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Selective Cleavage of *tert*-Butyldimethylsilylethers *ortho* to a Carbonyl Group by Ultrasound

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Abstract—A general method for the selective cleavage of *tert*-butyldimethylsilylethers *ortho* to a carbonyl group is established by sonication of a 0.1 M solution of the substrate in 1/1 (v/v) CH_3OH/CCl_4. Other phenolic *tert*-butyldimethylsilylethers are unaffected. This reaction performed on flavanoids is completed within 3 h and no special workup is required. Other substrates are also investigated and a mechanism is proposed. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Together with the increasing complexity of the molecules synthesized, there is a growing demand for better protective groups. These must be easy to introduce or to remove, and they should also be resistant to a wide variety of reaction conditions. The selectivity between several protecting groups and even between similar groups is especially valuable for the modern synthetic chemist. The *tert*-butyldimethylsilyl (TBDMS) group has become very popular during recent years because of all these characteristics.[1] We present a new deprotection method involving sonication with a classic ultrasonic cleaning bath.

Ultrasound has found many interesting applications in organic chemistry.[2,3] This technique derives its success not only from the simple rate enhancement of specific reactions, in particular in organo-metallic chemistry, but it also promotes radical pathways giving products which are normally not accessible via ionic reactions. The investigation of the use of ultrasound for deprotection purposes has only recently started. Schmittling applied sonication to accelerate the deprotection of phenolic silylethers by $KF-Al_2O_3$ in CH_3CN[4] and Lee cleaved primary TBDMS ethers selectively by sonication in a CH_3OH/CCl_4 solution without affecting phenolic groups.[5] Since Cavelier obtained some opposite results with this last method,[6] we found it worth investigating this technique within the scope of our research for new selective protections of flavanoids.

Results and Discussion

We wish to report the highly regioselective deprotection of several phenolic TBDMS ethers *ortho* to a carbonyl group under ultrasonic conditions. To achieve this, the substrate (0.1 M) was dissolved in a 1/1 (v/v) mixture of CH_3OH/CCl_4 and sonicated in an ultrasonic cleaning bath at 50–55°C (Fig. 1). The reactions were monitored by TLC and by mass spectrometry. After completion the solvent was evaporated in vacuo. The fast mono-deprotections gave pure end products. In the case of slower or consecutive desilylations, purification by preparative HPLC was sometimes necessary.

This regioselective reaction was first observed on persilylated taxifolin (Table 1, entry **1a**), whereas persilylated catechin (entry **2a**), the analogue of **1** lacking a carbonyl group, showed no deprotection. These reactions suggest that the carbonyl group plays a crucial role in the selective desilylation reaction. According to Lee,[5,7] sonication of a CH_3OH/CCl_4 mixture generates HCl in situ in analogy to the H_2O/CCl_4 mixture.[8] Mason observed a similar reaction.[9] By sonication of *tert*-butylchloride in aqueous ethanol he obtained the corresponding ether and HCl. As Luche[2] noted, this reaction probably follows a radical pathway[10] rather than the ionic pathway proposed by Mason. This radical pathway was proved by Eshuis,[11] when $CHBr_3$ was exposed to ultrasound. In contrast to this last reaction, where HBr is formed from two $CHBr_3$ molecules, CCl_4 needs a protic cosolvent, which delivers the hydrogen atom necessary for the formation of HCl. Consequently the created HCl

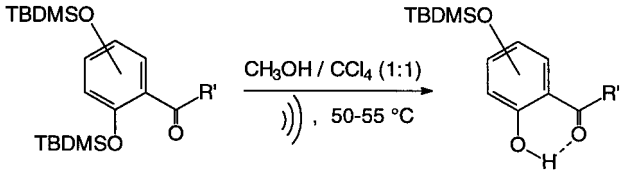

Figure 1.

Keywords: phenolics; protecting groups; sonochemistry; NMR.

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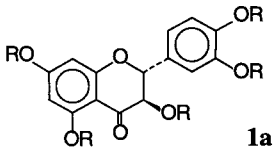
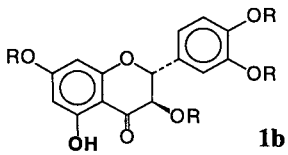
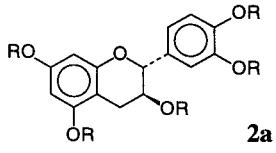
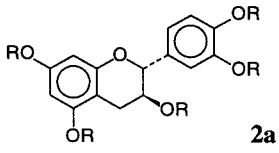
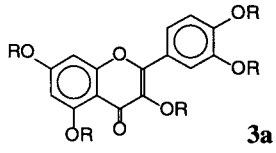
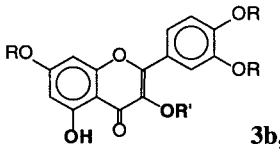
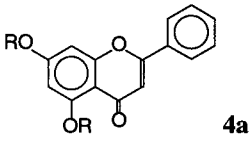
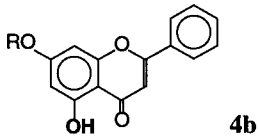
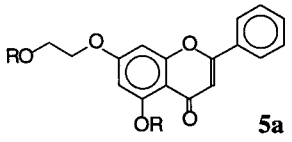
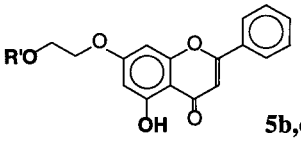
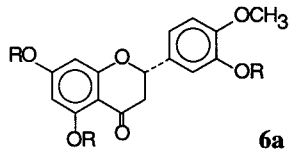
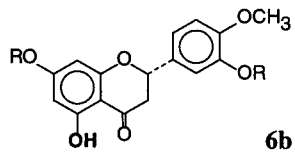
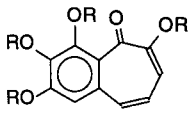
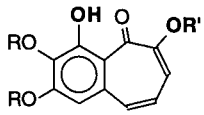
Table 1. Desilylation of *tert*-butyldimethylsilylethers near to a conformationally fixed carbonyl group

Substrate (R = TBDMS)	Product (R = TBDMS)	Reaction time	Yield (%)
 **1a**	 **1b**	15 min	98
 **2a**	 **2a**	> 2 days	100 % recovery
 **3a**	 **3b,c**	**3b:** R'= R: 1.5 h **3c:** R'= H: 24 h	93 63
 **4a**	 **4b**	1.5 h	95
 **5a**	 **5b,c**	**5b:** R'= R: 1.5 h **5c:** R'= H: 20 h	89 92
 **6a**	 **6b**	3 h	91
 **7a**	 **7b,c**	**7b:** R'= R: 3 h **7c:** R'= H: 48 h	90 45

temporarily protonates the carbonyl group and if the added proton is near enough to a silylether, it can catalyze its cleavage. Such a six-ring mechanism as shown in Fig. 2 is well known for Lewis acids, which catalyze selective deprotections *ortho* to a carbonyl group. Dean[12] described this mechanism for the selective deprotection of methyl ethers *ortho* to a carbonyl with boron trichloride. Benzyl-

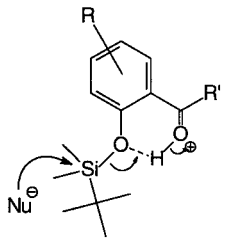


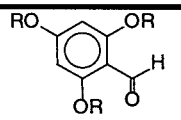
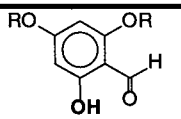
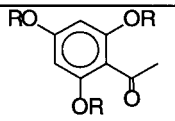
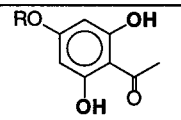
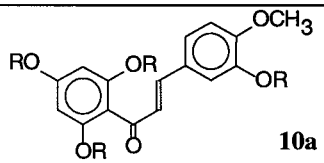
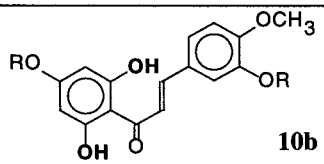
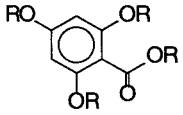
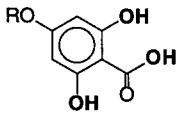
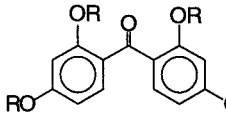
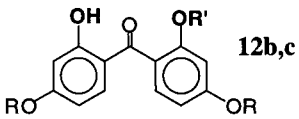
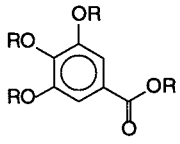
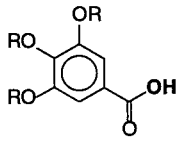
Figure 2.

ethers near a carbonyl group were reported to be selectively removed by $AlCl_3$[13] and $MgBr_2$[14]. To the best of our knowledge no selective deprotection of silylethers *ortho* to a carbonyl has yet been reported.

The flavanoid skeleton guarantees an ideal distance between the carbonyl group and the *ortho*-silylether and also a fixed planar position of the carbonyl group. Products **1** and **3**–**6** indeed give a fast desilylation at the 5-position. Product **5** shows that the carbonyl-group-catalyzed deprotection of the *ortho*-silylether is even faster than the desilylation of the primary alcohol[5] in the conditions mentioned above. As indicated, we could remove the silylether *ortho* to the carbonyl group, leaving the primary silylether unaffected.

