MHz, D_2O/CD_3OD) see table; ^{13}C NMR (101 MHz, D_2O, internal reference to CD_3OD at δ 49.0) δ 173.8, 169.5, 166.3, 155.5, 151.9, 142.2, 133.9, 128.3, 115.6, 102.6, 89.2, 84.1, 75.2, 73.1, 70.2, 56.6, 54.5, 40.9, 11.3; MS (FAB) m/z 517 (M + Na^+), 495 (M + H^+), 391, 329, 295, 237, 207, 179; exact mass (FAB) calcd for $C_{21}H_{28}N_4O_{10}$ (M + Na^+) 517.1547, (M + H^+) 495.1727, found (M + Na^+) 517.1564 (M + H^+), 495.1678.

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Supplementary Material Available: ^1H NMR spectra for compounds **28a,b**, **30a,b**, **35**, **38**, and **41** (7 pages). Ordering information is given on any current masthead page.

A Short and Facile Synthetic Route to Hydroxylated Flavones. New Syntheses of Apigenin, Tricin, and Luteolin

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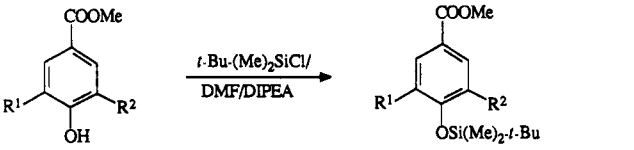
Reaction of the lithium polyanions generated from *o*-hydroxyacetophenones **3a-f** with O-silyloxylated benzoates **2a-d** gave 1-aryl-3-(2-hydroxyphenyl)-1,3-propanediones **4a-n**, which on treatment with acetic acid containing 0.5% H_2SO_4 at 95-100 °C afforded hydroxylated flavones **5-18** in high yields (76-92%).

Ring-A hydroxylated flavones are of current interest due to biological activities including inhibition of retroviral reverse transcriptases,[1-3] protein-tyrosine kinases,[4,5] and serine/threonine kinases.[4] They possess anticancer[6,7] and chemopreventative activities,[7] and certain ring-A hydroxylated flavones inhibit HIV-induced syncytium formation.[8] Although a number of methods are available for the synthesis of flavones,[9-18] they are not ideal for the preparation of ring-A hydroxylated flavones because the phenolic hydroxyl groups of the intermediates are derivatized as esters or ethers that must eventually be cleaved to regenerate the hydroxyl groups. This often results in only partial deprotection of the phenolic hydroxyl groups, which lowers the overall yield and complicates the product isolation procedure. We recently communicated a way to avoid this problem by making the lithium polyanions of di- and trihydroxylated acetophenones using enough lithium bis(trimethylsilyl)amide to deprotonate all of the phenolic hydroxyl groups and generate the lithium enolate of the ketone, followed by regioselective acylation of the carbon of the lithium enolate with an aroyl chloride to give a β-diketone intermediate directly.[19] The present report documents an investigation of the extension of this methodology in combination with *tert*-butyldimethylsilyl protection[20,21] of the ring-C phenolic hydroxyls to the preparation of a variety of flavones bearing hydroxyl groups on both the A and C rings. The desired polyhydroxylated flavones are produced in high yields, and tedious purifications are avoided. This methodology has resulted in improved syntheses of the naturally occurring flavones apigenin (**9**), luteolin (**11**), and tricin (**18**).

Scheme I



1a, $R^1 = R^2 = H$
1b, $R^1 = OH$, $R^2 = H$
1c, $R^1 = R^2 = OH$
1d, $R^1 = R^2 = OMe$

2a, $R^1 = R^2 = H$
2b, $R^1 = OSi(Me)_2$-*t*-Bu, $R^2 = H$
2c, $R^1 = R^2 = OSi(Me)_2$-*t*-Bu
2d, $R^1 = R^2 = OMe$

