

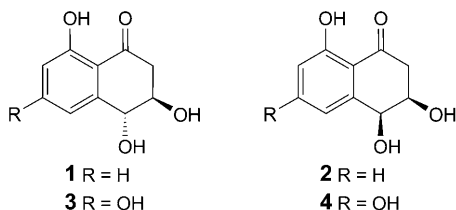
Stereoselective Synthesis of *cis*- and *trans*-3,4-Dihydro-3,4,8-trihydroxynaphthalen-1(2*H*)-one

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A short and efficient protocol for the stereoselective synthesis of racemic *trans*- and *cis*-3,4-dihydro-3,4,8-trihydroxynaphthalen-1(2*H*)-one (**1** and **2**, resp.), is described, comprising nine and eight steps starting from commercial juglone (= 5-hydroxynaphthalene-1,4-dione; **12**) (Scheme 4). Furthermore, an attempt to obtain **1** and **2** *via* phthalide annulation as the key step (Schemes 2 and 3) and a regioselective oxidation of the intermediate 1,2,3,4-tetrahydronaphthalene-1,2,4,5-tetrols **27** and **28** with activated MnO₂ were carried out (Scheme 4).

Introduction. – In our investigation on phytotoxic substances produced by *Ceratocystis fimbriata* sp. *coffea*, a fungus found in the canker of the coffee tree, we have reported the isolation and structure elucidation by spectroscopic methods of *trans*- and *cis*-3,4-dihydro-3,4,8-trihydroxynaphthalen-1(2*H*)-one (**1** and **2**, resp.) [1]. These natural polyhydroxylated α -tetralones (= 3,4-dihydronaphthalen-1(2*H*)-ones) are known as metabolites implicated in the branched pathway of fungal DHN-melanin biosynthesis [2–6]. Until now, only the natural (–)-*trans*-isomer has been isolated from six different fungal microorganisms [1][7–11]. In addition, the natural *cis*-isomer known also exclusively as the (–)-enantiomer has also been isolated from the mutagenic microorganism [12]. The control of the configuration of these natural products is achieved by a NADPH-dependent dehydrogenase, belonging to class B, *i.e.*, transferring the *pro-S* hydrogen from C(4) of the nicotinamide ring to the *Si* face of the naphthalenol substrate [4].



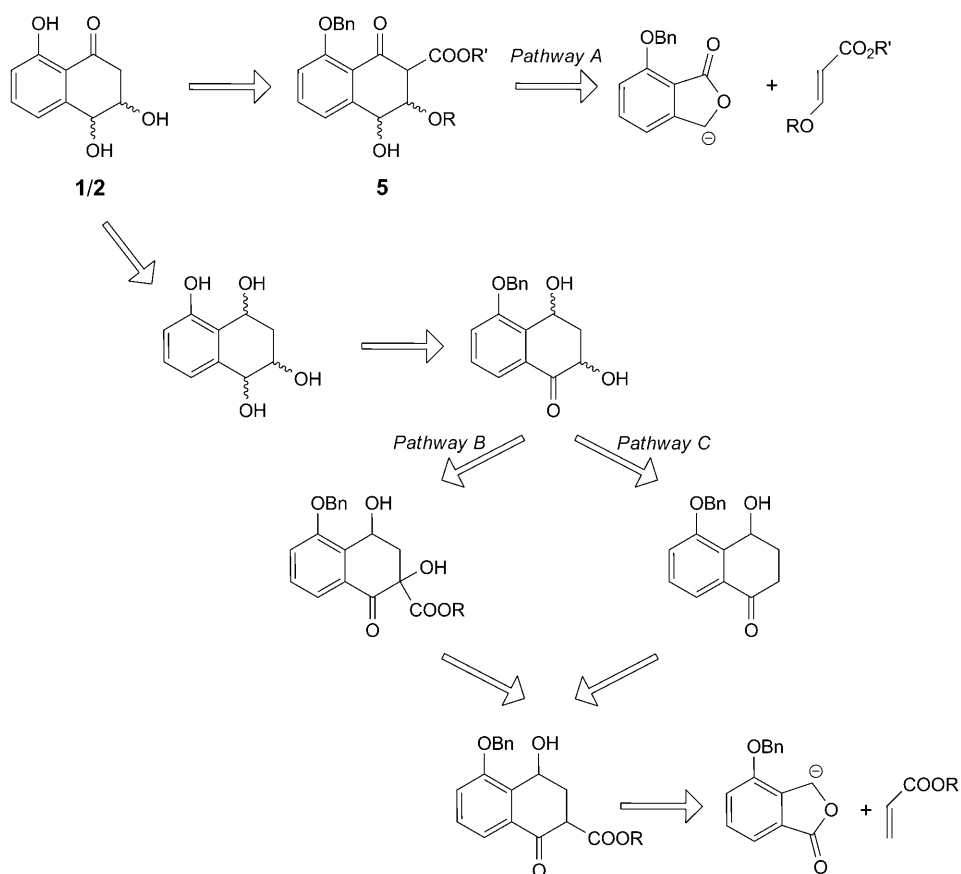
Our studies on the phytotoxicity of natural samples have shown that the metabolite **1** does not seem to develop necrosis in the cells of the coffee tree [13]. Furthermore, *Borgschulte* and co-workers have reported that **1** is toxic in contact with the leaves of

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the poplar tree [8]. At the same time, *Bürki et al.* [14] have established that the *trans*- and *cis*-4-hydroxycytalones (**3** and **4**, resp.) generate a partial toxicity in the leaves of the plane tree. The numerous contradictions encountered in various reports concerning the beneficial or the potential toxic effect of polyhydroxylated α -tetralone derivatives in contact with different vegetable species encouraged us to reexamine the biological activity of these compounds. In relation to this reexamination, we have now developed a stereoselective synthesis of **1** and **2**.

To synthesize the α -tetralones **1** and **2**, we decided to use the same protocol as in the synthesis of 3,4-dihydro-2,4,8-trihydroxynaphthalen-1(2*H*)-one [15]. This protocol involved the ring opening of a phthalide (= isobenzofuran-1(3*H*)-one). However, here, two alternatives could be considered. The first one involves the homologation of 7-(benzyloxy)phthalide in the presence of a *Michael* acceptor substituted by an alkoxy group in position 3 (*Pathway A* in *Scheme 1*). The second alternative is the ring opening of 4-(benzyloxy)phthalide with benzyl acrylate, followed by the introduction of the required additional OH group (*Pathway B*) or by direct decarboxylation and

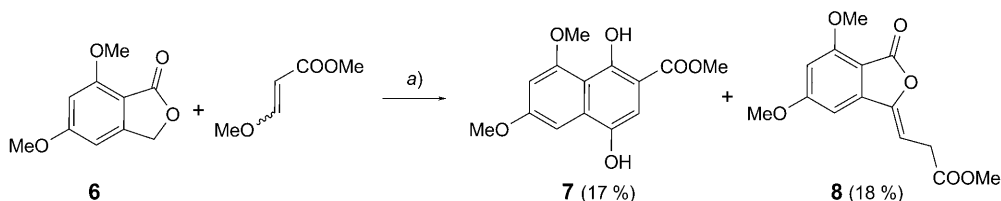
Scheme 1



subsequent oxidation (*Pathway C*). *Pathway A* could permit, *via* the direct formation of adduct **5**, followed by decarboxylation, a rapid access to **1** and **2**.

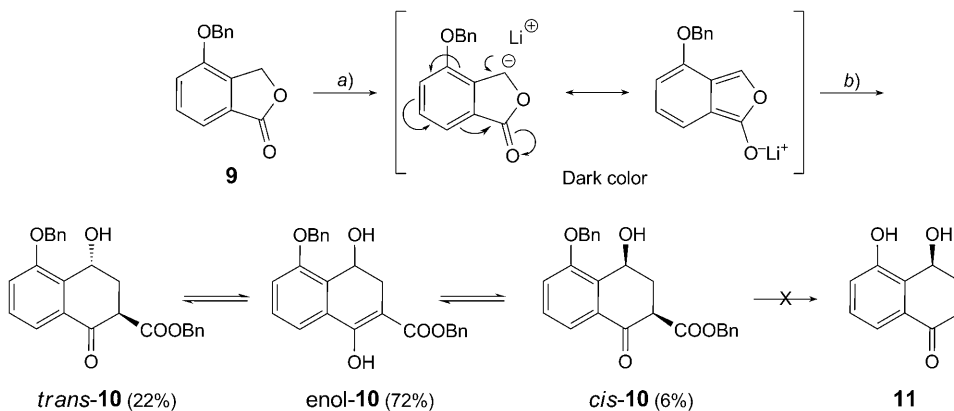
Results and Discussion. – The homologation reaction according to *Pathway A* was realized with 5,7-dimethoxyphthalide (**6**) and methyl 3-methoxyacrylate (= methyl 3-methoxyprop-2-enoate). However, several attempts under different conditions never yielded the desired compound but only the polysubstituted naphthalene-2-carboxylate **7** and the phthalide derivative **8** (*Scheme 2*).

Scheme 2. Ring Opening of 5,7-Dimethoxyphthalide (**6**) with Methyl 3-Methoxyacrylate (*Pathway A*)



a) **6** (1.0 equiv.), lithium diisopropylamide (LDA; 2.0 equiv.), MeOCH=CHCO₂Me (1.5 equiv.), THF, –40°; 35% (18% of **7** and 17% of **8**).

