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ELECTRONIC SUPPLEMENTARY INFORMATION

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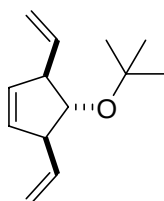
B E L O N G I N G T O T H E P A P E R

Regioselective [2+2]-Photocycloaddition Reactions of Chiral
Tetronates - Influence of Temperature, Pressure and Reaction
Medium

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1 Synthetic procedures and spectroscopical data

(*trans,trans*)-4-*tert*-Butoxy-3,5-divinylcyclopent-1-ene

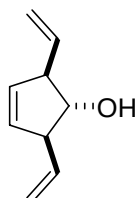


Under an atmosphere of ethene, 493 mg (3.00 mmol) 7-*tert*-butoxy-bicyclo[2.2.1]hepta-2,5-diene (**4**) were dissolved in 30 ml of dichloromethane. 50.0 mg (60.0 μ mol, 2 mol%) *Grubbs I* catalyst were added and the reaction mixture was stirred at r.t. for 48 h. Additional 25.0 mg (30.0 μ mol, 1 mol%) *Grubbs I* catalyst were added to the reaction mixture and stirring at r.t. was continued for additional 24 h. This procedure was repeated two times with each 12.5 mg (15.0 μ mol, 0.5 mol%) *Grubbs I* catalyst. After a total time of 120 h, the mixture was filtered over silica gel, the filtrate was charged with 3 g charcoal, and stirred for 16 h at r.t.. The mixture was filtered and the solvent was removed under reduced pressure. After flash chromatography (pentane/Et₂O = 80/1) 431 mg (2.24 mmol, 83%) (*trans,trans*)-4-*tert*-butoxy-3,5-divinylcyclopent-1-en were obtained as a colourless liquid. 50 mg (0.30 mmol) of starting material 7-*tert*-butoxy-bi-cyclo[2.2.1]hepta-2,5-diene (**4**) could also be reisolated.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.17 (s, 9 H, C7-H), 3.15 (dd, ³*J* = 3.2 Hz, 7.9 Hz, 2 H, C6-H), 3.67 (t, ³*J* = 3.2 Hz, 1 H, C4-H), 4.97 (dd, ²*J* = 1.8 Hz, ³*J* = 10.4 Hz, 2 H, C3-H), 5.03 (dd, ²*J* = 1.8 Hz, ³*J* = 17.5 Hz, 2 H, C3-H), 5.62 (s, 2 H, C2-H), 5.74 (ddd, ³*J* = 17.5 Hz, 10.4 Hz, 7.9 Hz, 2 H, C1-H).

^{13}C -NMR: (90.6 MHz, CDCl_3): δ [ppm] = 29.0 (q, C-7), 59.2 (d, C-6), 73.6 (s, C-5), 83.2 (d, C-4), 114.6 (t, C-3), 132.0 (d, C-2), 140.1 (d, C-1).

(*trans,trans*)-2,5-Divinylcyclopent-3-en-1-ol

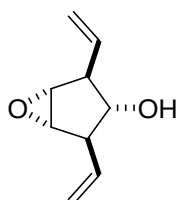


192 mg (1.00 mmol) (*trans,trans*)-4-*tert*-butoxy-3,5-divinylcyclopent-1-ene were dissolved in 4 ml of dichloromethane and 1 ml trifluoroacetic acid was added. The reaction mixture was stirred for 2 h at r.t. After neutralisation with Na_2CO_3 , 20 ml of H_2O and dichloromethane each were added, and the layers were separated and the aqueous layer was extracted two more times with 10 ml of dichloromethane. The organic layers were combined, washed with 20 ml of saturated aqueous NaCl solution and dried with Na_2SO_4 . After filtration the solvent was evaporated under reduced pressure. The compound was treated without further purification

^1H -NMR: (360 MHz, CDCl_3): δ [ppm] = 1.82 (s br, 1 H), 3.20 (virt. t, $^3J \cong 6.4$ Hz), 3.84 (t, $^3J = 5.9$ Hz, 1 H), 5.04 (dd, $^2J = 1.3$ Hz, $^3J = 10.2$ Hz, 2 H), 5.13 (dd, $^2J = 1.3$ Hz, $^3J = 16.5$ Hz, 2 H), 5.64 (s, 2 H), 5.80 (ddd, $^3J = 16.5$ Hz, 10.2 Hz, 7.8 Hz, 2 H).

^{13}C -NMR: (90.6 MHz, CDCl_3): δ [ppm] = 57.6 (d), 84.2 (d), 115.7 (t), 137.7 (d), 139.2 (d).

2,4-Divinyl-6-oxabicyclo[3.1.0]hexan-3-ol (5)



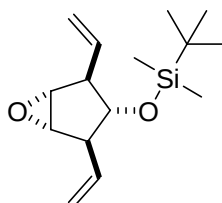
136 mg (1.00 mmol) (*trans,trans*)-2,5-divinylcyclopent-3-en-1-ol were dissolved in 5 ml of dichloromethane together with 26.5 mg (0.10 mmol) vanadyl(IV)acetylacetonate. At 0 °C 400 μl (5 M in decane, 2.00 mmol) *tert*-BuOOH were added to the mixture within 30 min, turning the solution dark red. The ice-bath was removed and the reaction mixture was stirred for 6 h at r.t. The solvent was removed under reduced pressure. After purification by flash chromatography

(pentane/Et₂O = 6/1) 83,0 mg (0.55 mmol, 55%) 2,4-divinyl-6-oxabicyclo[3.1.0]hexan-3-ol (**5**) were obtained as colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 2.40 (s br, 1 H), 2.93 (d, ³J = 7.7 Hz, 2 H), 3.68 (s, 2 H), 3.71 (s, br, 1 H), 5.12 (d virt. t, ³J = 10.4 Hz, ²J = ⁴J = 1.5 Hz, 2 H), 5.20 (d virt. t, ³J = 17.3 Hz, ²J = ⁴J = 1.5 Hz, 2 H), 5.65 (ddd, ³J = 17.3 Hz, 10.4 Hz, 7.5 Hz, 2 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 53.2 (d), 60.6 (d), 80.9 (d), 117.6 (t), 134.5 (d).

(2,4-Divinyl-6-oxabicyclo[3.1.0]hexan-3-yloxy)-*tert*-butyldimethylsilane

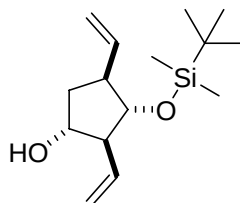


152 mg (1.00 mmol) 2,4-divinyl-6-oxabicyclo[3.1.0]hexan-3-ol (**5**) were dissolved in 5 ml of DMF and charged with 86.3 mg (1.30 mmol) imidazole. 433 µl (3 M in toluene, 1.30 mmol) TBDMS-Cl were added dropwise and the mixture was stirred for 16 h at r.t.. The reaction mixture was quenched by adding 20 ml of H₂O and extracted three times with 20 ml of Et₂O each. The organic layers were combined and washed with saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (pentane/Et₂O = 30/1) to yield 231 mg (0.86 mmol, 86%) (2,4-divinyl-6-oxabicyclo-[3.1.0]hexan-3-yloxy)-*tert*-butyldimethylsilane as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = -0.04 (s, 6 H), 0.88 (s, 9 H), 2.76 (d, ³J = 8.4 Hz, 2 H), 3.45 (s, 2 H), 3.94 (s, 1 H), 5.13 (d virt. t, ³J = 10.4 Hz, ²J = ⁴J = 1.4 Hz, 2 H), 5.17 (d virt. t, ³J = 17.4 Hz, ²J = ⁴J = 1.4 Hz, 2 H), 5.65 (ddd, ³J = 17.4 Hz, 10.4 Hz, 8.6 Hz, 2 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 4.47 (q), 18.3 (s), 25.9 (q), 54.3 (d), 61.0 (d), 84.4 (d), 116.9 (t), 136.0 (d).

