Supplementary Material for Organic & Biomolecular Chemistry

Supplementary data

Synthesis and "double-faced" antioxidant activity of polyhydroxylated 4-thiaflavans

Stefano Menichetti,*[a] Maria Chiara Aversa,[b] Francesco Cimino,[c] Caterina Viglianisi,[b] and Antonio Tomaino[c]

[a]Dipartimento di Chimica Organica, Polo Scientifico-Università di Firenze, via della Lastruccia 13, 50019, Sesto Fiorentino, Firenze, Italy, Tel:+39-055-4573535, Fax: +39-055-4573531, e-mail: stefano.menichetti@unifi.it
[b]Dipartimento di Chimica Organica e Biologica, Università di Messina, Salita Sperone 31, 98166, Messina, Italy
[c]Dipartimento Farmaco-Biologico, Università di Messina, Viale SS Annunziata, Messina, Italy

Experimental

General: ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300 and 75 MHz respectively, in $CDCl_3$ for silylated compounds and acetone-d_6 for hydroxy thiaflavans, unless otherwise specified, using signals of residual non-deuterated solvents as reference lines. Melting points are uncorrected. $CHCl_3$, DCM, THF, DMF, and Et_3N were dried following standard procedures. All the other commercial reagents were used as obtained from freshly opened containers. Silylated phenols **4a-d**, and **4f** were prepared by reaction of the commercially available hydroxy arenes with TBDMSCl and imidazole in dry DMF. Styrenes **7a-b** were obtained from 3-hydroxy- and 3,4-dihydroxy-benzaldehyde by silylation and subsequent Wittig reaction.[17] PhthNSCl and N-thiophthalimides **5** were prepared as reported elsewhere.[15,17]

Cycloaddition Reactions. General Procedure

To a solution of thiophthalimides **5** in dry $CHCl_3$ (roughly 0.1 M) styrenes **7** (1 equiv) and freshly distilled Et_3N (1 equiv) were added in sequence, the reaction mixtures heated at 60 °C and monitored, either by ^{1}H NMR or TLC, till the disappearance of **5**. Evaporation of the solvent and flash chromatography on silica gel allowed the isolation of cycloadducts **8**. Spectroscopic data of silylated derivatives **8** are as follows:

6-(*tert*-Butyl-dimethyl-silanyloxy)-2,3-dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin (8a)

Compound **8a** was obtained as a white solid by flash chromatography on silica gel with petroleum ether/DCM 4:1 as eluent; mp 89-90 °C, (67%). ^{1}H-NMR δ: 0.17 (s, 6H), 0.97 (s, 9H), 3.01 (dd, *J* = 13.0, 1.8 Hz, 1H), 3.28 (dd, *J* = 13.0, 9.6 Hz, 1H), 3.82 (s, 3H), 5.05 (dd, *J* = 9.6, 1.8 Hz, 1H), 6.51 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.61 (d, *J* = 2.7 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.93-6.95 (m, 2H), 7.32-7.35 (m, 2H); ^{13}C-NMR δ: -4.5 (q, 2C), 18.1 (s, 1C), 25.6 (q, 3C), 31.8 (t, 1C), 55.2 (q, 1C), 76.1 (d, 1C), 114.0 (d, 2C), 117.3(d, 1C), 117.6 (1s, 1d, 2C), 119.1 (d, 1C), 127.3 (d, 2C), 132.6 (s, 1C), 147.0 (s, 1C), 149.7 (s, 1C), 159.6 (s, 1C).

7-(*tert*-Butyl-dimethyl-silanyloxy)-2,3-dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin (8b)

Compound **8b** was obtained as a colourless oil by flash chromatography on silica gel with petroleum ether/DCM 3:1 as eluent; (63%). ^{1}H-NMR δ: 0.20 (s, 6H), 0.99 (s, 9H), 3.02 (dd, *J* = 13.2, 1.8 Hz, 1H), 3.25 (dd, *J* = 13.2, 9.6 Hz, 1H), 3.84 (s, 3H), 5.15 (dd, *J* = 9.6, 1.8 Hz, 1H), 6.44-6.49 (m, 2H), 6.93-6.98 (m, 3H), 7.34-7.36 (m, 2H); ^{13}C-NMR δ: -4.5 (q, 2C), 18.1 (s, 1C), 25.6 (q, 3C), 31.6 (t, 1C), 55.3 (q, 1C), 76.6 (d, 1C), 108.7 (s, 1C), 110.4 (d, 1C), 114.0 (d, 2C), 114.3 (d, 1C), 127.3 (d, 2C), 127.5 (d, 1C), 132.5 (s, 1C), 152.9 (s, 1C), 153.8 (s, 1C), 159.7 (s, 1C).

6-(*tert*-Butyl-dimethyl-silanyloxy)-2-[4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-2,3-dihydro-1,4-benzoxathiin (8c)

Compound **8c** was obtained as a white solid by flash chromatography on silica gel with petroleum ether/DCM 6:1 as eluent; mp 80-83 °C, (70%). ^{1}H-NMR δ: 0.20 (s, 6H), 0.23 (s, 6H), 1.00 (s, 9H), 1.02 (s, 9H), 3.01 (dd, *J* = 13.2, 1.8 Hz, 1H), 3.27 (dd, *J* = 13.2, 9.9 Hz, 1H), 5.05 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.52 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.62 (d, *J* = 2.7 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.87-6.91 (m, 2H), 7.27-7.30 (m, 2H); ^{13}C-NMR δ: -4.5 (q, 2C), -4.4 (q, 2C), 18.1 (s, 1C), 18.2 (s, 1C), 25.6 (q, 3C), 25.7 (q, 3C), 31.9 (t, 1C), 76.3 (d, 1C), 117.4 (d, 1C), 117.6 (d, s, 2C), 119.1 (d, 1C), 120.2 (d, 2C), 127.2 (d, 2C), 133.2 (s, 1C), 147.1 (s, 1C), 149.7 (s, 1C), 155.8 (s, 1C).

