Supporting Information

Locked π-Expanded Chlorins in Two Steps from Simple Tetraarylporphyrins

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NMR spectra were run in $CDCl_3$ or $C_2D_2Cl_4$ (at 50 to 85 °C) to avoid peak broadening. All compounds were analyzed by HRMS (Bruker MicroTOFF).

Nickel ketone Ni-4 from porphyrin Ni-2

A solution of nickel porphyrin **Ni-2** (0.6 g; 0.67 mmol) and benzoic anhydride (3 g; 13.3 mmol) in chlorobenzene (30 ml) was heated to 65 °C. Tin tetrachloride (1 mL; 8.8 mmol) was added at once and the reaction followed by TLC. As soon as the starting material was consumed (*ca* 15-20 min) the reaction mixture was added to a solution of sodium hydroxide (10 g) in water (100 mL) and stirred vigorously for 15 min. The organic phase was separated, diluted with CH_2Cl_2 (100 mL), washed with water (3 x 500 mL), and dried over Na_2SO_4. The solution was partially evaporated (to keep chlorobenzene). After addition of chloranil (1.2 g; 5 mmol) and $TsOH.H_2O$ (0.1 g), it was stirred at 25°C for 3 h. The solvent was evaporated and the residue chromatographed over silica gel (1 L; eluent gradient from cyclohexane + toluene 1:1 to pure toluene) gave ketone **Ni-4** as dark green needles from CH_2Cl_2 - MeOH (538 mg; 80.5%).
^{1}H NMR ($CDCl_3$): 8.91 and 8.55 (2d, 1+1 H, *J* = 5.1 Hz; pyrrole); 8.17 and 7.89 (2d, 1+1 H, *J* = 5.1 Hz; pyrrole); 8.11 and 8.03 (2d, 1+1 H, *J* = 4.8 Hz; pyrrole); 8.39 (d, 1 H, *J* = 7.5 Hz, cyclized phenyl); 7.85 (dd, 1 H, *J* = 7.5 and 2 Hz, cyclized phenyl); 7.85-7.45 (m, 18 H, all non-cyclized phenyl + 1 H of cyclized phenyl); 1.52, 1.49, 1.43, 1.33 (4s, 9+9+9+9 H, *t*-butyl).
UV-vis. (CH_2Cl_2) λ_{max} = 414 nm (ε = 73000), 466 (35000), 494 (36000), 714 (20000).
HRMS: calcd for $C_{67}H_{62}N_4ONi+H^+$ 997.4350; found 997.4350.

Diester Ni-6 (R = Et) from ketone Ni-4

In order to react zinc powder had to be activated in 20% aqueous HCl for 40 sec, then washed with water, acetone, and anhydrous ethyl ether, and used immediately.

A suspension of activated zinc powder (311 mg; 4.76 mmol) in dry benzene was brought to ebullition. A solution of ketone **Ni-4** (308 mg; 0.31 mmol) and ethyl 2-bromoacetate (519 mg; 3.11 mmol) in dry benzene (25 mL) was then added over 20 min. After the addition, the solution was kept under reflux for an additional 4 h. After cooling to room temperature, the reaction mixture was treated with water (3 mL), followed by Na_2SO_4. The organic phase was decanted from the solid and evaporated. The residue was chromatographed over silica gel (400 mL; eluent

cyclohexane + CH_2Cl_2 2:1). A little starting material (14 mg) was recovered followed by diester **Ni-6** (R = Et) as green crystals from CH_2Cl_2 - MeOH (169 mg; 48%).
^{1}H NMR ($CDCl_3$): 8.77 and 8.47 (2d, 1+1 H, *J* = 4.8 Hz; pyrrole); 8.13 and 7.93 (2d, 1+1 H, *J* = 5.1 Hz, pyrrole); 8.02 (s, 2 H, pyrrole); 8.56 (d, 1 H, *J* = 8.4 Hz, cyclized phenyl); 7.76 (dd, 1 H, *J* = 8.4 and 2.1 Hz, cyclized phenyl); 7.44 (d, 1 H, *J* = 2.1 Hz, cyclized phenyl); 7.85 and 7.64, 7.76 and 7.58, 7.55 and 7.44 (3 AB, 4+4+4 H, *J* = 8.7 Hz, remaining *meso*-aryl); 7.66-7.55 (m, 5H, phenyl on 6-membered ring); 2.94-3.18 (m, 8 H, all CH_2); 1.52, 1.48, 1.40, 1.30 (4s, 9+9+9+9 H, *t*-butyl); -0.12 (t, 6 H, *J* = 7 Hz, CH_3).
UV-vis. (CH_2Cl_2) λ_{max} = 450 nm (ε = 80000), 614 (8000), 670 (14000).
HRMS: calcd for $C_{75}H_{76}N_4O_4Ni+H^+$ 1155.5293; found 1155.5271.