Analogously to the ring opening of 7-(benzyloxy)phthalide [15], 4-(benzyloxy)phthalide (**9**) underwent homologation in the presence of benzyl acrylate (*Pathway B* or *C*) (*Scheme 3*). Unlike the 7-(benzyloxy)phthalide ring opening, the addition of the first drops of lithium diisopropylamide (LDA) to **9** gave a strongly dark-colored mixture. It is likely that the relocation of the benzylic anion at the aromatic moiety produces a strong bathochromic effect. In contrast to 7-(benzyloxy)phthalide, one equiv. of LDA was enough to convert all 4-(benzyloxy)phthalide (**9**) into the β -keto ester **10** (*Scheme 3*). A ¹H-NMR experiment in CDCl₃ with intermediate **10** established that the ratio between the keto forms and the enol form was 6% of the *cis*-isomer, 72% of enol, and 22% of the *trans*-isomer. The attribution of the *cis*- and *trans*-isomers and the enol form is based on the following ¹H-NMR signals: δ (H) 2.54 (*ddd*, *J* = 3.5, 4.4, 14.2, ¹H–C(3)), 4.21 (*dd*, *J* = 4.3, 12.6, H–C(2)), and 5.41 (*t*, *J* = 3.5, H–C(4)) for the *trans*-isomer, δ (H) 3.66 (*dd*, *J* = 4.3, 12.6, H–C(2)) for the *cis*-isomer, and δ (H) 2.69 (*dd*, *J* = 5.4, 17.3, H_{ax}–C(3)) and 3.19 (*dd*, *J* = 2.6, 17.3, H_{eq}–C(3)) for the enol form. Furthermore, the huge amount of the enol form was easily deduced from the OH signal at δ (H) 12.42. Soon, we will report the results of some phthalide annulations depending on different substitutions at the aromatic moiety; the choice of the attribution of ¹H-NMR signals to the *cis*- and *trans*-isomers or the enol form will then be discussed. In contrast to the hydrogenolysis of benzyl (benzyloxy)-1,2,3,4-tetrahydro-4-hydroxy-1-oxonaphthalene-2-carboxylate in THF, which gave isosclerone (= 3,4-dihydro-4,8-dihydroxynaphthalen-1(2*H*)-one in 41% yield [15], the study of the direct decarboxylation of **10** under the same conditions afforded, after purification, sclerone (= 3,4-dihydro-4,5-dihydroxynaphthalen-1(2*H*)-one; **11**) in a poor yield (< 5%). Subsequently to this result, the study of *Pathway C* has been given up.

Scheme 3. Ring Opening of 4-(Benzyloxy)phthalide (**9**) (Pathway C)

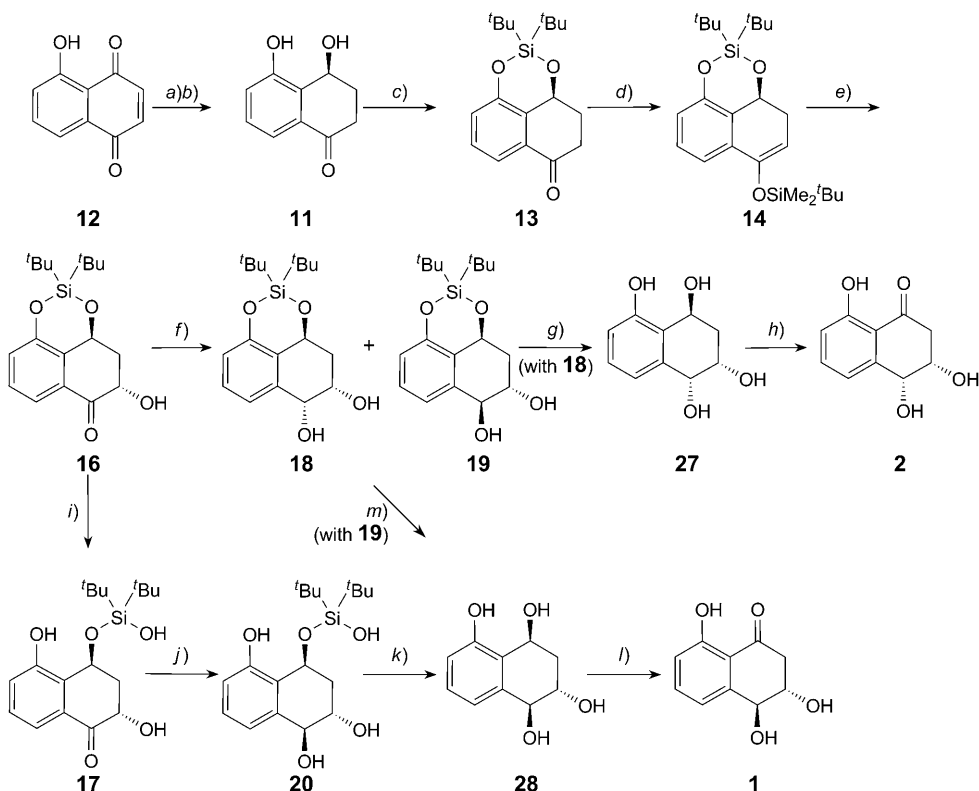
a) **9** (1.0 equiv.), LDA (1.0 equiv.), THF, -40° . b) $\text{H}_2\text{C}=\text{CHCO}_2\text{Bn}$ (1.5 equiv.), -10° , 1 h 30 min; 37% overall).

Like in the total synthesis of the 2,4,8-trihydroxy- α -tetralones [15], the metal enolate of **10** could be oxidized by treatment with an *N*-sulfonyloxaziridine and then could undergo a decarboxylation step (*Pathway B*) or follow the reverse procedure (*Pathway C*). However, the risk of epimerization at C(2) with exclusive formation of the *cis*-diastereoisomer during the hydrogenolysis in *Pathway B* did not encourage us to follow this method [15].

Consequently, **11** was prepared in two steps by reduction of juglone (=5-hydroxynaphthalene-1,4-dione; **12**) [16][17] (*Scheme 4*). To control the stereoselectivity during the subsequent reduction of the C=O group, we decided to use the di(*tert*-butyl)silylene protective group; thus, **11** was treated with di(*tert*-butyl)dichlorosilane at 80° in MeCN in the presence of Et_3N to give **13** in 83% yield. The reaction was completed in 48 h. With di(*tert*-butyl)silylene ditriflate ($(\text{CF}_3\text{SO}_3)_2\text{Si}^t\text{Bu}_2$) at room temperature, the reaction occurred in 3.5 h but gave a lower yield (51%). The benzylic O-atom at C(4) of compound **13** is in the equatorial conformation (naphthalene atom numbering). In the total synthesis of the 2,4,8-trihydroxy- α -tetralones [15], a keto group was transformed to a silyl enol ether by treatment with 3 equiv. of $^t\text{BuMe}_2\text{SiOTf}$ in the presence of Et_3N . Similarly, the sclerone derivative **13** gave silyl enol ether **14** in excellent yield with 1 equiv. of $^t\text{BuMe}_2\text{SiOTf}$ in the presence of 1.5 equiv. of Et_3N in 1,2-dichloroethane at room temperature after 20 min.

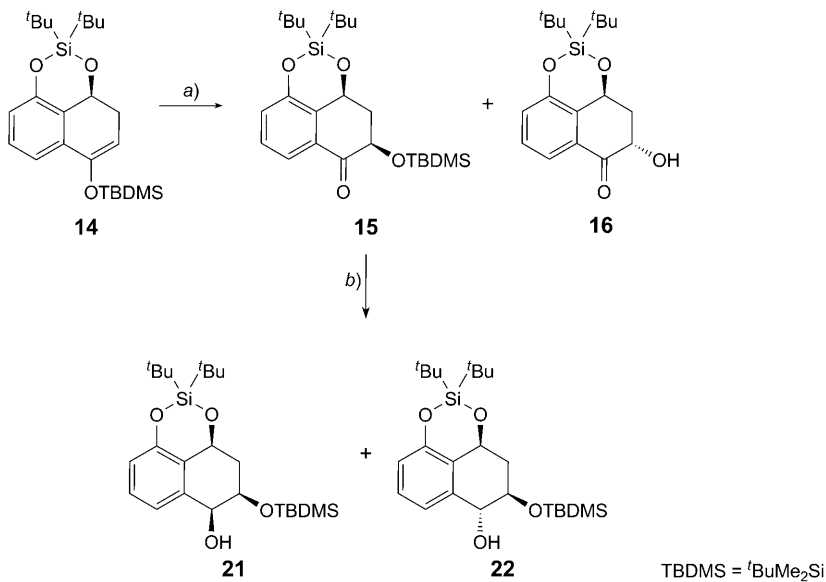
Intermediate **14** was subjected to oxidation with 3-chloroperbenzoic acid (*m*-CPBA) or with a catalytic amount of OsO_4 . When the oxidation of **14** was carried out with *m*-CPBA, the formation of compounds **15** and **16** in favor of the derivative **15** (de 10%) was observed (*Scheme 5*). During this oxidation, only the product **15** resulted from a rearrangement of the $^t\text{BuMe}_2\text{Si}$ group. This rearrangement allowed the easy separation of **15** and **16** by column chromatography. Thus, when the O-atom attack of *m*-CPBA on the C=C of the silyl enol ether moiety of **14** takes place *syn* to the $^t\text{Bu}_2\text{SiO}$ group at C(4), the epoxide-ring opening leads to a pseudo-equatorial conformation of the $^t\text{BuMe}_2\text{SiO}$ group at C(2) naphthalene atom numbering as for **13**. During this

Scheme 4. Total Synthesis of *trans*- and *cis*-3,4-Dihydro-3,4,8-trihydroxynaphthalen-1(2H)-ones (**1** and **2**, resp.)



a) SnCl_2 , 2 H_2O , 4M HCl, reflux, 1 h; 75%. b) NaBH_4 (0.6 equiv.), EtOH/ H_2O 99:1, r.t., 10 min; 43%. c) $\text{tBu}_2\text{SiCl}_2$ (1.1 equiv.), Et_3N (5.0 equiv.), HOBT (0.1 equiv.), MeCN, 80°, 48 h; 83%. d) $\text{tBuMe}_2\text{SiOTf}$ (1.0 equiv.), Et_3N (1.5 equiv.), 1,2-dichloroethane, r.t., 20 min; 92%. e) OsO_4 (2%), pyridine (cat.), $\text{K}_3[\text{Fe}(\text{CN})_6]$ (3.0 equiv.), K_2CO_3 (3.0 equiv.), MeSO_2NH_2 (1.0 equiv.), $\text{tBuOH}/\text{H}_2\text{O}$ 1:1, 0°, 20 h; 56%. f) NaBH_4 (1.0 equiv.), EtOH/ H_2O 99:1, r.t., 10 min; 82% (67% of **18** and 15% of **19**). g) HF·pyridine complex (3.0 equiv.) in HF, THF/pyridine 97:3, r.t., 25 min; 96%. h) Activated MnO_2 (9.0 equiv.), MeCl/MeOH 5:1, r.t., 24 h; 53%. i) Buffer soln. pH 10/THF 1:1, r.t., 3.5 h; 53%. j) NaBH_4 (1.0 equiv.), EtOH/ H_2O 99:1, r.t., 10 min; 76%. k) HF·pyridine complex (3.0 equiv.) in HF, THF/pyridine 97:3, r.t., 2.5 h; 57%. l) Activated MnO_2 (9.0 equiv.), $\text{CHCl}_3/\text{MeOH}$ 5:1, r.t., 24 h; 55%. m) HF·pyridine complex (3.0 equiv.) in HF, THF/pyridine 97:3, r.t., 25 min; 52%.

concerted process in which the cleavage of the Si–O bond would be simultaneous with the epoxide-ring opening, the OH group formed at C(2) is able to meet the tBuMe_2Si group and gives **15** (Fig. 1,a). On the other hand, when the attack of the O-atom of *m*-CPBA takes place *anti* to the tBu_2SiO group at C(4), the OH group formed at C(2), which is pushed in a pseudo-axial position, cannot meet the tBuMe_2Si group during epoxide-ring opening (Fig. 1,b).