7-(*tert*-Butyl-dimethyl-silanyloxy)-2-[4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-2,3-dihydro-1,4-benzoxathiin (8d)

Compound **8d** was obtained as a yellow oil by flash chromatography on silica gel with petroleum ether/DCM 6:1 as eluent; (42%). ^{1}H-NMR δ: 0.18 (s, 6H), 0.21 (s, 6H), 0.97 (s, 9H), 1.00 (s, 9H), 3.00 (dd, *J* = 13.2, 1.8 Hz, 1H), 3.23 (dd, *J* = 13.2, 9.6 Hz, 1H), 5.12 (dd, *J* = 9.6, 1.8 Hz, 1H), 6.42-6.47 (m, 2H), 6.85-6.95 (m, 3H), 7.24-7.29 (m, 2H); ^{13}C-NMR δ: -4.5 (q, 2C), -4.4 (q, 2C), 18.1 (s, 1C), 18.2 (s, 1C), 25.6 (q, 6C), 31.6 (t, 1C), 76.7 (d, 1C), 108.7 (s, 1C), 110.4 (d, 1C), 114.3 (d, 1C), 120.2 (d, 2C), 127.2 (d, 2C), 127.4 (d, 1C) 133.0 (s, 1C), 152.9 (s, 1C), 153.7 (s, 1C), 155.8 (s, 1C).

8-(*tert*-Butyl-dimethyl-silanyloxy)-2,3-dihydro-3-(4-methoxy-phenyl)-naphth[2,1-*b*][1,4]oxathiin (8e)

Compound **8e** was obtained as a white solid by flash chromatography on silica gel with petroleum ether/ethyl acetate 10:1 as eluent; (75%). ^{1}H-NMR δ: 0.25 (s, 6H), 1.03 (s, 9H), 3.21 (dd, *J* = 14.0, 2.6 Hz, 1H), 3.64 (dd, *J* = 14.0, 9.2 Hz, 1H), 3.84 (s, 3H), 5.23 (dd, *J* = 9.2, 2.6 Hz, 1H), 6.94-6.98 (m, 2H), 7.06-7.15 (m, 3H), 7.37-7.43 (m 3H), 7.79 (d, *J* = 8.6 Hz, 1H); ^{13}C-NMR δ: -4.4 (q, 2C), 18.2 (s, 1C), 25.7 (q, 3C), 31.5 (t, 1C), 55.2 (q, 1C), 76.1 (d, 1C), 110.3 (s, 1C), 114.1 (d, 2C), 115.8 (d, 1C), 120.3 (d, 1C), 122.0 (d, 1C), 123.9 (d, 1C) 124.5 (d, 1C), 127.3 (d, 2C), 130.5 (s, 2C), 132.5 (s, 1C), 148.7 (s, 1C), 152.2 (s, 1C), 159.7 (s, 1C).

9-(*tert*-Butyl-dimethyl-silanyloxy)-2,3-dihydro-3-(4-methoxy-phenyl)-naphth[2,1-*b*][1,4]oxathiin (8f)

Compound **8f** was obtained as a white solid by flash chromatography on silica gel with petroleum ether/DCM 3:1 as eluent; mp 113-115 °C, (79%). ^{1}H-NMR δ: 0.30 (s, 6H), 1.05 (s, 9H), 3.23 (dd, *J* = 13.2, 2.1 Hz, 1H), 3.34 (dd, *J* = 13.2, 9.3 Hz, 1H), 3.84 (s, 3H), 5.25 (dd, *J* = 9.3, 2.1 Hz, 1H), 6.95-7.02 (m, 4H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.37-7.41 (m, 2H), 7.47 (d, *J* = 8.7 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H); ^{13}C-NMR δ: -4.3 (q, 2C), 18.3 (s, 1C), 25.8 (q, 3C), 31.4 (t, 1C), 55.3 (q, 1C), 76.2 (d, 1C), 108.6 (s, 1C), 110.6 (d, 1C), 114.1 (d, 2C), 117.3 (d, 1C), 119.8 (d, 1C), 124.8 (s, 2C), 125.5 (d, 1C), 127.3 (d, 2C), 129.7 (d, 1C), 132.5 (s, 1C), 150.5 (s, 1C), 154.3 (s, 1C), 159.7 (s, 1C).

5,7-Bis-(*tert*-butyl-dimethyl-silanyloxy)-2,3-dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin (8g)

Compound **8g** was obtained as a white solid by flash chromatography on silica gel with petroleum ether/ethyl acetate from 100:1 to 6:1 as eluent; mp 96-99 °C, (64%). ^{1}H-NMR δ: 0.17 (s, 6H), 0.26 (s, 6H), 0.96 (s, 9H), 1.04 (s, 9H), 3.00 (dd, 1H, *J* = 13.0, 1.8 Hz); 3.16 (dd, 1H, *J* = 13.0, 9.4 Hz); 3.82 (s, 3H); 5.05 (dd, 1H, *J* = 9.4, 1.8 Hz); 6.02 (d, 1H, *J* = 2.4 Hz); 6.15 (d, 1H, *J* = 2.4 Hz); 6.91-6.96 (m, 2H); 7.31-7.35 (m, 2H); ^{13}C-NMR δ: -4.9 (q, 2C); -4.3 (q, 2C); 18.2 (s, 1C); 18.3 (s, 1C); 25.6 (q, 3C); 25.7 (q, 3C); 31.1 (t, 1C); 55.3 (q, 1C); 76.5 (d, 1C); 102.2 (d, 1C); 103.8 (d, 1C); 104.6 (s, 1C); 114.1 (d, 2C); 127.4 (d, 2C); 132.8 (s, 1C); 152.1 (s, 1C); 153.3 (s, 1C); 153.7 (s, 1C); 159.7 (s, 1C). *m/z* (EI): 518 (M^{+}, 19); 461 (50); 73 (100).

2-[3,4-Bis-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-2,3-dihydro-5,7-dimethoxy-1,4-benzoxathiin (8h)

Compound **8h** was obtained as a white solid by flash chromatography on silica gel with petroleum ether/ethyl acetate from 100:1 to 6:1 as eluent; mp 96-99 °C, (29%). ^{1}H-NMR δ: 0.18, 0.19, 0.20, (4s, 12H), 0.98 (s, 9H), 0.10 (s, 9H), 3.00-3.15 (m, 2H), 3.74 (s, 3H), 3.85 (s, 3H), 5.05 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.14 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 2.4, 1H), 6.84-6.85 (m, 3H); ^{13}C-NMR δ: -4.0 (q, 4C), 18.4 (s, 2C), 25.9 (q, 6C), 30.9 (t, 1C), 55.5 (q, 1C), 56.0 (q, 1C), 77.2 (d, 1C), 92.9 (d, 1C), 96.0 (d, 1C), 119.0 (d, 2C), 121.1 (d, s, 2C), 133.5 (s, 1C), 147.1 (s, 2C), 153.6 (s, 1C), 156.5 (s, 1C), 158.3 (s, 1C).