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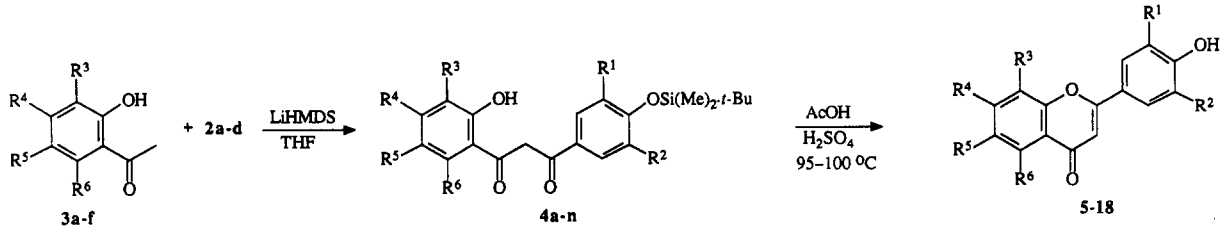
Scheme II

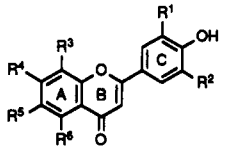


	R^3	R^4	R^5	R^6
3a	H	H	H	H
3b	H	H	H	OH
3c	H	H	OH	H
3d	H	OH	H	H
3e	OH	OH	H	H
3f	H	OH	H	OH

	R^1	R^2	R^3	R^4	R^5	R^6
4a	H	H	H	H	H	H
4b	H	H	H	H	H	OH
4c	H	H	H	H	OH	H
4d	H	H	H	OH	H	H
4e	H	H	H	OH	H	OH
4f	OR'	H	H	H	H	H
4g	OR'	H	H	OH	H	OH
4h	OR'	OR'	H	H	H	H
4i	OMe	OMe	H	H	H	H
4j	OMe	OMe	H	H	H	OH
4k	OMe	OMe	H	H	OH	H
4l	OMe	OMe	H	OH	H	H
4m	OMe	OMe	OH	OH	H	H
4n	OMe	OMe	H	OH	H	OH

R' = $Si(Me)_2$-t-Bu

Table I. Physical Characteristics and Yields of Flavones 5–18



compd	R^1	R^2	R^3	R^4	R^5	R^6	yield, %	mp, °C (lit. mp, °C)
5	H	H	H	H	H	H	86	270–271 (270)[13]
6	H	H	H	H	H	OH	88	238–240 (237–240)[23]
7	H	H	H	H	OH	H	92	320–322 (318–321)[24]
8	H	H	H	OH	H	H	88	316–318 (315–316)[13]
9	H	H	H	OH	H	OH	76	348–350 (348–350)[13]
10	OH	H	H	H	H	H	79	245–246 (246)[25]
11	OH	H	H	OH	H	OH	78	330–332 (330–331)[26]
12	OH	OH	H	H	H	H	81	300–302 (302)[13]
13	OMe	OMe	H	H	H	H	83	223–224 (223–224)[27]
14	OMe	OMe	H	H	H	OH	89	213–214
15	OMe	OMe	H	H	OH	H	91	218–220
16	OMe	OMe	H	OH	H	H	81	298–300
17	OMe	OMe	OH	OH	H	H	81	303–305
18	OMe	OMe	H	OH	H	OH	82	279–281 (276–279)[28]

The required methyl O-silyloxylated benzoates **2a–d** were prepared by the reaction of the corresponding phenols **1a–d** with *tert*-butyldimethylsilyl chloride in DMF in the presence of diisopropylethylamine (Scheme I). Subsequently, in the critical step in the process, 1 equiv of the methyl O-silyloxylated benzoates **2a–d** were condensed with the lithium polyanions generated from polyhydroxylated acetophenones **3a–f** to afford 1-aryl-3-(2-hydroxyphenyl)-1,3-propanediones **4a–n** (Scheme II). Consistent with our earlier studies, 3, 4, and 5 equiv of lithium bis(trimethylsilyl)amide were required as base for optimum yields of the diketones **4a–n** when mono-, di-, and trihydroxyacetophenones **3a–f** were employed as starting materials, respectively.[19] Longer reaction times were required for these esters **2a–d** as compared with the acid chlorides utilized in the prior study.[19] As revealed by TLC analyses of the reaction mixtures, 16–24 h were required for the complete disappearance of the starting materials. The ^1H NMR spectra of the intermediate diketones **4a–n** revealed that they were mixtures of tautomers,[22] and they were subjected to cyclodehydration with 0.5% sulfuric acid in acetic acid at 95–100 °C for 1 h. Under these reaction conditions, the *tert*-butyldimethylsilyl protecting groups were also cleaved to generate the desired phenols. The overall yields of these hydroxylated flavones **5–18** were 76–92% (Table I).