3-(*tert*-Butyldimethylsilanyloxy)-2,4-divinylcyclopentanol

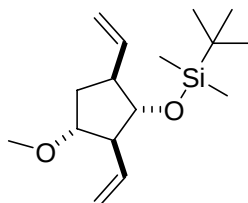


266 mg (1.00 mmol) (2,4-divinyl-6-oxabicyclo[3.1.0]hexan-3-yloxy)-*tert*-butyldimethylsilane were dissolved in 7.5 ml THF. After cooling down to 0 °C, 1.20 ml (1M in THF, 1.20 mmol) Super-Hydride® were added drop wise to the stirred solution. After 4.5 h the reaction was quenched by the addition of some ice. The reaction mixture was diluted with 20 ml of dichloromethane and 20 ml of saturated aqueous NH₄Cl solution and the layers were separated. The aqueous layer was extracted two more times with 15 ml of dichloromethane. The organic layers were combined and washed with 20 ml of saturated aqueous NaHCO₃ solution and 20 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 6/1) to yield 250 mg (0.93 mmol, 93%) 3-(*tert*-butyldimethylsilanyloxy)-2,4-divinylcyclopentanol as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 0.00 (s, 3 H), 0.01 (s, 3 H), 0.86 (s, 9 H), 1.79-2.00 (m, 3 H), 2.42 (virt. q, ³J ≅ 7.3 Hz), 2.71 (virt. quin., ³J ≅ 8.1 Hz), 3.62 (dd, ³J = 6.9 Hz, 6.9 Hz, 1 H), 3.95 (ddd, ³J = 6.7 Hz, 6.7 Hz, 4.6 Hz, 1 H), 4.98-5.18 (m, 4 H), 5.65 (ddd, ³J = 17.5 Hz, 9.8 Hz, 8.5 Hz, 1 H), 5.72 (ddd, ³J = 17.4 Hz, 9.8 Hz, 7.8 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = -3.9 (q), -3.8 (q), 18.1 (s), 26.0 (q), 37.8 (t), 50.3 (d), 62.0 (d), 75.0 (d), 82.2 (d), 115.2 (t), 117.5 (t), 138.2 (d), 140.5 (d).

tert-Butyl-(3-methoxy-2,5-divinylcyclopentyloxy)-dimethylsilane



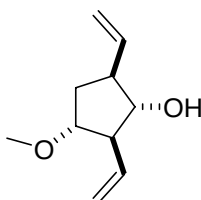
268 mg (1.00 mmol) 3-(*tert*-butyldimethylsilanyloxy)-2,4-divinylcyclopentanol were dissolved in 10 ml of THF and cooled to 0 °C. After addition of 48.0 mg (60% in mineral oil, 1.20 mmol) NaH, the solution was stirred at this temperature for 1 h. Then the solution was charged with 80.5 µl (1.30 mmol) MeI and stirred at r.t.. After 6 h the reaction mixture was quenched by adding 4 ml of saturated aqueous NH₄Cl-solution and stirred for additional 30 min. The reaction mixture was then

further diluted with 15 ml of H₂O and extracted three times with 20 ml of Et₂O each. The organic layers were combined, washed with 20 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 20/1) to yield 268 mg (0.95 mmol, 95%) *tert*-butyl-(3-methoxy-2,5-divinylcyclopentyloxy)-dimethylsilane as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = −0.02 (s, 3 H), −0.01 (s, 3 H), 0.85 (s, 9 H), 1.67 (ddd, ³J = 13.9 Hz, 8.3 Hz, 3.2 Hz 1 H), 1.90 (ddd, ³J = 13.9 Hz, 10.7 Hz, 7.4 Hz, 1 H), 2.46 (virt. q, ³J ≅ 7.5 Hz), 2.62 (virt. quin., ³J ≅ 8.9 Hz), 3.29 (s, 3 H), 3.48 (dd, ³J = 8.1 Hz, 8.1 Hz, 1 H), 3.46-3.52 (m, 1 H), 4.99-5.17 (m, 4 H), 5.69 (ddd, ³J = 17.1 Hz, 10.1 Hz, 8.8 Hz, 1 H), 5.76 (ddd, ³J = 17.0 Hz, 10.1 Hz, 7.7 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = −3.6 (q), −3.6 (q), 18.2 (s), 26.1 (q), 34.6 (t), 50.0 (q), 56.8 (d), 59.5 (d), 82.0 (d), 83.2 (d), 115.6 (t), 116.7 (t), 139.5 (d), 140.2 (d)

3-Methoxy-2,5-divinylcyclopentanol

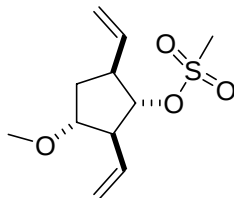


282 mg (1.00 mmol) *tert*-butyl-(3-methoxy-2,5-divinylcyclopentyloxy)-dimethylsilane were dissolved in 10 ml of MeOH. Three drops of concentrated hydrochloric acid were added and the solution was stirred for 2 h at r.t.. After neutralisation with saturated aqueous NaHCO₃ solution, 20 ml of H₂O were added and the aqueous layer was extracted three times with 20 ml of Et₂O each. The organic layers were combined and washed with 20 ml of saturated aqueous NaCl solution. After drying with Na₂SO₄, it was filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 3/1) to yield 151 mg (0.90 mmol, 90%) 3-methoxy-2,5-divinylcyclopentanol as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.67 (ddd, ³J = 14.1 Hz, 10.8 Hz, 6.7 Hz 1 H), 1.88 (s, br, 1 H), 1.94 (ddd, ³J = 14.1 Hz, 8.5 Hz, 2.8 Hz, 1 H), 2.43 (virt. q, ³J ≅ 8.5 Hz, 1 H), 2.58 (virt. quin., ³J ≅ 9.0 Hz), 3.26 (s, 3 H), 3.44 (dd, ³J = 8.3 Hz, 8.3 Hz, 1 H), 3.52 (ddd, ³J = 8.0 Hz, 6.7 Hz, 2.8 Hz, 1 H), 5.01-5.21 (m, 4 H), 5.71 (ddd, ³J = 17.2 Hz, 10.2 Hz, 7.8 Hz, 1 H), 5.80 (ddd, ³J = 17.2 Hz, 10.3 Hz, 8.2 Hz, 1 H)

^{13}C -NMR: (90.6 MHz, CDCl_3): δ [ppm] = 34.5 (t), 49.3 (q), 56.8 (d), 58.4 (d), 79.9 (d), 83.2 (d), 115.9 (t), 116.7 (t), 138.4 (d), 139.4 (d).

Methanesulfonic acid 3-methoxy-2,5-divinylcyclopentylester

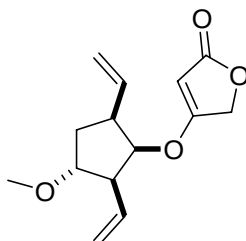


168 mg (1.00 mmol) *tert*-butyl-(3-methoxy-2,5-divinylcyclopentyl-oxy)-dimethylsilane were dissolved in 12 ml of dichloromethane and charged with 223 μl (1.60 mmol) triethylamine. Then the solution was cooled to 0 $^{\circ}\text{C}$ and 108 μl (1.40 mmol) methanesulfonyl chloride were slowly added to the stirred solution. After 4 h the reaction mixture was quenched with 20 ml of water and extracted three times with 20 ml of dichloromethane each. The organic layers were combined and washed with 20 ml of saturated aqueous NaCl solution. After drying with Na_2SO_4 and filtration, the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ Et_2O 3/1) to yield 197 mg (0.80 mmol, 80%) methanesulfonic acid 3-methoxy-2,5-divinylcyclopentylester as a colourless liquid.

^1H -NMR: (360 MHz, CDCl_3): δ [ppm] = 1.75 (ddd, $^3J = 13.9$ Hz, 10.9 Hz, 6.8 Hz 1 H), 2.03 (dddd, $^3J = 13.9$ Hz, 8.3 Hz, 2.8 Hz, $^4J = 1.0$ Hz, 1 H), 2.75-2.82 (m, 1 H), 2.92-3.10 (m., 1 H), 2.98 (s, 3 H), 3.31(s, 3 H), 3.55 (ddd, $^3J = 6.8$ Hz, 4.9 Hz, 2.8 Hz³, 1 H), 4.53 (dd, $^3J = 8.2$ Hz, 8.2 Hz, 1 H), 5.11-5.29 (m, 4 H), 5.79 (ddd, $^3J = 17.2$ Hz, 10.3 Hz, 7.8 Hz, 1 H), 5.86 (ddd, $^3J = 17.2$ Hz, 10.3 Hz, 8.4 Hz, 1 H)

^{13}C -NMR: (90.6 MHz, CDCl_3): δ [ppm] = 34.6 (t), 39.4 (q), 47.3 (d), 56.1 (d), 56.9 (d), 83.0 (d), 88.5 (d), 117.3 (t), 118.0 (t), 136.9 (d), 137.5 (d).

