $CDCl_3$): *cis*-**19**: δ = 173.17 (C); 172.17 (C); 61.21 (CH_2); 59.00 (C); 41.10 (CH_2); 40.67 (CH_2); 39.01 (CH); 37.83 (CH); 26.48 (CH_3); 16.55 (C); 14.87 (CH_3); 14.02 (CH_3); 11.98 (CH_2); –5.10 (CH_3); –5.89 (CH_3). *trans*-**19**: δ = 173.17 (C); 172.17 (C); 61.21 (CH_2); 58.29 (C); 43.54 (CH); 43.69 (CH); 42.90 (CH_2); 41.96 (CH_2); 26.48 (CH_3); 17.26 (CH_3); 16.55 (C); 15.75 (CH_2); 14.02 (CH_3); –4.73 (CH_3); –6.12 (CH_3). MS (EI): 311.2 (4, [M–OCH_2CH_3]$^+$); 300.3 (21); 299.3 (100, [M–C(CH_3)$_3$]$^+$); 182.1 (6); 181.1 (41); 73.0 (11); 32.0 (6); 28.0 (52). Anal. calcd. for $C_{19}H_{36}O_4Si$ (356.57): C 64.00; H 10.18. Found: C 63.74; H 10.03.

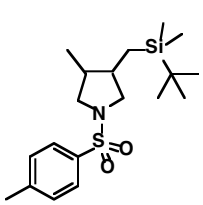
3-[(*tert*-Butyldimethylsilyl)methyl]- 4-methyltetrahydrofurane (20)



In a sealed tube, diallyl ether **15** (98 mg, 1 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (400 mg, 1.5 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (4 mL) and stirred for 4 h at 90 °C. Removal of the solvent *in vacuo* and purification by FC (pentane/ MTBE 30 : 1) afforded **20** (151 mg, 71 %) as a colorless oil. The diastereoisomeric ratio was determined by GC on the crude reaction mixture: dr (*cis : trans*) 2.5 : 1. I.R. (nujol): 2954*s*, 2928*s*, 2881*m*, 2856*s*, 1736*m*, 1253*m*, 1215*w*, 1192*w*, 1096*w*, 1043*w*, 911*w*, 831*s*, 808*m* cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): *cis*-**20**: δ = 3.89 (*d*×*d*, 2 H, J_1 = J_2 = 7.6 Hz, OCH_2); 3.49 (*d*×*d*, 1 H, J_1 = 8.1 Hz, J_2 = 3.4 Hz, OCH_2); 3.31 (*d*×*d*, 1 H, J_1 = J_2 = 8.3 Hz, OCH_2); 2.31–2.23 (*m*, 1 H, CH); 2.23–2.15 (*m*, 1 H, CH); 0.92 (*d*, 3 H, J = 7.1 Hz, CH–CH_3); 0.87 (*s*, 9 H, C(CH_3)$_3$); 0.67 (*d*×*d*, 1 H, J_1 = 14.7 Hz, J_2 = 5.4 Hz, Si(CH_2)); 0.44 (*d*×*d*, 1 H, J_1 = 14.7 Hz, J_2 = 9.4 Hz, Si(CH_2)); –0.02 (*s*, 3 H, Si(CH_3)); –0.05 (*s*, 3 H, Si(CH_3)). *trans*-**20**: δ = 4.02 (*d*×*d*, 1 H, J_1 = J_2 = 7.6 Hz, OCH_2); 3.97 (*d*×*d*, 1 H, J_1 = J_2 = 7.7 Hz, OCH_2); 3.33–3.28 (*m*, 1 H, OCH_2); 3.27 (*d*×*d*, 1 H, J_1 = J_2 = 7.0 Hz, OCH_2); 1.79–1.66 (*m*, 2 H, CH); 1.00 (*d*, 3 H, J = 6.4 Hz, CH–CH_3); 0.87 (*s*, 9 H, C(CH_3)$_3$); 0.94–0.87 (*m*, 1 H, Si(CH_2)); 0.35 (*d*×*d*, 1 H, J_1 = 14.7 Hz, J_2 = 10.7 Hz, Si(CH_2)); –0.04 (*s*, 3 H, Si(CH_3)); –0.07 (*s*, 3 H, Si(CH_3)). ^{13}C-NMR (133 MHz, $CDCl_3$): *cis*-**20**: δ = 75.08 (CH_3); 73.53 (CH_2); 38.51 (CH); 37.40 (CH); 26.47 (CH_3); 16.54 (C); 13.17 (CH_3); 9.16 (CH_2); –5.30 (CH_3); –5.88 (CH_3). *trans*-**20**: δ = 75.47 (CH_3); 74.64 (CH_2); 43.57 (CH); 43.53 (CH); 26.47 (CH_3); 16.54 (C); 15.37 (CH_3); 14.29 (CH_2); –5.11 (CH_3); –6.05 (CH_3). MS (EI): 199.1 (<1, [M–CH_3]$^+$); 158.1

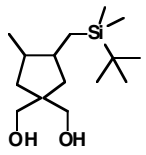
(11); 157.1 (68, $[M–C(CH_3)_3]^+$); 129.0 (19); 116.0 (12); 115.0 (100); 99.0 (30); 85.0 (16); 75.0 (68); 73.0 (40); 59.0 (24); 27.9 (10). Anal. calcd. for $C_{12}H_{26}OSi$ (214.42): C 67.22; H 12.22. Found: C 67.03; H 12.00.