Scheme 5. Oxidation of Silyl Enol Ether **14** with *m*-CPBA to give Racemic **21** and **22**

a) *m*-CPBA (1.0 equiv.), $\text{Cl}(\text{CH}_2)_2\text{Cl}$, -15° , then r.t. 1.5 h; 63% (35% of **15** and 28% of **16**). *b)* NaBH_4 (1.0 equiv.), EtOH/ H_2O 10:1, 10 min, r.t.; 71% (**21**/**22** 92:8).

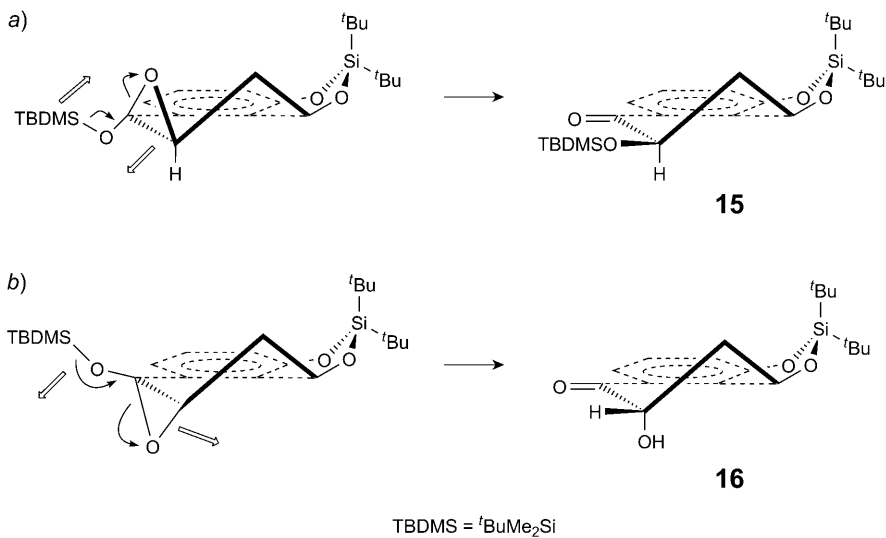


Fig. 1. Epoxide-ring opening to **15** and **16** (the \rightarrow represent the movement of each group formed during ring opening): *a)* The OH group formed at C(2) is able to meet the ${}^t\text{BuMe}_2\text{Si}$ group and triggers off the ${}^t\text{BuMe}_2\text{Si}$ rearrangement. *b)* The OH group formed at C(2) and the ${}^t\text{BuMe}_2\text{Si}$ group move away preventing ${}^t\text{BuMe}_2\text{Si}$ rearrangement (arbitrary atom numbering)

On oxidation with catalytic amounts of OsO₄, silyl enol ether **14** gave exclusively the *trans* compound **16** (Scheme 4). In this reaction, the control of the temperature is important to avoid formation of **17** in the basic medium. However, the ring opening of the dioxasilin of **16** in basic medium (\rightarrow **17**) is very useful for the control of the stereoselectivity in the subsequent reduction step. An X-ray study of intermediate **17** showed that OH–C(2) is in equatorial position, while the (hydroxysilyl)oxy group at C(4) is axial (Fig. 2), a conformation due to an intramolecular H-bond between the H-atom of the phenolic OH group and the O-atom of the hydroxysilyl group. Furthermore, the crystal packing of **17** (Fig. 3) shows that symmetry-related molecules are linked by H-bonding involving three OH groups (O(2), O(4), and O(5)); this forms a polymer extending in the *b* direction. On the other hand, in compound **16**, OH–C(2) is pseudo-axial, while the silyloxy moiety at C(4) is pseudo-equatorial. This difference of conformation between **16** and **17** was decisive during the reduction step which was

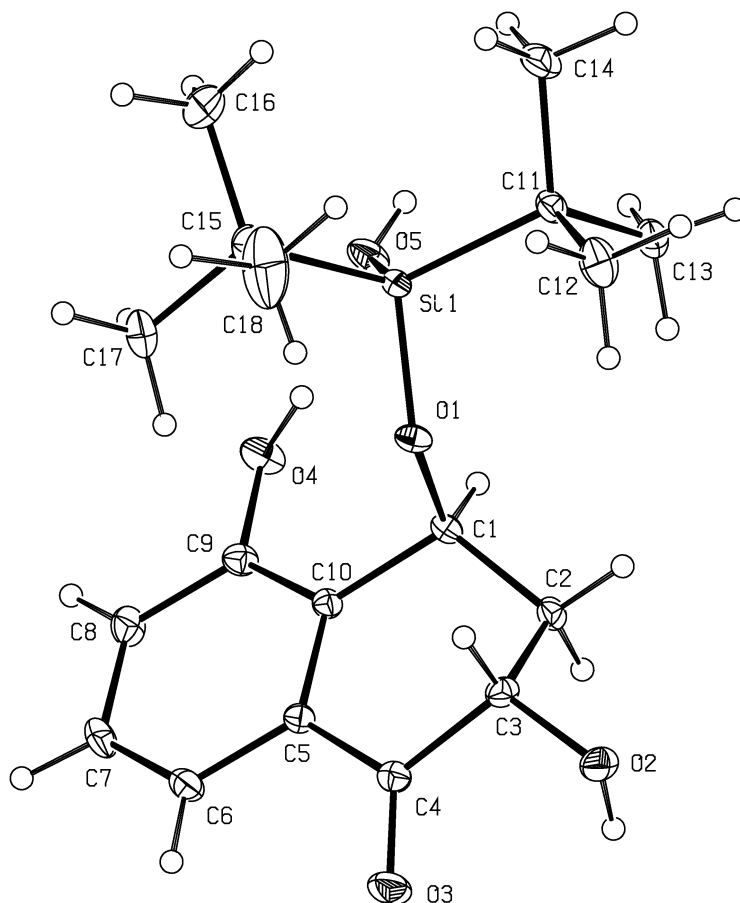


Fig. 2. View of the molecular structure of compound **17**. Thermal ellipsoids drawn at the 30% probability level; arbitrary atom numbering.

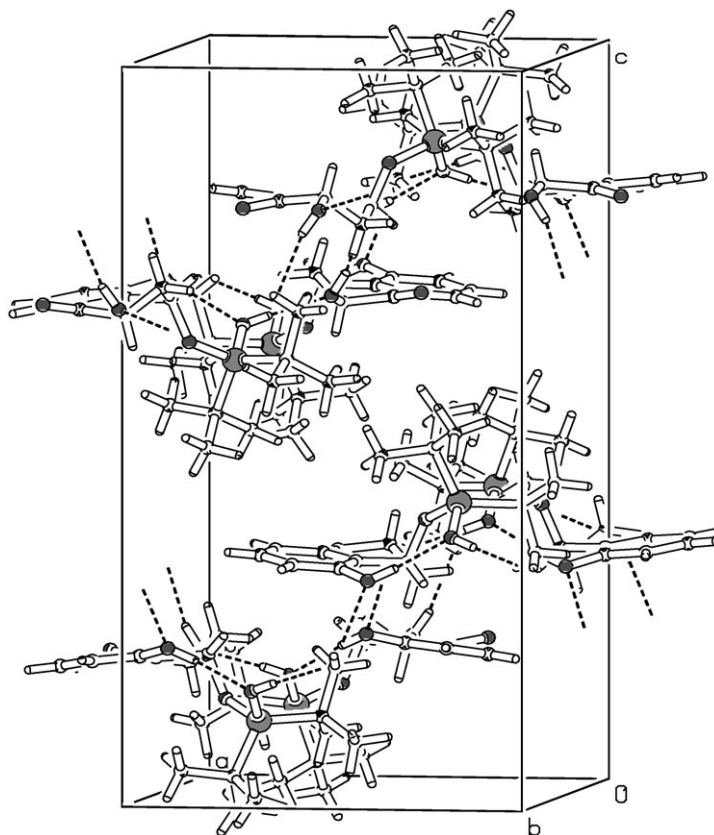


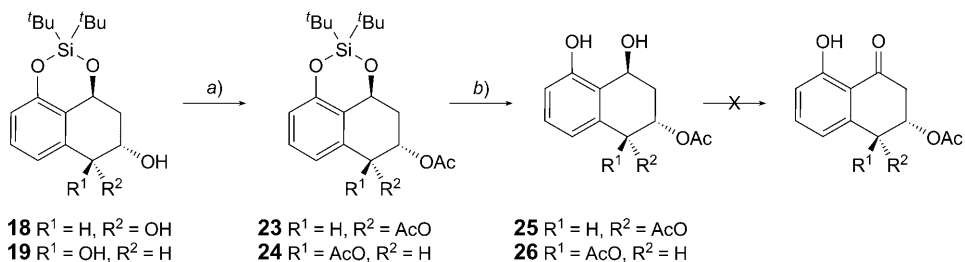
Fig. 3. Packing Structure of **17**

only studied with NaBH_4 in aqueous EtOH solution. Thus, reduction of **16** gave a mixture of the diastereoisomeric *cis*- and *trans*-1,2-diol **18** and **19**, respectively (*cis/trans* 79:21), which was separated by chromatography (silica gel), whereas reduction of **17** afforded *trans*-1,2-diol **20** with 100% diastereoisomer excess (*Scheme 4*). To improve the diastereoisomer excess of the *cis*-1,2-diol (\rightarrow de 84%), compound **15** was reduced to *cis*-1,2-diol **21** (*Scheme 5*).