Tetronic acid 3-methoxy-2,5-divinylcyclopentylester (1a)



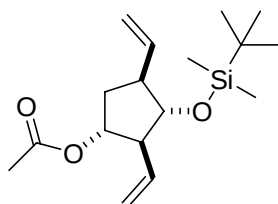
123 mg (0.50 mmol) methanesulfonic acid 3-methoxy-2,5-divinylcyclopentylester were dissolved in 7 ml DMF. 345 mg (2.50 mmol) potassium tetronate and 132 mg (0.50 mmol) 18-crown-6 were added and the mixture was stirred 16 h at 100 $^{\circ}\text{C}$. After this time the reaction mixture was

quenched with 40 ml of water and extracted three times with 15 ml of ethyl acetate each. The organic layers were combined, washed with 20 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 1.5/1) to yield 50 mg (0.20 mmol, 40%) tetronic acid 3-methoxy-2,5-divinylcyclopentylester as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.99 (ddd, ³J = 14.0 Hz, 8.7 Hz, 2.8 Hz 1 H), 2.10 (ddd, ³J = 14.0 Hz, 10.9 Hz, 7.8 Hz, 1 H), 2.83-2.88 (m, 1 H), 3.02-3.10 (m., 1 H), 3.34 (s, 3 H), 3.87 (ddd, ³J = 7.8 Hz, 5.8 Hz, 2.8 Hz, 1 H), 4.59 (s, 1 H), 4.59 (s, 1 H), 4.61 (dd, ³J = 4.3 Hz, 4.3 Hz, 1 H), 5.02-5.28 (m, 5 H), 5.70 (ddd, ³J = 17.3 Hz, 10.3 Hz, 8.3 Hz, 1 H), 5.76 (ddd, ³J = 17.4 Hz, 10.2 Hz, 7.4 Hz, 1 H)

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 34.8 (t), 46.6(d), 56.0 (d), 57.6 (q), 67.8 (t), 84.6 (d), 90.1 (d), 90.2 (d), 117.7 (t), 118.8 (t), 134.2 (d), 135.4 (d), 173.7 (s), 179.2 (s).

***tert*-Butyl-(3-acetoxy-2,5-divinylcyclopentyloxy)-dimethylsilane**

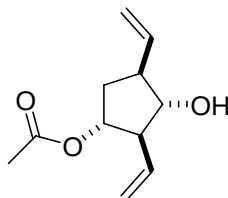


268 mg (1.00 mmol) 3-(*tert*-Butyldimethylsilyloxy)-2,4-divinylcyclopentanol were dissolved in 4 ml of Ac₂O and 4 ml of pyridine. After adding some crystals of DMAP, the mixture was stirred at r.t. for 16 h. The solvent was removed under reduced pressure, the crude product was dissolved in dichloromethane and filtered through a plug of silica gel. The solvent was removed under reduced pressure and purification was done by flash chromatography (pentane/Et₂O 8/1) to yield 295 mg (0.95 mmol, 95%) *tert*-butyl-(3-acetoxy-2,5-divinylcyclopentyloxy)-dimethylsilane as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = -0.01 (s, 3 H), 0.00 (s, 3 H), 0.86 (s, 9 H), 1.84-1.89 (m, 2 H), 2.03 (s, 3 H), 2.54 (virt. q, ³J ≅ 8.8 Hz), 2.65 (virt. quin., ³J ≅ 8.9 Hz), 3.48 (dd, ³J = 8.3 Hz, 8.3 Hz, 1 H), 4.86-4.91 (m, 1 H), 5.01-5.15 (m, 4 H), 5.73 (ddd, ³J = 17.1 Hz, 10.3 Hz, 8.6 Hz, 1 H), 5.69 (ddd, ³J = 17.2 Hz, 10.2 Hz, 8.0 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = −3.7 (q), −3.7 (q), 18.1 (s), 21.3 (q), 26.0 (q), 35.1 (t), 50.2 (d), 58.4 (d), 76.3 (d), 81.6 (d), 116.0 (t), 117.3 (t), 137.8 (d), 139.6 (d), 170.9 (s).

3-Acetoxy-2,5-divinylcyclopentanol

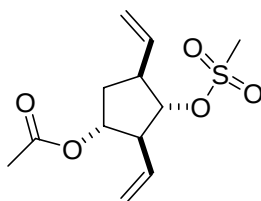


311 mg (1.00 mmol) *tert*-butyl-(3-acetoxy-2,5-divinylcyclopentyloxy)-dimethylsilane were dissolved in 15 ml of THF and cooled to 0 °C. Then 1.50 ml (1M in THF, 1.50 mmol) of TBAF were slowly added via a syringe. After 5 h the reaction mixture was quenched by adding 3 ml of saturated aqueous NH₄Cl-solution. The mixture was further diluted with 25 ml of H₂O and extracted three times with 15 ml of Et₂O each. The organic layers were combined, washed with 20 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 4/1) to yield 186 mg (0.90 mmol, 90%) 3-acetoxy-2,5-divinylcyclopentanol as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.89-1.94 (m, 2 H), 2.04 (s, 3 H), 2.43 (virt. q, ³J ≅ 7.8 Hz, 1 H), 2.58 (virt. quin., ³J ≅ 9.1 Hz), 3.44 (dd, ³J = 9.1 Hz, 9.1 Hz, 1 H), 4.91 (ddd, ³J = 6.9 Hz, 6.7 Hz, 4.4 Hz 1 H), 5.07-5.23 (m, 4 H), 5.74 (ddd, ³J = 17.1 Hz, 10.3 Hz, 7.7 Hz, 1 H), 5.83 (ddd, ³J = 17.3 Hz, 10.3 Hz, 7.9 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 21.3 (t), 35.2 (t), 49.3 (d), 57.3 (d), 76.1 (d), 79.6 (d), 116.4 (t), 117.3 (t), 137.1 (d), 138.9 (d), 170.8 (s).

Methanesulfonic acid 3-acetoxy-2,5-divinylcyclopentylester



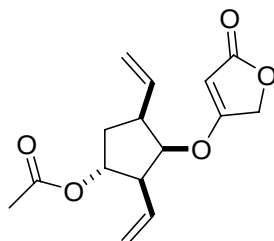
196 mg (1.00 mmol) *tert*-butyl-(3-acetoxy-2,5-divinylcyclopentyloxy)-dimethylsilane were dissolved in 12 ml of dichloromethane and charged with 223 µl (1.60 mmol) triethylamine. Then the solution was cooled to 0 °C and 108 µl (1.40 mmol) methanesulfonyl chloride were slowly

added to the stirred solution. After 4 h the reaction mixture was quenched with 20 ml of water and extracted three times with 20 ml of dichloromethane each. The organic layers were combined, washed with 20 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 3/1) to yield 255 mg (0.93 mmol, 93%) methanesulfonic acid 3-acetoxy-2,5-divinylcyclopentylester as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.89-2.00 (m, 2 H), 2.06 (s, 3 H), 2.86 (virt. q, ³J = 6.8 Hz, 1 H), 2.99 (s, 3 H), 3.00 (virt. quin., ³J = 8.3 Hz), 4.57 (dd, ³J = 7.8 Hz, 7.8 Hz, 1 H), 4.93 (ddd, ³J = 6.5 Hz, 5.1 Hz, 3.6 Hz³, 1 H), 5.14-5.28 (m, 4 H), 5.80 (ddd, ³J = 17.3 Hz, 10.3 Hz, 8.0 Hz, 1 H), 5.84 (ddd, ³J = 17.4 Hz, 10.0 Hz, 7.5 Hz, 1 H)

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 21.2 (q), 35.1 (t), 39.4 (q), 47.5 (d), 55.4 (d), 76.1 (d), 88.1 (d), 117.6 (t), 118.5 (t), 135.3 (d), 137.0 (d), 170.5 (s).

Tetronic acid 3-acetoxy-2,5-divinylcyclopentylester (1b)

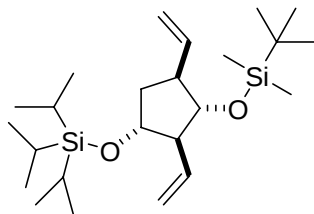


137 mg (0.50 mmol) methanesulfonic acid 3-acetoxy-2,5-divinylcyclopentylester were dissolved in 7 ml of DMF. 345 mg (2.50 mmol) potassium tetronate and 132 mg (0.50 mmol) 18-crown-6 were added and the mixture was stirred 24 h at 100 °C. After this the reaction mixture was quenched with 40 ml of water and extracted three times with 15 ml ethyl acetate each. The organic layers were combined and washed with 40 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate = 12/1 → 3/1) to yield 45 mg (0.16 mmol, 32%) tetronic acid 3-acetoxy-2,5-divinylcyclopentylester as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.90 (ddd, ³J = 14.4 Hz, 8.9 Hz, 3.0 Hz 1 H), 2.05 (s, 3 H), 2.30 (ddd, ³J = 14.4 Hz, 10.7 Hz, 8.3 Hz, 1 H), 2.94 (ddd, ³J = 8.3 Hz, 7.4 Hz, 4.2 Hz, 1 H), 3.02-3.11 (m., 1 H), 4.58 (s, 1 H), 4.58 (s, 1 H), 4.61 (dd, ³J = 4.2 Hz, 4.2 Hz, 1 H), 5.04-5.23 (m, 5 H), 5.70 (ddd, ³J = 17.4 Hz, 10.1 Hz, 7.8 Hz, 1 H), 5.72 (ddd, ³J = 17.4 Hz, 10.0 Hz, 7.4 Hz, 1 H)

^{13}C -NMR: (90.6 MHz, CDCl_3): δ [ppm] = 21.2 (q), 35.5(t), 46.6 (d), 54.9 (d), 67.7 (t), 89.4 (d), 90.2 (d), 90.3 (d), 118.1 (t), 119.4 (t), 132.7 (d), 134.8 (d), 170.7 (s), 173.5 (s), 179.1 (s).