3-[(*tert*-Butyldimethylsilyl)methyl]-4-methyl-*N*-(4-Toluenesulfonyl)-pyrrolidine (21)



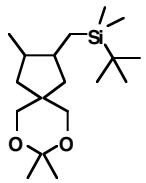
In a sealed tube, *N,N*-diallyl toluenesulfonamide **16** (251 mg, 1 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (400 mg, 1.5 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (4 mL) and stirred for 7 h at 90 °C. Removal of the solvent *in vacuo* and purification by FC (pentane/ MTBE 10 : 1) afforded **21** (280 mg, 76 %) as a colorless solid. The diastereoisomeric ratio was determined by GC on the crude reaction mixture: dr (*cis : trans*) 2.0 : 1. M.p. 52 – 53 °C. I.R. (KBr): 2954*s*, 2926*s*, 2881*s*, 2854*s*, 1922*w*, 1657*w*, 1598*w*, 1464*m*, 1341*s*, 1248*m*, 1157*s*, 828*s*, 812*s*, 672*s*, 589*s*, 548*s* cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): *cis*-**21**: δ = 7.70 (*d*, J = 8.3 Hz, 2 aromat. CH); 7.30 (*d*, J = 7.9 Hz, 2 aromat. CH); 3.38 (*d*×*d*, 1 H, J_1 = 9.6 Hz, J_2 = 7.1 Hz, $N(CH_2)$); 3.33 (*d*×*d*, 1 H, J_1 = 9.7 Hz, J_2 = 5.9 Hz, $N(CH_2)$); 3.02 (*d*×*d*, 1 H, J_1 = 9.7 Hz, J_2 = 3.1 Hz, $N(CH_2)$); 2.80 (*d*×*d*, 1 H, $J_1 = J_2$ = 16.6 Hz, $N(CH_2)$); 2.41 (*s*, 3 H, C_6H_4–CH_3); 2.12–1.98 (*m*, 2 H, CH); 0.79 (*s*, 9 H, $C(CH_3)_3$); 0.65 (*d*, J = 10.2 Hz, 3 H, CH–CH_3); 0.49 (*d*×*d*, 1 H, J_1 = 11.2 Hz, J_2 = 5.1 Hz, $Si(CH_2)$); 0.24 (*d*×*d*, 1 H, J_1 = 14.8 Hz, J_2 = 9.2 Hz, $Si(CH_2)$); –0.11 (2×*s*, 6 H, $Si(CH_3)$). *trans*-**21**: δ = 7.69 (*d*, J = 8.3 Hz, 2 aromat. CH); 7.30 (*d*, J = 8.5 Hz, 2 aromat. CH); 3.54 (*d*×*d*, 1 H, J_1 = 9.9 Hz, J_2 = 7.2 Hz, $N(CH_2)$); 3.46 (*d*×*d*, 1 H, J_1 = 11.2 Hz, J_2 = 7.4 Hz, $N(CH_2)$); 2.76 (*d*×*d*, 1 H, $J_1 = J_2$ = 17.4 Hz, $N(CH_2)$); 2.72 (*d*×*d*, 1 H, $J_1 = J_2$ = 19.1 Hz, $N(CH_2)$); 2.41 (*s*, 3 H, C_6H_4–CH_3); 1.63–1.49 (*m*, 1 H, CH); 1.49–1.38 (*m*, 1 H, CH); 0.81 (*s*, 9 H, $C(CH_3)_3$); 0.88 (*d*, J = 6.5 Hz, 3 H, CH–CH_3); 0.75 (*d*×*d*, 1 H, J_1 = 14.8 Hz, J_2 = 3.1 Hz, $Si(CH_2)$); 0.15 (*d*×*d*, 1 H, J_1 = 14.7 Hz, J_2 = 10.9 Hz, $Si(CH_2)$); –0.09 (*s*, 3 H, $Si(CH_3)$); –0.12 (*s*, 3 H, $Si(CH_3)$). ^{13}C-NMR (100 MHz, $CDCl_3$): *cis*-**21**: δ = 143.12 (C); 134.32 (C); 129.53 (CH); 127.35 (CH); 54.67 (CH_2); 53.05 (CH_2); 38.16 (CH); 37.10 (CH); 26.35 (CH_3); 21.46 (CH_3); 16.84 (C); 12.95 (CH_3); 9.66 (CH_2); –5.37 (CH_3); –5.98 (CH_3). *trans*-**21**: δ = 143.19 (C); 134.15 (C); 129.56 (CH); 127.40 (CH); 55.18 (CH_2); 54.29 (CH_2); 42.47 (CH); 42.36 (CH); 26.35 (CH_3); 21.46 (CH_3); 16.84 (C); 15.57 (CH_3); 14.23 (CH_2); –5.03 (CH_3); –6.18 (CH_3). MS (EI): 352.4 (3, $[M–CH_3]^+$); 312.4 (22); 311.4 (39); 310.4 (100, $[M–C(CH_3)_3]^+$); 149.1 (4); 91.1 (11); 73.1 (13); 28.0 (13).