The enolic silylether at the 3-position of persilylated quercetin (**3a**) is cleaved after prolonged reaction time. This result is also found for purpurogallin (**7**), which has a

Table 2. Desilylation of *tert*-butyldimethylsilylethers near to a conformationally free carbonyl group

Substrate (R = TBDMS)	Product (R = TBDMS)	Reaction time	Yield (%)
 **8a**	 **8b**	10 min	97
 **9a**	 **9b**	12 h	85
 **10a**	 **10b**	20 h	84
 **11a**	 **11b**	30 h	74
 **12a**	 **12b,c**	**12b:** R'= R : 24 h **12c:** R'= H : 6 d	84 37
 **13a**	 **13b**	10 h	98

similar substitution pattern around the carbonyl group. The oxygen atom of the enolic ethers is farther away from the carbonyl than the *ortho*-silylether oxygen atom, and after protonation only a five-membered ring can be formed.[12] In accordance with our proposed mechanism, the carbonyl group catalyzes less effectively the deprotection of the enolic silylether and so the *ortho* desilylated product can be isolated (**3b**). The out of plane oriented aliphatic silylether of the taxifolin derivative is not cleaved at all, even after prolonged reaction time (>2 days). In this case the silyl oxygen atom is clearly too far away from the carbonyl group. The less reactive character of the aliphatic ether must also be taken into account.

To test the generality of this desilylation, several compounds (**8**–**12**, Table 2) with a carbonyl containing functional group *ortho* to two silylethers and not fixed in a ring structure were studied. The results suggest that the selective desilylation reaction is general for all *ortho*-hydroxy-carbonyl compounds, but they also show that the reaction rate and selectivity decrease with increasing substituents on the carbonyl group. The proposed mechanism suggests that the carbonyl group has to be in the plane of the aromatic ring to play an ideal reaction promoting role. For **8**–**12** increasing sterical hindrance decreases the occurrence of this planar orientation, thus increasing the required reaction time. After deprotection of one of the *ortho*-silylethers the carbonyl group in the benzaldehyde **8** forms a stable hydrogen bond with the free hydroxyl group making it unavailable for desilylation of the second one. No further desilylation is seen even after three days of sonication. In the other compounds (**9**–**12**) the bulkier substituents prevent a planar conformation of the carbonyl group,[15,16] thereby destabilising an intramolecular hydrogen bond. The carbonyl group is now more available for a cleavage of the second *ortho*-silylether. This cleavage occurs slowly, due to steric hindrance of the bulky substituent hindering the carbonyl group from adopting an ideal planar conformation.

The aromatic silylester in **11** is also readily cleaved. However, the *ortho* hydroxyl group does not play any role here as can be seen from entry **13**.

In summary, aromatic and enolic *tert*-butyldimethylsilylethers *ortho* to a carbonyl group have been cleaved selectively, using a very simple ultrasound treatment in a CH_3OH/CCl_4 (1/1) mixture. Although the reaction seems to be quite general, effects that hamper the planar position of the carbonyl group relative to the *ortho*-silylether increase reaction times.

Experimental

Melting points are determined in glass capillaries on a

Tottoli apparatus and are uncorrected. ^{1}H, ^{13}C, COSY HETCOR and long-range HETCOR NMR spectra were recorded on a Varian Unity 400 spectrometer in deuterated chloroform using tetramethylsilane as an internal reference, unless otherwise mentioned. ^{1}H and ^{13}C were assigned with the aid of COSY, HETCOR and long-range HETCOR spectra where necessary, the latter is listed when measured. Assignments that could not be proved unambiguously, are marked with an asterisk: '*'. DCI-mass spectra were taken on a Ribermag R10-10B quadrupole mass spectrometer, using ammonia as reagent gas Preparative HPLC was performed on a Merck Novaprep 5000, using a Merck 250×50 self-packing column packed with Merck LiChroprep Si 60 (25–40 μm particle size).

Commercial dimethylformamide (DMF) was dried over calcium hydride and distilled. Commercial dichloromethane was dried over molecular sieves (4 Å). All other products were used as supplied by Acros, Aldrich or Sigma.

3,3′,4′,5,7-Penta-*O*-*tert*-butyldimethylsilyltaxifolin, 1a. Racemic taxifolin (0.5 g, 1.64 mmol) was dissolved in dry DMF (5 ml). Imidazole (1.1 g, 21 mmol) and *tert*-butyldimethylsilyl chloride (1.4 g, 9 mmol) were then added and the mixture was stirred at room temperature under a nitrogen atmosphere for 16 h. The reaction mixture was diluted with 40 ml ether and washed with water (5×20 ml). After drying over $MgSO_4$, the solvent was evaporated giving a pale yellow oil. It was purified by straight-phase preparative HPLC using a heptane/ether gradient, yielding 1.34 g (93%) colourless oil of **1a**. Anal. found: C, 61.91; H, 9.20; $C_{45}H_{82}O_7Si_5$ requires C, 61.73; H 9.44; δ ^{1}H ($CDCl_3$) 6.97 (d, 1H, *J*=2.4 Hz, H2′), 6.92 (dd, 1H, *J*=8.2,2.4 Hz, H6′), 6.84 (d, 1H, *J*=8.0 Hz, H5′), 6.10 (d, 2H, *J*=2.4 Hz, H8), 5.99 (d, 1H, *J*=2.4 Hz, H6), 4.97 (d, 1H, *J*=10.8 Hz, H2), 4.29 (d, 1H, *J*=10.8 Hz, H3), 1.06 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 1.02 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 1.01 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 0.98 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 0.70 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 0.284 (s, 3H, $\mathbf{CH}_3$Si–), 0.242 (s, 9H, $\mathbf{CH}_3$Si–), 0.223 (s, 3H, $\mathbf{CH}_3$Si–), 0.217 (s, 3H, $\mathbf{CH}_3$Si–), 0.207 (s, 6H, $\mathbf{CH}_3$Si–), 0.117 (s, 3H, $\mathbf{CH}_3$Si–), −0.17 (s, 3H, $\mathbf{CH}_3$Si–); δ ^{13}C ($CDCl_3$) 189.66 (C4), 163.26 (C9), 161.85 (C7), 158.05 (C5), 147.27 (C4′), 146.75 (C3′), 131.03 (C1′), 120.88 (C5′), 120.81 (C6′), 120.42 (C2′), 107.81 (C10), 106.77 (C6), 101.82 (C8), 83.46 (C2), 76.20 (C3), 26.04 (($\mathbf{CH}_3$)$_3$C–), 26.01 (($\mathbf{CH}_3$)$_3$C–), 25.85 (($\mathbf{CH}_3$)$_3$C–), 25.69 (($\mathbf{CH}_3$)$_3$C–), 25.58 (($\mathbf{CH}_3$)$_3$C–), 18.53 (($\mathbf{CH}_3$)$_3$**C**–), 18.49 (($\mathbf{CH}_3$)$_3$C–), 18.44 (($\mathbf{CH}_3$)$_3$C–), 18.25 (($\mathbf{CH}_3$)$_3$C–), −4.00 ($\mathbf{CH}_3$Si–), −4.06 ($\mathbf{CH}_3$Si–), −4.11 ($\mathbf{CH}_3$Si–), −4.15 ($\mathbf{CH}_3$Si–), −4.19 ($\mathbf{CH}_3$Si–), −4.25 ($\mathbf{CH}_3$Si–), −4.32 ($\mathbf{CH}_3$Si–), −4.33 ($\mathbf{CH}_3$Si–), −4.37 ($\mathbf{CH}_3$Si–), −5.76 ($\mathbf{CH}_3$Si–); Long-range HETCOR correlations: H2′→C:4′,6′,2; H6′→C:4′,2′,2; H5′→C:3′,1′; H8→C:9,7,10,6; H6→C:7,5,10,8; H2→C:4,1′,6′,2′,3; H3→C:2; *m*/*z* (DCI): 875 $[M+H]^+$, 817 $[M-57]^+$; IR (KBr) ν_{max}: 1631, 1520, 1251, 1167, 839, 782 cm^{-1}.