2-(*tert*-Butyldimethylsilanyloxy)-4-triisopropylsilanyloxy-1,3-divinylcyclopentane

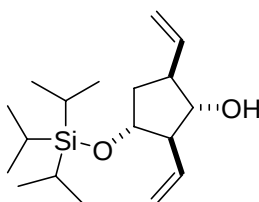


268 mg (1.00 mmol) 3-(*tert*-butyldimethylsilanyloxy)-2,4-divinylcyclopentanol were dissolved in 5 ml of DMF. After adding 136 mg (2.00 mmol) of imidazole and some crystals of DMAP, 533 μl (3M in toluene, 1.60 mmol) TIPS-Cl were added slowly by a syringe. The reaction mixture was stirred at r.t. for 40 h. After this the reaction mixture was quenched with 40 ml of H_2O and extracted three times with 25 ml of Et_2O each. The organic layers were combined and washed with 40 ml of saturated aqueous NaCl solution and dried with Na_2SO_4 . After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ Et_2O = 30/1) to yield 356 mg (0.84 mmol, 84%) 2-(*tert*-butyldimethylsilanyloxy)-4-triisopropylsilanyloxy-1,3-divinylcyclopentane as a colourless liquid.

^1H -NMR: (360 MHz, CDCl_3): δ [ppm] = -0.02 (s, 3 H), -0.01 (s, 3 H), 0.86 (s, 9 H), 1.03-1.05 (m, 21 H), 1.71 (ddd, 3J = 13.4 Hz, 10.1 Hz, 6.9 Hz 1 H), 1.83-1.90 (m, 1 H), 2.41-2.47 (m, 1 H), 2.72 (virt. quin., 3J $\cong$ 8.6 Hz, 1 H), 3.49 (dd, 3J = 8.1 Hz, 8.1 Hz, 1 H), 3.98-4.03 (m, 1 H), 4.98-5.12 (m, 4 H), 5.67 (ddd, 3J = 17.0 Hz, 10.2 Hz, 9.1 Hz, 1 H), 5.71 (ddd, 3J = 17.2 Hz, 10.3 Hz, 7.1 Hz, 1 H).

^{13}C -NMR: (90.6 MHz, CDCl_3): δ [ppm] = -3.7 (q), -3.6 (q), 12.4 (d), 17.9 (s), 18.2 (q), 18.2 (q) 26.1 (q), 39.2 (t), 50.1 (d), 62.9 (d), 75.4 (d), 82.1 (d), 115.1 (t), 116.9 (t), 139.5 (d), 140.8 (d).

3-Triisopropylsilanyloxy-2,5-divinylcyclopentanol

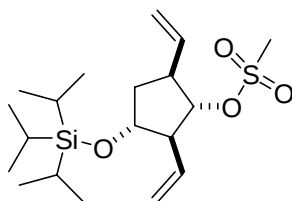


425 mg (1.00 mmol) 2-(*tert*-outyldimethylsilanyloxy)-4-triisopropylsilanyloxy-1,3-divinylcyclopentane were dissolved in 15 ml of THF/H₂O/HOAc (3/1/1) and stirred at r.t. for 48 h. The reaction mixture was neutralised with saturated aqueous NaHCO₃ solution, further diluted with 15 ml of H₂O and extracted four times with 15 ml of Et₂O each. The organic layers were combined, washed with 20 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 4/1) to yield 230 mg (0.74 mmol, 93%) 3-triisopropylsilanyloxy-2,5-divinylcyclopentanol as a colourless liquid and 85.0 mg (0.20 mmol) of 2-(*tert*-butyldimethylsilanyloxy)-4-triisopropylsilanyloxy-1,3-divinylcyclopentane.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.04-1.06 (m, 21 H), 1.76 (ddd, ³*J* = 13.7 Hz, 10.1 Hz, 6.7 Hz 1 H), 1.93-2.00 (m, 1 H), 2.48-2.54 (m, 1 H), 2.58 (virt. quin., ³*J* ≅ 8.6 Hz), 3.54 (dd, ³*J* = 4.0 Hz, 4.0 Hz, 1 H), 4.09-4.14 (m, 1 H), 5.02-5.20 (m, 4 H), 5.72 (ddd, ³*J* = 17.3 Hz, 9.9 Hz, 8.1 Hz, 1 H), 5.78 (ddd, ³*J* = 17.4 Hz, 10.2 Hz, 7.6 Hz, 1 H)

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 12.3 (d), 18.5 (q), 18.6 (q), 39.4 (t), 50.0 (d), 61.8 (d), 76.2 (d), 80.9 (d), 115.3 (t), 117.0 (t), 138.2 (d), 140.2 (d).

Methanesulfonic acid 3-triisopropylsilanyloxy-2,5-divinylcyclopentylester



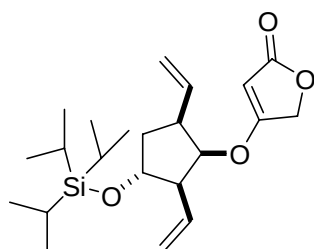
311 mg (1.00 mmol) 3-triisopropylsilanyloxy-2,5-divinylcyclopentanol were dissolved in 12 ml of dichloromethane and charged with 223 μl (1.60 mmol) triethylamine. Then the solution was cooled to 0 °C and 108 μl (1.40 mmol) methanesulfonyl chloride were slowly added to the stirred solution. After 4 h the reaction mixture was quenched with 20 ml of water and extracted three times with 20 ml of dichloromethane each. The organic layers were combined, washed with 20 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 6/1) to yield 354 mg (0.91 mmol, 91%) methanesulfonic acid 3-triisopropylsilanyloxy-2,5-divinylcyclopentylester as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.03-1.06 (m, 21 H), 1.78 (ddd, ³*J* = 13.4 Hz, 10.4 Hz, 6.1 Hz 1 H), 1.92-2.01 (m, 1 H), 2.71-2.80 (m, 1 H), 2.98 (s, 3 H), 3.10 (virt. quin., ³*J* ≅ 6.2 Hz), 4.09-4.12 (m, 1 H), 4.54 (dd, ³*J* = 7.6 Hz,

7.6 Hz, 1 H), 5.09-5.25 (m, 4 H), 5.78 (ddd, $^3J = 17.4$ Hz, 10.0 Hz, 7.8 Hz, 1 H), 5.83 (ddd, $^3J = 17.3$ Hz, 10.1 Hz, 8.5 Hz, 1 H)

^{13}C -NMR: (90.6 MHz, CDCl_3): δ [ppm] = 12.5 (d), 18.4 (q), 18.4 (q), 39.3 (t), 47.5 (d), 59.9 (d), 75.6 (d), 89.3 (d), 117.0 (t), 118.3 (t), 137.1 (d), 138.2 (d).

Tetronic acid 3-triisopropylsilanyloxy-2,5-divinylcyclopentylester (1c)

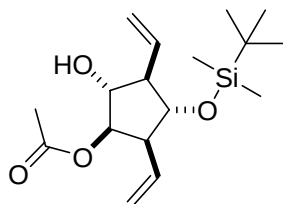


144 mg (0.50 mmol) methanesulfonic acid 3-triisopropylsilanyloxy-2,5-divinylcyclopentylester were dissolved in 7 ml of DMF. 345 mg (2.50 mmol) potassium tetronate and 132 mg (0.50 mmol) 18-crown-6 were added and the mixture was stirred 16 h at 100 °C. After this the reaction mixture was quenched with 40 ml of water and extracted three times with 15 ml of ethyl acetate each. The organic layers were combined, washed with 40 ml of saturated aqueous NaCl solution and dried with Na_2SO_4 . After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate = 12/1 $\rightarrow$ 3/1) to yield 72 mg (0.18 mmol, 37%) tetronic acid 3-triisopropylsilanyloxy-2,5-divinylcyclopentylester as a colourless liquid.