3-[(*tert*-Butyldimethylsilyl)methyl]-1,1-bis(hydroxymethyl)-4-methylcyclopentane (22)



In a sealed tube, 4,4-bis(hydroxymethyl)-1,6-heptadiene **17** (79 mg, 0.5 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (400 mg, 1.5 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (2 mL) and stirred for 4 h at 90 °C. Removal of the solvent *in vacuo* and purification by FC (pentane/ MTBE 1 : 2) afforded **22** (84 mg, 62 %) as a colorless solid. The diastereoisomeric ratio was determined by GC on the crude reaction mixture: dr (*cis : trans*) 2.3 : 1. M.p. 64 °C. I.R. (KBr): 3329*br. m*, 2952*s*, 2933*s*, 2857*s*, 2710*w*, 1470*s*, 1374*m*, 1360*m*, 1245*s*, 1033*s*, 1015*s*, 827*s*, 804*m* cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): *cis*-**22**: δ = 3.65–3.50 (*m*, 4 H, C*H*$_2$OH); 2.26–2.17 (*m*, 2 H, OH); 2.08–1.98 (*m*, 2 H, CH_2/CH); 1.66–1.56 (*m*, 2 H, CH_2/CH); 1.21–1.14 (*m*, 2 H, CH_2/CH); 0.84 (*d*, *J* = 4.9 Hz, 3 H, CH–C*H*$_3$); 0.85 (*s*, 9 H, C(CH_3)$_3$); 0.64 (*d*×*d*, 1 H, J_1 = 14.6 Hz, J_2 = 5.0 Hz, Si(CH_2)); 0.42 (*d*×*d*, 1 H, J_1 = 14.7 Hz, J_2 = 9.0 Hz, Si(CH_2)); –0.05 (2×*s*, 6 H, Si(CH_3)). *trans*-**22**: δ = 3.65–3.50 (*m*, 4 H, C*H*$_2$OH); 2.36–2.26 (*m*, 2 H, OH); 1.81–1.71 (*m*, 2 H, CH_2/CH); 1.45–1.25 (*m*, 2 H, CH_2/CH); 1.25–1.21 (*m*, 2 H, CH_2/CH); 0.93 (*d*, *J* = 8.5 Hz, 3 H, CH–C*H*$_3$); 0.85 (*s*, 9 H, C(CH_3)$_3$); 0.97–0.89 (*m*, 1 H, Si(CH_2)); 0.18 (*d*×*d*, 1 H, J_1 = 14.5 Hz, J_2 = 11.2 Hz, Si(CH_2)); –0.05 (*s*, 3 H, Si(CH_3)); –0.07 (*s*, 3 H, Si(CH_3)). ^{13}C-NMR (100 MHz, $CDCl_3$): *cis*-**22**: δ = 72.73 (CH_2); 70.96 (CH_2); 47.24 (C); 39.02 (CH_2); 38.67 (CH_2); 38.11 (CH); 37.49 (CH); 26.52 (CH_3); 16.60 (C); 15.82 (CH_3); 12.54 (CH_2); –4.99 (CH_3); –5.79 (CH_3). *trans*-**22**: δ = 71.54 (CH_2); 71.32 (CH_2); 47.24 (C); 43.14 (CH); 42.93 (CH); 41.23 (CH_2); 40.32 (CH_2); 26.52 (CH_3); 17.63 (CH_3); 16.60 (C); 16.15 (CH_2); –4.59 (CH_3); –6.10 (CH_3). MS (EI): 237.5 (4); 215.4 (20, [M–C(CH_3)$_3$)]$^+$); 197.5 (42); 123.3 (47); 121.3 (28); 95.2 (53); 81.3 (71); 76.4 (40); 75.4 (100); 73.4 (57); 67.2 (46); 55.1 (46); 43.1 (19).