5,7-Bis-(*tert*-butyl-dimethyl-silanyloxy)-2-[3,4-bis-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-2,3-dihydro-1,4-benzoxathiin (8i)

Compound **8i** was obtained as a white solid by flash chromatography on silica gel with petroleum ether/ethyl acetate from 100:1 to 6:1 (or with petroleum ether/DCM 5:1) as eluent; mp 85-89 °C, (40%). ^{1}H-NMR δ: 0.18 (s, 6H), 0.19-0.21 (m, 12H), 0.26 (s, 6H), 0.96 (s, 9H), 0.99 (2s, 18H), 1.04 (s, 9H), 2.97-3.14 (m, 2H), 4.98 (dd, *J* = 9.3 , 2.1 Hz, 1H), 6.02 (d, *J* = 2.4 Hz, 1H), 6.16 (d, *J* = 2.4 Hz, 1H), 6.84-6.85 (m, 3H); ^{13}C-NMR δ: -4.5 (q, 2C), -4.3 (q, 2C), -4.1 (q, 2C), -4.1 (q, 2C), 18.2 (s, 1C), 18.3 (s, 1C), 18.4 (s, 2C), 25.6 (q, 3C), 25.7 (q, 3C), 25.9 (q, 6C), 31.2 (t, 1C), 76.3 (d, 1C), 102.1 (s, 1C), 103.8 (d, 1C), 104.4 (d, 1C), 118.9 (d, 2C), 121.0 (d, 1C), 133.6 (s, 1C), 146.9 (s, 2C), 152.1 (s, 1C), 153.2 (s, 1C), 153.6 (s, 1C).

Oxidation Reactions to Silylated Sulfoxides (indicated as 10a' and 10b'). General Procedure

To a solution of cycloadducts **8a** or **8b**, in DCM (0.04 M) kept at 0°C, a solution of MCPBA (1 equiv.) in DCM was added and the reactions monitored by TLC till the disappearance of sulfides **8** (30-40 min). The mixtures were diluted with DCM, washed with 10% $Na_2S_2O_3$, saturated $NaHCO_3$ and water. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. ^{1}H NMR of the crude mixture allowed the attribution of the *cis*/*trans* ratio, purification by flash chromatography on silica gel allowed the isolation of *trans*-**10a'** and *cis*- and *trans*-**10b'**.

***trans*-6-(*tert*-Butyl-dimethyl-silanyloxy)-2,3-dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin 4-Oxide (*trans*-10a')**

Compound *trans*-**10a'** was obtained as a white solid by flash chromatography on silica gel with petroleum ether/ethyl acetate 2:1 as eluent; mp 139 °C dec., (65%). ^{1}H-NMR δ: 0.20 (s, 6H), 0.99 (s, 9H), 3.07 (dd, *J* = 14.4, 12.0 Hz, 1H), 3.24 (dd, *J* = 14.4, 1.5 Hz, 1H), 3.84 (s, 3H), 5.61 (br d, 1H), 6.94-6.98 (m, 4H), 7.13-7.14 (m, 1H), 7.40-7.45 (m, 2H), ^{13}C-NMR δ: -4.5 (q, 2C), 18.1 (s, 1C), 25.6 (q, 3C), 49.8 (t, 1C), 55.3 (q, 1C), 67.4 (d, 1C), 114.2 (d, 2C), 120.2 (d, 1C), 122.1 (d, 1C), 122.4 (s, 1C), 126.9 (d, 1C), 127.9 (d, 2C), 130.6 (s, 1C), 147.7 (s, 1C), 149.7 (s, 1C), 160.1 (s, 1C).

***trans*-7-(*tert*-Butyl-dimethyl-silanyloxy)-2,3-dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin 4-Oxide (*trans*-10b')**

Compound *trans*-**10b'** was obtained as a white solid by flash chromatography on silica gel with petroleum ether/ethyl acetate 3:1 as eluent; mp 146 °C dec., (72%). ^{1}H-NMR δ: 0.21 (s, 6H), 0.97 (s, 9H), 3.05 (dd, *J* = 14.4, 11.8 Hz, 1H), 3.22 (dd, *J* = 14.4, 1.5 Hz, 1H), 3.84 (s, 3H), 5.67 (dd, *J* = 11.8, 1.5 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.96-6.98 (m, 2H), 7.42-7.45 (m, 2H), 7.54 (d, *J* = 8.7 Hz, 1H). ^{13}C-NMR δ: -4.5 (q, 2C), 18.2 (s, 1C), 25.5 (q, 3C), 49.4 (t, 1C), 55.4 (q, 1C), 67.3 (d, 1C), 109.8 (d, 1C), 114.3 (d, 2C), 114.8 (d, 1C), 115.7 (s, 1C), 128.0 (d, 2C), 130.5 (s, 1C), 133.8 (d, 1C), 154.9 (s, 1C), 160.1 (s, 1C), 161.0 (s, 1C).

***cis*-7-(*tert*-Butyl-dimethyl-silanyloxy)-2,3-dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin 4-Oxide (*cis*-10b')**

Compound ***cis*-10b'** was obtained as a yellow oil by flash chromatography on silica gel with petroleum ether/ethyl acetate 3:1 as eluent; (18%). ^{1}H-NMR δ: 0.20 (s, 6H), 0.97 (s, 9H), 3.36 (ap t, *J* = 12.0 Hz, 1H), 3.66 (dd, *J* = 12.6, 1.2 Hz, 1H), 3.84 (s, 3H), 5.21 (br d, *J* = 11.4 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 6.66 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.94-6.99 (m, 2H), 7.34-7.39 (m, 2H), 7.58 (d, *J* = 8.7 Hz, 1H). ^{13}C-NMR δ: -4.5 (q, 2C), 18.2 (s, 1C), 25.5 (q, 3C), 51.9 (t, 1C), 55.4 (q, 1C), 74.2 (d, 1C), 108.8 (d, 1C), 114.4 (d, 2C), 115.5 (d, 1C), 118.8 (s, 1C), 127.7 (d, 2C), 129.4 (d, 1C), 129.8 (s, 1C), 154.3 (s, 1C), 159.7 (s, 1C), 160.3 (s, 1C).

Oxidation Reactions to Silylated Sulfones (indicated as 11a', 11b', 11g', 11h'). General Procedure

To a solution of cycloadducts **8**, in DCM (0.04 M) at rt, a solution of MCPBA (2.2 equiv.) in DCM was added and the reactions monitored by TLC till the disappearance of sulfides **8** (4-8 h). The mixtures were diluted with DCM, washed with 10% $Na_2S_2O_3$, saturated $NaHCO_3$ and water. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness to give sulfones **11'** not needing of purification before desilylation.