^1H -NMR: (360 MHz, CDCl_3): δ [ppm] = 1.04-1.05 (m, 21 H), 1.91 (ddd, $^3J = 13.6$ Hz, 8.5 Hz, 2.7 Hz 1 H), 2.11 (ddd, $^3J = 13.6$ Hz, 10.4 Hz, 7.1 Hz, 1 H), 2.83 (virt. quin., $^3J \cong 4.7$ Hz, 1 H), 3.11-3.19 (m., 1 H), 4.33-4.37 (m, 1 H), 4.57 (s, 1 H), 4.57 (s, 1 H), 4.63 (dd, $^3J = 4.9$ Hz, 4.9 Hz, 1 H), 5.03-5.19 (m, 5 H), 5.67 (ddd, $^3J = 17.1$ Hz, 10.2 Hz, 7.8 Hz, 1 H), 5.71 (ddd, $^3J = 17.2$ Hz, 10.2 Hz, 8.2 Hz, 1 H)

^{13}C -NMR: (90.6 MHz, CDCl_3): δ [ppm] = 12.3 (d), 18.1 (q), 39.4(t), 46.0 (d), 59.0 (d), 67.8 (t), 89.6 (d), 90.1 (d), 117.3 (t), 119.1 (t), 134.1 (d), 135.8 (d), 173.8 (s), 179.2 (s).

Acetic acid-3-*tert*-butyldimethylsilanyloxy-5-hydroxy-2,4-divinyl-cyclopentylester

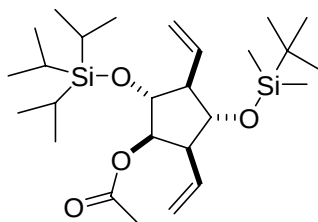


133 mg (500 μ mol) (2,4-divinyl-6-oxabicyclo[3.1.0]hexan-3-yloxy)-*tert*-butyldimethyl-silane were dissolved in 4.00 ml of 1.5 M NaOAc/HOAc buffer solution and stirred for 6 h at 100 °C. Then two third of the solvent was removed under reduced pressure and the residue was neutralised with saturated aqueous NaHCO₃ solution and extracted three times with 20 ml of ethyl acetate each. The organic layers were combined, washed with 40 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 12/1 $\rightarrow$ 3/1) to yield 50.5 mg (155 μ mol, 49%) acetic acid-3-*tert*-butyldimethylsilanyloxy-5-hydroxy-2,4-divinyl-cyclopentyl-ester as a colourless liquid and 48.1 mg (180 μ mol) (2,4-divinyl-6-oxabicyclo[3.1.0]hexan-3-yloxy)-*tert*-butyldimethyl-silane.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = -0.01 (s, 3 H), 0.00 (s, 3 H), 0.88 (s, 9 H), 2.06 (s, 3 H), 2.39 (virt. q, ³*J* $\cong$ 8.5 Hz, 1 H), 2.60 (s br, 1 H), 2.84 (virt. quin., ³*J* $\cong$ 8.6 Hz, 1 H), 3.75 (virt. t, ³*J* $\cong$ 8.4 Hz, 1 H), 3.79 (dd, ³*J* = 8.5 Hz, 4.8 Hz, 1 H), 4.87 (dd, ³*J* = 8.6 Hz, 4.8 Hz, 1 H), 5.09-5.25 (m, 4 H), 5.66 (d virt. t, ²*J* = 16.8 Hz, ³*J* $\cong$ 10.0 Hz, 1 H), 5.73 (ddd, ³*J* = 17.1 Hz, 9.9 Hz, 8.6 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 3.90 (q), 3.79 (q), 17.9 (s), 20.9 (q), 25.8 (q), 53.4 (d), 57.9 (d), 78.6 (d), 78.8 (d), 81.4 (d), 118.3 (t), 119.0 (t), 134.3 (d), 137.4 (d), 171.4(s).

Acetic acid-3-*tert*-butyldimethylsilanyloxy-5-triisopropylsilanyloxy-2,4-divinyl-cyclopentylester



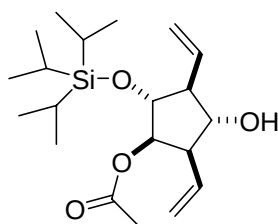
327 mg (1.00 mmol) acetic acid-3-*tert*-butyldimethylsilanyloxy-5-hydroxy-2,4-divinyl-cyclopentyl-ester were dissolved in 5 ml of DMF together with 165 mg (2.50 mmol) imidazole and

some crystals of DMAP. 491 μ l (3 M in toluene, 1.30 mmol) TIPS-Cl were added slowly by a syringe. The reaction mixture was stirred at 55 $^{\circ}$ C for 36 h. After this the reaction mixture was quenched with 50 ml of H₂O and extracted three times with 30 ml of Et₂O each. The organic layers were combined, washed with 40 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 50/1) to yield 405 mg (0.84 mmol, 84%) acetic acid-3-*tert*-butyldimethylsilanyloxy-5-triisopropylsilanyloxy-2,4-divinyl-cyclopentylester as colourless crystals.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = -0.02 (s, 3 H), -0.01 (s, 3 H), 0.85 (s, 9 H), 1.02-1.06 (m, 21 H), 2.02 (s, 3 H), 2.43 (d virt. t, ³J = 9.2 Hz, ³J $\cong$ 6.4 Hz, 1 H), 2.89 (virt. q, ³J $\cong$ 7.9 Hz, 1 H), 3.80 (virt. t, ³J $\cong$ 7.5 Hz, 1 H), 3.97 (dd, ³J = 3.9 Hz, 5.7 Hz, 1 H), 5.00 (dd, ³J = 3.9 Hz, 6.8 Hz, 1 H), 5.09-5.15 (m, 4 H), 5.61 (d virt. t, ³J = 17.1 Hz, ³J $\cong$ 9.7 Hz, 1 H), 5.71 (d virt. t, ³J = 17.0 Hz, ³J $\cong$ 9.8 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = -3.6 (d), -3.5 (q), 12.7 (q), 18.3 (s), 18.3 (q), 18.4 (q), 21.3 (q), 26.2 (q), 53.7 (d), 60.8 (d), 79.6 (t), 80.4 (d), 82.0 (d), 117.7 (t), 118.9 (t), 135.0 (d), 139.1 (d), 170.2 (s).

Acetic acid-3-hydroxy-5-triisopropylsilanyloxy-2,4-divinyl-cyclopentylester

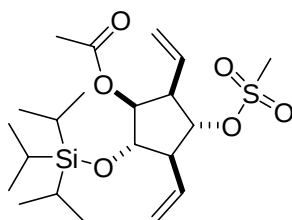


241 mg (0.50 mmol) acetic acid-3-*tert*-butyldimethylsilanyloxy-5-triisopropylsilanyloxy-2,4-divinyl-cyclopentylester were dissolved in 6 ml of EtOH and charged with 3 drops of concentrated hydrochloric acid. The reaction mixture was stirred at r.t. After 7 h the reaction mixture was neutralised with saturated aqueous NaHCO₃ solution and extracted three times with 10 ml of ethyl acetate each. The organic layers were combined, washed with 30 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 3/1) to yield 151 mg (0.41 mmol, 82%) acetic acid-3-*tert*-butyldimethylsilanyloxy-5-hydroxy-2,4-divinyl-cyclopentylester as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.01-1.09 (m), 1.74 (s br, 1 H), 2.02 (s, 3 H), 2.44 (d virt. t, ³J ≅ 5.7 Hz, ³J ≅ 8.2 Hz, 1 H), 2.86 (virt. q, ³J ≅ 8.0 Hz, 1 H), 3.84 (virt. t, ³J ≅ 8.9 Hz, 1 H), 4.00 (dd, ³J = 2.7 Hz, 5.4 Hz, 1 H), 5.06 (dd, ³J = 2.7 Hz, 6.4 Hz, 1 H), 5.15-5.28 (m, 4 H), 5.71 (ddd, ³J = 17.3 Hz, 10.3 Hz, 8.2 Hz, 1 H), 5.82 (ddd, ³J = 17.0 Hz, 10.2 Hz, 8.9 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 12.4 (d), 18.09 (q), 18.12 (q), 21.0 (q), 52.7 (d), 60.1 (d), 78.2 (d), 79.9 (d), 81.5 (d), 117.6 (t), 118.8 (t), 133.9 (d), 138.1 (d).