2-[(*tert*-Butyldimethylsilyl)methyl]-3,8,8-trimethyl-7,9-dioxaspiro[4.5]decane (23)

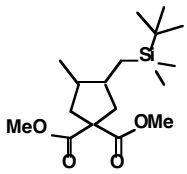


In a sealed tube, 5,5-diallyl-2,2-dimethyl-1,3-dioxane **18** (98 mg, 0.5 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (200 mg, 0.75 mmol) and AIBN (25 mg, 0.15 mmol) were dissolved in hexane (2 mL) and stirred for 4 h at 90 °C. Removal of the solvent *in vacuo* and purification by FC (pentane/ MTBE 30 : 1) afforded **23** (113 mg, 72 %) as a colorless oil. The diastereoisomeric ratio was determined by GC on the crude reaction mixture: dr (*cis : trans*) 2.6 : 1. I.R. (nujol): 2992*s*, 2953*s*, 2855*s*, 1471*s*, 1464*s*, 1381*s*, 1368*s*, 1249*s*, 1209*s*, 1195*s*, 1157*m*, 1080*s*, 1032*m*, 831*s*, 574*m* cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): *cis*-**23**: δ = 3.62–3.44 (*m*, 4 H, OCH_2); 2.02–1.92 (*m*, 1 H, CH/CH_2); 1.85 (*d*×*d*, J_1 = 13.3 Hz, J_2 = 7.0 Hz, 1 H, CH_2); 1.76 (*d*×*d*, J_1 = 13.3 Hz, J_2 = 7.2 Hz, 1 H, CH_2); 1.60 (*d*×*d*, J_1 = 13.8

Hz, J_2 = 7.0 Hz, 1 H, CH_2); 1.24–1.15 (*m*, 2 H, CH/CH_2); 1.38 (*br. s*, 6 H, $OC(CH_3)_2$); 0.80 (*d*, *J* = 6.8 Hz, 3 H, CHCH_3); 0.84 (*s*, 9 H, $C(CH_3)_3$); 0.62 (*d*×*d*, J_1 = 14.6 Hz, J_2 = 5.1 Hz, 1 H, $Si(CH_2)$); 0.39 (*d*×*d*, J_1 = 14.8 Hz, J_2 = 8.9 Hz, 1 H, $Si(CH_2)$); –0.05 (*s*, 3 H, $Si(CH_3)$); –0.06 (*s*, 3 H, $Si(CH_3)$). *trans*-**23**: δ = 3.62–3.44 (*m*, 4 H, OCH_2); 2.02–1.92 (*m*, 3 H, CH/CH_2); 1.24–1.15 (*m*, 3 H, CH/CH_2); 1.38 (*br. s*, 6 H, $OC(CH_3)_2$); 0.92 (*d*, *J* = 6.4 Hz, 3 H, CHCH_3); 0.84 (*s*, 9 H, $C(CH_3)_3$); 0.97–0.87 (*m*, 1 H, $Si(CH_2)$); 0.16 (*d*×*d*, J_1 = 14.4 Hz, J_2 = 11.0 Hz, 1 H, $Si(CH_2)$); –0.05 (*s*, 3 H, $Si(CH_3)$); –0.07 (*s*, 3 H, $Si(CH_3)$). ^{13}C-NMR (100 MHz, $CDCl_3$): *cis*-**23**: δ = 97.43 (C); 71.50 (CH_2); 69.98 (CH_2); 42.86 (C); 40.83 (CH_2); 40.66 (CH_2); 38.09 (CH); 37.33 (CH); 26.51 (CH_3); 24.57 (CH_3); 23.16 (CH_3); 16.58 (C); 15.77 (CH_3); 12.60 (CH_2); –5.04 (CH_3); –5.81 (CH_3). *trans*-**23**: δ = 97.53 (C); 70.50 (CH_2); 70.28 (CH_2); 43.12 (CH_2); 42.86 (C); 42.24 (CH_2); 40.59 (CH); 39.69 (CH); 26.51 (CH_3); 24.23 (CH_3); 23.50 (CH_3); 17.73 (CH_3); 16.58 (C); 16.40 (CH_2); –4.64 (CH_3); –6.12 (CH_3). MS (EI): 297.4 (5, $[M–CH_3]^+$); 198.2 (10); 197.2 (45); 167.2 (12); 121.1 (14); 89.1 (11); 75.1 (100); 73.1 (23), 28.0 (6).

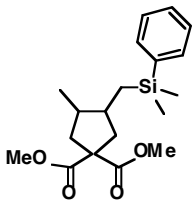
Dimethyl bis-allyl malonate (24) was prepared in two steps from dimethyl malonate in analogy to diethyl bis-allyl malonate (**14**)[4] using methanol as a solvent in 64%. The spectroscopic data are in agreement with those reported in the literature.[7]

Dimethyl 3-[(*tert*-butyldimethylsilyl)methyl]-4-methyl-cyclopentane-1,1-dicarboxylate (25)