The corresponding methyl ester **Ni-6** (R = Me) was prepared in 40% yield following the same procedure, starting from ketone **Ni-4** and methyl bromoacetate.
^{1}H NMR ($CDCl_3$): 8.79 and 8.47 (2d, 1+1 H, *J* = 4.8 Hz; pyrrole); 8.13 and 7.91 (2d, 1+1 H, *J* = 5.1 Hz, pyrrole); 8.02 (s, 2 H, pyrrole); 8.55 (d, 1 H, *J* = 8.4 Hz, cyclized phenyl); 7.79 (dd, 1 H, *J* = 8.4 and 2.1 Hz, cyclized phenyl); 7.46 (d, 1 H, *J* = 2.1 Hz, cyclized phenyl); 7.85 and 7.64, 7.75 and 7.58, 7.55 and 7.44 (3 AB, 4+4+4 H, *J* = 8.7 Hz, remaining *meso*-aryl); 7.66-7.55 (m, 5H, phenyl on 6-membered ring); 3.07 and 2.94 (AB, 4 H, *J* = 16.2 Hz, CH_2); 2.57 (s, 6H, CH_3); 1.53, 1.49, 1.42, 1.32 (4s, 9+9+9+9 H, *t*-butyl).
UV-vis. (CH_2Cl_2) λ_{max} = 450 nm (ε = 84000), 616 (7900), 668 (14000).
HRMS: calcd for $C_{73}H_{72}N_4O_4Ni+H^+$ 1127.4980; found 1127.5023.

Palladium ketone Pd-4 from porphyrin Pd-2

A solution of palladium porphyrin **Pd-2** (0.6 g; 0.67 mmol) and benzoic anhydride (3 g; 13.3 mmol) in chlorobenzene (30 mL) was heated to 65°C. Tin tetrachloride (1 mL; 8.8 mmol) was added at once and the reaction followed by TLC. As soon as the starting material was consumed (*ca* 15-20 min), the reaction mixture was added to a solution of sodium hydroxide (10 g) in water (100 mL) and stirred vigorously for 15 min. The organic phase was separated, diluted with CH_2Cl_2 (100 mL), washed with water (3 x 500 mL), and dried over Na_2SO_4. The solution was partially evaporated (to keep chlorobenzene) and, after addition of chloranil (1.2 g; 5 mmol) and TsOH.H_2O (0.1 g), it was stirred overnight at 25 °C. The solvent was evaporated and the residue chromatographed over silica gel (1 L; eluent gradient from cyclohexane + toluene 1:1 to pure toluene) gave ketone **Pd-4** as dark green needles from CH_2Cl_2 - MeOH (528 mg; 79%).
^{1}H NMR ($CDCl_3$): 9.17 and 8.59 (2d, 1+1 H, *J* = 4.8 Hz, pyrrole); 8.30 and 8.25 (2d, 1+1 H, *J* = 4.8 Hz, pyrrole); 8.24 and 7.88 (2d, 1+1 H, *J* = 4.8 Hz, pyrrole); 8.80 (d, 1 H, *J* = 8.7 Hz, cyclized phenyl); 7.94 (dd, 1 H, *J* = 8.7 and 2.1 Hz, cyclized phenyl); 7.90 (d, 1 H, *J* = 2.1 Hz, cyclized phenyl); 7.97 and 7.72, 7.88 and 7.65, 7.58 and 7.54 (3 AB, 4+4+4H, remaining *meso* aryl), 7.74-7.55 (m, 5 H, phenyl on six-membered ring), 1.58, 1.53, 1.48, 1.38 (4s, 9+9+9+9 H, *t*-butyl).
UV-vis. (C_6H_6): λ_{max} = 412 nm (ε = 122000), 462 (48000), 488 (58000), 686 (40000).
HRMS: calcd for $C_{67}H_{62}N_4OPd+H^+$ 1045.4053; found 1045.4074.