Acetic acid 3-methanesulfonyloxy-5-triisopropylsilanyloxy-2,4-divinylcyclopentylester

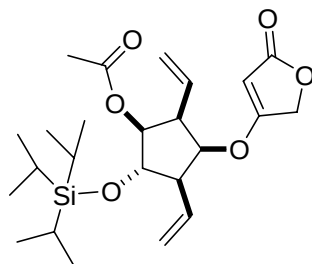


185 mg (0.50 mmol) acetic acid-3-*tert*-butyldimethylsilyloxy-5-hydroxy-2,4-divinyl-cyclopentylester were dissolved in 7 ml of dichloromethane and charged with 112 μl (0.80 mmol) triethylamine. Then the solution was cooled to -30 °C and 54.0 μl (0.70 mmol) methanesulfonyl chloride were slowly added to the stirred solution. After 5 h the reaction mixture was quenched with 20 ml of water and extracted three times with 20 ml of dichloromethane each. The organic layers were combined, washed with 20 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 4/1) to yield 187 mg (0.42 mmol, 84%) acetic acid 3-methanesulfonyloxy-5-triisopropylsilyloxy-2,4-divinylcyclopentylester as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.04-1.07 (m, 21 H), 2.04 (s, 3 H), 2.70-2.80 (m, 1 H), 2.99 (s, 3 H), 3.18-3.27 (m, 1 H), 4.00 (dd., ³J = 3.5 Hz, 2.5 Hz, 1 H), 4.85 (dd, ³J = 8.9 Hz, 6.5 Hz, 1 H), 4.99-5.03 (m, 1 H), 5.19-5.34 (m, 4 H), 5.677 (ddd, ³J = 17.4 Hz, 10.1 Hz, 8.6 Hz, 1 H), 5.84 (ddd, ³J = 17.4 Hz, 10.0 Hz, 9.1 Hz, 1 H)

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 12.2 (d), 18.0 (q), 18.1 (q), 20.9 (q), 39.3 (q), 50.7 (d), 58.3 (d), 79.3 (t), 80.9 (d), 87.6 (d), 118.3 (t), 120.2 (t), 132.2 (d), 136.7 (d), 169.7 (s).

Tetronic acid 4-acetoxy-3-triisopropylsilanyloxy-2,5-divinylcyclopentylester

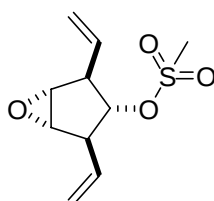


97.3 mg (0.25 mmol) methanesulfonic acid 3-triisopropylsilanyloxy-2,5-divinylcyclopentylester were dissolved in 5 ml of DMF/DMSO. 1.71 g (5.00 mmol) tetrabutylammonium tetronate were added and the mixture was stirred 16 h at 90 °C. After this the reaction mixture was quenched with 40 ml of water and extracted three times with 20 ml of ethyl acetate each. The organic layers were combined, washed with 40 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate = 12/1 → 4/1) to yield 32 mg (0.07 mmol, 28%) tetronic acid 4-acetoxy-3-triisopropylsilanyloxy-2,5-divinylcyclopentylester as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.03-1.05 (m, 21 H), 2.05 (s, 3 H), 2.82 (ddd, ³J = 9.5 Hz, 6.7 Hz, 6.0 Hz, 1 H), 3.29-3.35 (m, 1 H), 4.38 (dd., ³J = 6.7 Hz, 4.2 Hz, 1 H), 4.60 (s, 1 H), 4.60 (s, 1 H), 4.65 (dd, ³J = 6.0 Hz, 6.0 Hz, 1 H), 5.03 (s, 1H), 5.09 (dd, ³J = 7.5 Hz, 4.2 Hz, 1 H), 5.15-5.23 (m, 4 H), 5.61 (ddd, ³J = 17.2 Hz, 10.1 Hz, 9.5 Hz, 1 H), 5.75 (ddd, ³J = 17.1 Hz, 10.1 Hz, 9.5 Hz, 1 H)

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 12.5 (d), 18.1 (q), 18.1 (q), 21.0 (q), 48.8(d), 55.9 (d), 67.7 (t), 80.5 (d), 81.3 (d), 87.1(d), 90.5 (d), 120.2 (t), 120.9 (t), 130.0 (d), 133.3 (d), 169.9 (s), 173.5 (s), 178.8 (s).

Methanesulfonic acid-2,4-divinyl-6-oxabicyclo[3.1.0]hex-3-yl-ester



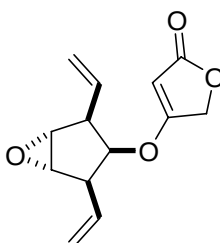
152 mg (1.00 mmol) 2,4-divinyl-6-oxabicyclo[3.1.0]hexan-3-ol (**5**) were dissolved in 12 ml of dichloromethane and charged with 223 µl (1.60 mmol) triethylamine. Then the solution was cooled to 0 °C and 108 µl (1.40 mmol) methanesulfonyl chloride were slowly added to the stirred solution. After 4 h the reaction mixture was quenched with 20 ml of water and extracted three times with

20 ml of dichloromethane each. The organic layers were combined, washed with 20 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 6/1) to yield 193 mg (0.84mmol, 84%) methanesulfonic acid-2,4-divinyl-6-oxabicyclo[3.1.0]hex-3-yl-ester as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 3.01 (s, 3 H), 3.18 (d, ³J = 7.7 Hz, 2 H), 3.59 (s, 2 H), 4.77 (s, 1 H), 5.23 (d, ³J = 10.6 Hz, 2 H), 5.29 (d, ³J = 17.6 Hz, 2 H), 5.72 (ddd, ³J = 17.6 Hz, 10.6 Hz, 7.7 Hz, 2 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 38.8 (q), 51.2 (d), 60.1 (d), 87.9 (d), 119.0 (t), 133.4 (d).

4'-(2,4-Divinyl-6-oxabicyclo[3.1.0]hex-3-yloxy)-5'H-furanone (7)

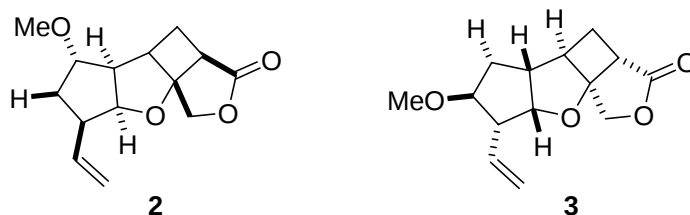


115 mg (0.50 mmol) methanesulfonic acid 3-triisopropylsilanyloxy-2,5-divinylcyclopentylester were dissolved in 7 ml of DMF. 345 mg (2.50 mmol) potassium tetronate and 132 mg (0.50 mmol) 18-crown-6 were added and the mixture was stirred for 3 d at 110 °C. After this the reaction mixture was quenched with 40 ml of water and extracted three times with 15 ml of ethyl acetate each. The organic layers were combined, washed with 40 ml of saturated aqueous NaCl solution and dried with Na₂SO₄. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et₂O = 1/1) to yield 16 mg (0.07 mmol, 14%) 4-(2,4-divinyl-6-oxabicyclo[3.1.0]hex-3-yloxy)-5H-furanone (7) as a colourless liquid.

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 3.41 (dd, ³J = 8.1 Hz, 8.0 Hz, 2 H), 3.57 (s, 2 H), 4.50 (t, ³J = 8.0 Hz, 1 H), 4.55 (d, ⁴J = 1.1 Hz, 2 H), 5.09 (d, ⁴J = 1.1 Hz, 1 H), 5.22-5.28 (m, 4 H), 5.69 (ddd, ³J = 17.2 Hz, 10.4 Hz, 8.1 Hz, 2 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 45.6 (d), 58.4(d), 67.9 (t), 82.0 (d), 90.6 (d), 120.5 (t), 131.3 (t), 173.3 (s), 178.2 (s).

2,12-Dioxa-4-vinyl-5/6-methoxy-tetracyclo[6.5.0.0^{1,10}.0^{3,7}]tridecan-11-one



2:

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.75 (ddd, ³J = 13.6 Hz, 12.3 Hz, 5.8 Hz, 1 H), 1.88 (ddd, ³J = 13.6 Hz, 6.6 Hz, 0.1 Hz, 1 H), 2.14 (ddd, ³J = 13.2 Hz, 10.4 Hz, 5.4 Hz, 1 H), 2.31 (ddd, ³J = 13.2 Hz, 8.3 Hz, 4.6 Hz, 1 H), 2.51-2.55 (m, 1 H), 2.86-2.93 (m, 2 H), 3.00 (ddd, ³J = 10.4 Hz, 4.6 Hz, 1.3 Hz, 1 H), 3.27 (s, 3 H), 3.46-3.50 (m, 1 H), 4.31 (s, 1 H), 4.31 (s, 1 H), 4.54 (dd, ³J = 4.7 Hz, 4.7 Hz, 1 H), 5.09-5.17 (m, 2 H), 5.91 (ddd, ³J = 17.5 Hz, 10.2 Hz, 7.4 Hz, 1 H).