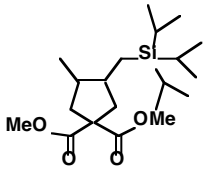
In a sealed tube, dimethyl bis-allyl malonate **24** (208 mg, 0.98 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (393 mg, 1.48 mmol) and AIBN (52 mg, 0.32 mmol) were dissolved in hexane (4 mL) and heated to 90 °C for 7 h. Removal of the solvent *in vacuo* and purification by FC (pentane/ MTBE 25 : 1) afforded **25** (270 mg, 0.82 mmol, 84 %) as a colorless oil. The diastereoisomeric ratio was determined by GC on the crude reaction mixture: dr (*cis : trans*) 3.8 : 1. The NMR-data for the *trans*-isomer are in agreement with those reported in the literature.[8] *cis*-**25**: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.70 (*s*, 6 H, OCH_3); 2.40–2.32 (*m*, 2 H, CH_2/CH); 2.16–2.01 (*m*, 3 H, CH_2/CH); 1.88 (*d*×*d*, 1 H, J_1 = 13.2 Hz, J_2 = 9.8 Hz, C–CH_2); 0.85 (*s*, 9 H, $C(CH_3)_3$); 0.81 (*d*, 3 H, *J* = 6.6 Hz, CH–CH_3); 0.61 (*d*×*d*, 1 H, J_1 = 14.6 Hz, J_2 = 4.6 Hz, $Si(CH_2)$); 0.41 (*d*×*d*, 1 H, J_1 = 14.6 Hz, J_2 = 9.0 Hz, $Si(CH_2)$); –0.04 (2×*s*, 6 H, $Si(CH_3)_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 174.03 (C); 173.82 (C); 59.24 (C); 53.04 (CH_3); 53.01 (CH_3); 41.60 (CH_2); 41.18 (CH_2); 39.44 (CH); 38.21 (CH); 26.87 (CH_3); 16.96 (C); 15.24 (CH_3); 12.35 (CH_2); –4.70 (CH_3); –5.49 (CH_3).

Dimethyl 3-[(dimethylphenylsilyl)methyl]-4-methyl-cyclopentane-1,1-dicarboxylate (26)



In a sealed tube, dimethyl bis-allyl malonate **24** (211 mg, 1 mmol), 3-dimethylphenylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **7** (518 mg, 1.8 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (4 mL) and heated to 90 °C. After 4, and 8 h, AIBN was added (2×50 mg, 0.6 mmol). Heating was continued for 4 h at 90 °C. Removal of the solvent *in vacuo* and purification by FC (pentane/ MTBE 40 : 1) afforded **26** (198 mg, 0.57 mmol, 57 %) as a colorless oil. The diastereoisomeric ratio was determined by GC on the crude reaction mixture: dr (*cis : trans*) 4.4 : 1. The NMR-data for the *trans*-isomer are in agreement with those reported in the literature.[8] I.R. (nujol): 2954*s*, 1734*s*, 1432*m*, 1251*s*, 1200*m*, 1151*m*, 1113*m*, 836*m*, 730*m*, 701*m* cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): *cis*-**26**: δ = 7.52–7.48 (*m*, 2 aromat. H); 7.36–7.32 (*m*, 3 aromat. H); 3.68 (*s*, 3 H, OCH_3); 3.67 (*s*, 3 H, OCH_3); 2.37–2.29 (*m*, 2 H, CH_2/CH); 2.14–1.98 (*m*, 3 H, CH_2/CH); 1.88 (*d*×*d*, 1 H, J_1 = 13.6 Hz, J_2 = 9.6 Hz, CH_2); 0.94–0.85 (*m*, 1 H, Si(CH_2)); 0.79 (*d*, 3 H, J = 6.8 Hz, CH–CH_3); 0.69 (*d*×*d*, 1 H, J_1 = 14.6 Hz, J_2 = 9.2 Hz, Si(CH_2)); 0.30 (2×*s*, 6 H, Si(CH_3)). ^{13}C-NMR (75 MHz, $CDCl_3$): *cis*-**26**: δ = 173.5 (C); 173.3 (C); 139.4 (C); 133.5 (CH); 128.8 (CH); 127.7 (CH); 58.8 (C); 52.59 (CH_3); 52.56 (CH_3); 41.11 (CH_2); 40.51 (CH_2); 38.80 (CH); 37.67 (CH); 15.87 (CH_2); 14.83 (CH_3); –2.18 (CH_3); –2.49 (CH_3). MS (EI): 348.3 (4, $[M]^+$); 333.2 (35, $[M–CH_3]^+$); 271.1 (12); 151.1 (30); 145.0 (25); 135.1 (100); 108.1 (8); 28.0 (19).