3,3′,4′,7-Tetra-*O*-*tert*-butyldimethylsilyltaxifolin, 1b. A solution of **1a** (0.9 g, 1 mmol) in methanol (2 ml) and tetrachloromethane (2 ml) was sonicated in a Bransor 2200 cleaning bath (47 kHz) at 50–55°C. The reaction was monitored by TLC and after 15 min the solvents were removed in vacuo. The resulting light brown oil was held overnight under high vacuum and purified by straight-phase preparative HPLC using a heptane/ether gradient, yielding 769 mg (98%) of pure **1b** as a colourless oil. Anal. found: C, 61.41; H, 9.03; $C_{39}H_{68}O_7Si_4$ requires C, 61.53; H 9.00; δ ^{1}H ($CDCl_3$) 11.78 (s, 1H, –O**H**5), 6.95 (d, 1H, *J*=2.1 Hz, H2′), 6.91 (dd, 1H, *J*=8.2,2.1 Hz, H6′), 6.85 (d, 1H, *J*=8.1 Hz, H5′), 6.02 (d, 1H, *J*=2.1 Hz, H6), 5.96 (d, 1H, *J*=2.1 Hz, H8), 5.00 (d, 1H, *J*=11.1 Hz, H2), 4.41 (d, 1H, *J*=11.1 Hz, H3) 1.002 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 0.997 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 0.96 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 0.72 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 0.24 (s, 6H, $\mathbf{CH}_3$Si–), 0.211 (s, 3H, $\mathbf{CH}_3$Si–), 0.205 (s, 3H, $\mathbf{CH}_3$Si–), 0.20 (s, 6H, $\mathbf{CH}_3$Si–), 0.07 (s, 3H, $\mathbf{CH}_3$Si–), −0.27 (s, 3H $\mathbf{CH}_3$Si–); δ ^{13}C ($CDCl_3$) 196.93 (C4), 164.85 (C7), 163.84 (C5), 162.48 (C9), 147.60 (C4′), 146.90 (C3′), 130.31 (C1′), 120.98 (C6′), 120.93 (C5′), 120.52 (C2′), 102.30 (C6), 102.30 (C10), 99.84 (C8), 83.87 (C2) 75.03 (C3), 26.01 (($\mathbf{CH}_3$)$_3$C–), 25.98 (($\mathbf{CH}_3$)$_3$C–), 25.61 (($\mathbf{CH}_3$)$_3$C–), 25.51 (($\mathbf{CH}_3$)$_3$C–), 18.49 (($\mathbf{CH}_3$)$_3$**C**–), 18.43 (($\mathbf{CH}_3$)$_3$**C**–), 18.32 (($\mathbf{CH}_3$)$_3$**C**–), 18.21 (($\mathbf{CH}_3$)$_3$**C**–), −4.00 ($\mathbf{CH}_3$Si–), −4.06 ($\mathbf{CH}_3$Si–), −4.11 ($\mathbf{CH}_3$Si–), −4.15 ($\mathbf{CH}_3$Si–), −4.37 ($\mathbf{CH}_3$Si–), −4.45 ($\mathbf{CH}_3$Si–); Long-range HETCOR correlations: H5→C:5,10,6; H2′→C:4′,6′; H6′→C:2′; H5′→C:3′,1′; H6→C:7,5,10,8; H8→C:9,10; H2→C:4,6′,3; H3→C:2. *m*/*z* (DCI): 761 $[M+H]^+$ 703 $[M-57]^+$; IR (KBr) ν_{max}: 1650, 1513, 1256, 1172, 837, 784 cm^{-1}.

3,3′,4′,5,7-Penta-*O*-*tert*-butyldimethylsilylquercetin, 3a. Quercetin (0.5 g, 1.48 mmol) was dissolved in dry dichloromethane (5 ml) and DBU (1.5 ml, 10 mmol) *tert*-butyldimethylsilyl chloride (1.4 g, 9 mmol) was then added and the mixture was stirred at room temperature under a nitrogen atmosphere for 6 h. The reaction mixture was diluted with 20 ml dichloromethane and washed with water (5×20 ml). After drying over $MgSO_4$, the solvent was evaporated giving a yellow-brown oil. It was purified by straight-phase preparative HPLC using a heptane/dichloromethane gradient yielding 1.25 g (97%) of **1a** as a yellow oil. Anal. found: C, 61.64; H, 8.97; $C_{45}H_{80}O_7Si_5$ requires C, 61.87; H 9.23; δ ^{1}H ($CDCl_3$) 7.47 (dd, 1H, *J*=8.4,2.1 Hz, H6′), 7.38 (d, 1H, *J*=2.1 Hz, H2′), 6.92 (d, 1H, *J*=8.5 Hz H5′), 6.34 (d, 1H, *J*=2.1 Hz, H8), 6.28 (d, 1H, *J*=2.1 Hz, H6), 1.02 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 1.01 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 1.00 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 0.87 (s, 10H, ($\mathbf{CH}_3$)$_3$Si–), 0.86 (s, 9H, ($\mathbf{CH}_3$)$_3$Si–), 0.27 (s, 6H, $\mathbf{CH}_3$Si–), 0.25 (s, 6H, $\mathbf{CH}_3$Si–), 0.23 (s, 6H, $\mathbf{CH}_3$Si–), 0.15 (s, 6H, $\mathbf{CH}_3$Si–), 0.03 (s, 6H, $\mathbf{CH}_3$Si–); δ ^{13}C ($CDCl_3$) 178.20 (C4), 161.92 (C5), 161.77 (C7), 156.49 (C9), 153.18 (C4′*), 147.51 (C2*), 146.79 (C3′), 135.69 (C3), 124.52 (C1′), 123.21 (C6′), 121.79 (C2′), 120.81 (C5′), 106.15 (C10), 102.95 (C6), 98.14 (C8), 25.96 (($\mathbf{CH}_3$)$_3$C–), 25.76 (($\mathbf{CH}_3$)$_3$C–), 25.73 (($\mathbf{CH}_3$)$_3$C–), 25.67 (($\mathbf{CH}_3$)$_3$C–), 25.57 (($\mathbf{CH}_3$)$_3$C–), 18.62 (($\mathbf{CH}_3$)$_3$**C**–), 18.59 (($\mathbf{CH}_3$)$_3$**C**–), 18.46 (($\mathbf{CH}_3$)$_3$**C**–), 18.23 (($\mathbf{CH}_3$)$_3$**C**–), 18.11 (($\mathbf{CH}_3$)$_3$**C**–), −3.57 ($\mathbf{CH}_3$Si–), −4.03 ($\mathbf{CH}_3$Si–), −4.03 ($\mathbf{CH}_3$Si–), −4.15 ($\mathbf{CH}_3$Si–), −4.36 ($\mathbf{CH}_3$Si–); Long-range HETCOR correlations: H6′→C:2,4′,2′; H2′→C:2,4′,3′,6′; H5′→C:3′,1′; H8→C:7,9,10,6; H6→C:5,7,10,8; *m*/*z* (DCI): 873 $[M+H]^+$, 815 $[M-57]^+$; IR (KBr) ν_{max}: 1644, 1611, 1499, 1350, 1313, 1253, 1181, 1014, 839, 779 cm^{-1}.

3,3′,4′,7-Tetra-*O*-*tert*-butyldimethylsilylquercetin, 3b. Sonication of **3a** following a procedure similar to the one

described for **1b** gave **3b** after 90 min. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a yellow oil. Yield 1.01 g (93%). Anal. found: C, 61.57; H, 8.83; $C_{39}H_{66}O_7Si_4$ requires C, 61.69; H, 8.76; δ ^{1}H ($CDCl_3$) 12.67 (s, 1H, –O**H**5), 7.45 (dd, 1H, *J*=8.4,2.2 Hz, H6′), 7.35 (d, 1H, *J*=2.1 Hz, H2′), 6.90 (d, 1H, *J*=8.5 Hz, H5′), 6.33 (d, 1H, *J*=2.1 Hz, H8), 6.26 (d, 1H, *J*=2.1 Hz, H6), 1.01 (s, 9H, (C**H**$_3$)$_3$Si–), 1.00 (s, 9H, (C**H**$_3$)$_3$Si–), 0.99 (s, 9H, (C**H**$_3$)$_3$Si–), 0.84 (s, 9H, (C**H**$_3$)$_3$Si–), 0.26 (s, 6H, C**H**$_3$Si–), 0.24 (s, 6H, C**H**$_3$Si–), 0.21 (s, 6H, C**H**$_3$Si–), 0.12 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 178.23 (C4), 161.91 (C5), 161.80 (C7), 156.50 (C9), 153.22 (C4′*), 149.25 (C2*), 146.81 (C3′), 135.70 (C3), 124.52 (C1′), 123.22 (C6′), 121.75 (C2′), 120.80 (C5′), 106.17 (C10), 102.96 (C6), 98.17 (C8), 25.98 ((**C**H$_3$)$_3$C–), 25.76 ((**C**H$_3$)$_3$C–), 25.73 ((**C**H$_3$)$_3$C–), 25.59 ((**C**H$_3$)$_3$C–), 18.63 ((CH$_3$)$_3$**C**–), 18.61 ((CH$_3$)$_3$**C**–), 18.48 ((CH$_3$)$_3$**C**–), 18.26 ((CH$_3$)$_3$**C**–), −4.02 (**C**H$_3$Si–), −4.13 (**C**H$_3$Si–), −4.34 (**C**H$_3$Si–); Long-range HETCOR correlations: H5→C:5, 10,6; H6′→C:2,4′,2′; H2′→C:2,4′(3′,6′; H5′→C:3′1′; H8→C:7,9,10,6; H6→C:5,7,10,8; *m/z* (DCI): 759 $[M+H]^+$, 701 $[M-57]^+$; IR (KBr) ν_{max}: 1652, 1601, 1509, 1352, 1309, 1253, 1188, 1164, 1004, 841, 781 cm^{-1}.