Diester Pd-6 (R = Me) from ketone Pd-4

A suspension of activated zinc powder (608 mg; 9.3 mmol) in dry benzene (125 mL) was brought to reflux. A solution of ketone **Pd-4** (603 mg; 0.58 mmol) and methyl 2-bromoacetate (879 mg; 5.75 mmol) in dry benzene (125 mL) was then added dropwise over 25 min. After the addition the solution was kept under reflux for an additional 22 h. After cooling to room temperature, the mixture was treated with water (10 mL), followed by Na_2SO_4. The organic phase was decanted from the solid and evaporated. The residue was chromatographed over silica gel (600 mL; eluent gradient from cyclohexane + toluene 1:1 to 1:3). Starting material (124 mg, 20%) was revovered followed by diester **Pd-6** as blue-green crystals from MeOH-water 8:2 (160 mg; 24%).

^{1}H NMR (at 50 °C in deuterated 1,1,2,2-tetrachloroethane): 9.11 and 8.57 (2d, 1+1 H, *J* = 4.8 Hz, pyrrole); 8.22 and 7.66 (2d, 1+1 H, *J* = 5.1 Hz, pyrrole); 8.29 (broad s, 2 H, pyrrole); 8.95 (d, 1 H, *J* = 8.7 Hz, cyclized phenyl); 7.93 (dd, 1 H, *J* = 8.7 and 2.1 Hz, cyclized phenyl); 7.57 (d, 1 H, *J* = 2.1 Hz, cyclized phenyl); 8.02 and 7.74, 7.91 and 7.65, 7.75 and 7.52 (3 AB, 4+4+4 H, *J* ca 8 Hz, remaining *meso*-aryl); 7.76-7.51 (m, 5H, phenyl on 6-membered ring); 3.34 and 3.18 (AB, 2+2 H, *J* = 15.9 Hz, CH_2), 2.67 (s, 6H, methyl), 1.59, 1.54, 1.49, 1.38 (4s, 9+9+9+9 H, *t*-butyl).
UV-vis. (C_6H_6): λ_{max} = 448 nm (ε = 170000), 606 (15500), 648 (40000).
HRMS: calcd for $C_{73}H_{72}N_4O_4Pd+H^+$ 1175.4685; found 1175.4704.

Hydroxyester Ni-5

To a solution of lithium bistrimethylsilylamide in THF (10 mL; 1 M) cooled to -78 °C under argon was added dropwise AcOEt (1 mL). This solution was stirred for 15 min and a solution of ketone **Ni-4** (270 mg; 0.27 mM) in dry THF (5 mL) added dropwise over 5 min. The reaction mixture was stirred at -78 °C for 5 min, then quenched with 20% HCl (2 mL), let warm to 20 °C, diluted with water and CH_2Cl_2, washed with water (3x), and dried over Na_2SO_4. Only one spot was detectable on tlc. The product was crystallized from wet MeOH to give purple crystals (274 mg; 91%).
^{1}H NMR (at 85 °C in deuterated 1,1,2,2-tetrachloroethane): 8.59 (d, 1H, *J* = 8.9 Hz, cyclized phenyl); 8.51 and 8.19 (2d, 1+1H, *J* = 5 Hz); 8.09 and 8.07 (2d, 1+1H, *J* = 5.3 Hz, pyrrole); 7.9-7.5 (m, 21H, all remaining aryl H + 2 pyrrole H); 3.17 (broad s, 1H, OH), 3.03 and 2.96 (AB, 1+1H, J = 14.7 Hz, side-chain CH_2); 3.07-2.95 (m, 2H, ethyl CH_2); 1.58, 1.54, 1.48, 1.37 (4s, 9+9+9+9H, *t*-butyl); -0.03 (t, 3H, J = 6.9 Hz, ethyl CH_3).
UV-vis. (CH_2Cl_2): λ_{max} = 448 nm (ε = 90000), 620 (8500), 664 (15000); + TsOH.H_2O (0.1 g / 3 mL solution in CH_2Cl_2): λ_{max} = 407 nm (ε = 33000), 499 (21500), 720 (10000), 792 (9800), 875 (10600).
HRMS: calcd for $C_{71}H_{70}N_4O_3Ni+H^+$ 1085.4874; found 1085.4877.