Conditions were also sought for the preparation of flavones with the *tert*-butyldimethylsilyl group intact. This could result in a way to synthesize flavones having a wider variety of substituents. A careful study utilizing *p*-toluenesulfonic acid in benzene at reflux and azeotropic separation of water, treatment with glacial acetic acid at different temperatures between 25 and 75 °C, reaction with concentrated sulfuric acid below 0 °C, as well as other conditions always resulted in the formation of mixtures of hydroxyl protected and deprotected flavones or incomplete cyclodehydration reactions. However, when a solution of 5 mmol of the 1,3-propanedione **4c** was stirred in 10 mL of glacial acetic acid containing 5 drops of con-

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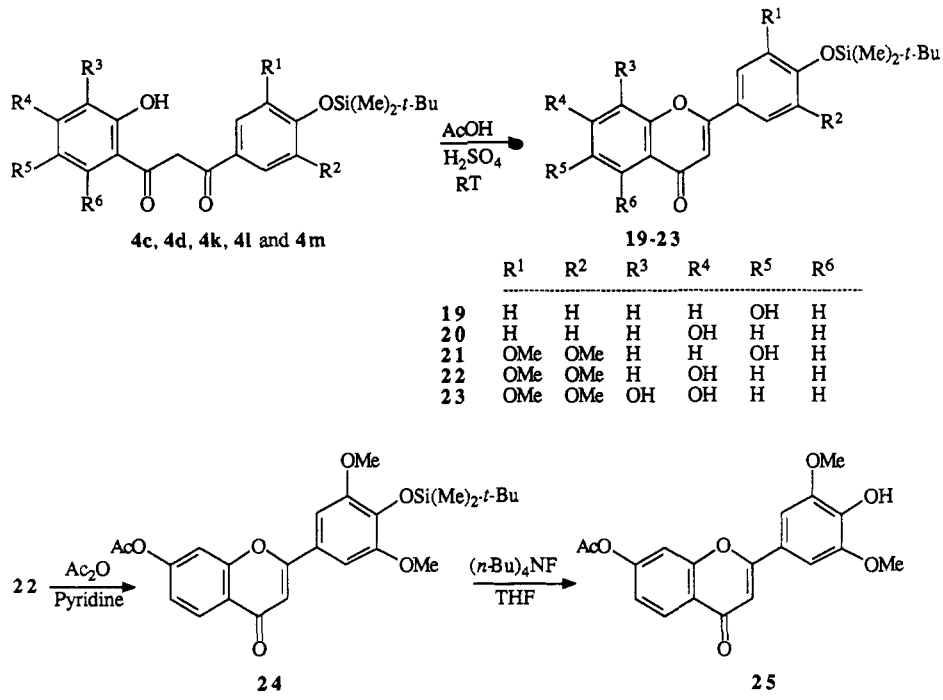
Scheme III



	R^1	R^2	R^3	R^4	R^5	R^6
19	H	H	H	H	OH	H
20	H	H	H	OH	H	H
21	OMe	OMe	H	H	OH	H
22	OMe	OMe	H	OH	H	H
23	OMe	OMe	OH	OH	H	H

centrated sulfuric acid for 30 min at room temperature, the silyl-protected flavone **19** was obtained as a single product in good yield. Utilizing these reaction conditions, the silyloxylated flavones **19–23** were obtained in 83–92% yields from the corresponding 1,3-propanediones **4**. The flavone **25**, bearing methoxy, acetoxy, and hydroxy substituents, was prepared using the methods developed here (Scheme III). Reaction of **22** with acetic anhydride in pyridine gave **24**, which on subsequent treatment with tetra-*n*-butylammonium fluoride in THF gave **25** in 92% yield from **22**.

In summary, the methodology reported here has resulted in improved syntheses of polyhydroxylated flavones, including the natural products apigenin (**9**), luteolin (**11**), and tricin (**18**).

Experimental Section

Microanalyses were performed at the Purdue Microanalysis Laboratory, and all values were within 0.4% of the calculated compositions. Solutions of lithium bis(trimethylsilyl)amide in THF and tetra-*n*-butylammonium fluoride in THF were obtained from commercial sources.