6-(*tert*-Butyl-dimethyl-silanyloxy)-2,3-dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin 4,4-Dioxide (11a')

Compound **11a'** was obtained as a white solid; mp 93-96 °C, (99%). ^{1}H-NMR δ: 0.21 (s, 6H), 0.98 (s, 9H), 3.46 (dd, *J* = 14.1, 1.5 Hz, 1H), 3.71 (dd, *J* = 14.1, 12.0 Hz, 1H), 3.84 (s, 3H), 5.70 (dd, *J* = 12.0, 1.5 Hz, 1H), 6.91-6.99 (m, 4H), 7.24-7.26 (m, 1H), 7.36-7.40 (m, 2H); ^{13}C-NMR δ: -4.5 (q, 2C), 18.1 (s, 1C), 25.6 (q, 3C), 55.4 (t, 1C), 55.9 (q, 1C), 77.3 (d, 1C), 113.4 (d, 1C), 114.5 (d, 2C), 120.0 (d, 1C), 125.5 (s, 1C), 127.1 (d, 1C), 127.7 (d, 2C), 129.3 (s, 1C), 147.6 (s, 1C), 150.5 (s, 1C), 160.5 (s, 1C).

7-(*tert*-Butyl-dimethyl-silanyloxy)-2,3-dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin 4,4-Dioxide (11b')

Compound **11b'** was obtained as a colourless oil; (94%). ^{1}H-NMR δ: 0.22 (s, 6H), 0.97 (s, 9H), 3.43 (dd, *J* = 13.9, 1.3 Hz, 1H), 3.71 (dd, *J* = 13.9, 12.1 Hz, 1H), 3.83 (s, 3H), 5.75 (br d, 1H, *J* = 12.1 Hz), 6.47 (d, *J* = 2.1 Hz, 1H), 6.64 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.96-6.99 (m, 2H), 7.37-7.40 (m, 2H), 7.70 (d, *J* = 8.7 Hz, 1H);^{13}C-NMR δ: -4.5 (q, 2C), 18.1 (s, 1C), 25.4 (q, 3C), 55.3 (t, 1C), 55.5 (q, 1C), 76.6 (d, 1C), 109.1 (d, 1C), 114.4 (d, 2C), 115.4 (d, 1C), 118.5 (s, 1C), 125.1 (d, 1C), 127.7 (d, 2C), 129.1 (s, 1C), 154.9 (s, 1C), 160.4 (s, 1C), 161.0 (s, 1C).

5,7-Bis-(*tert*-butyl-dimethyl-silanyloxy)-2,3-dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin 4,4-Dioxide (11g')

Compound **11g'** was obtained as a yellow oil; (93%). ^{1}H-NMR δ: 0.20 (s, 6H), 0.34 (s, 6H), 0.95 (s, 9H), 1.07 (s, 9H), 3.36 (dd, *J* = 13.9, 1.3 Hz, 1H), 3.71 (dd, *J* = 13.9, 12.1 Hz, 1H), 3.83 (s, 3H), 5.59 (br d, 1H, *J* = 11.1 Hz), 6.04 (d, *J* = 2.2 Hz, 1H), 6.08 (d, *J* = 2.2 Hz, 1H), 6.94-6.97 (m, 2H), 7.34-7.37 (m, 2H); ^{13}C-NMR δ: -4.4 (q, 2C), -4.2 (q, 1C), -4.1 (q, 1C), 18.2 (s, 1C), 18.3 (s, 1C), 25.5 (q, 3C), 25.6 (q, 3C), 55.4 (q, 1C), 55.8 (t, 1C), 77.1 (d, 1C), 102.3 (d, 1C), 103.4 (d, 1C), 114.5 (d, 2C), 127.7 (d, 2C), 127.9 (s, 1C), 129.3 (s, 1C), 154.9 (s, 1C), 156.0 (s, 1C), 160.5 (s, 1C), 160.6 (s, 1C).

2-[3,4-Bis-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-2,3-dihydro-5,7-dimethoxy-1,4-benzoxathiin 4,4-Dioxide (11h')

Compound **11h'** was obtained as a white solid; mp 63-65 °C, (90%). ^{1}H-NMR δ: 0.20-0.21 (m, 12H), 0.99 (s, 18H), 3.42 (dd, *J* = 13.9, 1.2 Hz, 1H), 3.70 (dd, *J* = 13.9, 12.1 Hz, 1H), 3.78 (s, 3H), 3.95 (s, 3H), 5.55 (br d, *J* = 11.4 Hz, 1H), 6.12 (d, *J* = 2.4 Hz, 1H), 6.17 (d, *J* = 2.4 Hz, 1H), 6.88 (ap s, 3H); ^{13}C-NMR δ: -4.1 (2q, 2C), 18.4 (s, 2C), 25.8 (q, 6C), 55.6 (q, 1C), 56.6 (q, 1C), 58.0 (t, 1C), 77.1 (d, 1C), 94.0 (d, 1C), 94.3 (d, 1C), 108.3 (s, 1C), 119.2 (d, 1C), 119.5 (d, 1C), 121.3 (d, 1C), 129.7 (s, 1C), 147.3 (s, 1C), 148.1 (s, 1C), 156.3 (s, 1C), 159.6 (s, 1C), 164.4 (s, 1C).

Desilylation Reactions. General Procedure

To a solution of compounds **8**, **10'**, and **11'**, in dry THF (0.04 M) at 0 °C, a solution of TBAF·3H$_2$O in DCM (1 equiv for each TBDMSO group) was added and the reaction monitored by TLC till the disappearance of silylated starting product. The crude mixture was diluted with ethyl acetate, washed with saturated NH_4Cl and water. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. Purification of the residue by flash chromatography on silica gel afforded the required products **9**, **10**, and **11**. Spectroscopic data are as follows:

2,3-Dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin-6-ol (9a)

Compound **9a** was obtained as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 20:1 as eluent; mp 110-111 °C, (95%). ^{1}H-NMR δ: 3.12 (dd, *J* = 13.2, 2.1 Hz, 1H), 3.25 (dd, *J* = 13.2, 9.3 Hz, 1H), 3.80 (s, 3H), 5.02 (dd, *J* = 9.3, 2.1 Hz, 1H), 6.51 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.57 (d, *J* = 3.0 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 1H), 6.93-6.98 (m, 2H), 7.37-7.42 (m, 2H), 8.01 (br s, 1H); ^{13}C-NMR δ: 32.1 (t, 1C), 55.5 (q, 1C), 76.8 (d, 1C), 113.3 (d, 1C), 113.6 (d, 1C), 114.7 (d, 2C), 118.9 (s, 1C), 120.0 (d, 1C), 128.3 (d, 2C), 133.8 (s, 1C), 146.7 (s, 1C), 152.5 (s, 1C), 160.6 (s, 1C). Found: C, 65.71; H, 5.17. Calc. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14.