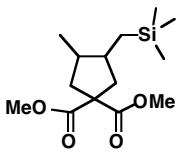
Dimethyl 4-methyl-3-[(triisopropylsilyl)methyl]cyclopentane-1,1-dicarboxylate (27)



In a sealed tube, dimethyl bis-allyl malonate **24** (217 mg, 1.02 mmol), 2,4-dimethoxy-3-methyl-3-triisopropylsilyl-1,4-cyclohexadiene **8** (666 mg, 2.15 mmol) and di-*tert*-butyl peroxide (100 μL, 0.54 mmol) were dissolved in hexane (4 mL) and heated to 140 °C for 6 h. Removal of the solvent *in vacuo* and purification by FC (pentane/ MTBE 40 : 1) afforded **27** (311 mg, 0.84 mmol, 82 %) as a colorless oil. The diastereoisomeric ratio was determined by GC on the crude reaction mixture: dr (*cis : trans*) 2.6 : 1. I.R. (nujol): 2944*s*, 2891*m*, 2866*s*, 1736*s*, 1362*m*, 1435*m*, 1254*s*, 1202*m*, 1153*m*, 882*m* cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): *cis*-**27**: δ = 3.70 (*s*, 3 H, OCH_3); 3.69 (*s*, 3 H, OCH_3); 2.41 (*d*×*d*, 1 H, J_1 = 13.1 Hz, J_2 = 6.4 Hz, C–CH_2); 2.38–2.33 (*m*, 1 H, C–CH_2); 2.20–2.00 (*m*, 3 H, CH_2/CH); 1.91 (*d*×*d*, 1 H, J_1 = 13.1 Hz, J_2 = 10.4 Hz, C–CH_2); 1.11–0.98 (*m*, 3 H, C*H*(CH_3)$_2$); 1.03 (*br. s*, 18 H, CH(CH_3)$_2$); 0.85 (*d*, J = 6.9 Hz, 3 H, CH–CH_3); 0.69 (*d*×*d*, 1 H, J_1 = 15.0 Hz, J_2 = 3.5 Hz,

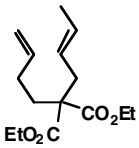
Si(CH_2)); 0.49 (*d*×*d*, 1 H, J_1 = 14.9 Hz, J_2 = 10.3 Hz, Si(CH_2)). *trans*-**27**: δ = 3.70 (*s*, 3 H, OCH_3); 3.69 (*s*, 3 H, OCH_3); 2.62 (*d*×*d*, 1 H, J_1 = 14.1 Hz, J_2 = 8.2 Hz, C–CH_2); 2.50 (*d*×*d*, 1 H, J_1 = 13.6 Hz, J_2 = 6.9 Hz, C–CH_2); 1.73–1.63 (*m*, 2 H, CH/CH_2); 1.52–1.44 (*m*, 2 H, CH/CH_2); 1.11–0.98 (*m*, 3 H, C*H*(CH_3)$_2$); 1.03 (*br. s*, 18 H, CH(CH_3)$_2$); 0.85 (*d*, *J* = 6.9 Hz, 3 H, CH–CH_3); 0.76 (*d*×*d*, 1 H, J_1 = 15.0 Hz, J_2 = 3.4 Hz, Si(CH_2)); 0.36 (*d*×*d*, 1 H, J_1 = 15.0 Hz, J_2 = 11.3 Hz, Si(CH_2)). ^{13}C-NMR (75 MHz, $CDCl_3$): *cis*-**27**: δ = 173.6 (C); 173.4 (C); 59.0 (C); 52.6 (CH_3); 41.0 (CH_2); 40.6 (CH_2); 38.4 (2×CH); 18.8 (CH_3); 14.8 (CH_3); 11.4 (CH); 8.9 (CH_2). *trans*-**27**: δ = 173.6 (C); 173.4 (C); 58.2 (C); 52.6 (CH_3); 44.1 (CH); 43.2 (CH); 42.0 (2×CH_2); 24.4 (CH_3); 18.2 (CH_3); 11.4 (CH); 9.3 (CH_2). MS (EI): 329.1 (8); 328.2 (25); 327.1 (100, [M–CH(CH_3)$_2$]$^+$); 325.1 (26); 145.1 (14); 117.1 (16); 75.0 (12); 28.0 (34).

Dimethyl 4-methyl-3-[(trimethylsilyl)methyl]cyclopentane-1,1-dicarboxylate (28)



In a sealed tube, dimethyl bis-allyl malonate **24** (206 mg, 1 mmol), 3-methyl-3-trimethylsilyl-1,4-cyclohexadiene **9** (241 mg, 1.54 mmol) and di-*tert*-butyl peroxide (92 μL, 0.5 mmol) were dissolved in hexane (4 mL) and heated to 140 °C for 5 h. Removal of the solvent *in vacuo* and purification by FC (pentane/ MTBE 20 : 1) afforded **28** (214 mg, 0.79 mmol, 81 %) as a colorless oil. The diastereoisomeric ratio was determined by GC on the crude reaction mixture: dr (*cis : trans*) 3.1 : 1. The spectroscopic data are in agreement with those reported in the literature.[9]

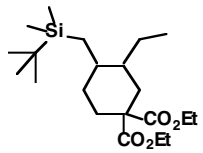
Diethyl 1,7-nonadiene-5,5-dicarboxylate (29)