Methyl 4-[(*tert*-Butyldimethylsilyl)oxy]benzoate (2a). A solution of methyl 4-hydroxybenzoate (3.80 g, 25 mmol) in dry DMF (150 mL) under argon atmosphere was cooled to 0 °C, and to this was added *N,N*-diisopropylethylamine (6.50 g, 50 mmol) over 5 min. *tert*-Butyldimethylsilyl chloride (4.22 g, 28 mmol) was added over 30 min, and the reaction mixture was allowed to warm to room temperature over a period of 1 h. After 4 h, the reaction mixture was poured into ice water (500 mL) and extracted with ethyl ether (3 × 50 mL). The combined extracts were washed with brine (3 × 50 mL) and dried (Na_2SO_4). Evaporation of solvents and drying of the residue at reduced pressure for 24 h gave methyl 4-[(*tert*-butyldimethylsilyl)oxy]benzoate (6.46 g, 97%) as a single product. An analytical sample was prepared by passing a solution of a small amount of **2a** in hexane through a pad of neutral alumina: oil; ^1H NMR ($CDCl_3$) δ 7.75 (d, J = 8.6 Hz, 2 H), 6.86 (d, J = 8.6 Hz, 2 H), 3.86 (s, 3 H), 0.98 (s, 9 H), 0.16 (s, 6 H); CIMS (isobutane) m/z 267 (MH^+, 100). Anal. Calcd for $C_{14}H_{22}O_3Si$: C, 63.12; H, 8.32. Found: C, 63.42; H, 8.28.

Methyl 3,4-Bis[(*tert*-butyldimethylsilyl)oxy]benzoate (2b). This compound was prepared by utilizing the procedure described above with methyl 3,4-dihydroxybenzoate (4.20 g, 25 mmol), *N,N*-diisopropylethylamine (13.0 g, 100 mmol), and *tert*-butyldimethylsilyl chloride (8.44 g, 56 mmol) in DMF (200 mL) (9.50 g, 96%). The crude product was pure enough for subsequent reactions, and an analytical sample was prepared by crystallization from absolute ethanol: mp 46–47 °C; ^1H NMR ($CDCl_3$) δ 7.52 (dd, 1 H), 7.42 (d, J = 2.1 Hz, 1 H), 6.90 (d, J = 8.4 Hz, 1 H), 3.80 (s, 3 H), 0.96 (s, 18 H), 0.22 (s, 6 H), 0.19 (s, 6 H); CIMS (isobutane) m/z 397 (MH^+, 100). Anal. Calcd for $C_{20}H_{36}O_4Si_2$: C, 60.56; H, 9.15. Found: C, 60.82; H, 9.37.

Methyl 3,4,5-Tris[(*tert*-butyldimethylsilyl)oxy]benzoate (2c). Reaction of methyl 3,4,5-trihydroxybenzoate (4.60 g, 25 mmol) with *tert*-butyldimethylsilyl chloride (12.66 g, 84 mmol) in DMF (200 mL) in presence of *N,N*-diisopropylethylamine (19.5 g, 150 mmol) gave methyl 3,4,5-tris[(*tert*-butyldimethylsilyl)-oxy]benzoate (**2c**, 12.23 g, 93%). An analytical sample was prepared by recrystallization from ethanol: mp 70–71 °C; ^1H NMR ($CDCl_3$) δ 7.21 (s, 2 H), 3.85 (s, 3 H), 0.99 (s, 9 H), 0.95 (s, 18 H), 0.23 (s, 12 H), 0.13 (s, 6 H); CIMS (isobutane) m/z 527 (MH^+, 100). Anal. Calcd for $C_{26}H_{50}O_5Si_3$: C, 59.26; H, 9.56. Found: C, 59.44; H, 9.43.

Methyl 4-[(*tert*-Butyldimethylsilyl)oxy]-3,5-dimethoxybenzoate (2d). Reaction of methyl 3,5-dimethoxy-4-hydroxybenzoate (5.03 g, 25 mmol) with *tert*-butyldimethylsilyl chloride (4.22 g, 28 mmol) in DMF (200 mL) in presence of *N,N*-diisopropylethylamine (6.5 g, 50 mmol) gave compound **2d** (8.22 g, 97%). An analytical sample was prepared by recrystallization from ethanol: mp 98–100 °C; ^1H NMR ($CDCl_3$) δ 7.27 (s, 2 H), 3.89 (s, 3 H), 3.85 (s, 6 H), 1.00 (s, 9 H), 0.14 (s, 6 H); CIMS (isobutane) m/z 327 (MH^+, 100). Anal. Calcd for $C_{16}H_{26}O_5Si$: C, 58.87; H, 8.03. Found: C, 58.94; H, 8.26.