2,3-Dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin-7-ol (9b)

Compound **9b** was obtained as a colourless glassy solid by flash chromatography on silica gel with DCM/ethyl acetate 20:1 as eluent; (96%). ^{1}H-NMR δ: 3.06-3.23 (m, 2H), 3.79 (s, 3H), 5.13 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.42 (d, *J* = 2.5 Hz, 1H), 6.46 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.93-6.96 (m, 2H), 7.36-7.39 (m, 2H), 8.32 (br s, 1H); ^{13}C-NMR δ: 31.8 (t, 1C), 55.5 (q, 1C), 77.5 (d, 1C), 106.2 (d, 1C), 107.5 (s, 1C), 110.5 (d, 1C), 114.6 (d, 2C), 128.3 (d, 2C), 128.5 (d, 1C), 133.5 (s, 1C), 154.0 (s, 1C), 156.5 (s, 1C), 160.5 (s, 1C). Found: C, 65.83; H, 5.20. Calc. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14.

2,3-Dihydro-2-(4-hydroxy-phenyl)-1,4-benzoxathiin-6-ol (9c)

Compound **9c** was obtained as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 10:1 as eluent; mp 180-183 °C, (90%). ^{1}H-NMR δ: 3.12 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.23 (dd, *J* = 13.0, 9.4 Hz, 1H), 4.96 (dd, *J* = 9.4, 1.9 Hz, 1H), 6.51 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.58 (d, *J* = 2.8 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 1H), 6.84-6.89 (m, 2H), 7.26-7.30 (m, 2H), 8.25 (br s, 2H); ^{13}C-NMR δ: 32.1 (t, 1C), 76.9 (d, 1C), 113.3 (d, 1C), 113.6 (d, 1C), 116.0 (d, 2C), 118.8 (s, 1C), 119.9 (d, 1C), 128.3 (d, 2C), 132.6 (s, 1C), 146.8 (s, 1C), 152.3 (s, 1C), 158.1 (s, 1C). Found: C, 64.77; H, 4.52. Calc. for $C_{14}H_{12}O_3S$: C, 64.60; H, 4.65.

2,3-Dihydro-2-(4-hydroxy-phenyl)-1,4-benzoxathiin-7-ol (9d)

Compound **9d** was obtained as a colourless oil by flash chromatography on silica gel with DCM/ethyl acetate 10:1 as eluent; (79%). ^{1}H-NMR δ: 3.06-3.23 (m, 2H), 5.09 (dd, *J* = 9.1, 2.2 Hz, 1H), 6.39 (d, *J* = 2.5 Hz, 1H), 6.44 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.84-6.89 (m, 3H), 7.27-7.32 (m, 2H), 8.39 (br s, 2H); ^{13}C-NMR δ: 31.8 (t, 1C), 77.7 (d, 1C), 106.2 (d, 1C), 107.5 (s, 1C), 110.5 (d, 1C), 116.1 (d, 2C), 128.4 (d, 2C), 128.5 (d, 1C), 132.5 (s, 1C), 154.1 (s, 1C), 156.6 (s, 1C), 158.3 (s, 1C). Found: C, 64.68; H, 4.56. Calc. for $C_{14}H_{12}O_3S$: C, 64.60; H, 4.65.

2,3-Dihydro-3-(4-methoxy-phenyl)-naphth[2,1-*b*][1,4]oxathiin-8-ol (9e)

Compound **9e** was obtained as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 20:1 as eluent; (32%). ^{1}H-NMR (400 MHz) δ: 3.34-3.35 (m, 2H), 3.82 (s, 3H), 5.22 (dd, *J* = 6.8, 4.4 Hz, 1H), 6.97-7.03 (m, 3H), 7.15-7.18 (m, 2H), 7.40-7.48 (m, 3H), 7.71-7.73 (m, 1H), 8.53 (br s, 1H); ^{13}C-NMR (acetone-d_6, 100 MHz) δ: 31.6 (t, 1C), 55.6 (q, 1C), 76.8 (d, 1C), 111.0 (d, 1C), 111.3 (s, 1C), 114.7 (d, 2C), 119.1 (d, 1C), 121.1 (d, 1C), 124.6 (d, 1C), 124.9 (d, 1C), 126.4 (s, 1C), 128.4 (d, 2C), 131.8 (s, 1C), 133.6 (s, 1C), 149.0 (s, 1C), 155.0 (s, 1C), 160.7 (s, 1C). Found: C, 70.28; H, 4.86. Calc. for $C_{19}H_{16}O_3S$: C, 70.35; H, 4.97.

2,3-Dihydro-3-(4-methoxy-phenyl)-naphth[2,1-*b*][1,4]oxathiin-9-ol (9f)

Compound **9f** was obtained as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 20:1 as eluent; mp 160-163 °C, (93%). ^{1}H-NMR δ: 3.30 (d, *J* = 5.4 Hz, 2H), 3.79 (s, 3H), 5.22 (t, *J* = 5.4 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 6.93-6.98 (m, 2H), 7.04 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.39-7.44 (m, 2H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 8.76 (br s, 1H); ^{13}C-NMR δ: 31.5 (t, 1C), 55.5 (q, 1C), 76.9 (d, 1C), 105.7 (d, 1C), 109.2 (s, 1C), 114.7 (d, 2C), 116.8 (d, 1C), 117.8 (d, 1C), 124.9 (s, 1C), 126.4 (d, 1C), 128.3 (d, 2C), 130.9 (s, 1C), 133.5 (s, 1C), 133.7 (s, 1C), 151.4 (s, 1C), 156.9 (s, 1C), 160.6 (s, 1C). Found (%): C, 70.17; H, 5.05. Calc. for $C_{19}H_{16}O_3S$: C, 70.35; H, 4.97.