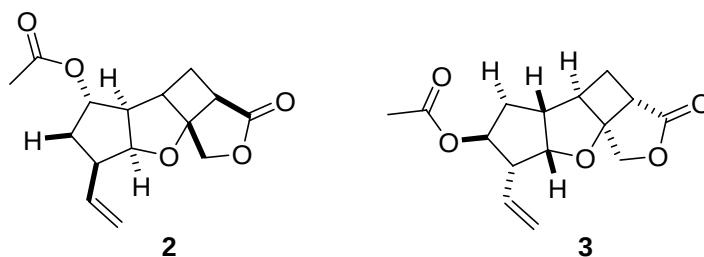
¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 26.5 (t), 34.9 (t), 40.4 (d), 47.0 (d), 48.7(d), 56.9 (d), 59.3 (d), 73.0 (t), 88.2 (d), 88.6 (d), 89.7(d), 115.6 (t), 137.1 (d), 178.1 (s).

3 :

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.73 (ddd, ³J = 13.8 Hz, 7.5 Hz, 6.0 Hz, 1 H), 1.88 (ddd, ³J = 13.8 Hz, 10.7 Hz, 6.4 Hz, 1 H), 2.07 (ddd, ³J = 13.0 Hz, 10.4 Hz, 5.8 Hz, 1 H), 2.24 (ddd, ³J = 13.0 Hz, 8.1 Hz, 4.4 Hz, 1 H), 2.59-2.70 (m, 2 H), 2.81 (dd, ³J = 8.1 Hz, 5.8 Hz, 1 H), 2.98 (ddd, ³J = 10.4 Hz, 4.4 Hz, 1.3 Hz, 1 H), 3.31 (s, 3 H), 3.77 (virt. q, ³J ≅ 7.0 Hz, 1 H), 4.33 (d, ²J = 9.7 Hz, 1 H), 4.37 (d, ²J = 9.7 Hz, 1 H), 4.66 (t, ³J = 4.3 Hz, 1 H), 5.16-5.30 (m, 2 H), 5.96 (ddd, ³J = 17.3 Hz, 10.3 Hz, 8.4 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 25.7 (t), 37.1 (t), 40.2 (d), 47.5 (d), 49.9(d), 55.1 (d), 57.9 (d), 72.8 (t), 84.9 (d), 88.0 (d), 89.0(d), 117.6 (t), 135.9 (d), 177.9 (s).

2,12-Dioxa-4-vinyl-5/6-acetoxy-tetracyclo[6.5.0.0^{1,10}.0^{3,7}]tridecan-11-one



2:

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.83 (ddd, ³J = 14.2 Hz, 6.7 Hz, 1.0 Hz, 1 H), 1.90-2.10 (m, 2 H), 2.04 (s, 3 H), 2.05-2.14 (m, 1 H), 2.32 (ddd, ³J = 13.1 Hz, 8.4 Hz, 4.5 Hz, 1 H), 2.52 (d, ³J = 4.5 Hz, 1 H), 2.88-2.96 (m, 1 H), 3.00 (ddd, ³J = 10.5 Hz, 4.5 Hz, 1.3 Hz, 1 H), 3.06-3.11 (m, 1 H), 4.30 (d, ³J = 9.7 Hz, 1 H), 4.34 (d, ³J = 9.7 Hz, 1 H), 4.75 (t, ³J = 4.6 Hz, 1 H), 4.80 (dd, ³J = 5.8 Hz, 1.0 Hz, 1 H), 5.10-5.20 (m, 2 H), 5.91 (ddd, ³J = 17.5 Hz, 10.4 Hz, 7.4 Hz, 1 H).

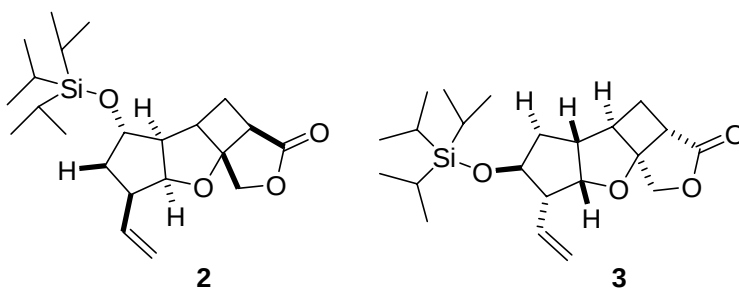
¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 21.3 (q), 26.1 (t), 35.6 (t), 40.1 (d), 47.0 (d), 48.0(d), 59.5 (d), 72.6 (t), 80.9 (d), 88.3 (d), 89.1 (d), 116.7 (t), 136.2 (d), 170.7 (s), 177.7 (s).

3 :

¹H-NMR : (360 MHz, CDCl₃): δ [ppm] = 1.86-2.12 (m, 6 H), 2.25 (ddd, ³J = 13.2 Hz, 8.0 Hz, 4.5 Hz, 1 H), 2.65-2.76 (m, 2 H), 2.83 (dd, ³J = 8.0 Hz, 6.0 Hz, 1 H), 2.99 (ddd, ³J = 10.4 Hz, 4.4 Hz, 1.2 Hz, 1 H), 4.33 (d, ²J = 10.2 Hz, 1 H), 4.31 (d, ²J = 10.2 Hz, 1 H), 4.68 (t, ³J = 4.4 Hz, 1 H), 5.04-5.12 (m, 1 H), 5.12-5.23 (m, 2 H), 5.91 (ddd, ³J = 17.3 Hz, 10.3 Hz, 8.2 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 21.2 (q), 25.6 (t), 37.3 (t), 40.2 (d), 47.5 (d), 49.9(d), 54.0 (d), 72.8 (t), 77.3 (d), 88.0 (d), 88.2 (d), 118.2 (t), 134.4 (d), 170.9 (s), 177.8 (s).

2,12-Dioxa-4-vinyl-5/6-triisopropylsilanyloxy-tetracyclo[6.5.0.0^{1,10}.0^{3,7}]tridecan-11-one



2:

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.00-1.06 (m, 21 H), 1.69-1.85 (m, 2 H), 2.12 (ddd, ³J = 13.1 Hz, 10.4 Hz, 5.3 Hz, 1 H), 2.30 (ddd, ³J = 13.1 Hz, 8.3 Hz, 4.6 Hz, 1 H), 2.55 (d, ³J = 4.8 Hz, 1 H), 2.83-2.89 (m, 1 H), 2.96-3.04 (m, 2 H), 4.04 (d, ³J = 4.8 Hz), 4.30 (s, 1 H), 4.30 (s, 1 H), 4.80 (t, ³J = 4.8 Hz, 1 H), 5.09-5.21 (m, 2 H), 5.92 (ddd, ³J = 17.6 Hz, 10.3 Hz, 7.5 Hz, 1 H).

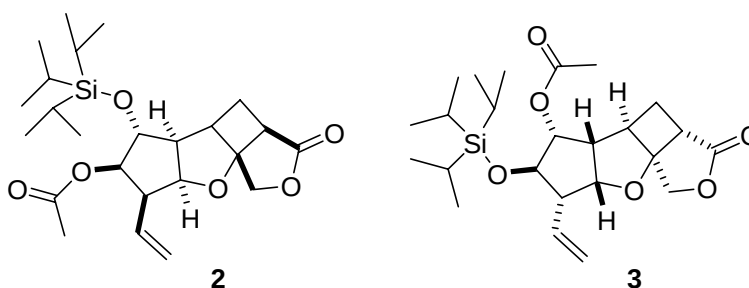
^{13}C -NMR: (90.6 MHz, CDCl_3): δ [ppm] = 12.2 (d), 18.1 (q), 18.2 (q), 26.3 (t), 29.8 (t), 39.2 (d), 40.2 (d), 46.7(d), 48.2 (d), 63.4 (d), 72.9 (t), 79.3 (d), 88.3 (d), 116.1 (t), 137.1 (d), 177.9 (s).

3 :

^1H -NMR: (360 MHz, CDCl_3): δ [ppm] = 0.97-1.10 (m, 21 H), 1.65 (ddd, $^3J = 13.4$ Hz, 7.0 Hz, 6.0 Hz, 1 H), 1.89 (ddd, $^3J = 13.4$ Hz, 10.5 Hz, 6.0 Hz, 1 H), 2.05 (ddd, $^3J = 13.3$ Hz, 10.5 Hz, 5.8 Hz, 1 H), 2.21 (ddd, $^3J = 13.3$ Hz, 7.0 Hz, 4.4 Hz, 1 H), 2.50-2.56 (m, 1 H), 2.65 (ddd, $^3J = 10.5$ Hz, 7.0 Hz, 5.8 Hz, 1 H), 2.73-2.77 (m, 1 H), 2.90 (ddd, $^3J = 10.5$ Hz, 4.4 Hz, 1.3 Hz, 1 H), 4.21 (virt. q, $^3J \cong 4.7$ Hz), 4.29 (s, 1 H), 4.29 (s, 1 H), 4.65 (dd, $^3J = 4.7$ Hz, 4.7 Hz, 1 H), 5.10-5.20 (m, 2 H), 5.84 (ddd, $^3J = 17.3$ Hz, 10.2 Hz, 9.1 Hz, 1 H).