Sodium (230 mg, 10 mmol) was dissolved in ethanol (7 mL). The soln. was treated with ethyl 2-ethoxycarbonyl-4-hexenoate (1.46 g, 6.8 mmol), which was prepared according to a literature procedure.[10] After stirring for 1 h at room temperature, 3-butenylbromide (1.01 mL, 10 mmol) was added. The mixture was refluxed over night. The solvent was removed *in vacuo.* The residue was dissolved in MTBE. The soln. was washed with sat. NH_4Cl-soln. and brine and was dried over $MgSO_4$. Removal of the solvent *in vacuo* and purification by FC (pentane/MTBE 25 : 1) afforded **29** (521 mg, 29 %) as a colorless oil. I.R. (nujol): 3470*br. w*, 2980*m*, 2937*w*, 1732*s*, 1447*m*, 1385*w*, 1367*w*, 1298*w*, 1266*m*, 1240*m*, 1203*s*, 1134*m*, 1096*w*, 1035*w* cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.86–5.72 (*m*, 1 H, CH_2=C*H*); 5.57–5.45 (*m*, 1 H, CH=CH); 5.30–5.20 (*m*, 1 H, CH=CH); 5.05–4.94 (*m*, 2 H, CH_2=CH); 4.17 (*q*, *J* = 7.1 Hz, 4 H, OCH_2); 2.58 (*d*, *J* = 7.3 Hz, 2 H, CH=CH–CH_2); 2.02–1.87 (*m*, 4 H, CH_2–CH_2); 1.64 (*d*, *J* = 6.4 Hz, 3 H, CH=CH–CH_3); 1.24 (*t*, *J* = 7.1 Hz, 6 H, OCH_2CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 171.7 (C); 138.1 (CH_2); 129.9 (CH); 125.1 (CH); 115.3

(CH); 61.4 (CH_2); 57.7 (C); 36.2 (CH_2); 31.8 (CH_2); 28.7 (CH_2); 18.4 (CH_3); 14.5 (CH_3). MS (EI): 268.2 (2, $[M]^+$); 213.2 (34); 194.2 (31); 167.1 (42); 153.1 (100); 127.1 (25); 125.1 (24); 122.1 (52); 121.2 (40); 107.1 (23); 81.1 (29); 79.1 (24); 55.1 (31); 29.1 (53); 28.0 (37).

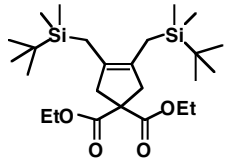
Diethyl 4-[(*tert*-butyldimethylsilyl)methyl]-3-ethyl-cyclohexane-1,1-dicarboxylate (30)



In a sealed tube, diethyl 1,7-nonadiene-5,5-dicarboxylate **29** (110 mg, 1 mmol), 3-*tert*-butyldimethylsilyl-2,4-dimethoxy-3-methyl-1,4-cyclohexadiene **6** (400 mg, 1.5 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (4 mL) and stirred at 90 °C. After 4 h, AIBN (50 mg, 0.3 mmol) was added. After 4 h, removal of the solvent *in vacuo* and purification by FC (pentane/MTBE 50 : 1) afforded **30** (233 mg, ca. 95 % pure, 0.58 mmol, 61 %) as a colorless oil. The diastereoisomers could not be separated completely by GC: dr (*cis : trans*) ≈ 1 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): *cis*- and *trans*-**30**: δ = 4.22–4.13 (*m*, 8 H); 2.41–2.27 (*m*, 2 H); 2.09–2.04 (*m*, 2 H); 1.83–1.58 (*m*, 8 H); 1.40–1.11 (*m*, 20 H); 0.88–0.83 (*m*, 6 H); 0.85 (*s*, 9 H, $C(CH_3)_3$); 0.83 (*s*, 9 H, $C(CH_3)_3$); 0.48–0.42 (*m*, 2 H); 0.14–0.06 (*m*, 2 H); –0.04 (*s*, 3 H, $Si(CH_2)_2$); –0.05 (*s*, 3 H, $Si(CH_2)_2$); –0.07 (*s*, 3 H, $Si(CH_2)_2$); –0.10 (*s*, 3 H, $Si(CH_2)_2$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.8; 171.3; 61.2; 61.0; 60.9; 55.3; 42.3; 40.3; 37.1; 36.1; 32.0; 31.6; 31.3; 30.9; 28.4; 26.5; 26.1; 25.6; 25.5; 16.0; 14.1; 14.0; 11.5; 10.4; –4.0, –4.3; –5.4; –5.8.