The last steps of the total synthesis of the targets **1** and **2** were planned to consist of a series of protection and deprotection reactions followed by a regioselective oxidation of the benzylic alcohol moiety. Thus, the protection of the 1,2-diol moiety of **18** and **19** by acetylation with Ac_2O in the presence of catalytic amounts of *N,N*-dimethylpyridin-4-amine (DMAP) in CH_2Cl_2 yielded the diacetyl derivatives **23** and **24** (*Scheme 6*). Subsequent deprotection of the silylene group with $\text{HF} \cdot \text{pyridine}$ complex provided **25** and **26**. Unfortunately, the oxidation of the benzylic alcohol moiety of **25** and **26** by different methods (*Dess–Martin*, tetrapropylammonium perruthenate (TPAP), MnO_2) failed to afford the desired products and resulted in the decomposition of starting material. Finally, the targets **1** and **2** were obtained by direct deprotection of the

silylene group of **18** and **20** with HF·pyridine complex in dry THF/pyridine via the tetrols **27** and **28**, respectively, regioselectively oxidized at room temperature with activated MnO₂ for 20 h in MeOH/CHCl₃ 1:5 (Scheme 4).

Scheme 6. Acetylation of Compounds **18** and **19** to Give Racemic **25** and **26**



a) Ac₂O (10.0 equiv.), DMAP (0.3 equiv.), CH₂Cl₂; 70–93%. b) HF·pyridine complex (3.0 equiv.) in HF, THF/pyridine 97:3, r.t., 30 min; 64–78%.

Conclusions. – The stereoselective total synthesis of *trans*- and *cis*-3,4-dihydro-3,4,8-trihydroxynaphthalen-1(2*H*)-ones (**1** and **2**, resp.) was elaborated in nine and eight steps, respectively, from juglone (**12**). The stereoselectivity was controlled by the presence of the protective di(*tert*-butyl)silylene group. As described earlier in the asymmetric synthesis of 3,4-dihydro-2,4,8-trihydroxy-naphthalen-1(2*H*)-one [15], the asymmetric *Sharpless* dihydroxylation of silyl enol ether **14** permitted to achieve easily the enantioselective synthesis of **1** or **2**.

Currently, the total synthesis of racemic vermelone (= 3,4-dihydro-3,8-dihydroxynaphthalen-1(2*H*)-one) is described in eleven steps from 3-oxopentanedioic acid diethyl ester, and the asymmetric synthesis of (–)-(3*R*)-vermelone in five steps from the natural product (+)-(3*R*)-scytalone (= (3*R*)-3,4-dihydro-3,6,8-trihydroxynaphthalen-1(2*H*)-one) [5][6][18][19]. Intermediate **16** could be used to synthesize vermelone in only three steps by catalytic hydrogenolysis under pressure (5 bar) in acetone, followed by deprotection of the di(*tert*-butyl)silylene group and regioselective oxidation with MnO₂.

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Experimental Part

General. Activated MnO₂ was purchased from *Fluka* (ref. 63548). Solvents and reagents were distilled by standard procedures prior to use, and air-sensitive compounds were handled under either N₂ or Ar. Reactions were monitored by TLC. TLC: *Macherey-Nagel* silica gel 60 F₂₅₄ plates; visualization by UV light and/or spraying with 5% (v/v) H₂SO₄/EtOH followed by heating. Column chromatography (CC): *Macherey-Nagel* silica gel 60. M.p.: *Büchi-B510* apparatus. IR Spectra: *Perkin-Elmer FT-IR-1720-X* spectrometer; $\bar{\nu}$ in cm⁻¹. ¹H- and ¹³C-NMR Spectra: *Bruker AMX-400* spectrometer; chemical shifts δ in ppm rel. to the residual H-atom resonances of the solvent used, *J* in Hz. MS: *Finnigan LCQ* apparatus; in *m/z*. Microanalyses were performed in the Mikroelementaranalytisches Laboratorium, ETH-Zürich.

Methyl 1,4-Dihydroxy-6,8-dimethoxynaphthalene-2-carboxylate (7) and Methyl 3-(4,6-Dimethoxy-3-oxoisobenzofuran-1(3H)-ylidene)propanoate (8). To 5,7-dimethoxyphthalide (200 mg, 1.03 mmol; **6**) [20] in freshly distilled THF (40 ml) at -40° under Ar, commercial 2M LDA (1.03 ml, 2.06 mmol) was added dropwise with a syringe (\rightarrow light-orange soln.) After 5 min stirring, methyl 3-methoxyacrylate (152 μ l, 1.54 mmol) [21] in dry THF (3 ml) was slowly added by syringe while maintaining the temp. at -40° . Then, the burgundy mixture was allowed to warm to r.t. within 2 h and quenched by the addition of 1M HCl (40 ml). The aq. layer was extracted with AcOEt (3×20 ml), the combined org. extract washed with H₂O (2×10 ml) and brine (20 ml) and dried (MgSO₄), the solvent evaporated, and the residue purified by CC (SiO₂, AcOEt/hexane 2:3): 50.2 mg (18%) of **7** and 49.3 mg (17%) of **8**.

Data of 7: Pale yellow solid. R_f (AcOEt/hexane 2:3) 0.31. IR (KBr): 3400, 1655, 1631, 1611, 1261, 1220. ¹H-NMR (400 MHz, CDCl₃): 4.03 (s, MeO); 4.04 (s, MeO); 4.06 (s, MeO); 6.71 (d, $J = 2.4$, H-C(5)); 7.27 (d, $J = 2.4$, H-C(7)); 7.30 (s, H-C(3)); 8.65 (s, OH); 11.99 (s, OH). ¹³C-NMR (100 MHz, CDCl₃): 51.78; 55.05; 55.75; 94.05 (C(7)); 99.13 (C(5)); 103.11; 106.42 (C(3)); 112.21; 133.58; 143.55; 156.98; 160.78; 161.20; 171.44 (C(9)). EI-MS (70 eV): 278 (M^+), 218, 116, 91, 58.

Data of 8: White solid. M.p. $167-170^{\circ}$ (hexane/AcOEt). R_f (AcOEt/hexane 2:3) 0.22. IR (KBr): 1784, 1733, 1617, 1600. ¹H-NMR (400 MHz, CDCl₃): 3.51 (d, $J = 7.3$, CH₂(2)); 3.74 (s, MeO); 3.92 (s, MeO); 3.96 (s, MeO); 5.74 (t, $J = 7.3$, H-C(3)); 6.45 (d, $J = 2.8$, H-C(5')); 6.68 (d, $J = 2.8$, H-C(7')). ¹³C-NMR (100 MHz, CDCl₃): 30.91 (C(2)); 52.09; 55.98; 56.05; 95.20 (C(5')); 99.59 (C(3)); 100.30 (C(7')); 105.58; 143.19; 146.80; 159.26; 164.27; 167.03; 171.18 (C(1)). EI-MS (70 eV): 278 (M^+), 219, 191, 161. Anal. calc. for C₁₄H₁₄O₆ (278.3): C 60.43, H 5.07; found: C 60.24, H 4.95.

4-(Benzyloxy)isobenzofuran-1(3H)-one (= 4-(Benzyloxy)phthalide; 9). To 4-hydroxyphthalide (3 g, 20 mmol) [22] and K₂CO₃ (8.3 g, 60 mmol) in DMF (50 ml) at 0° under Ar, BnBr (3.8 g, 22 mmol) in dry DMF (10 ml) was added dropwise. The mixture was stirred at r.t. for 48 h and then quenched by addition of H₂O (50 ml) at 5° . The aq. layer was extracted with Et₂O (3×100 ml), the combined org. extract washed with brine (20 ml) and dried (MgSO₄), the solvent evaporated, and the residue purified by CC (SiO₂, AcOEt/hexane 1:1): 3.5 g (72%) of **9**. White solid. M.p. $110-111^{\circ}$ (hexane/AcOEt). IR (KBr): 1760, 1610, 1498, 1281. ¹H-NMR (400 MHz, CDCl₃): 5.20 (s, CH₂(3)); 5.31 (s, PhCH₂); 7.18 (d, $J = 7.8$, H-C(5)); 7.36-7.48 (m, 6 H); 7.53 (t, $J = 8.0$, H-C(6)). ¹³C-NMR (100 MHz, CDCl₃): 68.63 (PhCH₂); 70.84 (C(3)); 116.53 (C(5)); 118.03; 127.84; 127.94; 128.87; 129.20; 131.21; 135.75; 136.25; 153.79 (C(4)); 171.55 (C(1)). Anal. calc. for C₁₅H₁₂O₃ (240.3): C 74.99, H 5.03; found: C 74.80, H 5.04.

Benzyl 5-(Benzyloxy)-1,2,3,4-tetrahydro-4-hydroxy-1-oxonaphthalene-2-carboxylate (10). To **9** (500 mg, 2.08 mmol) in freshly distilled THF (100 ml) at -40° under Ar, 2M LDA (1.04 ml, 2.08 mmol) was added dropwise with a syringe (\rightarrow dark soln.). After 5 min stirring, benzyl acrylate (439 mg, 2.70 mmol) in dry THF (5 ml) was slowly added by syringe while maintaining the temp. at -40° (\rightarrow pale yellow soln.). Then, the mixture was allowed to warm to -10° within 1 h 30 min and quenched by the addition of 1M HCl (20 ml) followed by H₂O (80 ml). The aq. layer was extracted with AcOEt (3×70 ml), the combined org. extract washed with brine (25 ml) and dried (MgSO₄), the solvent evaporated and the residue purified by CC (SiO₂, AcOEt/hexane 3:7): 308 mg (37%) of **10**. Pale yellow oil. R_f (AcOEt/hexane 3:7) 0.36. ¹H-NMR (400 MHz, CDCl₃): enol-**10**: 2.69 (dd, $J = 5.4$, 17.3, 1 H, CH₂(3)); 3.19 (dd, $J = 2.6$, 17.3, 1 H, CH₂(3)); 5.29-5.31 (m, 2 PhCH₂O, H-C(4)); 7.11 (dd, $J = 0.9$, 8.3, H-C(6)); 7.31-7.48 (m, 12 H); 7.60 (d, $J = 7.8$, H-C(8)); 12.42 (s, OH); *trans*-**10**: 2.54 (ddd, $J = 3.5$, 4.4, 14.2, 1 H, CH₂(3)); 2.65-2.72 (m, 1 H, CH₂(3)); 4.21 (dd, $J = 4.3$, 12.6, H-C(2)); 5.19 (s, PhCH₂O); 5.29-5.31 (m, PhCH₂O); 5.41 (t, $J = 3.5$, H-C(4)); 7.23 (dd, $J = 1.0$, 8.2, H-C(6)); 7.31-7.48 (m, 11 H); 7.67 (dd, $J = 0.9$, 8.0, H-C(8)); *cis*-**10**: 3.66 (dd, $J = 4.3$, 12.6, H-C(2)). ¹³C-NMR (100 MHz, CDCl₃): enol-**10**: 29.28 (C(3)); 59.89 (C(4)); 66.78; 71.04; 94.37 (C(2)); 115.53; 117.98; 127.76; 128.18; 128.51; 128.62; 128.72; 129.05; 129.16; 129.31; 130.43; 136.24; 136.99; 155.85 (C(5)); 164.13 (C(1)); 173.03 (C(11)); *trans*-**10**: 32.95 (C(3)); 49.89 (C(2)); 60.94 (C(4)); 67.39; 71.16; 119.95; 127.38; 127.86; 127.96; 128.67; 128.89; 128.94; 129.00; 129.38; 132.28; 136.16; 136.46; 156.41 (C(5)); 170.67 (C(11)); 193.75 (C(1)). ESI-MS (neg.): 401 ([$M - H$]⁻).