Typical Experimental Procedure for the Preparation of Hydroxyflavones 5–18: 2-(4-Hydroxyphenyl)-5-hydroxy-4*H*-benzopyran-4-one (6). A solution of LiHMDS in THF (1 M, 40 mL, 40 mmol) was added to a well-stirred solution of 2',6'-dihydroxyacetophenone (**3b**) (1.52 g, 10 mmol) in THF (50 mL) under argon at −78 °C over 15 min. The reaction mixture was stirred at −78 °C for 1 h and at −10 °C for 2 h and was cooled again to −78 °C, and a solution of methyl 4-[(*tert*-butyldimethylsilyl)oxy]benzoate (**2a**, 2.66 g, 10 mmol) in THF (5 mL) was added in one portion. Stirring was continued at −78 °C for 1 h and at room temperature for 16 h (until the disappearance of the starting material **3b** as determined by ^1H NMR). The reaction mixture was poured into a mixture of ice (200 g) and concd HCl (10 mL) and extracted with $CHCl_3$ (3 × 25 mL). Solvents were evaporated from the dried (Na_2SO_4) extracts, and the residue was dried under vacuum for 24 h. The residue was mixed with glacial acetic acid (40 mL) and H_2SO_4 (0.2 mL) and

heated at 95–100 °C under an argon atmosphere for 1 h. About 30 mL of acetic acid was distilled off at reduced pressure, and the residue was poured into water (300 mL). The precipitated product was filtered, washed with water, and dried. An analytical sample was prepared by recrystallization from acetone and hexane. Physical characteristics and yields of flavones 5–18 are summarized in Table I. Compounds were prepared on a 10-mmol scale using 3, 4, and 5 equiv of lithium bis(trimethylsilyl)amide for mono-, di-, and trihydroxy compounds respectively.

2-(4-Hydroxy-3,5-dimethoxyphenyl)-5-hydroxy-4*H*-benzopyran-4-one (14): ^{1}H NMR (DMSO-d_6) δ 12.82 (bs, 1 H, exchanges with D_2O), 9.43 (bs, 1 H, exchanges with D_2O), 7.66 (dd, 1 H), 7.37 (s, 2 H), 7.23 (d, J = 8.7 Hz, 1 H), 7.14 (s, 1 H), 6.79 (d, J = 8.7 Hz, 1 H), 3.88 (s, 6 H); CIMS (isobutane) m/z 315 (MH^+, 100). Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97; H, 4.49. Found: C, 65.03; H, 4.67.

2-(4-Hydroxy-3,5-dimethoxyphenyl)-6-hydroxy-4*H*-benzopyran-4-one (15): ^{1}H NMR (DMSO-d_6) δ 10.01 (bs, 1 H, exchanges with D_2O), 9.22 (bs, 1 H, exchanges with D_2O), 7.69 (d, J = 8.9 Hz, 1 H), 7.34 (s, 2 H), 7.31 (d, J = 3.0 Hz, 1 H), 7.24 (dd, 1 H), 6.99 (s, 1 H), 3.89 (s, 6 H); CIMS (isobutane) m/z 315 (MH^+, 100). Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97; H, 4.49. Found: C, 64.98; H, 4.52.

2-(4-Hydroxy-3,5-dimethoxyphenyl)-7-hydroxy-4*H*-benzopyran-4-one (16): ^{1}H NMR (DMSO-d_6) δ 10.74 (bs, 1 H, exchanges with D_2O), 9.24 (bs, 1 H, exchanges with D_2O), 7.88 (d, J = 8.9 Hz, 1 H), 7.33 (s, 2 H), 7.05 (d, J = 3.0 Hz, 1 H), 6.93 (s, 1 H), 6.91 (dd, 1 H), 3.89 (s, 6 H); CIMS (isobutane) m/z 315 (MH^+, 100). Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97; H, 4.49. Found: C, 65.21; H, 4.53.