^{13}C -NMR: (90.6 MHz, CDCl_3): δ [ppm] = 12.4 (d), 18.2 (q), 18.2 (q), 25.9 (t), 29.8 (t), 40.2 (d), 41.2 (d), 47.7(d), 49.8 (d), 58.1 (d), 72.9 (t), 88.1 (d), 89.0 (d), 118.0 (t), 135.9 (d), 178.0 (s).

2,12-Dioxa-4-vinyl-5/6-acetoxy-5/6-triisopropylsilanyloxy-tetracyclo[6.5.0.0^{1,10}.0^{3,7}]tridecan-11-one



2 :

^1H -NMR: (360 MHz, CDCl_3): δ [ppm] = 1.00-1.10 (m, 21 H), 2.13 (s, 3 H), 2.16 (ddd, $^3J = 13.3$ Hz, 10.3 Hz, 5.2 Hz, 1 H), 2.34 (ddd, $^3J = 13.3$ Hz, 8.2 Hz, 4.7 Hz, 1 H), 2.64-2.67 (m, 1 H), 2.91-2.97 (m, 1 H), 3.01 (ddd, $^3J = 10.3$ Hz, 4.7 Hz, 1.3 Hz, 1 H), 3.08 (ddd, $^3J = 8.9$ Hz, 5.4 Hz, 5.3 Hz, 1 H), 4.03 (dd, $^3J = 2.0$ Hz, 2.0 Hz, 1 H), 4.35 (d, $^3J = 9.9$ Hz, 1 H), 4.35 (d, $^3J = 9.9$ Hz, 1 H), 4.94 (dd, $^3J = 5.7$ Hz, 5.4 Hz, 1 H), 5.06 (dd, $^3J = 5.4$ Hz, 2.0 Hz, 1 H), 5.20 (dd, $^3J = 10.1$ Hz, 1.6 Hz, 1 H), 5.25 (d, $^3J = 17.4$ Hz, 1 H), 5.82 (ddd, $^3J = 17.4$ Hz, 10.1 Hz, 8.9 Hz, 1 H).

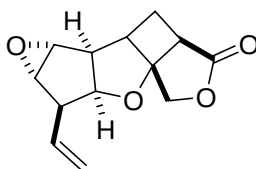
¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 12.2 (d), 18.0 (q), 18.1 (q), 21.1 (q), 26.7 (t), 40.2 (d), 47.8 (d), 49.6(d), 61.7 (d), 73.4 (t), 82.3 (d), 83.2 (d), 88.7 (d), 89.6 (d), 118.9 (t), 132.0 (d), 169.7 (s), 177.7 (s).

3:

¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 1.00-1.10 (m, 21 H), 2.08-2.13 (m, 3 H), 2.29 (ddd, ³J = 13.0 Hz, 8.0 Hz, 4.1 Hz, 1 H), 2.57 (ddd, ³J = 9.1 Hz, 9.3 Hz, 4.3 Hz, 1 H), 2.77 (dd, ³J = 8.0 Hz, 7.3 Hz, 1 H), 2.96 (dd, ³J = 9.3 Hz, 4.8 Hz, 1 H), 3.00 (ddd, ³J = 10.3 Hz, 4.1 Hz, 0.8 Hz, 1 H), 4.25 (dd, ³J = 9.1 Hz, 6.6 Hz, 1 H), 4.28 (d, ²J = 9.7 Hz, 1 H), 4.31 (d, ²J = 9.7 Hz, 1 H), 4.76 (dd, ³J = 4.8 Hz, 4.3 Hz, 1 H), 4.88 (dd, ³J = 9.1 Hz, 6.5 Hz, 1 H), 5.24 (d, ³J = 9.9 Hz, 1 H), 5.28 (d, ³J = 17.5 Hz, 1 H), 5.92 (ddd, ³J = 17.5 Hz, 9.9 Hz, 9.3 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 12.6 (d), 18.1 (q), 18.2 (q), 21.0 (q), 25.6 (t), 40.1 (d), 43.3 (d), 49.6(d), 53.1 (d), 72.1 (t), 79.5 (d), 80.4 (d), 80.7 (d), 87.7 (d), 88.5 (d), 119.2 (t), 134.9 (d), 170.3 (s), 177.6 (s).

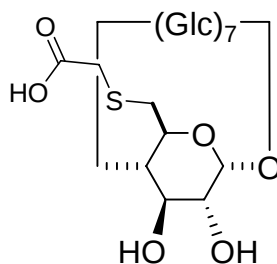
2,6,13-Trioxa-4-vinyl-pentacyclo[7.5.0.0^{1,11}.0^{3,8}.0^{5,7}]tetradecan-12-one (8)



¹H-NMR: (360 MHz, CDCl₃): δ [ppm] = 2.15 (ddd, ³J = 13.4 Hz, 10.4 Hz, 5.0 Hz, 1 H), 2.30 (ddd, ³J = 13.4 Hz, 8.3 Hz, 5.1 Hz, 1 H), 2.80 (dd, ³J = 8.4 Hz, 5.3 Hz, 1 H), 2.86 2.90 (m, 1 H), 2.93 (dd, ³J = 8.3 Hz, 5.0 Hz, 1 H), 3.02 (ddd, ³J = 10.4 Hz, 5.1 Hz, 1.3 Hz, 1 H), 3.38 (dd, ³J = 2.2 Hz, 0.9 Hz, 1 H), 3.47 (dd, ³J = 2.2 Hz, 0.9 Hz, 1 H), 4.35 (d, ²J = 10.4 Hz, 1 H), 4.41 (d, ²J = 10.4 Hz, 1 H), 4.71-4.74 (m, 1 H), 5.21-5.27 (m, 2 H), 5.74 (ddd, ³J = 17.3 Hz, 10.7 Hz, 8.4 Hz, 1 H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ [ppm] = 25.7 (t), 40.3 (d), 44.6 (d), 49.0 (d), 54.7(d), 61.7 (d), 62.3 (d), 73.4 (t), 88.6 (d), 91.7 (d), 118.4 (t), 133.4 (d), 177.3 (s).

6^A-(thioacetic acid)-6^A-deoxy-γ-cyclodextrin.



106 mg sodium carbonate (1.00 mmol) were dissolved in 3 ml of H₂O and added dropwise with stirring to a solution of 290 mg (0.20 mmol) 6^A-O-tosyl-γ-cyclodextrin¹ and 46.0 mg (0.50 mmol) thioacetic acid (46 mg, 0.5 mmol) in 20 ml of DMF. The resulting mixture was stirred at 70 °C for 2 d. After the reaction mixture had been allowed to cool down to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in 10 ml of H₂O, adjusted to neutral pH with 0.5M HCl, and applied to a reversed-phase chromatography with a gradient elution from 5% to 40% aqueous EtOH. The fraction containing sodium salt of the titled compound was concentrated and recrystallized from acetone/2M HCl (3:1) to give 124 mg (0.09 mmol) 6^A-(thioacetic acid)-6^A-deoxy-γ-cyclodextrin as a colourless solid.

¹H NMR (400 MHz, D₂O): δ [ppm] = 5.08 (d, ³J = 3.6 Hz, 1 H), 5.03-4.99 (m, 6 H), 4.97 (d, ³J = 3.6 Hz, 1 H), 4.57 (m, 1 H), 3.97-3.76 (m, 24 H), 3.66-3.49 (m, 18 H), 3.09-3.04 (m, 3 H), 3.08-3.05 (m, 2 H), 2.86-2.82 (m, 2 H).

¹³C NMR (100 MHz, D₂O): δ [ppm] = 174.3, 101.5, 101.3, 100.8, 99.5, 99.3, 95.6, 91.6, 82.8, 81.2, 76.9, 75.8, 75.6, 74.2, 72.8, 72.7, 72.5, 72.0, 71.4, 71.2, 71.0, 70.7, 70.3, 69.6, 69.3, 60.5, 60.4, 60.1, 59.9, 34.7, 33.5.

¹ K. Fujita, T. Tahara, T. Koga, T. Imoto, *Bull. Chem. Soc. Jpn.* **1989**, 62, 3150;

Photolysis under high pressure. Irradiations under high pressure were performed in a pressure vessel which was equipped with three sapphire windows for irradiation and was connected to a pump (the whole system was designed and manufactured by Teramex Co., Kyoto). A 0.15-mL quartz cuvette (light path 0.2 cm) filled with a sample solution was placed in the high-pressure vessel, which was maintained at a constant temperature by circulating a 1:1 mixture of water and ethylene glycol through the reactor body. The pressure was applied with a plunger pump and its magnitude was measured by a pressure gauge. The sample solution was irradiated at 254 nm through one of the sapphire windows using an Asahi Spectra LAX 101/102 light source.