3′,4′,7-Tri-*O*-*tert*-butyldimethylsilylquercetin, 3c. After 24 h **3c** was obtained from **3b** in 63% yield (0.54 g) as a yellow oil by a procedure similar to the one described for **3b**. Anal. found: C, 61.33; H, 8.01; $C_{33}H_{52}O_7Si_3$ requires C, 61.45; H, 8.13; δ ^{1}H ($CDCl_3$) 11.70 (s, 1H, –O**H**5), 7.84 (d, 1H, *J*=2.2 Hz, H2′), 7.68 (dd, 1H, *J*=8.5,2.3 Hz, H6′), 6.96 (d, 1H, *J*=8.6 Hz, H5′), 6.64 (s, 1H, –O**H**3), 6.41 (d, 1H, *J*=2.0 Hz, H8), 6.30 (d, 1H, *J*=2.0 Hz, H6), 1.03 (s, 9H, (C**H**$_3$)$_3$Si–), 1.02 (s, 9H, (C**H**$_3$)$_3$Si–), 1.01 (s, 9H, (C**H**$_3$)$_3$Si–), 0.284 (s, 6H, C**H**$_3$Si–), 0.275 (s, 6H, C**H**$_3$Si–), 0.254 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 175.30 (C4), 162.43 (C7*), 160.86 (C5), 156.59 (C9*), 149.17 (C4′), 147.02 (C3′), 145.58 (C2), 135.76 (C3), 123.94 (C1′), 121.22 (C6′), 121.05 (C5′), 120.65 (C2′), 104.40 (C10), 103.15 (C6), 98.61 (C8), 26.00 ((**C**H$_3$)$_3$C–), 25.89 ((**C**H$_3$)$_3$C–), 25.56 ((**C**H$_3$)$_3$C–), 18.56 ((CH$_3$)$_3$**C**–), 18.52 ((CH$_3$)$_3$**C**–), 18.27 ((CH$_3$)$_3$**C**–), −4.06 (**C**H$_3$Si–), −4.12 (**C**H$_3$Si–), −4.34 (**C**H$_3$Si–); Long-range HETCOR correlations: H5→C:5, 10,6; H6′→C:4′; H5′→C:3′,1′; H3→C:2,3; H6→C:10; *m/z* (DCI): 645 $[M+H]^+$, 587 $[M-57]^+$; IR (KBr) ν_{max}: 1659, 1602, 1512, 1352, 1309, 1254, 1186, 1167, 1009, 842, 777 cm^{-1}.

5,7-Di-*O*-*tert*-butyldimethylsilylchrysin, 4a. 4a was formed from 500 mg of chrysin by a procedure similar to the one described for **3a**. Recrystallization from ethanol afforded a yellow crystalline material, mp 152.5°C. Yield 885 mg (93%). Anal. found: C, 66.92; H, 8.17; $C_{27}H_{38}O_4Si_2$ requires C, 67.17; H 7.93; δ ^{1}H ($CDCl_3$) 7.81 (m, 2H, H2′+H6′), 7.44 (m, 3H, H3′+H5′+H4′), 6.569 (d, 1H, *J*=2.2 Hz, H8), 6.565 (s, 1H, H3), 6.28 (d, 1H, *J*=2.2 Hz, H6), 1.07 (s, 9H, (C**H**$_3$)$_3$Si–), 0.99 (s, 9H, (C**H**$_3$)$_3$Si–), 0.28 (s, 6H, C**H**$_3$Si–), 0.26 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 177.26 (C4), 160.73 (C2), 159.99 (C7), 159.05 (C9), 156.85 (C5), 131.71 (C1′), 130.95 (C4′), 128.75 (C3′+C5′), 125.85 (C2′+C6′), 112.14 (C10), 109.90 (C6), 108.38 (C3), 101.73 (C8), 25.87 ((**C**H$_3$)$_3$C–), 25.48 ((**C**H$_3$)$_3$C–), 18.57 ((CH$_3$)$_3$**C**–), 18.16 ((CH$_3$)$_3$**C**–), −4.41 (**C**H$_3$Si–), −4.42 (**C**H$_3$Si–); Long-range HETCOR correlations: H2′+H6′→C:2,4′,6′; H3′+H5′→C:5′; H8→C:7, 9,10,6; H3→C:4,2,1′,10; H6→C:7,5,10,8; *m/z* (DCI): 483 $[M+H]^+$, 425 $[M-57]^+$; IR (KBr) ν_{max}: 1642, 1619, 1450, 1352, 1170, 1100, 853, 840, 778 cm^{-1}

7-*O*-*tert*-Butyldimethylsilylchrysin, 4b. Sonication of **4a** following a procedure similar to the one described for **1b** gave **4b** after 90 min. Recrystallization from ethanol afforded a yellow crystalline material, mp 153.5°C. Yield 643 mg (95%). Anal. found C, 68.60; H, 6.57; $C_{21}H_{24}O_4Si$ requires C, 68.45; H, 6.56; δ ^{1}H ($CDCl_3$) 12.65 (s, 1H, –O**H**5), 7.91 (m, 2H, H2′+H6′), 7.53 (m, 3H, H3′+H5′+H4′), 6.66 (s, 1H, H3), 6.45 (d, 1H, *J*=2.0 Hz, H8), 6.31 (d, 1H, *J*=2.0 Hz H6), 1.00 (s, 9H, (C**H**$_3$)$_3$Si–), 0.28 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 182.50 (C4), 163.95 (C2), 162.36 (C7), 162.12 (C5), 157.62 (C9), 131.74 (C4′), 131.36 (C1′), 129.00 (C3′+C5′), 126.26 (C2′+C6′), 106.21 (C10), 105.82 (C3), 103.92 (C6), 98.74 (C8), 25.51 ((**C**H$_3$)$_3$C–), 18.21 ((CH$_3$)$_3$**C**–), −4.38 (**C**H$_3$Si–); Long-range HETCOR correlations: H5→C:5,10,6; H2′+H6′→C:2,4′,6′; H3′+H5′→C:5′; H3→C:4,2,1′,10; H8→C:7,9, 10,6; H6→C:7,10,8; *m/z* (DCI): 369 $[M+H]^+$, 311 $[M-57]^+$; IR (KBr) ν_{max}: 1652, 1618, 1451, 1349, 1169, 1102, 857, 839, 780 cm^{-1}.

5-*O*-*tert*-Butyldimethylsilyl-7-*O*-(2-*tert*-butyldimethylsilyloxyethyl)chrysin, 5a. 5a was formed from 500 mg of 7-*O*-(2-hydroxyethyl)chrysin by a procedure similar to the one described for **3a.** Recrystallization from methanol/water gave a deep yellow crystalline material, mp 92°C. Yield 840 mg (95%). Anal. found: C, 66.36; H, 8.15; $C_{29}H_{42}O_5Si_2$ requires C, 66.12; H 8.04; δ ^{1}H ($CDCl_3$) 7.89 (m, 2H, H2′+H6′), 7.55 (m, 3H, H3′+H5′ and H4′), 6.70 (d, 1H, *J*=2.4 Hz, H8), 6.65 (s, 1H, H3), 6.46 (d, 1H, *J*=2.4 Hz, H6), 4.21 (t, 2H, *J*=5.2 Hz, H1′′), 4.12 (t, 2H, *J*=5.2 Hz, H2′′), 1.08 (s, 9H, (C**H**$_3$)$_3$Si–), 0.92 (s, 9H, (C**H**$_3$)$_3$Si–), 0.28 (s, 6H, C**H**$_3$Si–), 0.12 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 176.80 (C4), 162.53 (C7), 160.32 (C2), 159.05 (C9), 156.57 (C5), 130.77 (C1′), 130.76 (C4′), 128.59 (C3′+C5′), 125.57 (C2′+C6′), 111.43 (C10), 108.25 (C3), 105.45 (C6), 94.97 (C8), 69.73 (C1′′), 61.52 (C2′′), 26.59 ((**C**H$_3$)$_3$C–), 26.53 ((**C**H$_3$)$_3$C–), 19.44 ((CH$_3$)$_3$**C**–), 19.15 ((CH$_3$)$_3$**C**–), −3.81 (**C**H$_3$Si–), −4.71 (**C**H$_3$Si–); Long-range HETCOR correlations: H2′+H6′→C:2,4′,6′; H3′+H5′→C:4′; H8→C:7,9,10; H3→C:2,10; H6→C:7,5,10; H1′′→C:7; *m/z* (DCI): 527 $[M+H]^+$, 469 $[M-57]^+$; IR (KBr) ν_{max}: 1645, 1611, 1450, 1350, 1254, 1174, 1136, 1102, 836, 777 cm^{-1}.

7-*O*-(2-*tert*-Butyldimethylsilyloxyethyl)chrysin, 5b. Sonication of **5a** following a procedure similar to the one described for **1b** gave **5b** after 90 min. Recrystallization from ethanol afforded a deep yellow crystalline material, mp 107.5°C. Yield 585 mg (89%). Anal. found: C, 66.89; H, 6.80; $C_{23}H_{28}O_5Si$ requires C, 66.96; H, 6.84; δ ^{1}H ($CDCl_3$) 13.95 (s, 1H, –O**H**5), 7.88 (m, 2H, H2′+H6′), 7.52 (m, 3H, H3′+H5′+H4′), 6.66 (s, 1H, H3), 6.52 (d, 1H, *J*=2.3 Hz, H8), 6.38 (d, 1H, *J*=2.3 Hz, H6), 4.12 (t, 2H, *J*=5.2 Hz, H1′′), 4.00 (t, 2H, *J*=5.2 Hz, H2′′), 0.96 (s, 9H, (C**H**$_3$)$_3$Si–), 0.55 (s, 5H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 182.47 (C4), 165.07 (C7), 164.00 (C2), 162.25 (C5), 157.84 (C9), 131.78 (C4′), 131.47 (C1′), 129.08 (C3′+C5′), 126.32 (C2′+C6′), 105.95 (C3), 105.94 (C10), 98.78 (C6), 93.24

(C8), 70.03 (C1′′), 61.73 (C2′′), 25.88 (($\mathbf{C}H_3)_3C$–), 18.38 (($CH_3)_3C$–), −5.20 ($\mathbf{C}H_3Si$–); Long-range HETCOR correlations: H5→C:5,10,6; H2′+H6′→C:2,4′,6′; H3′+H5′→C:4′; H3→C:2,10; H8→C:7,9,10; H6→C:7,5,10; H1′′→C:7; *m/z* (DCI): 413 $[M+H]^+$, 355 $[M-57]^+$; IR (KBr) ν_{max}: 1663, 1622, 1449, 1353, 1255, 1172, 1101, 838, 771, 762 cm^{-1}.