Ketone free base H_2-4

Nickel ketone **Ni-4** (1 g; 1 mmol), dissolved in trifluoroacetic acid (50 mL), was treated with conc. H_2SO_4 (10 mL). After 1 h, the solution was poured into a mixture of CH_2Cl_2 (200 mL), water (200 mL) and ice (500 mL) and neutralized by careful addition of $NaHCO_3$. The organic

phase was then washed with water (3x) and dried over Na_2SO_4. The solvent was evaporated and the residue crystallized from CH_2Cl_2 + MeOH to give **H_2-4** as a green felt (896 mg; 95%).
^{1}H NMR: 9.20 and 8.55 (2d, 2H, J = 4.8 Hz, pyrrole); 8.40 and 8.07 (2d, 2H, J = 5.1 Hz, pyrrole); 8.34 and 8.31 (2d, 2H, J = 5.1 Hz, pyrrole); 8.98 (d, 1H, J = 9 Hz, cyclized phenyl); 7.96 (dd, 1H, J = 9 and 2.1 Hz, cyclized phenyl); 7.90 (d, 1H, J = 2.1 Hz, cyclized phenyl); 8.06 and 7.75, 7.96 and 7.68, 7.56 and 7.03 (AB, 4+4+4H, J = 8.4 Hz, remaining *meso*-aryl); 7.70-7.55 (m, 5H, phenyl on six-membered ring); 1.59, 1.54, 1.50, 1.39 (4s, 9+9+9+9H, *t*-butyl); 0.47 (broad s, 2H, NH). UV-vis. (C_6H_6): λ_{max} = 410 nm (ε = 115000), 424 (108000), 468 (56000), 510 (38000), 638 (16000), 688 (29000), 724 (26000).
HRMS: calcd for $C_{67}H_{64}N_4O+H^+$ 941.5153; found 941.5122.

Zinc ketone Zn-4

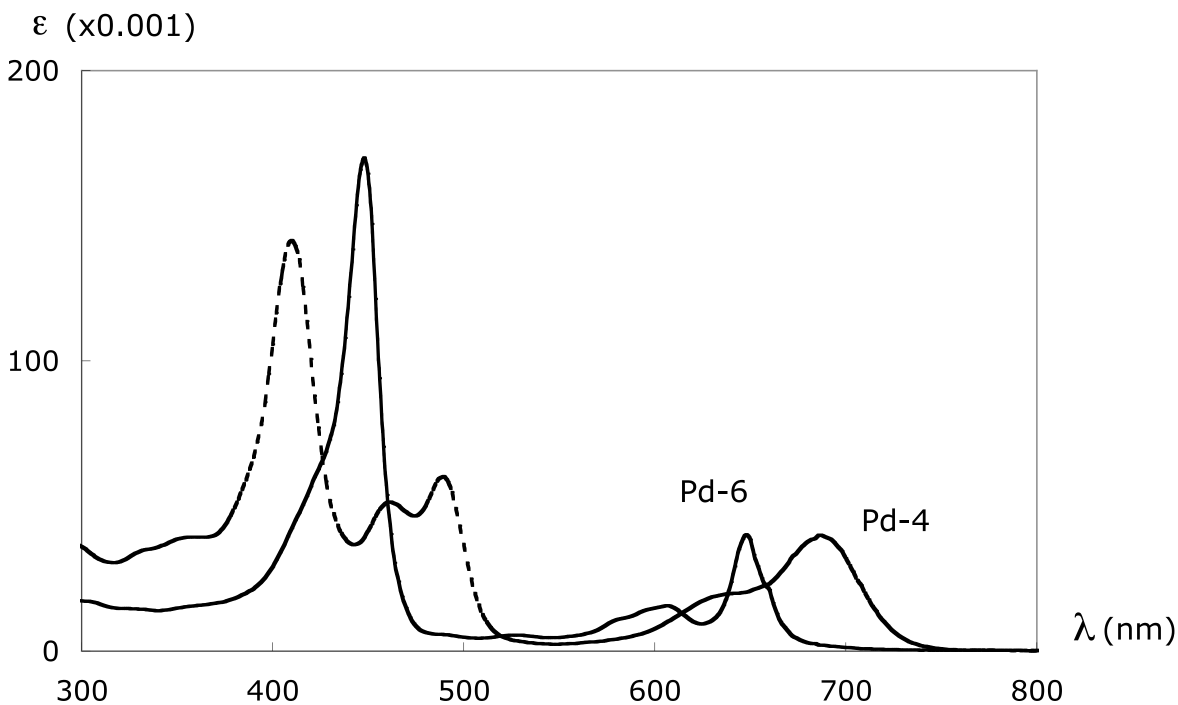
A solution of base **H_2-4** (192 mg; 0.19 mmol) in boiling CH_2Cl_2 was treated with $Zn(OAc)_2$ (500 mg) in MeOH (15 mL). After 15 min of reflux, the solution was washed with water (3x) an dried over Na_2SO_4. The solvent was evaporated and green **Zn-4** crystallized from CH_2Cl_2 - MeOH (168 mg; 87%).
^{1}H NMR: 9.12 and 8.51 (2d, 2H, J = 4.2 Hz, pyrrole); 8.25 and 7.83 (2d, 2H, J = 4.8 Hz, pyrrole); 8.24 (s, 2H, pyrrole); 8.87 (d, 1H, J = 8.7 Hz, cyclized phenyl); 7.92 (dd, 1H, J = 8.7 and 2.4 Hz, cyclized phenyl); 7.60 (d, 1H, J = 2.4 Hz, cyclized phenyl); 8.00 and 7.73, 7.90 and 7.65, 7.64 and 7.56 (AB, 4+4+4H, J = 8.1 Hz, remaining *meso*-aryl); 7.74-7.54 (m, 5H, phenyl on six-membered ring); 1.58, 1.53, 1.48, 1.38 (4s, 9+9+9+9H, *t*-butyl).
UV-vis. (C_6H_6): λ_{max} = 416 nm (ε = 109000), 478 (45000), 510 (sh., *ca* 35000), 660 (sh., *ca* 16000), 724 (32000).
HRMS: calcd for $C_{67}H_{62}N_4OZn+H^+$ 1003.4288; found 1003.4263.