7,8-Dihydroxy-2-(4-hydroxy-3,5-dimethoxyphenyl)-4*H*-benzopyran-4-one (17): ^{1}H NMR (DMSO-d_6) δ 10.22 (bs, 1 H, exchanges with D_2O), 9.51 (bs, 1 H, exchanges with D_2O), 9.25 (bs, 1 H, exchanges with D_2O), 7.47 (d, J = 8.7 Hz, 1 H), 7.34 (s, 2 H), 6.97 (d, J = 8.7 Hz, 1 H), 6.93 (s, 1 H), 3.91 (s, 6 H); CIMS (isobutane) m/e 331 (MH^+, 100). Anal. Calcd for $C_{17}H_{14}O_7$: C, 61.82; H, 4.27. Found: C, 62.01; H, 4.51.

General Procedure for the Preparation of Products 19–23. Concentrated H_2SO_4 (5 drops) was added to a well-stirred solution of 1,3-propanediones 4 (5 mmol) in glacial acetic acid (10 mL) at room temperature. After 30 min, the reaction mixture was kept at 0–5 °C for 2 h, and the product was filtered, washed with water, and dried under vacuum for 4 h. Analytical samples were prepared by recrystallization from ethanol.

2-[4-[(*tert*-Butyldimethylsilyl)oxy]phenyl]-6-hydroxy-4*H*-benzopyran-4-one (19): 1.53 g; 83%; mp 333–335 °C; ^{1}H NMR (DMSO-d_6) δ 10.10 (bs, 1 H, exchanges with D_2O), 8.12 (d, J = 8.6 Hz, 2 H), 7.64 (d, J = 8.7 Hz, 1 H), 7.43 (d, J = 3.0 Hz, 1 H), 7.37 (dd, 1 H), 7.15 (d, J = 8.6 Hz, 2 H), 6.97 (s, 1 H), 0.98 (s, 9 H), 0.26 (s, 6 H); CIMS (isobutane) m/z 369 (MH^+, 100). Anal. Calcd for $C_{21}H_{24}O_4Si$: C, 68.45; H, 6.56. Found: C, 68.52; H, 6.74.

2-[4-[(*tert*-Butyldimethylsilyl)oxy]phenyl]-7-hydroxy-4*H*-benzopyran-4-one (20): 1.68 g; 91%; mp 252–254 °C; ^{1}H NMR (DMSO-d_6) δ 10.91 (bs, 1 H, exchanges with D_2O), 8.00 (d, J = 8.5 Hz, 2 H), 7.89 (d, J = 8.7 Hz, 1 H), 7.04 (d, J = 8.5 Hz, 2 H), 7.00 (s, 1 H), 6.94 (d, J = 8.7 Hz, 1 H), 6.81 (s, 1 H), 0.98 (s, 9 H), 0.25 (s, 6 H); CIMS (isobutane) m/z 369 (MH^+, 100). Anal. Calcd for $C_{21}H_{24}O_4Si$: C, 68.45; H, 6.56. Found: C, 68.39; H, 6.64.

2-[4-[(*tert*-Butyldimethylsilyl)oxy]-3,5-dimethoxyphenyl]-6-hydroxy-4*H*-benzopyran-4-one (21): 1.88 g; 88%; mp 178–180 °C; ^{1}H NMR (DMSO-d_6) δ 10.04 (bs, 1 H, exchanges with D_2O), 7.71 (d, J = 8.7 Hz, 1 H), 7.36 (s, 2 H), 7.33 (dd, 1 H), 7.27 (d, J = 3.0 Hz, 1 H), 7.05 (s, 1 H), 3.89 (s, 6 H), 0.99 (s, 9 H), 0.14 (s, 6 H); CIMS (isobutane) m/z 429 (MH^+, 100). Anal. Calcd for $C_{23}H_{28}O_6Si$: C, 64.46; H, 6.59. Found: C, 64.52; H, 6.58.

2-[4-[(*tert*-Butyldimethylsilyl)oxy]-3,5-dimethoxyphenyl]-7-hydroxy-4*H*-benzopyran-4-one (22): 1.97 g; 92%; mp 208–210 °C; ^{1}H NMR (DMSO-d_6) δ 10.77 (bs, 1 H, exchanges with D_2O), 7.89 (d, J = 8.9 Hz, 1 H), 7.33 (s, 2 H), 7.06 (d, J = 3.0 Hz, 1 H), 6.98 (s, 1 H), 6.94 (dd, 1 H), 3.88 (s, 6 H), 0.98 (s, 9 H), 0.13 (s, 6 H); CIMS (isobutane) m/z 429 (MH^+, 100). Anal. Calcd for $C_{23}H_{28}O_6Si$: C, 64.46; H, 6.59. Found: C, 64.27; H, 6.78.