7-*O*-(2-Hydroxyethyl)chrysin, 5c. Sonication of **5b** following a procedure similar to the one described for **1b** gave **5c** after 20 h. Recrystallization from ethanol gave a yellow crystalline material, mp 162°C. Yield 390 mg (92%). Anal. found: C, 68.31; H, 4.65; $C_{17}H_{14}O_5$ requires C, 68.45; H, 4.73; δ ^{1}H ($CDCl_3$) 12.65 (s, 1H, –O**H**5), 7.83 (m, 2H, H2′+H6′), 7.50 (m, 3H, H3′+H5′+H4′), 6.47 (d, 1H, *J*=2.1 Hz, H8), 6.34 (d, 1H, *J*=2.1 Hz, H6), 4.14 (t, 2H, *J*=4.5 Hz, H1′′), 4.01 (br.q., 2H, *J*=4.6 Hz, H2′′), 2.65 (br.s, 1H, –O**H**2′′); δ ^{13}C ($CDCl_3$) 182.38 (C4), 164.66 (C7), 164.04 (C2), 162.19 (C5), 157.71 (C9), 131.80 (C4′), 131.24 (C1′), 129.03 (C3′+C5′), 126.25 (C2′+C6′), 105.86 (C10), 105.82 (C3), 98.69 (C6), 93.17 (C8), 69.94 (C1′′), 61.07 (C2′′); Long-range HETCOR correlations: H5→C:5,10,6; H2′+H6′→C:2,4′,6′+2′; H3′+H5′→ C:1′,5′+3′; H8→C:7,9,10; H6→C:7,5,10; H1′′→C:7; *m/z* (DCI): 299 $[M+H]^+$; IR (KBr) ν_{max}: 3500–3300(OH), 1665, 1615, 1451, 1380, 1174 cm^{-1}.

3′,5,7-Tri-*O*-*tert*-butyldimethylsilylhesperetin, 6a. 6a was formed from 500 mg of hesperetin by a procedure similar to the one described for **3a**. Recrystallization from methanol/water gave a yellow crystalline material, mp 82°C. Yield 950 mg (89%). Anal. found: C, 63.13; H, 8.64. $C_{34}H_{56}O_6Si_3$ requires C, 63.31; H 8.75; δ ^{1}H ($CDCl_3$) 6.97 (dd, 1H, *J*=8.3,2.2 Hz, H6′), 6.91 (d, 1H, *J*=2.3 Hz, H2′), 6.85 (d, 1H, *J*=8.4 Hz, H5′), 6.11 (d, 1H, *J*=2.3 Hz, H8), 5.94 (d, 1H, *J*=2.3 Hz, H6), 5.24 (dd, 1H, *J*=12.7,2.7 Hz, H2), 3.79 (s, 3H, C**H**$_3$), 2.94 (dd, 1H, *J*=12.9,16.4 Hz, H3a), 2.67 (dd, 1H, *J*=16.4,2.8 Hz, H3b), 1.03 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 0.98 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 0.95 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 0.24 (s, 3H, C**H**$_3$Si–), 0.23 (s, 3H, C**H**$_3$Si–), 0.21 (s, 6H, C**H**$_3$Si–), 0.15 (s, 3H, C**H**$_3$Si–), 0.14 (s, 3H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 189.16 (C4), 164.05 (C9), 162.01 (C7), 158.25 (C5), 151.21 (C4′), 145.28 (C3′), 131.67 (C1′), 119.55 (C6′), 119.06 (C2′), 112.23 (C5′), 109.25 (C10), 106.63 (C6), 102.09 (C8), 78.59 (C2), 55.57 (C**H**$_3$), 45.71 (C3a), 25.84 (($\mathbf{C}H_3)_3C$–), 25.73 (($\mathbf{C}H_3)_3C$–), 25.55 (($\mathbf{C}H_3)_3C$–), 18.51 (($CH_3)_3\mathbf{C}$–), 18.45 (($CH_3)_3\mathbf{C}$–), 18.22 (($CH_3)_3\mathbf{C}$–), −4.26 ($\mathbf{C}H_3Si$–), −4.32 ($\mathbf{C}H_3Si$–), −4.33 ($\mathbf{C}H_3Si$–), −4.56 ($\mathbf{C}H_3Si$–), −4.57 ($\mathbf{C}H_3Si$–); Long-range HETCOR correlations: H6′→C:4′,2′; H2′→C:4′,3′,6′; H5′→C:3′,1′,5′; H8→C:9,7,10,6; H6→C:7,5,10,8; H2→C:4,6′,2′,2; C**H**$_3$→C:4′; H3a→C:4,2; H3b→C:4; *m/z* (DCI): 645 $[M+H]^+$, 587 $[M-57]^+$; IR (KBr) ν_{max}: 1687, 1602, 1515, 1257, 1166, 1098, 839, 783 cm^{-1}.

3′,7-Di-*O*-*tert*-butyldimethylsilylhesperetin, 6b. Sonication of **6a** following a procedure similar to the one described for **1b** gave **6b** after 3 h. Recrystallization from ethanol afforded a light yellow crystalline material, mp 143°C. Yield 711 mg (91%). Anal. found: C, 63.47; H, 8.04. $C_{28}H_{42}O_6Si_2$ requires C, 63.36; H, 7.98. δ ^{1}H ($CDCl_3$) 11.93 (s, 1H, –O**H**5), 6.99 (dd, 1H, *J*=8.3,2.3 Hz, H6′), 6.94 (d, 1H, *J*=2.1 Hz, H2′), 6.88 (d, 1H, *J*=8.3 Hz, H5′) 6.00 (d, 1H, *J*=2.1 Hz, H6), 5.99 (d, 1H, *J*=2.1 Hz, H8), 5.31 (dd, 1H, *J*=12.7,2.9 Hz, H2), 3.82 (s, 3H, C**H**$_3$), 3.06 (dd, 1H, *J*=17.1,12.8 Hz, H3a), 2.78 (dd, 1H, *J*=17.0,2.9 Hz, H3b), 1.01 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 0.97 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 0.247 (s, 6H, C**H**$_3$Si–), 0.174 (s, 3H, C**H**$_3$Si–), 0.169 (s, 3H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 196.09 (C4), 164.95 (C7), 163.99 (C5), 162.86 (C9), 151.45 (C4′), 145.41 (C3′), 131.07 (C1′), 119.65 (C6′), 119.10 (C2′), 112.28 (C5′), 103.72 (C10), 101.17 (C6), 99.90 (C8), 78.87 (C2), 55.58 (C**H**$_3$), 43.31 (C3a), 25.73 (($\mathbf{C}H_3)_3C$–), 25.51 (($\mathbf{C}H_3)_3C$–), 18.45 (($CH_3)_3\mathbf{C}$–), 18.19 (($CH_3)_3\mathbf{C}$–), −4.37 ($\mathbf{C}H_3Si$–), −4.56 ($\mathbf{C}H_3Si$–); Long-range HETCOR correlations: H5→C:5,10,6; H6′→C:2′; H2′→C:3′,6′; H5′→C:3′,1′; H6→C:7; H8→C:7,9; H3a→C:4,2; *m/z* (DCI): 531 $[M+H]^+$, 473 $[M-57]^+$; IR (KBr) ν_{max}: 1698, 1609, 1509, 1256, 1172, 1094, 843, 785 cm^{-1}.

2,7,8,9-Tetra-*O*-*tert*-butyldimethylsilylpurpurogallin, 7a. 7a was formed from 0.5 g of purpurogallin by a procedure similar to the one described for **3a**. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a brown oil. Yield 1.27 g (83%). Anal. found: C, 61.88; H, 9.69. $C_{35}H_{64}O_5Si_4$ requires C, 62.07; H 9.53; δ ^{1}H ($CDCl_3$) 6.77 (d, 1H, *J*=11.3 Hz, H5), 6.66 (s, 1H, H6) 6.34 (d, 1H, *J*=8.1 Hz, H3), 6.26 (dd, 1H, *J*=11.4,8.8 Hz, H4), 1.04 (s, 9H ($C\mathbf{H}_3)_3Si$–), 1.03 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 1.02 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 0.98 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 0.30 (s, 6H, C**H**$_3$Si–), 0.29 (s, 6H, C**H**$_3$Si–), 0.21 (s, 6H, C**H**$_3$Si–), 0.08 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 184.72 (C1), 155.25 (C2), 150.73 (C7), 148.28 (C9), 140.40 (C8), 131.05 (C5), 130.48 (C11), 126.20 (C10), 121.77 (C4), 115.44 (C3), 115.05 (C6), 26.65 (($\mathbf{C}H_3)_3C$–), 26.44 (($\mathbf{C}H_3)_3C$–), 26.14 (($\mathbf{C}H_3)_3C$–), 25.86 (($\mathbf{C}H_3)_3C$–), 18.77 (($CH_3)_3\mathbf{C}$–), 18.58 (($CH_3)_3\mathbf{C}$–), 18.10 (($CH_3)_3\mathbf{C}$–), 17.98 (($CH_3)_3\mathbf{C}$–), −3.47 ($\mathbf{C}H_3Si$–), −3.61 ($\mathbf{C}H_3Si$–), −3.61 ($\mathbf{C}H_3Si$–), −3.83 ($\mathbf{C}H_3Si$–); Long-range HETCOR correlations: H5→C:10,3,6; H6→C:7,8,10; H3→C:1,5; H4→C:2,11; *m/z* (DCI): 677 $[M+H]^+$, 619 $[M-57]^+$; IR (KBr) ν_{max}: 1619, 1432, 1386, 1253, 1014, 851, 769 cm^{-1}.