Diester Zn-6 and base H_2-6

The Reformatsky reaction was run as for the nickel complexes (see above). However, to facilitate the isolation of the products, the crude reaction mixture was treated with conc. HCl (1 mL), neutralized (aq. $NaHCO_3$), washed with water (3x) and chromatographed (alumina, toluene, then silicagel, CH_2Cl_2). The base crystallized from wet MeOH (27 mg; 20%) and could also be metallated quantitatively to the zinc complex **Zn-6** (see above).
Zn-6. ^{1}H NMR (at 50°C in deuterated 1,1,2,2-tetrachloroethane): 9.06 and 8.48 (2d, 1+1 H, J = 4.5 Hz, pyrrole); 8.21 and 7.55 (2d, 1+1 H, J = 4.8 Hz, pyrrole); 8.26 and 8.17 (2d, 1+1 H, J = 4.5 Hz, pyrrole); 9.10 (d, 1 H, J = 8.7 Hz, cyclized phenyl); 7.92 (dd, 1 H, J = 8.7 and 2.1 Hz, cyclized phenyl); 7.59 (d, 1 H, J = 2.1 Hz, cyclized phenyl); 8.04 and 7.72, 7.90 and 7.62, 7.77 and 7.50 (3 AB, 4+4+4 H, J ca 8 Hz, remaining *meso*-aryl); 7.70-7.58 (m, 5H, phenyl on 6-membered ring); 3.36 and 3.19 (AB, 2+2 H, J = 16.8 Hz, CH_2), 2.71 (s, 6H, methyl), 1.59, 1.54, 1.49, 1.38 (4s, 9+9+9+9 H, *t*-butyl). UV-vis. (C_6H_6): λ_{max} = 346 nm (ε = 18500), 370 (19000), 452 (153000), 634 (15000), 670 (25000).
HRMS: calcd for $C_{73}H_{72}N_4O_4Zn$ 1132.4840; found 1132.4849 (this highly oxidizable compound was detected as its cation-radical).

H_2-6. ^{1}H NMR: 8.91 and 8.30 (2d, 1+1 H, *J* = 5.1 Hz, pyrrole); 8.18 and 7.69 (2d, 1+1 H, *J* = 5.1 Hz, pyrrole); 8.11 and 7.74 (2d, 1+1 H, *J* = 5.1 Hz, pyrrole); 9.21 (d, 1 H, *J* = 8.4 Hz, cyclized phenyl); 7.91 (dd, 1 H, *J* = 8.4 and 2.1 Hz, cyclized phenyl); 7.94 (d, 1 H, *J* = 2.1 Hz, cyclized phenyl); 8.10 and 7.72, 7.92 and 7.64, 7.80 and 7.51 (3 AB, 4+4+4 H, *J* ca 8 Hz, remaining *meso*-aryl); 7.70-7.55 (m, 5H, phenyl on 6-membered ring); 3.29 and 3.16 (AB, 2+2 H, *J* = 16.8 Hz, CH_2), 2.54 (s, 6H, methyl), 1.58, 1.53, 1.47, 1.37 (4s, 9+9+9+9 H, *t*-butyl); the NH signals were not detected, but small coupling (≤ 0.5 Hz) could be observed on the pyrrolic proton signals at 8.91 and 8.30 ppm. UV-vis. (C_6H_6): λ_{max} = 340 nm (ε = 20000), 444 (200000), 462 (91000), 564 (10000), 602 (18000), 632 (17000), 686 (27000).
HRMS: calcd for $C_{73}H_{74}N_4O_4$+H^+ 1071.5783; found 1071.5763.