2-[4-[(*tert*-Butyldimethylsilyl)oxy]-3,5-dimethoxyphenyl]-7,8-dihydroxy-4*H*-benzopyran-4-one (23): 1.86 g; 84%; mp 224–226 °C; ^{1}H NMR (DMSO-d_6) δ 10.23 (bs, 1 H, exchanges with D_2O), 9.52 (bs, 1 H, exchanges with D_2O), 7.42 (s, 2 H), 7.06 (d, J = 8.7 Hz, 1 H), 6.96 (s, 1 H), 6.94 (d, J = 8.7 Hz, 1 H), 3.88 (s, 6 H), 0.99 (s, 9 H), 0.13 (s, 6 H); CIMS (isobutane) m/z 445 (MH^+, 100). Anal. Calcd for $C_{23}H_{28}O_7Si$: C, 62.14; H, 6.35. Found: C, 62.33; H, 6.71.

7-Acetoxy-2-[4-[(*tert*-butyldimethylsilyl)oxy]-3,5-dimethoxyphenyl]-4*H*-benzopyran-4-one (24). Compound **22** (0.888 g, 2 mmol) was mixed with acetic anhydride (5 mL) and pyridine (10 mL), and the mixture was stirred at room temperature for 3 h. Excess acetic anhydride and pyridine were removed at reduced pressure, and the residue was treated with water (20 mL). The solid formed was filtered, washed with water, and dried (0.96 g, 96%): mp 189–190 °C; ^{1}H NMR ($CDCl_3$) δ 8.26 (d, J = 8.7 Hz, 1 H), 7.45 (d, J = 3.0 Hz, 1 H), 7.15 (dd, 1 H), 7.10 (s, 2 H), 6.75 (s, 1 H), 3.89 (s, 6 H), 2.37 (s, 3 H), 1.03 (s, 9 H), 0.17 (s, 6 H); CIMS (isobutane) m/z 471 (MH^+, 100). Anal. Calcd for $C_{25}H_{30}O_7Si$: C, 63.81; H, 6.43. Found: C, 63.72; H, 6.60.

7-Acetoxy-2-(4-hydroxy-3,5-dimethoxyphenyl)-4*H*-benzopyran-4-one (25). A solution of tetra-*n*-butylammonium fluoride in THF (1 M, 3 mL, 3 mmol) was added to a solution of compound **24** (0.47 g, 1 mmol) in THF (10 mL), and the stirring was continued for 15 min. THF was distilled off at reduced pressure, and the residue was treated with water (25 mL). The product precipitated was filtered, washed with water, and dried (0.34 g, 95.5%); mp 296–299 °C; ^{1}H NMR (DMSO-d_6) δ 9.92 (bs, 1 H, exchanges with D_2O), 7.92 (d, J = 8.7 Hz, 1 H), 7.03 (s, 2 H), 6.88 (d, J = 3.0 Hz, 1 H), 6.84 (dd, 1 H), 6.53 (s, 1 H), 3.87 (s, 6 H), 2.39 (s, 2 H); CIMS (isobutane) m/z 357 (MH^+, 100). Anal. Calcd for $C_{19}H_{16}O_7$: C, 64.04; H, 4.53. Found: C, 64.28; H, 4.61.

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Registry No. **1a**, 99-76-3; **1b**, 2150-43-8; **1c**, 99-24-1; **1d**, 884-35-5; **2a**, 133642-20-3; **2b**, 134178-06-6; **2c**, 121056-97-1; **2d**, 134178-07-7; **3a**, 118-93-4; **3b**, 699-83-2; **3c**, 490-78-8; **3d**, 89-84-9; **3e**, 528-21-2; **3f**, 480-66-0; **5**, 4143-63-9; **6**, 6665-67-4; **7**, 63046-09-3; **8**, 2196-14-7; **9**, 520-36-5; **10**, 4143-64-0; **11**, 491-70-3; **12**, 126432-36-8; **13**, 132018-15-6; **14**, 134178-08-8; **15**, 134178-09-9; **16**, 134178-10-2; **17**, 134178-11-3; **18**, 520-32-1; **19**, 134178-12-4; **20**, 134178-13-5; **21**, 134178-14-6; **22**, 134178-15-7; **23**, 134178-16-8; **24**, 134178-17-9; **25**, 134178-18-0.