2,7,8-Tri-*O*-*tert*-butyldimethylsilylpurpurogallin, 7b. Sonication of **7a** following a procedure similar to the one described for **1b** gave **7b** after 3 h. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a brown oil. Yield 0.95 g (90%). Anal. found: C, 61.64; H, 8.76. $C_{29}H_{50}O_5Si_3$ requires C, 61.87; H, 8.95; δ ^{1}H ($CDCl_3$) 15.34 (s, 1H, –O**H**9), 7.09 (dd, 1H, *J*=12.3,0.8 Hz, H5), 6.90 (dd, 1H, *J*=9.5,0.8 Hz, H3), 6.67 (s, 1H, H6), 6.48 (dd, 1H, *J*=11.4,9.5 Hz, H4), 1.03 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 1.00 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 0.99 (s, 9H, ($C\mathbf{H}_3)_3Si$–), 0.29 (s, 5H, C**H**$_3$Si–), 0.27 (s, 6H, C**H**$_3$Si–), 0.24 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 186.49 (C1), 157.71 (C9), 154.92 (C2), 151.96 (C7), 136.71 (C8), 135.57 (C5), 133.12 (C11), 122.48 (C3), 122.43 (C4), 117.52 (C10), 114.87 (C6), 26.04 (($\mathbf{C}H_3)_3C$–), 26.02 (($\mathbf{C}H_3)_3C$–), 25.91 (($\mathbf{C}H_3)_3C$–), 18.90 (($CH_3)_3\mathbf{C}$–), 18.81 (($CH_3)_3\mathbf{C}$–), 18.69 (($CH_3)_3\mathbf{C}$–), −3.66 ($\mathbf{C}H_3Si$–), −3.75 ($\mathbf{C}H_3Si$–), −3.97 ($\mathbf{C}H_3Si$–); Long-range HETCOR correlations: H9→C:9,8,10; H5→C:10,6; H3→C:1,*2*,*4*; H6→C:7,8,10; H4→C:2,11; *m/z* (DCI): 563 $[M+H]^+$, 505 $[M-57]^+$; IR (KBr) ν_{max}: 1631, 1424, 1378, 1258, 1007, 845, 767 cm^{-1}.

7,8-Di-*O*-*tert*-butyldimethylsilylpurpurogallin, 7c. Sonication of **7b** following a procedure similar to the one described for **1b** gave **7c** after 48 h. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a brown oil. Yield 0.34 g (45%). Anal. found: C, 61.73; H, 8.18. $C_{23}H_{36}O_5Si_2$ requires C, 61.57; H, 8.09; δ ^{1}H ($CDCl_3$) 14.70 (s, 1H, –O**H**9), 8.49 (s, 1H, –O**H**2), 7.21 (dd, 1H, *J*=12.3,0.7 Hz, H5), 7.10 (dd, 1H, *J*=9.2,0.8 Hz, H3), 6.77 (s, 1H, H6), 6.70 (dd, 1H, *J*=11.2,9.2 Hz, H4), 1.04 (s, 9H, (C**H**$_3$)$_3$Si–), 1.01 (s, 9H, (C**H**$_3$)$_3$Si–), 0.306 (s, 6H, C**H**$_3$Si–), 0.247 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 182.62 (C1), 156.94 (C9), 154.84 (C2), 153.05 (C7), 134.96 (C8), 134.60 (C5), 134.29 (C11), 124.06 (C4), 116.54 (C10), 115.67 (C3), 114.96 (C6), 26.01 ((**C**H$_3$)$_3$C–), 25.97 ((**C**H$_3$)$_3$C–), 18.74 ((CH$_3$)$_3$**C**–), 18.04 ((CH$_3$)$_3$**C**–), −3.65 (**C**H$_3$Si–), −3.77 (**C**H$_3$Si–); Long-range HETCOR correlations: H9→C:9,8,10; H5→C:10,6; H3→C:1,*2*,*4*; H6→C:7,8,10; H4→C:2,11; *m*/*z* (DCI): 449 $[M+H]^+$, 391 $[M-57]^+$; IR (KBr) ν_{max}: 1635, 1427, 1377, 1254, 1003, 846, 763 cm^{-1}.

2,4,6-Tri-*tert*-butyldimethylsilyloxybenzaldehyde, 8a. 8a was formed from 0.5 g of 2,4,6-trihydroxybenzaldehyde by a procedure similar to the one described for **1a.** Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a light brown oil. Yield 1.5 g (93%). Anal. found: C, 60.10; H, 9.91. $C_{25}H_{48}O_4Si_3$ requires C, 60.43; H 9.74; δ ^{1}H ($CDCl_3$) 10.27 (s, 1H, H1), 5.93 (s, 2H, H3′+H5′), 1.00 (s, 18H, (C**H**$_3$)$_3$Si–), 0.97 (s, 9H, (C**H**$_3$)$_3$Si–), 0.24 (s, 12H, C**H**$_3$Si–), 0.23 (, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 188.07 (C1), 166.33 (C4′), 159.89 (C2′+C6′), 114.89 (C1′), 106.48 (C3′+C5′), 25.61 ((**C**H$_3$)$_3$C–), 25.49 ((**C**H$_3$)$_3$C–), 18.41 ((CH$_3$)$_3$**C**–), 18.19 ((CH$_3$)$_3$**C**–), −4.38 ((**C**H$_3$Si–), −4.42 ((**C**H$_3$Si–). *m*/*z* (DCI): 497 $[M+H]^+$, 439 $[M-57]^+$; IR (KBr) ν_{max}: 1627, 1604, 1477, 1319, 1251, 1160, 1078, 846, 779 cm^{-1}.

4,6-Di-*tert*-butyldimethylsilyloxy-2-hydroxybenzaldehyde, 8b. Sonication of **8a** following a procedure similar to the one described for **1b** gave **8b** after 10 min. Purification by straight-phase preparative HPLC using a heptane/ether gradient gave a light brown oil. Yield 1.12 g (97%). Anal. found: C, 59.53; H, 8.98. $C_{19}H_{34}O_4Si_2$ requires C, 59.64; H, 8.96; δ ^{1}H ($CDCl_3$) 12.11 (s, 1H, OH2′), 10.10 (d, 1H, *J*=0.5 Hz, H1), 5.99 (dd, 1H, *J*=2.3,0.7 Hz, H3′), 5.80 (d, 1H, *J*=2.1 Hz, H5′) 1.01 (s, 9H, (C**H**$_3$)$_3$Si–), 0.97 (s, 9H, (C**H**$_3$)$_3$Si–), 0.29 (s, 6H, C**H**$_3$Si–), 0.25 (s, 6H, C**H**$_3$Si–), δ ^{13}C ($CDCl_3$) 192.44 (C1), 165.50 (C2′), 164.82 (C4′), 160.78 (C6′), 109.13 (C1′), 102.41 (C5′), 101.30 (C3′), 25.64 ((**C**H$_3$)$_3$C–), 25.52 ((**C**H$_3$)$_3$C–), 18.35 ((CH$_3$)$_3$**C**–), 18.26 ((CH$_3$)$_3$**C**–), −4.40 (**C**H$_3$Si–), −4.43 (**C**H$_3$Si–); Long-range HETCOR correlations: H1→C:**2**′,1′; H2′+H6′→C:2′,***4***′,1′,3′; H3′+H5′→C:2′,4′,1′,5′; H5′→C:4′,6′,1′,3′; *m*/*z* (DCI): 383 $[M+H]^+$, 325 $[M-57]^+$; IR (KBr) ν_{max}: 1642, 1605, 1475, 1321, 1255, 1156, 1078, 845, 776 cm^{-1}.

2′,4′,6′-Tri-*tert*-butyldimethylsilyloxyacetophenone, 9a. 9a was formed from 0.5 g of 2′,4′,6′-trihydroxyacetophenone by a procedure similar to the one described for **3a**. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a colourless oil. Yield 1.31 g (95%). Anal. found: C, 60.96; H, 9.97. $C_{26}H_{50}O_4Si_3$ requires C, 61.12; H 9.86; δ ^{1}H ($CDCl_3$) 5.92 (s, 2H, H3′+H5′), 2.38 (s, 3H, H2), 0.92 (s, 9H, (C**H**$_3$)$_3$Si–), 0.90 (s, 18H, (C**H**$_3$)$_3$Si–), 0.15 (s, 18H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 202.21 (C1), 157.08 (C4′), 153.55 (C2′+C6′), 120.60 (C1′), 104.81 (C3′+C5′), 32.46 (C2), 25.60 ((**C**H$_3$)$_3$C–), 25.57 ((**C**H$_3$)$_3$C–), 18.19 ((CH$_3$)$_3$**C**–), 18.02 ((CH$_3$)$_3$**C**–), −4.41 (**C**H$_3$Si–); *m*/*z* (DCI): 511 $[M+H]^+$, 453 $[M-57]^+$; IR (KBr) ν_{max}: 1615, 1280, 1252, 1171, 835, 781 cm^{-1}.