2,3-Dihydro-2-(4-methoxy-phenyl)-1,4-benzoxathiin-5,7-diol (9g)

Compound **9g** was obtained as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 3:1 or DCM/methanol 7:1 as eluent; mp 167-170 °C, (84%). ^{1}H-NMR δ: 3.08-3.11 (m, 2H), 3.83 (s, 3H), 5.05-5.09 (m, 1H), 6.10 (d, *J* = 2.4 Hz, 1H), 6.11 (d, *J* = 2.4 Hz, 1H), 6.94-6.98 (m, 2H), 7.37-7.41 (m, 2H), 8.09 (s, 1H), 8.66 (s, 1H); ^{13}C-NMR δ: 31.1 (t, 1C), 55.5 (q, 1C), 77.4 (d, 1C), 96.3 (s, 1C), 97.1 (d, 1C), 98.1 (d, 1C), 114.7 (d, 2C), 128.3 (d, 2C), 133.9 (s, 1C), 154.8 (s, 1C), 155.0 (s, 1C), 156.3 (s, 1C), 160.6 (s, 1C). Found: C, 61.88; H, 4.73. Calc. for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86.

2,3-Dihydro-2-(3,4-dihydroxy-phenyl)-5,7-dimethoxy-1,4-benzoxathiin (9h)

Compound **9h** was obtained as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 3:1 as eluent; mp 127-130 °C, (83%). ^{1}H-NMR δ: 3.06-3.08 (m, 2H), 3.73 (s, 3H), 3.81 (s, 3H), 4.95-4.99 (m, 1H), 6.13 (d, *J* = 2.4 Hz, 1H), 6.20 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 1.9 Hz, 1H), 8.00 (br s, 2H); ^{13}C-NMR δ: 31.0 (t, 1C), 55.6 (q, 1C), 56.3 (q, 1C), 77.5 (d, 1C), 93.2 (d, 1C), 96.6 (d, 1C), 98.8 (s, 1C), 114.2 (d, 1C), 116.0 (d, 1C), 118.7 (d, 1C), 133.4 (s, 1C), 146.0 (s, 2C), 154.5 (s, 1C), 157.4 (s, 1C), 159.1 (s, 1C). Found: C, 60.11; H, 4.95. Calc. for $C_{16}H_{16}O_5S$ (%): C, 59.99; H, 5.03.

2,3-Dihydro-2-(3,4-dihydroxy-phenyl)-1,4-benzoxathiin-5,7-diol (9i)

Compound **9i** was obtained as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 1:1 as eluent; mp 203-205°C, (70%). ^{1}H-NMR δ: 3.04-3.06 (m, 2H), 4.94-4.98 (m, 1H), 5.98 (d, *J* = 2.4 Hz, 1H), 6.10 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.93 (d, *J* = 1.9 Hz, 1H), 7.98 (s, 1H), 7.00 (s, 1H), 8.11 (s, 1H), 8.67 (s, 1H); ^{13}C-NMR δ: 31.2 (t, 1C), 77.6 (d, 1C), 96.3 (s, 1C), 97.0 (d, 1C), 98.0 (d, 1C), 114.2 (d, 1C), 116.0 (d, 1C), 118.7 (d, 1C), 133.7 (s, 1C), 145.9 (s, 2C), 154.8 (s, 1C), 154.9 (s, 1C), 156.3 (s, 1C). Found: C, 57.37; H, 4.07. Calc. for $C_{14}H_{12}O_5S$: C, 57.53; H, 4.14.

***trans*-2,3-Dihydro-2-(4-methoxy-phenyl)-4-oxo-1,4-benzoxathiin-6-ol (*trans*-10a)**

Compound *trans*-**10a** was obtained as a white solid by flash chromatography on silica gel with ethyl acetate/DCM 2:1 as eluent; mp 178 °C dec., (65%). ^{1}H-NMR (DMSO-d_6) δ: 3.26 (dd, *J* = 14.5, 1.2 Hz, 1H), 3.47 (dd, *J* = 14.5, 12.0 Hz, 1H), 3.77 (s, 3H), 5.38 (br d, *J* = 11.1 Hz, 1H), 6.94-7.02 (m, 5H), 7.44-7.48 (m, 2H), 9.56 (br s, 1H); ^{13}C-NMR (DMSO-d_6, 75 MHz) δ: 48.4 (t, 1C), 55.2 (q, 1C), 67.1 (d, 1C), 114.0 (d, 2C), 116.5 (d, 1C), 119.8 (d, 1C), 122.0 (d, 1C), 123.1 (s 1C), 128.5 (d, 2C), 130.9 (s, 1C), 145.5 (s, 1C), 151.3 (s, 1C), 159.5 (s, 1C). Found: C, 62.25; H, 4.69. Calc. for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86.

***trans*-2,3-Dihydro-2-(4-methoxy-phenyl)-4-oxo-1,4-benzoxathiin-7-ol (*trans*-10b)**

Compound *trans*-**10b** was obtained as a white solid by flash chromatography on silica gel with ethyl acetate/DCM 2:1 as eluent; mp 162 °C dec., (82%). ^{1}H-NMR (DMSO-d_6) δ: 3.19-3.47 (m, 2H), 3.78 (s, 3H), 5.47 (br d, *J* = 11.1, 2.2 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 1H), 6.54 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.98-7.01 (m, 2H), 7.46-7.53 (m, 3H), 10.31 (br s, 1H); ^{13}C-NMR (DMSO-d_6, 75 MHz) δ: 48.0 (t, 1C), 55.2 (q, 1C), 67.0 (d, 1C), 103.9 (d, 1C), 109.9 (d, 1C), 114.0 (d, 2C), 114.3 (s, 1C), 128.6 (d, 2C), 130.7 (d, 1C), 133.8 (s, 1C), 154.5 (s, 1C), 159.5 (s, 1C), 162.4 (s, 1C). Found: C, 62.31; H, 5.04. Calc. for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86.

***cis*-2,3-Dihydro-2-(4-methoxy-phenyl)-4-oxo-1,4-benzoxathiin-7-ol (*cis*-10b)**

Compound *cis*-**10b** was obtained as a white solid by flash chromatography on silica gel with DCM/methanol 10:1 as eluent; mp 137 °C dec., (81%). ^{1}H-NMR ($CDCl_3$) δ: 3.42 (dd, *J* = 12.5, 11.4 Hz, 1H), 3.69 (dd, *J* = 12.5, 0.9 Hz, 1H), 3.84 (s, 3H), 5.17 (br d, *J* = 11.4 Hz, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 6.58 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.94-6.97 (m, 2H), 7.35-7.38 (m, 2H), 7.49 (d, *J* = 9.0 Hz, 1H). Further analysis on *cis*-**10b** failed due to its instability (see above).