(4RS)-3,4-Dihydro-4,5-dihydroxynaphthalen-1(2H)-one (= Sclerone; 11). To β -hydrojuglone (= 2,3-dihydro-5-hydroxynaphthalene-1,4-dione [16] (1.45 g, 8.24 mmol) in EtOH (180 ml) at 0° , NaBH₄ (187 mg, 0.494 mmol) in H₂O (1.8 ml) was added. The mixture was stirred for 10 min and then quenched with H₂O (100 ml). After addition of 1M HCl until pH 7 was reached, EtOH was evaporated and the aq.

layer extracted with AcOEt (3 × 200 ml). Then the combined org. extract was washed with brine (150 ml) and dried (MgSO₄), the solvent evaporated, and the residue purified by CC (SiO₂, AcOEt/hexane 1:1): 632 mg (43%) of **11**. White solid. *R*_f (AcOEt/hexane 1:1) 0.21. ¹H-NMR (400 MHz, CDCl₃): 1.72 (br., OH); 2.23 (*m*, 1 H, CH₂(3)); 2.53–2.61 (*m*, 1 H, CH₂(2), 1 H, CH₂(3)); 2.84 (*dt*, *J* = 5.0, 16.2, 1 H, CH₂(2)); 5.37 (*dd*, *J* = 4.9, 9.9, H–C(4)); 7.13 (*dd*, *J* = 1.3, 8.1, H–C(6)); 7.32 (*dt*, *J* = 0.6, 8.0, H–C(7)); 7.60 (*dd*, *J* = 1.2, 7.8, H–C(8)); 8.46 (br., OH). ¹³C-NMR (100 MHz, CDCl₃): 32.38 (C(3)); 36.01 (C(2)); 68.44 (C(4)); 119.17 (C(4a)); 122.27 (C(7)); 128.53 (C(5)); 129.50 (C(6)); 132.22 (C(8a)); 155.93 (C(5)); 196.77 (C(1)). ESI-MS (pos.): 179 ([*M* + H]⁺).

(4*RS*)-4,5-[[*Bis*(1,1-dimethylethyl)silylene]dioxy]-3,4-dihydronaphthalen-1(2*H*)-one (= (3*aRS*)-2,2-*Bis*(1,1-dimethylethyl)-4,5-dihydronaphtho[1,8-*de*]-1,3,2-dioxasilin-6(3*aH*)-one; **13**). To **11** (480 mg, 2.69 mmol) in dry MeCN (15 ml), HOBT (= 1-hydroxy-1*H*-benzotriazole; 37 mg, 0.27 mmol), Et₃N (1.88 ml, 13.5 mmol; freshly distilled from CaH₂) and ^tBu₂SiCl₂ (626 μl, 2.96 mmol) were added. The mixture was stirred at 80° for 48 h. Then, the soln. was cooled to r.t. and poured into ice (25 g). The aq. layer was further extracted with Et₂O (3 × 30 ml), the combined org. extract washed with sat. NaHCO₃ soln. (25 ml) and brine (25 ml) and dried (MgSO₄), the solvent evaporated, and the brown oily residue purified by CC (silica gel, AcOEt/hexane 1:9): 709 mg (83%) of **13**. Pale yellow solid. Recrystallization from hexane gave a white solid. M.p. 115° (hexane). *R*_f (AcOEt/hexane 1:9) 0.65. IR (KBr): 2926, 2857, 1689, 1594, 1467, 1284, 1263, 829. ¹H-NMR (400 MHz, CDCl₃): 0.97 (*s*, Me₃C); 1.17 (*s*, Me₃C); 2.07–2.16 (*m*, 1 H, CH₂(3)); 2.50–2.63 (*m*, 1 H, CH₂(2), 1 H, CH₂(3)); 2.77–2.84 (*m*, 1 H, CH₂(2)); 5.30 (*dd*, *J* = 4.9, 11.2, H–C(4)); 7.16 (*dd*, *J* = 1.3, 8.0, H–C(6)); 7.31 (*t*, *J* = 8.0, H–C(7)); 7.65 (*dd*, *J* = 1.3, 7.8, H–C(8)). ¹³C-NMR (100 MHz, CDCl₃): 21.56; 21.92; 27.32; 27.35; 33.17 (C(3)); 37.23 (C(2)); 69.65 (C(4)); 120.35 (C(8)); 124.92 (C(6)); 129.33 (C(7)); 132.02; 133.16; 154.17 (C(5)); 197.29 (C(1)). ESI-MS (pos.): 319 ([*M* + H]⁺). Anal. calc. for C₁₈H₂₆O₃Si (318.5): C 67.88, H 8.23; found: C 68.04, H 8.17.

(*IRS*)-1,8-[[*Bis*(1,1-dimethylethyl)silylene]dioxy]-4-[[1,1-dimethylethyl]dimethylsilyloxy]-1,2-dihydronaphthalene (= (3*aRS*)-2,2-*Bis*(1,1-dimethylethyl)-6-[[1,1-dimethylethyl]dimethylsilyloxy]-3*a*,4-dihydronaphtho[1,8-*de*]-1,3,2-dioxasilin; **14**). To **13** (709 mg, 2.23 mmol) in 1,2-dichloroethane (20 ml) at r.t. under Ar, Et₃N (467 μl, 3.35 mmol; freshly distilled from KOH) was added by syringe. Then, at r.t., ^tBuMe₂SiOTf (512 μl, 2.23 mmol) was added dropwise by syringe. The mixture was stirred for 25 min, then SiO₂ (5 g) was directly added to the soln. The solvent was evaporated and the residue purified by CC (SiO₂, AcOEt/hexane 2:98): 886 mg (92%) of **14**. Colorless oil. *R*_f (AcOEt/hexane 2:98): 0.72. IR (KBr): 2933, 2891, 2860, 1579, 1471, 1353, 1261. ¹H-NMR (400 MHz, CDCl₃): 0.21 (*s*, MeSi); 0.24 (*s*, MeSi); 1.02 (*s*, Me₃C); 1.05 (*s*, Me₃C); 1.11 (*s*, Me₃C); 2.43–2.59 (*m*, CH₂(2)); 5.06 (*dd*, *J* = 2.5, 6.8, H–C(3)); 5.31 (*dd*, *J* = 7.5, 14.0, H–C(1)); 6.84 (*dd*, *J* = 1.2, 8.0, H–C(7)); 7.08 (*dd*, *J* = 1.2, 7.7, H–C(5)); 7.16 (*t*, *J* = 7.8, H–C(6)). ¹³C-NMR (100 MHz, CDCl₃): –4.17; –4.08; 18.68; 21.80; 26.24; 27.23; 27.30; 32.35 (C(2)); 70.39 (C(1)); 101.81 (C(3)); 115.70 (C(5)); 119.47 (C(7)); 124.19; 128.54 (C(6)); 133.75; 148.04 (C(4)); 152.92 (C(8)). ESI-MS (pos.): 433 ([*M* + H]⁺).

(2*RS*,4*SR*)-4,5-[[*Bis*(1,1-dimethylethyl)silylene]dioxy]-2-[[1,1-dimethylethyl]dimethylsilyloxy]-3,4-dihydronaphthalen-1(2*H*)-one (= (3*aRS*,5*SR*)-2,2-*Bis*(1,1-dimethylethyl)-5-[[1,1-dimethylethyl]silyloxy]-4,5-dihydronaphtho[1,8-*de*]-1,3,2-dioxasilin-6(3*aH*)-one; **15**). To **14** (158 mg, 0.366 mmol) in 1,2-dichloroethane (7 ml) at –15° under Ar, 70% *m*-CPBA (90 mg, 0.366 mmol) in 1,2-dichloroethane (2 ml) was added dropwise by syringe. The mixture was stirred at r.t. for 90 min. Then, the solvent was evaporated and the residue purified by CC (SiO₂, AcOEt/hexane 5:95): 57 mg (35%) of **15** and 34 mg (28%) of **16**. **15**: Colorless oil. *R*_f (AcOEt/hexane 5:95) 0.65. IR (KBr): 2934, 2861, 1699, 1595, 1468, 1281, 1263. ¹H-NMR (400 MHz, CDCl₃): 0.05 (*s*, MeSi); 0.18 (*s*, MeSi); 0.85 (*s*, Me₃C); 0.96 (*s*, Me₃C); 1.19 (*s*, Me₃C); 2.12 (*ddd*, *J* = 2.2, 10.2, 12.5, 1 H, CH₂(3)); 2.69 (*dt*, *J* = 4.1, 12.5, 1 H, CH₂(3)); 4.35 (*dd*, *J* = 2.1, 3.8, H–C(2)); 5.58 (*dd*, *J* = 4.9, 10.2, H–C(4)); 7.17 (*dd*, *J* = 1.2, 8.0, H–C(6)); 7.33 (*t*, *J* = 8.0, H–C(7)); 7.64 (*dd*, *J* = 1.2, 7.8, H–C(8)). ¹³C-NMR (100 MHz, CDCl₃): –4.78; –4.44; 18.52; 21.56; 25.99; 27.36; 41.47 (C(3)); 65.66 (C(4)); 72.84 (C(2)); 121.10 (C(8)); 124.80 (C(6)); 129.38 (C(7)); 130.16; 133.18; 154.11 (C(5)); 194.59 (C(1)). ESI-MS (pos.): 471 ([*M* + Na]⁺).