4′-*tert*-Butyldimethylsilyloxy-2′,6′-dihydroxyacetophenone, 9b. Sonication of **9a** following a procedure similar to the one described for **1b** gave **9b** after 12 h. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a colourless oil. Yield 615 mg (85%). Anal. found: C, 59.66; H, 7.92. $C_{14}H_{22}O_4Si$ requires C, 59.54; H, 7.85; δ ^{1}H ($CDCl_3$) 5.94 (s, 2H, H3′+H5′), 2.75 (s, 3H, H2), 0.94 (s, 9H, (C**H**$_3$)$_3$Si–), 0.20 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 204.56 (C1), 163.61 (C2′+C6′), 163.42 (C4′), 105.82 (C1′), 100.08 (C3′+C5′), 32.52 (C2), 25.42 ((**C**H$_3$)$_3$C–), 18.107 ((CH$_3$)$_3$**C**–), −4.48 (**C**H$_3$Si–); *m*/*z* (DCI): 283 $[M+H]^+$, 225 $[M-57]^+$; IR (KBr) ν_{max}: 1632, 1282, 1252, 1167, 830, 777 cm^{-1}.

2′3,4′,6′-Tetra-*tert*-butyldimethylsilyloxy-4-methoxychalcone, 10a. 10a was formed from 80 mg of 3,2′,4′,6′-tetrahydroxy-4-methoxychalcone by a procedure similar to the one described for **3a**. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a yellow oil. Yield 175 mg (87%). Anal. found: C, 63.11; H, 9.44; $C_{40}H_{70}O_6Si_4$ requires C, 63.27; H 9.29 δ ^{1}H ($CDCl_3$) 7.20 (d, 1H, *J*=16.1 Hz, Hβ), 7.02 (dd, 1H, *J*=8.2,2.1 Hz, H6), 7.00 (d, 1H, *J*=2.0 Hz, H2) 6.80 (d, 1H, *J*=8.2 Hz, H5), 6.74 (d, 1H, *J*=16.0 Hz, Hα), 6.00 (s, 2H, H3′+H5′), 3.80 (s, 3H, C**H**$_3$), 0.99 (s, 9H, (C**H**$_3$)$_3$Si–), 0.98 (s, 9H, (C**H**$_3$)$_3$Si–), 0.86 (s, 18H, (C**H**$_3$)$_3$Si–), 0.22 (s, 6H, C**H**$_3$Si–), 0.15 (s, 12H, C**H**$_3$Si–) 0.14 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 194.38 (Cβ′), 157.10 (C4′), 154.41 (C2′+C6′), 153.00 (C4), 145.24 (C3) 144.38 (Cβ), 127.47 (Cα), 123.21 (C6), 119.82 (C2), 118.88 (C1′), 111.82 (C5), 104.89 (C3′+C5′), 55.35 (**C**H$_3$) 25.66 ((**C**H$_3$)$_3$C–), 25.65 ((**C**H$_3$)$_3$C–), 25.51 ((**C**H$_3$)$_3$C–), 18.38 ((**C**H$_3$)$_3$**C**–), 18.24 ((CH$_3$)$_3$**C**–), 17.96 ((CH$_3$)$_3$**C**–), −4.36 (**C**H$_3$Si–), −4.37 (**C**H$_3$Si–), −4.69 (**C**H$_3$Si–); Long-range HETCOR correlations: Hβ→C:β′,6,2 H6→C:4,3,β,2; H2→C:4,3,β,6; H5→C:3,1; Hα→C:1; H3′+H5′→C:4′,2′+6′; C**H**$_3$→C:4; *m*/*z* (DCI): 759 $[M+H]^+$, 701 $[M-57]^+$; IR (KBr) ν_{max}: 1615, 1509, 1253, 1157, 1104, 837, 764 cm^{-1}.

3,4′-Di-*tert*-butyldimethylsilyloxy-2′,6′-dihydroxy-4-methoxychalcone, 10b. Sonication of **10a** following a procedure similar to the one described for **1b** gave **10b** after 20 h. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a brown oil. Yield 103 mg (84%). Anal. found: C, 63.41; H, 8.04; $C_{28}H_{42}O_6Si_2$ requires C, 63.36; H, 7.98; δ ^{1}H ($CDCl_3$) 10.5 (br.s, 2H, –O**H**2′+6′), 7.95 (d, 1H, *J*=15.6 Hz, Hβ), 7.58 (d, 1H, *J*=15.4 Hz, Hα), 7.11 (dd, 1H, *J*=8.6,2.3 Hz, H6), 7.03 (d, 1H, *J*=2.1 Hz, H2), 6.81 (d, 1H, *J*=8.5 Hz, H5), 5.84 (s, 2H, H3′+H5′), 3.77 (s, 3H, C**H**$_3$), 0.92 (s, 9H, (C**H**$_3$)$_3$Si–), 0.89 (s, 9H, (C**H**$_3$)$_3$Si–), 0.17 (s, 6H, C**H**$_3$Si–),

0.09 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 192.78 (Cβ'), 163.26 (C2′+C6′), 162.65 (C4′), 153.28 (C4), 145.32 (C3), 143.47 (Cβ), 124.91 (Cα), 123.64 (C6), 120.35 (C2), 111.98 (C5), 106.20 (C1′), 100.54 (C3′+C5′), 55.51 (**C**H$_3$), 25.75 ((**C**H$_3$)$_3$C–), 25.57 ((**C**H$_3$)$_3$C–), 18.49 ((CH$_3$)$_3$**C**–), 18.23 ((CH$_3$)$_3$**C**–), −4.31 (**C**H$_3$Si–), −4.56 (**C**H$_3$Si–); Long-range HETCOR correlations: H2′+H6′→C:1′,2′+6′,3′+′5; Hβ→C:β',6,2; Hα→C:1; H6→C:4,3,β,2; H2→C:4,3,β,6; H5→C:3,1; H3′+H5′→C:4′2′+6′; C**H**$_3$→C:4; *m/z* (DCI): 531 $[M+H]^+$, 473 $[M-57]^+$; IR (KBr) ν_{max}: 1607, 1510, 1256, 1154, 1100, 839, 761 cm^{-1}.

***tert*-Butyldimethylsilyl 2′,4′,6′-tri-*tert*-butyldimethylsilyloxybenzoate, 11a. 11a** was formed from 0.5 g of 2′,4′,6′-trihydroxybenzoic acid by a procedure similar to the one described for **1a**. Recrystallization from methanol/water gave a white crystalline material, mp 184°C. Yield 1.466 g (88%). Anal. found: C, 59.20; H, 10.18; $C_{31}H_{62}O_5Si_4$ requires C, 59.37; H 9.96; δ ^{1}H ($CDCl_3$) 5.94 (s, 2H, H3′+H5′), 0.964 (s, 9H, (C**H**$_3$)$_3$Si–), 0.960 (s, 18H (C**H**$_3$)$_3$Si–), 0.93 (s, 9H (C**H**$_3$)$_3$Si–), 0.34 (s, 6H, C**H**$_3$Si–), 0.22 (s, 12H, C**H**$_3$Si–), 0.19 (s, 6H C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 166.72 (C1), 156.46 (C2′+C6′), 153.81 (C4′), 115.46 (C1′), 104.36 (C3′+C5′), 25.87 ((**C**H$_3$)$_3$C–), 25.70 ((**C**H$_3$)$_3$C–), 25.65 ((**C**H$_3$)$_3$C–), 18.38 ((CH$_3$)$_3$**C**–), 18.23 ((CH$_3$)$_3$**C**–), 17.66 ((CH$_3$)$_3$**C**–), −4.03 (**C**H$_3$Si), −4.36 (**C**H$_3$Si); *m/z* (DCI): 627 $[M+H]^+$, 569 $[M-57]^+$; IR (KBr) ν_{max}: 1629, 1284, 1164, 1065, 834 cm^{-1}.

4′-*tert*-Butyldimethylsilyloxy-2′,6′-dihydroxybenzoic acid, 11b. Sonication of **11a** following a procedure similar to the one described for **1b** gave **11b** after 30 h. Recrystallization from methanol/water afforded a white crystalline material, mp 199°C. Yield 493 mg (74%). Anal. found: C, 54.88; H, 7.08. $C_{13}H_{20}O_5Si$ requires C, 54.91; H, 7.09; δ ^{1}H (acetone-d6) 5.87 (s, 2H, H3′+H5′), 0.94 (s, 9H, (C**H**$_3$)$_3$Si–), 0.20 (s, 6H, C**H**$_3$Si–); δ ^{13}C (acetone-d6) 172,03 (C1′), 163,56 (C4′), 160,03 (C2′+C6′), 100,02 (C1′), 95,48 (C3′+C5′), 25,89 ((**C**H$_3$)$_3$C–), 18,76 ((CH$_3$)$_3$**C**–), −4,28 (**C**H$_3$Si–); *m/z* (CDI): 285 $[M+H]^+$, 241 $[M-44]^+$, 227 $[M-57]^+$; IR (KBr) ν_{max}: 1637, 1472, 1279, 1254, 1166, 1066, 837, 740 cm^{-1}.