2,3-Dihydro-2-(4-methoxy-phenyl)-4,4-dioxo-1,4-benzoxathiin-6-ol (11a)

Compound **11a** was obtained as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 1:1 (or DCM/methanol 6:1) as eluent; mp 201-206 °C, (79%). ^{1}H-NMR δ: 3.63 (dd, *J* = 14.1, 1.5 Hz, 1H), 3.83 (s, 3H), 3.94 (dd, *J* = 14.1, 12.1 Hz, 1H), 5.65 (dd, *J* = 12.1, 1.5 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 6.00-7.08 (m, 3H), 7.17 (d, *J* = 2.7 Hz, 1H), 7.54-7.56 (m, 2H), 8.71 (br s, 1H); ^{13}C-NMR δ: 55.6 (q, 1C), 55.8 (t, 1C), 78.3 (d, 1C), 108.6 (d, 1C), 114.9 (d, 2C), 121.0 (d, 1C), 123.3 (d, 1C), 127.0 (s, 1C), 129.1 (d, 2C), 130.8 (s, 1C), 147.4 (s, 1C), 152.8 (s, 1C), 161.3 (s, 1C). Found: C, 58.97; H, 4.69. Calc. for $C_{15}H_{14}O_5S$: C, 58.81; H, 4.61.

2,3-Dihydro-2-(4-methoxy-phenyl)-4,4-dioxo-1,4-benzoxathiin-7-ol (11b)

Compound **11b** was obtained as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 20:1 as eluent; mp 199-203 °C, (38%). ^{1}H-NMR δ: 3.58 (dd, *J* = 14.1, 1.5 Hz, 1H), 3.85 (s, 3H), 3.93 (dd, *J* = 14.1, 12.3 Hz, 1H), 5.73 (dd, *J* = 12.3, 1.5 Hz, 1H), 6.46 (d, *J* = 2.2 Hz, 1H), 6.71 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.01-7.06 (m, 2H), 7.55-7.60 (m, 2H), 7.63 (d, *J* = 8.8 Hz, 1H), 9.44 (br s, 1H); ^{13}C-NMR δ: 55.5 (q, 1C), 55.7 (t, 1C), 78.8 (d, 1C), 104.7 (d, 1C), 111.5 (d, 1C), 115.0 (d, 2C), 118.7 (s, 1C), 126.1 (d, 1C), 129.2 (d, 2C), 130.7 (s, 1C), 156.2 (s, 1C), 161.4 (s, 1C), 163.3 (s, 1C). Found: C, 58.57; H, 4.35. Calc. for $C_{15}H_{14}O_5S$: C, 58.81; H, 4.61.

2,3-Dihydro-2-(4-methoxy-phenyl)-4,4-dioxo-1,4-benzoxathiin-5,7-diol (11g)

Compound **11g** was obtained as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 2:1 (or DCM/methanol 7:1) as eluent; mp 216-219°C, (92%). ^{1}H-NMR δ: 3.49 (dd, *J* = 13.8, 1.5 Hz, 1H), 3.84 (s, 3H), 3.90 (dd, *J* = 13.8, 12.1 Hz, 1H), 5.62 (dd, *J* = 12.1, 1.5 Hz, 1H), 6.00 (d, *J* = 2.1 Hz, 1H), 6.19 (d, *J* = 2.1 Hz, 1H), 7.00-7.05 (m, 2H), 7.52-7.58 (m, 2H), 9.36 (br s, 1H); ^{13}C-NMR δ: 55.6 (q, 1C), 57.8 (t, 1C), 78.1 (d, 1C), 96.7 (d, 1C), 98.3 (d, 1C), 107.9 (s, 1C), 114.9 (d, 2C), 129.2 (d, 2C), 130.6 (s, 1C), 157.1 (s, 1C), 158.6 (s, 1C), 161.3 (s, 1C) 163.1 (s, 1C). Found: C, 55.67; H, 4.17. Calc. for $C_{15}H_{14}O_6S$: C, 55.89; H, 4.38.

2,3-Dihydro-2-(3,4-dihydroxy-phenyl)-5,7-dimethoxy-1,4-benzoxathiin 4,4-Dioxide (11h)

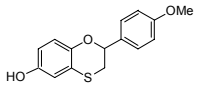
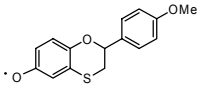
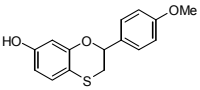
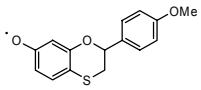
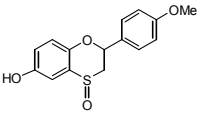
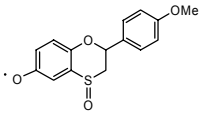
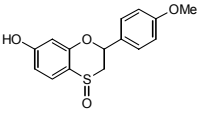
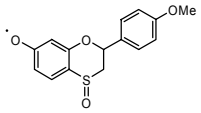
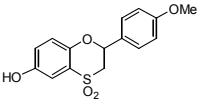
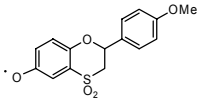
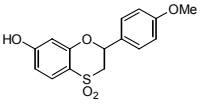
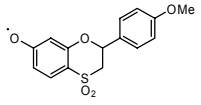
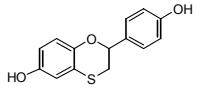
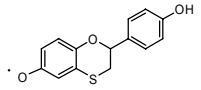
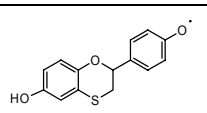
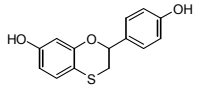
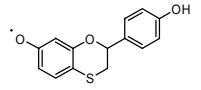
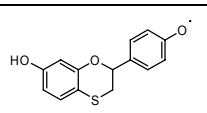
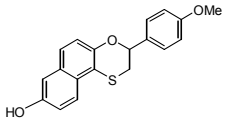
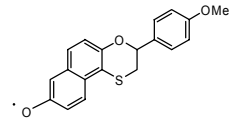
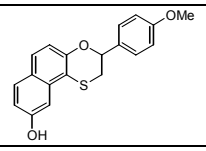
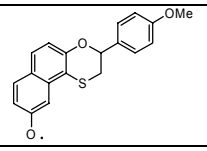
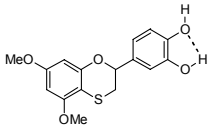
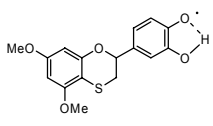
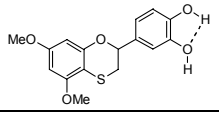
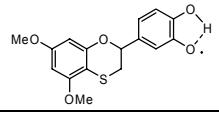
Compound **11h** was obtained by desilylation of **11h'** as a white solid after purification by flash chromatography on silica gel with DCM/ethyl acetate 3:1 as eluent, mp 127-130 °C, (18%) yield, or, more conveniently, by MCPBA oxidation of the corresponding oxathiin **9h**, (83%). ^{1}H-NMR δ: 3.45 (dd, *J* = 13.9, 1.2 Hz, 1H), 3.82 (s, 3H), 3.89 (s, 3H), 3.74-3.90 (m, 1H), 5.49 (dd, *J* = 12.1, 1.5 Hz, 1H), 6.16 (d, *J* = 2.4 Hz, 1H), 6.31 (d, *J* = 2.4 Hz, 1H), 6.87-6.92 (m, 2H), 7.07 (d, *J* = 2.1 Hz, 1H), 8.24 (br s, 2H); ^{13}C-NMR δ: 56.1 (q, 1C), 56.8 (q, 1C), 58.3 (t, 1C), 78.4 (d, 1C), 94.4 (d, 1C), 95.2 (d, 1C), 109.9 (s, 1C), 114.9 (d, 1C), 116.1 (d, 1C), 119.5 (d, 1C), 130.0 (s, 1C), 146.2 (s, 1C), 146.9 (s, 1C), 157.2 (s, 1C), 160.5 (s, 1C), 165.2 (s, 1C). Found: C, 54.67; H, 4.29. Calc. for $C_{16}H_{16}O_7S$: C, 54.54; H, 4.58.