(2*RS*,4*RS*)-4,5-[[*Bis*(1,1-dimethylethyl)silylene]dioxy]-3,4-dihydro-2-hydroxynaphthalen-1(2*H*)-one (= (3*aRS*,5*RS*)-2,2-*Bis*(1,1-dimethylethyl)-4,5-dihydro-5-hydroxynaphtho[1,8-*de*]-1,3,2-dioxasilin-6(3*aH*)-one; **16**). To a soln. of K₂CO₃ (276 mg, 2.00 mmol), K₃[Fe(CN)₆] (418 mg, 2.00 mmol), and pyridine (2 μl, 0.013 mmol) in H₂O (3.7 ml), ^tBuOH (1 ml) and 2.5% OsO₄ soln. in ^tBuOH (140 μl, 0.013 mmol) were

added, followed by MeSO₂NH₂ (63 mg, 0.66 mmol). Then, the mixture was cooled to 0°, **14** (288 mg, 0.66 mmol) diluted in *t*-BuOH (2.7 ml) was added, and the mixture was stirred overnight at 0°. After quenching with Na₂SO₃ (500 mg), the mixture was stirred for 1 h at r.t., and then H₂O (10 ml) was added. The aq. layer was extracted with AcOEt (3 × 25 ml), the combined org. extract washed with brine (20 ml) and dried (MgSO₄), the solvent evaporated, and the residue purified by CC (SiO₂, AcOEt/hexane 1:4): 126 mg (56%) of **16**. White solid. M.p. 124° (hexane). *R*_f (AcOEt/hexane 2:8) 0.25. IR (KBr): 3474, 2962, 2935, 2860, 1686, 1594, 1467, 1296, 1263. ¹H-NMR (400 MHz, CDCl₃): 0.94 (s, Me₃C); 1.19 (s, Me₃C); 2.43 (ddd, *J* = 5.7, 7.0, 12.7, 1 H, CH₂(3)); 2.61 (ddd, *J* = 4.7, 7.0, 12.7, 1 H, CH₂(3)); 4.49 (dd, *J* = 4.7, 7.0, H-C(2)); 5.46 (t, *J* = 6.3, H-C(4)); 7.21 (dd, *J* = 1.1, 8.0, H-C(6)); 7.36 (t, *J* = 8.0, H-C(7)); 7.58 (dd, *J* = 1.1, 7.7, H-C(8)). ¹³C-NMR (100 MHz, CDCl₃) 21.65; 21.95; 27.39; 27.45; 37.74 (C(3)); 65.09 (C(4)); 70.45 (C(2)); 120.39 (C(8)); 125.27 (C(6)); 129.74; 129.93 (C(7)); 132.37; 154.83 (C(5)); 197.43 (C(1)). ESI-MS (pos.): 357 ([*M* + Na]⁺). Anal. calc. for C₁₈H₂₆O₄Si (334.5): C 64.64, H 7.83; found: C 64.66, H 7.69.

(2*RS*,4*RS*)-4-[[*Bis*(1,1-dimethylethyl)hydroxysilyl]oxy]-3,4-dihydro-2,5-dihydroxynaphthalen-1(2*H*)-one (**17**). A soln. of **16** (62 mg, 0.186 mmol) in buffer soln. pH 10/THF 1:1 (10 ml) was stirred at r.t. for 90 min and then neutralized with 2*M* HCl (→ pH 7). The aq. layer was extracted with AcOEt (3 × 20 ml), the combined org. extract washed with brine (20 ml) and dried (MgSO₄), the solvent evaporated, and the residue purified by CC (SiO₂, AcOEt/hexane 1:4): 35 mg (53%) of **17**. White solid. *R*_f (AcOEt/hexane 2:8) 0.15. IR (KBr): 3435, 2935, 2860, 1694, 1062. ¹H-NMR (400 MHz, CDCl₃): 0.85 (s, Me); 1.07 (s, Me, Me₃C); 1.16 (s, Me); 2.23 (dt, *J* = 2.8, 13.0, 1 H, CH₂(3)); 2.83 (ddd, *J* = 3.3, 5.2, 13.0, 1 H, CH₂(3)); 5.07 (dd, *J* = 5.1, 12.7, H-C(2)); 5.52 (t, *J* = 2.9, H-C(4)); 7.21 (dd, *J* = 1.1, 7.7, H-C(6)); 7.38 (t, *J* = 8.0, H-C(7)); 7.71 (dd, *J* = 1.1, 7.7, H-C(8)). ¹³C-NMR (100 MHz, CDCl₃): 20.19; 20.51; 27.10; 27.63; 27.67; 40.39 (C(3)); 63.27 (C(4)); 69.21 (C(2)); 120.65 (C(8)); 124.80 (C(6)); 130.46; 130.62 (C(7)); 130.69; 154.29 (C(5)); 200.18 (C(1)). ESI-MS (neg.): 351 ([*M* - H]⁻).

X-Ray Crystal Structure of 17. X-Ray crystal data for C₁₈H₂₈O₅Si (*M*_r 352.51): Orthorhombic space group *Pbca*, *D*_c = 1.229 g · cm⁻³, *Z* = 8; *a* = 11.640, *b* = 14.381, *c* = 22.761 Å, *α* = *β* = *γ* = 90°, *V* = 3809.8 Å³; MoK_α radiation, *λ* = 0.71073 Å, 2.42 < *θ* < 25.89°; number of reflections measured 27881, number of independent reflections 3666, number of observed reflections 3056 (*I* > 2σ(*I*)), *T* 153 K. Suitable crystals of **17** were grown from benzene as pale yellow blocks. Intensity data were collected at 153 K with a *Stoe-Image-Plate-Diffraction* system [23] and MoK_α graphite-monochromated radiation. Image-plate distance 70 mm, *φ* oscillation scans 0–198°, step Δ*φ* = 1.0°, 2*θ* range 3.27–52.1°, *d*_{max} – *d*_{min} = 12.45–0.81 Å. The structure was solved by direct methods with the program SHELXS-97 [24]. The refinement and all further calculations were carried out with SHELXL-97 [25]. The H-atoms were located from *Fourier* difference maps and refined isotropically. The non-H-atoms were refined anisotropically by means of weighted full-matrix least-squares on *F*². All-data refinement of 319 parameters based on *F*² converged at *R*(*F*) = 0.0431 and *wR*(*F*²) = 0.0955. The molecular structure and crystallographic numbering scheme are illustrated in the PLATON drawing [26] (Fig. 2) CCDC-602497 contains the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request.cif.

(1*RS*,2*SR*,4*SR*)- and (1*RS*,2*RS*,4*RS*)-4,5-[[*Bis*(1,1-dimethylethyl)silylene]dioxo]-1,2,3,4-tetrahydronaphthalene-1,2-diol (= (3*aRS*,5*RS*,6*SR*)- and (3*aRS*,5*RS*,6*RS*)-2,2-*Bis*(1,1-dimethylethyl)-3*a*,4,5,6-tetrahydronaphtho[1,8-*de*]-1,3,2-dioxasilin-5,6-diol, resp.; **18** and **19**). To a soln. of **16** (277 mg, 0.829 mmol) in EtOH (20 ml) at r.t., NaBH₄ (32 mg, 0.829 mmol) in H₂O (4 ml) was added. The mixture was stirred for 10 min and then H₂O (20 ml) was added. After neutralization of the soln. (→ pH 7) with 1*M* HCl, EtOH was evaporated and the aq. layer extracted with AcOEt (3 × 40 ml). The combined org. extract was washed with brine (20 ml) and dried (MgSO₄), the solvent evaporated, and the residue purified by CC (SiO₂, AcOEt/hexane 3:7): 186 mg (67%) of **18** and 43 mg (15%) of **19**.

Data of 18: White solid. M.p. 120° (hexane/AcOEt). *R*_f (AcOEt/hexane 3:7) 0.30. IR (KBr): 3390, 2934, 2860, 1602, 1584, 1473, 1455, 1266, 968. ¹H-NMR (400 MHz, CDCl₃): 0.94 (s, Me₃C); 1.15 (s, Me₃C); 1.81 (ddd, *J* = 1.8, 10.2, 12.0, 1 H, CH₂(3)); 2.59 (dt, *J* = 5.6, 12.0, 1 H, CH₂(3)); 3.00 (br., OH); 4.17–4.20 (*m*, H-C(2)); 4.64 (*d*, *J* = 3.4, H-C(1)); 5.34 (dd, *J* = 5.9, 10.2, H-C(4)); 6.85 (*d*, *J* = 7.9, H-C(6)); 7.10 (*d*, *J* = 7.7, H-C(8)), 7.22 (t, *J* = 7.8, H-C(7)). ¹³C-NMR (100 MHz, CDCl₃): 21.71; 21.87; 27.51; 27.59;

37.12 (C(3)); 66.27 (C(4)); 69.42 (C(2)); 70.30 (C(1)); 118.47 (C(6)); 120.37 (C(8)); 127.19; 129.51 (C(7)); 136.73; 154.41 (C(5)). ESI-MS (pos.): 359 ($[M + Na]^+$).

Data of 19: White solid. R_f (AcOEt/hexane 3:7) 0.23. $^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3 + \text{D}_2\text{O}$): 0.91 (s, Me_3C); 1.15 (s, Me_3C); 2.25 (t, $J = 5.9$, $\text{CH}_2(3)$); 3.98 (q, $J = 5.9$, $\text{H-C}(2)$); 4.44 (d, $J = 6.0$, $\text{H-C}(1)$); 5.23 (t, $J = 6.7$, $\text{H-C}(4)$); 6.89 (dd, $J = 0.5$, 7.9, $\text{H-C}(6)$); 7.07 (d, $J = 7.7$, $\text{H-C}(8)$); 7.24 (t, $J = 7.9$, $\text{H-C}(7)$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 21.65; 21.92; 27.49; 27.52; 35.66 (C(3)); 66.31 (C(4)); 70.75 (C(2)); 72.96 (C(1)); 118.94 (C(6)); 120.27 (C(8)); 126.59; 129.72 (C(7)); 136.75; 154.58 (C(5)). ESI-MS (pos.): 359 ($[M + Na]^+$).