2,2′,4,4′-Tetra-*tert*-butyldimethylsilyloxybenzophenone, 12a. 12a was formed from 0.5 g of 2,2′,4,4′-tetrahydroxybenzophenone by a procedure similar to the one described for **3a**. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a yellow oil. Yield 1.37 g (96%). Anal. found: C, 63.03; H, 9.33. $C_{37}H_{66}O_5Si_4$ requires C, 63.19; H 9.46; δ ^{1}H ($CDCl_3$) 7.35 (d, 2H, *J*=8.4 Hz, H6 (+6′)), 6.42 (dd, 2H, *J*=8.5,2.3 Hz, H5 (+5′)), 6.24 (d, 2H, *J*=2.2 Hz, H3 (+3′)), 0.96 (s, 18H, (C**H**$_3$)$_3$Si–), 0.79 (s, 18H, (C**H**$_3$)$_3$Si–), 0.19 (s, 12H, C**H**$_3$Si–), 0.05 (s, 12H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 193.89 (**C**=O), 159.27 (C2+C2′*), 155.83 (C4+C4′*), 132.80 (C6+C6′), 126.41 (C1+C1′), 112.90 (C5+C5′), 111.35 (C3+C3′), 25.66 ((**C**H$_3$)$_3$C–), 25.59 ((**C**H$_3$)$_3$C–), 18.18 ((CH$_3$)$_3$**C**–), 18.15 ((CH$_3$)$_3$**C**–), −4.37 (**C**H$_3$Si), −4.41 (**C**H$_3$Si–); Long-range HETCOR correlations: H6+H6′→C:CO,2,4; H5+H5′→C:1,3; H3+H3′→C:2,4,1,5; *m/z* (DCI): 703 $[M+H]^+$, 645 $[M-57]^+$; IR (KBr) ν_{max}: 1619, 1497, 1257, 1168, 1106, 852, 775 cm^{-1}.

2′,4,4′-Tri-*tert*-butyldimethylsilyloxy-2-hydroxybenzophenone, 12b. Sonication of **12a** following a procedure similar to the one described for **1b** gave **12b** after 24 h. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a yellow oil. Yield 962 mg (84%). Anal. found: C, 63.09; H, 8.83. $C_{31}H_{52}O_5Si_3$ requires C, 63.21; H, 8.90; δ ^{1}H ($CDCl_3$) 12.555 (s, 1H, –O**H**2), 7.30 (d, 1H, *J*=9.0 Hz, H6), 7.20 (d, 1H, *J*=8.3 Hz, H6′), 6.55 (dd, 1H, *J*=8.3,2.4 Hz, H5′), 6.40 (d, 1H, *J*=2.3 Hz, H3), 6.36 (d, 1H, *J*=2.1 Hz, H3′), 6.28 (dd, 1H, *J*=8.8,2.4 Hz, H5), 1.00 (s, 9H, (C**H**$_3$)$_3$Si–), 0.98 (s, 9H, (C**H**$_3$)$_3$Si–), 0.73 (s, 9H, (C**H**$_3$)$_3$Si–), 0.24 (s, 6H, C**H**$_3$Si–), 0.23 (s, 6H, C**H**$_3$Si–), 0.07 (s, 6H, C**H**$_3$Si–), δ ^{13}C ($CDCl_3$) 200.26 (**C**=O), 165.16 (C2), 162.93 (C4), 158.69 (C2′*), 153.77 (C4′*), 135.95 (C6), 130.17 (C6′), 124.72 (C1′), 115.51 (C1), 115.51 (C5′), 111.94 (C5), 111.65 (C3′), 107.78 (C3), 25.66 ((**C**H$_3$)$_3$C–), 25.59 ((**C**H$_3$)$_3$C–), 25.32 ((**C**H$_3$)$_3$C–), 18.27 (2X, (CH3)3$^+$C–), 17.86 ((CH$_3$)$_3$**C**–), −4.34 (**C**H$_3$Si–), −4.36 (**C**H$_3$Si–), −4.54 (**C**H$_3$Si–); Long-range HETCOR correlations: H2→ C:2,1,3; H6→C:CO,2,4; H6′→C:CO,2′,4′; H5′→C:1′,3′; H3→C:1,5; H3′→C:1′,5′; H5→C:1; *m/z* (DCI): 589 $[M+H]^+$, 531 $[M-57]^+$; IR (KBr) ν_{max}: 1627, 1496, 1259, 1102, 839, 783 cm^{-1}.

4,4′Di-*tert*-butyldimethylsilyloxy-2,2′-dihydroxybenzophenone, 12c. Sonication of **12b** following a procedure similar to the one described for **1b** gave **12c** after six days. Purification by straight-phase preparative HPLC using a heptane/dichloromethane gradient gave a yellow oil. Yield 289 mg (37%; the remaining fraction consists of the mono-silylether and the unprotected benzophenone derivative). Anal. found: C, 63.17; H, 8.03. $C_{25}H_{38}O_5Si_2$ requires C, 63.25; H, 8.07; δ ^{1}H ($CDCl_3$) 11.12 (s, –O**H**2+2′), 7.51 (d, H, *J*=8.8 Hz, H6 (+6′)), 6.48 (d, H, *J*=2.4 Hz, H3 (+3′)), 6.40 (dd, H, *J*=8.8,2.4 Hz, H5 (+5′)), 1.00 (s, H, *J*=18.3 Hz, (C**H**$_3$)$_3$Si–), 0.27 (s, H, *J*=10.2 Hz, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 199.53 (**C**=O), 164.30 (C2+C2′), 162.48 (C4+C4′), 134.52 (C6+C6′), 114.39 (C1+C1′), 111.81 (C5+C5′), 108.63 (C3+C3′), 25.57 ((**C**H$_3$)$_3$C–), 18.26 ((CH$_3$)$_3$**C**–), −4.31 (**C**H$_3$Si–); Long-range HETCOR correlations: H2+H2′→C:2; H6+H6′→C:2,4; H3+H3′→C:1,5; H5+H5′→C:3; *m/z* (DCI): 475 $[M+H]^+$, 417 $[M-57]^+$; IR (KBr) ν_{max}: 1632, 1509, 1259, 1172, 1092, 838, 786 cm^{-1}.

***tert*-Butyldimethylsilyl 3′,4′,5′-tri-*O*-*tert*-butyldimethylsilylgallate, 13a. 13a** was formed from 0.5 g of gallic acid by a procedure similar to the one described for **1a**. ^{1}H NMR did not show any impurities and product was further used without purification. Yield 1.63 g (98%). Anal. found: C, 59.32; H, 9.85. $C_{31}H_{62}O_5Si_4$ requires C, 59.37; H 9.96; δ ^{1}H ($CDCl_3$) 7.23 (s, 2H, H2′+H6′), 1.02 (s, 9H, (C**H**$_3$)$_3$Si–), 1.01 (s, 9H, (C**H**$_3$)$_3$Si–), 0.96 (s, 18H, (C**H**$_3$)$_3$Si–), 0.36 (s, 5H, C**H**$_3$Si–), 0.25 (s, 12H, C**H**$_3$Si–), 0.15 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 166.12 (C1), 148.33 (C3′+C5′), 143.19 (C4′), 123.40 (C1′), 116.05 (C2′+C6′), 26.24 ((**C**H$_3$)$_3$C–), 26.18 ((**C**H$_3$)$_3$C–), 25.66 ((**C**H$_3$)$_3$C–), 18.81 ((CH$_3$)$_3$**C**–), 18.49 ((CH$_3$)$_3$**C**–**),** 17.72 ((CH$_3$)$_3$**C**–), −3.60 (**C**H$_3$Si–), −3.83 (**C**H$_3$Si–), −4.75 (**C**H$_3$Si–); *m/z* (DCI): 627 $[M+H]^+$, 569 $[M-57]^+$; IR (KBr) ν_{max}: 1627, 1496, 1259, 1180, 1104, 839, 783 cm^{-1}.

3′,4′,5′-Tri-*O*-*tert*-butyldimethylsilylgallic acid, 13b. Sonication of **13a** following a procedure similar to the one described for **1b** gave **13b** after 10 h. Recrystallization from methanol afforded white needles, mp 237°C. Yield 1.31 g (98%). Anal. found: C, 58.60; H, 9.43. $C_{25}H_{48}O_5Si_3$ requires C, 58.54; H, 9.43; δ ^{1}H ($CDCl_3$) 7.29 (s, 2H, H2′+H6′), 1.00 (s, 9H, (C**H**$_3$)$_3$Si–), 0.96 (s, 18H, (C**H**$_3$)$_3$Si–), 0.25 (s, 12H, C**H**$_3$Si–), 0.16 (s, 6H, C**H**$_3$Si–); δ ^{13}C ($CDCl_3$) 171.75 (C1), 148.53 (C3′+C5′), 144.10 (C4′), 121.13 (C1′), 116.17 (C2′+C6′), 26.22 ((**C**H$_3$)$_3$C–), 26.15 ((**C**H$_3$)$_3$C–), 18.83 ((CH$_3$)$_3$**C**–), 18.54 ((CH$_3$)$_3$**C**–), −3.61 (**C**H$_3$Si–), −3.84 (**C**H$_3$Si–); *m/z* (DCI): 513 $[M+H]^+$, 469 $[M-44]^+$, 455 $[M-57]^+$.

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