UV-visible spectra of selected compounds



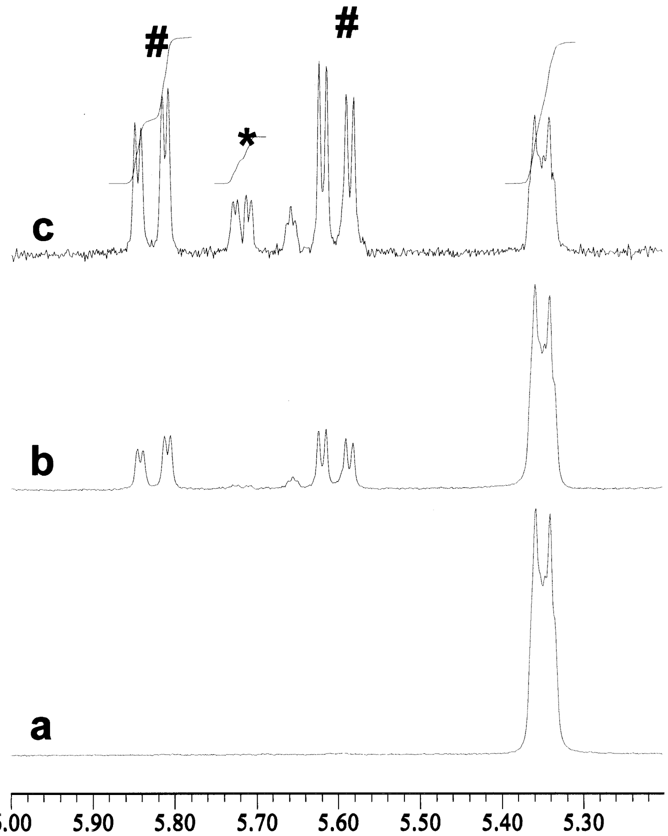
Cholesterol photooxidation

Experimental procedure:

A round bottomed flask containing a benzene (20 mL) solution of cholesterol (2×10^{-3} mol/L) and photosensitizer (10^{-5} mol/L) was placed in an aqueous bath of potassium dichromate used as light filter.

The electronic spectrum of the solution was recorded before and after irradiation and the absorbances compared in order to evaluate the stability of the photosensitizer. The concentration of potassium dichromate was adjusted in such a way that 1 cm of the solution transmitted less than 1% light at 510 nm. The solution was then irradiated with a 250 W slide projector bulb through 5 cm of the filter solution.

After a given period of time, an aliquot of the solution was taken, evaporated to dryness, dried under vacuum, redissolved in deuterated chloroform and analyzed by ^{1}H NMR. Typical NMR spectra (only the olefinic part is represented) recorded after irradiation with different photosensitizers are shown (a: **Ni-6** after 3 hours; b: **Pd-6** after 3 hours; c: **Pd-4** after 10 hours). Integration of the signals allowed to determine the respective amounts of remaining cholesterol and generated products. The olefinic proton of cholesterol was found at 5.35 ppm. The hydroperoxide **7**, the product of the initial ene reaction, gave two dd signals indicated by #. Isomerization of this primary product (see figure) gave an additional dd signal indicated by *, corresponding to the olefinic proton of **8**.


#
#
*
c
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a
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5.90
5.80
5.70
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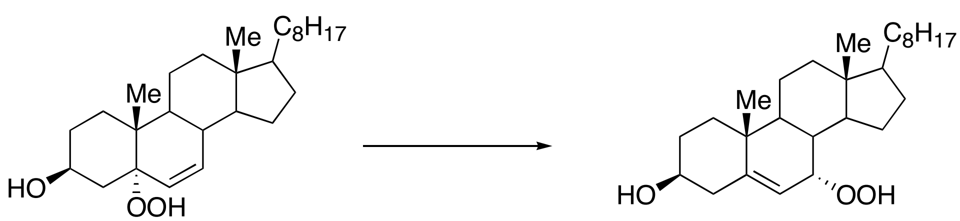
Me
C8H17
Me
HO
OOH
Me
C8H17
Me
HO
OOH

7 **8**