(*IRS,2RS,4RS*)-4- $\{[Bis(1,1\text{-dimethylethyl})\text{hydroxysilyl}]\text{oxy}\}$ -1,2,3,4-tetrahydronaphthalene-1,2,5-triol (**20**). As described for **18/19**, with **17** (41 mg, 0.116 mmol) in EtOH (3 ml) and NaBH_4 soln. (600 μl , $c = 9.3 \text{ g l}^{-1}$, 0.14 mmol) in H_2O : 32 mg (76%) of **20**. White solid. R_f (AcOEt/hexane 1:1) 0.22. IR (KBr): 3412, 2932, 2858, 1589, 1471, 1053. $^1\text{H-NMR}$ (400 MHz, $\text{CD}_3\text{COCD}_3 + \text{D}_2\text{O}$): 0.84 (s, Me); 0.99 (s, Me, Me_3C); 1.06 (s, Me); 1.83 (ddd, $J = 3.2$, 11.8, 13.1, 1 H, $\text{CH}_2(3)$); 2.37 (dt, $J = 3.4$, 13.1, 1 H, $\text{CH}_2(3)$); 4.23 (ddd, $J = 3.3$, 8.4, 11.7, $\text{H-C}(2)$); 4.34 (d, $J = 8.5$, $\text{H-C}(1)$); 5.34 (t, $J = 3.2$, $\text{H-C}(4)$); 6.76 (ddd, $J = 0.7$, 1.2, 7.5, $\text{H-C}(6)$); 7.12–7.17 (m, $\text{H-C}(7)$, $\text{H-C}(8)$). $^{13}\text{C-NMR}$ (100 MHz, CD_3COCD_3): 20.10; 20.45; 20.99; 27.11; 27.38; 27.51; 39.44 (C(3)); 64.75 (C(4)); 68.82 (C(2)); 75.80 (C(1)); 115.33 (C(6)); 119.61; 124.83; 129.30; 140.09; 154.75 (C(5)). ESI-MS (neg.): 353 ($[M - H]^-$).

(*IRS,2SR,4RS*)- and (*IRS,2RS,4SR*)-4,5- $\{[Bis(1,1\text{-dimethylethyl})\text{silylene}]\text{dioxy}\}$ -2- $\{[(1,1\text{-dimethylethyl})\text{dimethylsilyl}]\text{oxy}\}$ -1,2,3,4-tetrahydronaphthalen-1-ol (= (*3aRS,5SR,6SR*)- and (*3aRS,5SR,6SR*)-2,2-Bis(1,1-dimethylethyl)-5- $\{[(1,1\text{-dimethylethyl})\text{dimethylsilyl}]\text{oxy}\}$ -3a,4,5,6-tetrahydronaphtho[1,8-de]-1,3,2-dioxasilin-6-ol; **21** and **22**, resp.). As described for **18/19**, with **15** (23 mg, 0.0513 mmol) in EtOH (1 ml) and NaBH_4 soln. (100 μl , $c = 19.5 \text{ g l}^{-1}$, 0.0513 mmol) in H_2O : 17 mg (71%) of **21/22** (ratio 92:8). Colorless oil mixture.

Data of 21: Colorless oil. Hexane/AcOEt. R_f (AcOEt/hexane 3:7) 0.36. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.16 (s, Me); 0.19 (s, Me); 0.88 (s, Me_3C); 0.95 (s, Me_3C); 1.15 (s, Me_3C); 1.85 (ddd, $J = 1.6$, 10.3, 13.5, 1 H, $\text{CH}_2(3)$); 2.45 (d, $J = 10.8$, OH); 2.53 (dt, $J = 5.6$, 13.5, 1 H, $\text{CH}_2(3)$); 4.36 (ddd, $J = 1.6$, 3.8, 5.5, $\text{H-C}(2)$); 4.61 (dd, $J = 3.8$, 10.8, $\text{H-C}(1)$); 5.34 (dd, $J = 5.6$, 10.3, $\text{H-C}(4)$); 6.84 (d, $J = 7.9$, $\text{H-C}(6)$); 7.20–7.26 (m, $\text{H-C}(7)$, $\text{H-C}(8)$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): –4.83; –4.49; 14.54; 18.50; 21.65; 26.14; 27.46; 27.51; 38.51 (C(3)); 66.49 (C(4)); 70.20 (C(1)); 70.65 (C(2)); 118.01 (C(6)); 121.00; 127.02; 129.21; 137.99; 153.89 (C(5)). ESI-MS (neg.): 450 ($[M - H]^-$).

Data of 22: Colorless oil. Hexane/AcOEt. R_f (AcOEt/hexane 3:7) 0.36. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.23 (s, Me); 0.26 (s, Me); 0.94 (s, Me_3C); 1.00 (s, Me_3C); 1.15 (s, Me_3C); 1.81–1.89 (m, 1 H, $\text{CH}_2(3)$); 2.70 (dt, $J = 5.6$, 13.5, 1 H, $\text{CH}_2(3)$); 4.20–4.24 (m, $\text{H-C}(2)$); 4.80 (d, $J = 5.6$, $\text{H-C}(1)$); 5.40 (dd, $J = 5.6$, 10.3, $\text{H-C}(4)$); 6.84 (d, $J = 7.9$, $\text{H-C}(6)$); 6.99 (d, $J = 7.8$, $\text{H-C}(8)$); 7.21–7.24 (m, $\text{H-C}(7)$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): –4.28; –3.84; 21.68; 21.87; 21.97; 26.23; 27.51; 27.61; 36.77 (C(3)); 66.37 (C(4)); 69.77 (C(2)); 71.51 (C(1)); 118.21 (C(6)); 120.50 (C(8)); 127.27; 129.13 (C(7)); 136.84; 154.35 (C(5)). ESI-MS (neg.): 450 ($[M - H]^-$).

(*IRS,2SR,4SR*)-4,5- $\{[Bis(1,1\text{-dimethylethyl})\text{silylene}]\text{dioxy}\}$ -1,2,3,4-tetrahydronaphthalene-1,2-diyl Diacetate (= (*3aRS,5RS,6SR*)-2,2-Bis(1,1-dimethylethyl)-3a,4,5,6-tetrahydronaphtho[1,8-de]-1,3,2-dioxasilin-5,6-diol Diacetate; **23**). To a soln. of **18** (92 mg, 0.274 mmol) in dry CH_2Cl_2 (5 ml) at r.t. under Ar, DMAP (10 mg, 0.0822 mmol) and then dry Ac_2O (259 μl , 0.274 mmol) were added by syringe. The mixture was stirred for 48 h and then quenched with H_2O (5 ml). The aq. layer was extracted with CH_2Cl_2 (3 \times 10 ml), the combined org. extract washed with brine (20 ml) and dried (MgSO_4), the solvent evaporated, and the residue purified by CC (SiO_2 , AcOEt/hexane 3:7): 107 mg (93%) of **23**. White solid. M.p. 116–117° (hexane/AcOEt). R_f (AcOEt/hexane 3:7) 0.44. IR (KBr): 2934, 2858, 1749, 1586, 1268, 1249. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.92 (s, Me_3C); 1.17 (s, Me_3C); 2.05 (s, MeCOO); 2.03–2.10 (m, 1 H, $\text{CH}_2(3)$); 2.14 (s, MeCOO); 2.62 (dt, $J = 6.3$, 12.8, 1 H, $\text{CH}_2(3)$); 5.31 (dd, $J = 6.4$, 8.9, $\text{H-C}(4)$); 5.61 (ddd, $J = 2.8$, 6.2, 8.9, $\text{H-C}(2)$); 6.10 (d, $J = 3.5$, $\text{H-C}(1)$); 6.84 (d, $J = 7.7$, $\text{H-C}(6)$); 6.91 (d, $J = 8.0$, $\text{H-C}(8)$); 7.23 (t, $J = 8.0$, $\text{H-C}(7)$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 21.36; 21.43; 21.71; 21.90; 27.46; 27.54; 34.58 (C(3)); 66.37 (C(4)); 68.96 (C(2)); 70.05 (C(1)); 119.16 (C(8)); 120.05 (C(6)); 127.29 (C(7)); 129.59; 132.64; 154.73 (C(5)); 170.95; 171.05. ESI-MS (pos.): 443 ($[M + Na]^+$). Anal. calc. for $\text{C}_{22}\text{H}_{32}\text{O}_6\text{Si}$ (420.6): C 62.83, H 7.67; found: C 62.85, H 7.55.

(*IRS,2RS,4RS*)-4,5-[[*Bis*(1,1-dimethylethyl)silylene]dioxo]-1,2,3,4-tetrahydronaphthalene-1,2-diyl Diacetate (= (*3aRS,5RS,6RS*)-2,2-*Bis*(1,1-dimethylethyl)-3a,4,5,6-tetrahydronaphtho[1,8-de]-1,3,2-dioxasilin-5,6-diol Diacetate; **24**). As described for **23**, with **19** (14 mg, 0.0417 mmol) in dry CH₂Cl₂ (2 ml), DMAP (1.5 mg, 0.0125 mmol), and Ac₂O (39 μ l, 0.417 mmol): 12 mg (70%) of **24**. White solid. *R*_f (AcOEt/hexane 3 : 7) 0.44. IR (KBr): 2963, 2934, 2860, 1747, 1602, 1584, 1474, 1368, 1247, 1227. ¹H-NMR (400 MHz, CDCl₃): 0.96 (s, Me₃C); 1.16 (s, Me₃C); 2.05 (s, MeCOO); 2.11 (s, MeCOO); 2.12–2.18 (m, 1 H, CH₂(3)); 2.51 (ddt, *J* = 1.2, 4.3, 13.9, 1 H, CH₂(3)); 5.18 (dd, *J* = 5.9, 10.6, H–C(4)); 5.23 (ddd, *J* = 2.8, 5.8, 7.0, H–C(2)); 5.87 (d, *J* = 2.7, H–C(1)); 6.93–6.95 (m, H–C(6), H–C(7)); 7.22 (dt, *J* = 0.6, 8.0, H–C(8)). ¹³C-NMR (100 MHz, CDCl₃): 21.45; 21.60; 21.64; 21.92; 27.42; 27.50; 32.51 (C(3)); 65.97 (C(4)); 68.80 (C(1)); 70.44 (C(2)); 119.71; 123.02; 127.95; 129.58 (C(7)); 132.34; 154.44 (C(5)); 170.25; 170.34. ESI-MS (pos.): 443 ([*M* + Na]⁺).