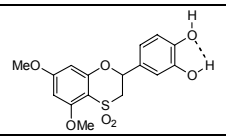
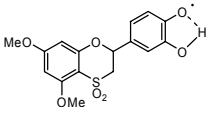
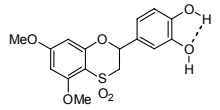
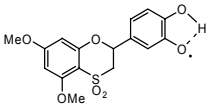
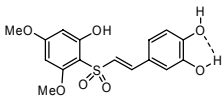
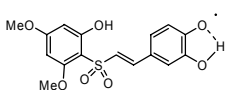
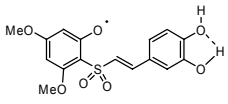
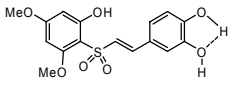
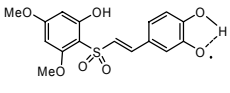
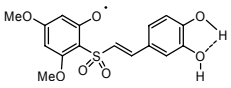
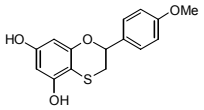
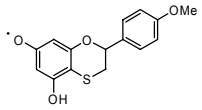
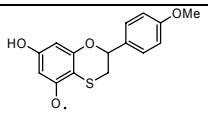
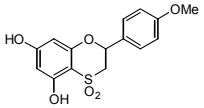
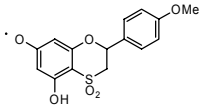
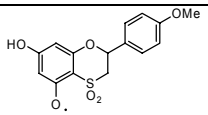
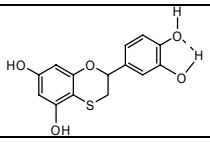
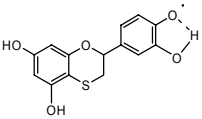
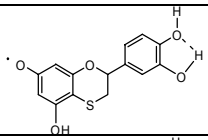
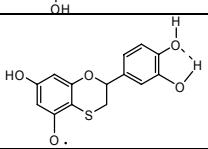
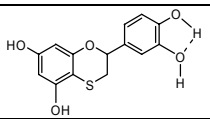
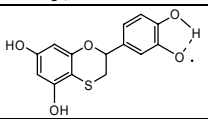
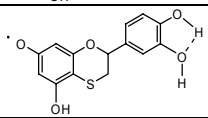
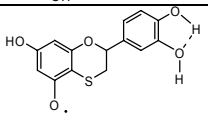
***trans*-4-[2-(2-Hydroxy-4,6-dimethoxy-benzenesulfonyl)-vinyl]-benzene-1,2-diol (12h)**

Compound **12h** was obtained during desilylation of **11h'**. It becomes the unique product of the reaction when an excess of TBAF at rt is used. **12h** was isolated as a white solid by flash chromatography on silica gel with DCM/ethyl acetate 3:1 as eluent; mp 197 °C dec., (72%). ^{1}H-NMR δ: 3.82 (s, 3H), 3.88 (s, 3H), 6.08 (d, *J* = 2.2 Hz, 1H), 6.15 (d, *J* = 2.2 Hz, 1H), 6.88(d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 15.3 Hz, 1H), 7.20 (d, *J* = 2.1 Hz, 1H), 7.50 (d, *J* = 15.3 Hz, 1H) 8.43 (br s, 3H); ^{13}C-NMR δ: 56.1 (q, 1C), 56.8 (q, 1C), 92.5 (d, 1C), 95.4 (d, 1C), 106.1 (s, 1C), 115.8 (d, 1C), 116.5 (d, 1C), 123.3 (d, 1C), 125.5 (d, 1C), 125.8 (s, 1C), 143.8 (d, 1C), 146.4 (s, 1C), 149.4 (s, 1C), 160.4 (s, 1C), 160.9 (s, 1C), 166.7 (s, 1C). Found: C, 54.76; H, 4.89. Calc. for $C_{16}H_{16}O_7S$: C, 54.54; H, 4.58.

BDE of compounds **9**, **10**, **11** and **12**.

BDE = E_{tot} (Radical) + E_{tot} ($H^{\bullet}$) – E_{tot} (Phenol): E_{tot} = Total energy of minimized structure.
HyperChem 6.3, PM3 UHF *in vacuo*. Convergence SCF: 10^{-5}. Gradient: 0.01 kcal/mol/Ang

	Compound	Radical	BDE Kcal/mol
9a			75.08
9b			75.73
1a			76.09
10b			79.03
11a			77.12
11b			81.19
9c			75.11
			77.54
9d			75.83
			77.64
9e			74.28
9f			74.75
9h			72.31
			72.57

11h			72.46
			72.80
12h			71.22
			77.16
			73.30
			77.71
9g			77.22
			76.52
11g			83.06
			81.14
9i			72.26
			77.07
			76.36
			72.49
			77.32
			76.56