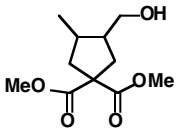
Diethyl di(prop-2-ynyl)malonate (31) was prepared according to a literature procedure.[11]

1,2-Bis[(*tert*-butyldimethylsilyl)methyl]-4,4-di(ethoxycarbonyl)-cyclopent-1-ene (32)



In a sealed tube, diethyl di(prop-2-ynyl)malonate **31** (118 mg, 0.5 mmol), 2,4-dimethoxy-3-methyl-3-*tert*-butyl-dimethylsilyl-1,4-cyclohexadiene **6** (530 mg, 2 mmol) and TBHN (35 mg, 0.2 mmol) were dissolved in hexane (2 mL) and stirred at 90 °C. After 2, 4, and 6 h, TBHN (3×35 mg, 0.6 mmol) was added to the reaction mixture. Heating was continued for 2 h. Removal of the solvent *in vacuo* and purification by FC (pentane/ MTBE 40 : 1) afforded **32** (129 mg, 55 %) as a colorless oil. The spectral data are in agreement with those reported in the literature.[12]

Dimethyl 3-hydroxymethyl-4-methyl-cyclopentane-1,1-dicarboxylate (35)



Acetic anhydride (5.4 mL, 57 mmol) was treated with 3 drops of conc. sulfuric acid and cooled to 0 °C. To this solution, hydrogen peroxide (3.60 mL, 35% in water, 42 mmol) was added. The resulting solution was stirred at room temperature for 30 min. In 6 mL of this solution, dimethyl 3-[(dimethylphenylsilyl)methyl]-4-methyl-cyclopentane-1,1-dicarboxylate **26** (171 mg, 0.49 mmol) was dissolved and treated with $Hg(OAc)_2$ (263 mg, 0.79 mmol).[13] The solution was stirred for 5 h at room temperature. Diethyl ether (80 mL) was added. The organic phase was separated and consecutively washed with sat. $Na_2S_2O_3$-soln., H_2O, $NaHCO_3$-soln. and brine. The organic phase was dried over $MgSO_4$. Filtration and removal of the solvent *in vacuo* yielded the crude product which was purified by FC (pentane/ MTBE 1 : 1) to afford **35** (83 mg, 0.36 mmol, 74 %) as a colorless oil. The diastereoisomeric ratio was determined with GC on the crude reaction mixture: dr (*cis : trans*) 4 : 1. The NMR-data for the *trans*-isomer are in agreement with those reported in the literature.[8] *cis*-**35**: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.65 (*s*, 6 H, OCH_3); 3.60 (*d*×*d*, 1 H, J_1 = 11.0 Hz, J_2 = 5.6 Hz, CH_2OH); 3.45 (*d*×*d*, 1 H, J_1 = 10.7 Hz, J_2 = 6.3 Hz, CH_2OH); 2.43 (*d*×*d*, 1 H, J_1 = 13.4 Hz, J_2 = 6.8 Hz, C–CH_2); 2.33–2.09 (*m*, 4 H, CH_2/CH); 1.86 (*d*×*d*, 1 H, J_1 = 13.4 Hz, J_2 = 7.3 Hz, C–CH_2); 1.81 (*br. s*, 1 H, OH); 0.88 (*d*, 3 H, *J* = 6.8 Hz, CH–CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 173.9 (C); 173.6 (C); 63.1 (CH_2); 59.4 (C); 53.1 (CH_3); 53.0 (CH_3); 44.8 (CH); 42.2 (CH_2); 36.7 (CH_2); 35.6 (CH); 15.1 (CH_3).

References

1. Mendenhall, G. D. *Tetrahedron Lett.* **1983**, *24,* 451.
2. Piers, E.; Grierson, J. R. *J. Org. Chem.* **1977**, *42,* 3755.
3. Charlton, J. L.; Williams, G. J.; Lypka, G. N. *Can. J. Chem.* **1980,** *58,* 1271.
4. Beaulieu, N.; Deslongchamps, P. *Can. J. Chem.* **1980,** *58,* 875.
5. Gilbert, B. C.; Kalz, W.; Lindsay, C. I.; McGrail, P. T.; Parsons, A. F.; Whittaker, D. T. E. *J. Chem. Soc., Perkin Trans. 1* **2000,** 1187.
6. Samu, E.; Huszthy, P.; Somogyi, L.; Hollósi, M. *Tetrahedron: Asymmetry* **1999,** *10,* 2775.
7. Zhang, S.-W.; Mitsudo, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1993,** *450,* 197.
8. Widenhoefer, R. A.; Stengone, C. N. *J. Org. Chem.* **1999,** *64,* 8681.
9. Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1993**, *66,* 2348.
10. Eccott, E. N.; Linstead, R. P. *J. Chem. Soc.* **1929,** 2153. The spectroscopic data are in agreement with those reported in the literature: Takeuchi, R.; Kashio, M. *J. Am. Chem. Soc.* **1998,** *120,* 8647.

11. Bhatarah, P.; Smith, E. H. *J. Chem. Soc., Perkin Trans. 1* **1990,** 2603.
12. Ojima, I.; Zhu, J.; Vidal, E. S.; Kass, D. F. *J. Am. Chem. Soc.* **1998,** *120,* 6690.
13. Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987,** *28,* 4229.