(*IRS,2SR,4SR*)-1,2,3,4-Tetrahydro-4,5-dihydroxynaphthalene-1,2-diyl Diacetate (= (*IRS,2SR,6SR*)-1,2,3,4-Tetrahydronaphthalene-1,2,4,5-tetrol 1,2-Diacetate; **25**). To a soln. of **23** (90 mg, 0.214 mmol) in dry THF (5 ml) in a plastic flask at r.t., and dry pyridine (323 μ l, 2.97 mmol) and then 70% HF/pyridine (161 mg, 4.27 mmol) were added by syringe. The mixture was stirred for 30 min, then AcOEt (15 ml) was added. The mixture was washed with brine (10 ml) and dried (MgSO₄), the solvent evaporated, and the residue purified by CC (SiO₂, AcOEt/hexane 1 : 1): 47 mg (78%) of **25**. White solid. M.p. 141° (hexane/AcOEt). *R*_f (AcOEt/hexane 1 : 1) 0.22. IR (KBr): 3481, 3242, 1734, 1719, 1595, 1471, 1368, 1260, 1229. ¹H-NMR (400 MHz, CD₃COCD₃): 1.99 (s, MeCOO); 2.04 (s, MeCOO); 2.06–2.10 (m, 1 H, CH₂(3)); 2.45 (ddd, *J* = 5.1, 10.8, 13.4, 1 H, CH₂(3)); 3.84 (br., OH); 5.26 (t, *J* = 4.7, H–C(4)); 5.53 (dt, *J* = 3.3, 10.8, H–C(2)); 6.13 (d, *J* = 3.4, H–C(1)); 6.78 (d, *J* = 7.7, H–C(6)); 6.88 (dd, *J* = 1.1, 8.0, H–C(8)); 7.19 (t, *J* = 7.8, H–C(7)). ¹³C-NMR (100 MHz, CD₃COCD₃): 20.44; 20.46; 32.48 (C(3)); 63.58 (C(4)); 67.91 (C(2)); 69.07 (C(1)); 116.10 (C(8)); 120.83 (C(6)); 125.33; 129.64 (C(7)); 134.15; 156.27 (C(5)); 170.11; 170.27. ESI-MS (neg.): 279 ([*M* – H][–]). Anal. calc. for C₁₄H₁₆O₆ (280.3): C 60.00, H 5.75; found: C 60.14, H 5.91.

(*IRS,2RS,4RS*)-2-Acetoxy-4,5-dihydroxy-1,2,3,4-tetrahydronaphthalene-1,2-diyl Diacetate (= (*IRS,2RS,3RS*)-1,2,3,4-Tetrahydronaphthalene-1,2,4,5-tetrol 1,2-Diacetate; **26**). As described for **25**, with **24** (15 mg, 0.0286 mmol) in dry THF (2 ml), dry pyridine (76 μ l, 0.698 mmol), and 70% HF/pyridine (25 mg, 0.662 mmol): 5 mg (64%) of **26**. White solid. *R*_f (AcOEt/hexane 1 : 1) 0.24. ¹H-NMR (400 MHz, CD₃COCD₃): 2.01 (s, MeCOO); 2.10 (s, MeCOO); 2.26–2.29 (m, CH₂(3)); 4.74 (br., OH); 5.19–5.22 (m, H–C(4)); 5.37–5.42 (m, H–C(2)); 5.92 (d, *J* = 6.4, H–C(1)); 6.75 (d, *J* = 7.7, H–C(6)); 6.83 (dd, *J* = 1.1, 8.1, H–C(8)); 7.18 (t, *J* = 7.8, H–C(7)); 8.86 (br., OH). ¹³C-NMR (100 MHz, CD₃COCD₃): 20.43; 20.49; 33.79 (C(3)); 63.77 (C(4)); 69.58 (C(2)); 71.11 (C(1)); 115.75 (C(8)); 119.94 (C(6)); 125.23; 129.48 (C(7)); 134.53; 156.46 (C(5)); 169.77; 170.25. ESI-MS (neg.): 279 ([*M* – H][–]).

(*IRS,2SR,4SR*)-1,2,3,4-Tetrahydronaphthalene-1,2,4,5-tetrol (**27**). To a soln. of **18** (103 mg, 0.307 mmol) in dry THF (10 ml) in a plastic flask at r.t., dry pyridine (465 μ l, 4.27 mmol) and then 70% HF/pyridine (231 mg, 6.11 mmol) were added by syringe. The mixture was stirred for 30 min and then AcOEt (15 ml) was added. The mixture was poured over SiO₂ (1.5 g), the solvent evaporated, and the residue purified by CC (SiO₂, AcOEt): 58 mg (96%) of **27**. White solid. *R*_f (AcOEt) 0.24. ¹H-NMR (400 MHz, CD₃OD): 1.95 (ddt, *J* = 1.0, 3.5, 13.4, 1 H, CH₂(3)); 2.30 (ddd, *J* = 4.8, 11.1, 13.4, 1 H, CH₂(3)); 4.24 (dt, *J* = 3.3, 11.1, H–C(2)); 4.61 (d, *J* = 3.5, H–C(1)); 5.20 (t, *J* = 4.2, H–C(4)); 6.78 (dd, *J* = 1.1, 8.0, H–C(8)); 6.91 (dd, *J* = 0.6, 7.6, H–C(6)); 7.17 (t, *J* = 7.8, H–C(7)). ¹³C-NMR (100 MHz, CD₃OD): 34.26 (C(3)); 63.91 (C(4)); 66.67 (C(2)); 70.09 (C(1)); 114.74 (C(8)); 121.16 (C(6)); 124.21; 129.16 (C(7)); 138.58; 156.08 (C(5)). ESI-MS (neg.): 195 ([*M* – H][–]).

(*IRS,2RS,4RS*)-1,2,3,4-Tetrahydronaphthalene-1,2,4,5-tetrol (**28**). As described for **27**, with **19** (20 mg, 0.0594 mmol) in dry THF (5 ml) dry pyridine (90 μ l, 0.828 mmol), and 70% HF/pyridine (45 mg, 1.19 mmol): 6 mg (52%) of **28**. White solid. As described for **27**, with **20** (14 mg, 0.0395 mmol) in dry THF (1.4 ml), dry pyridine (63 μ l, 0.578 mmol), and 70% HF/pyridine (32 mg, 8.48 mmol) but for 2 h 30 min: 4.4 mg (57%) of **28**. White solid. *R*_f (AcOEt) 0.15. ¹H-NMR (400 MHz, CD₃OD): 1.92 (ddd, *J* = 4.5, 11.0, 13.5, 1 H, CH₂(3)); 2.22 (dt, *J* = 3.6, 13.5, 1 H, CH₂(3)); 4.05 (ddd, *J* = 3.3, 7.8, 11.0, H–C(2)); 4.33 (d, *J* = 7.7, H–C(1)); 5.15 (t, *J* = 4.1, H–C(4)); 6.73 (ddd, *J* = 0.7, 1.1, 7.9, H–C(8)); 7.06 (dt, *J* = 0.9, 7.8, H–C(6)); 7.16 (t, *J* = 7.9, H–C(7)). ¹³C-NMR (100 MHz, CD₃OD): 37.25 (C(3)); 63.48 (C(4)); 68.96 (C(2)); 74.44 (C(1)); 113.90 (C(8)); 118.63 (C(6)); 124.04; 129.10 (C(7)); 139.71; 155.82 (C(5)). ESI-MS (neg.): 195 ([*M* – H][–]).

cis-(3RS,4SR)-3,4-Dihydro-3,4,8-trihydroxynaphthalen-1(2H)-one (**2**). Under stirring, **27** (31 mg, 0.158 mmol) was dissolved in MeOH (1.7 ml), and then CHCl₃ (8.6 ml) was added. At r.t., activated MnO₂ (151 mg, ca. 1.56 mmol; *Fluka* ref. 63548) was added by spatula. The mixture was stirred overnight and then filtered over SiO₂. The SiO₂ was washed with AcOEt and then the solvent evaporated: 16.3 mg (53%) of **2**. Pale yellow solid. *R*_f (AcOEt) 0.33. ¹H-NMR (400 MHz, CD₃OD): 2.88 (*dd*, *J* = 3.9, 17.4, 1 H, CH₂(2)); 2.99 (*dd*, *J* = 7.2, 17.4, 1 H, CH₂(2)); 4.30 (*ddd*, *J* = 2.8, 3.9, 6.9, H-C(3)); 4.86 (*d*, *J* = 2.8, H-C(4)); 6.88 (*ddd*, *J* = 0.5, 1.0, 8.4, H-C(5)); 7.12 (*dt*, *J* = 1.0, 7.5, H-C(7)); 7.54 (*dd*, *J* = 7.5, 8.4, H-C(6)). ¹³C-NMR (100 MHz, CD₃OD): 42.90 (C(2)); 69.45 (C(3)); 70.29 (C(4)); 115.65 (C(9)); 116.82 (C(5)); 119.02 (C(7)); 136.93 (C(6)); 144.65 (C(10)); 162.22 (C(5)); 203.72 (C(1)). ESI-MS (neg.): 193 ([*M* - H]⁻).

trans-(3RS,4RS)-3,4-Dihydro-3,4,8-trihydroxynaphthalen-1(2H)-one (**1**). As described for **2**, with **28** (6 mg, 0.0306 mmol), MeOH (0.3 ml), CHCl₃ (1.7 ml), and activated MnO₂ (30 mg, ca. 0.3 mmol): 3.3 mg (55%) of **1**. Pale yellow solid. *R*_f (AcOEt) 0.33. ¹H-NMR (400 MHz, CD₃OD): 2.72 (*dd*, *J* = 8.0, 17.2, 1 H, CH₂(2)); 3.11 (*dd*, *J* = 4.0, 17.2, 1 H, CH₂(2)); 4.05–4.11 (*m*, H-C(3)); 4.63 (*d*, *J* = 7.0, H-C(4)); 6.88 (*dd*, *J* = 0.6, 8.6, H-C(5)); 7.14 (*dt*, *J* = 0.6, 7.4, H-C(7)); 7.56 (*dd*, *J* = 7.4, 8.4, H-C(6)). ESI-MS (neg.): 193 ([*M* - H]⁻).

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