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Easy and Green Synthesis of 6-(Arylvinyl)-4-hydroxy-3-(phenylsulfanyl)-2*H*-pyran-2-ones in Aqueous Potassium Hydroxide[1]

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Abstract—A convenient green procedure have been proposed for the synthesis of 6-(2-arylvinyl)-4-hydroxy-3-(phenylsulfanyl)-2*H*-pyran-2-ones by condensation of 6-(arylvinyl)-4-hydroxy-2*H*-pyran-2-ones with *S*-phenyl benzenesulfonothioate in aqueous potassium hydroxide at room temperature.

Keywords: Dehydroacetic acid, 4-hydroxy-6-methyl-2*H*-pyran-2-one, KOH/H_2O, 6-(arylvinyl)-4-hydroxy-3-(phenylsulfanyl)-2*H*-pyran-2-one

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2*H*-Pyran-2-one derivatives [1–5] are widespread in nature, and they exhibit a wide range of biological activities, in particular anxiolytic, antifungal, cytotoxic, and neurotoxic [2, 6–11]. 4-Hydroxy-2*H*-pyran-2-one fragment functionalized by a sulfide group at the 3-position is the key structural unit of a new class of HIV protease inhibitors [12–14]. Inhibiting effect of unsaturated γ-lactones on the central nervous system [15] has stimulated search for new strategies for the synthesis of such bioactive compounds.

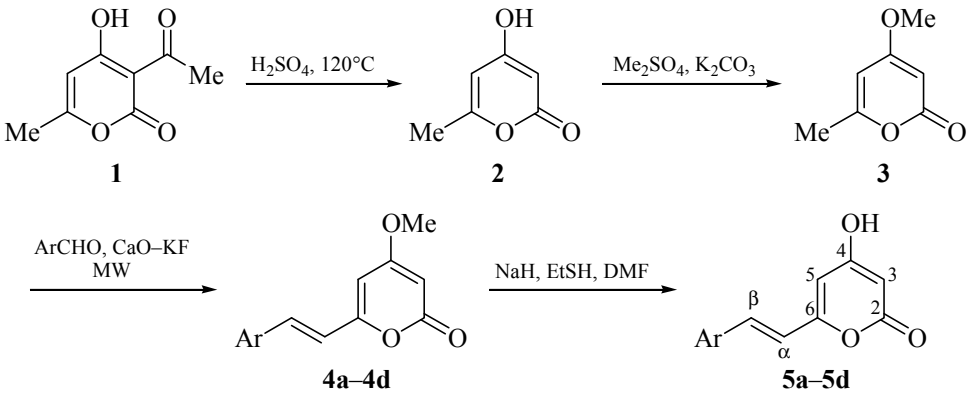
Herein we describe the synthesis of 4-hydroxy-6-styryl-2*H*-pyran-2-ones and 6-methyl- and 6-(arylvinyl)-4-hydroxy-3-(phenylsulfanyl)-2*H*-pyran-2-ones starting from dehydroacetic acid (**1**). Deacetylation of **1** on heating in sulfuric acid (95 %) gave 4-hydroxy-6-methyl-2*H*-pyran-2-one (**2**) [16–19] which was identified by TLC and UV-Vis, IR, ^1H and ^{13}C NMR, and mass spectra. Compound **2** was converted to 4-methoxypyranone **3** in 89% yield by methylation with dimethyl sulfate in the presence of K_2CO_3 according to [20]. Unlike the procedures reported previously [21–23], we synthesized 4-methoxy-6-styryl-2*H*-pyran-2-ones **4a**–**4d** by condensation of **3** with aromatic aldehydes in methylene chloride in the presence of CaO–KF as basic heterogenous catalyst under microwave irradiation. The subsequent removal of the MeO protecting group from **4a**–**4d** by treatment with sodium ethanethiolate in DMF afforded 67–79% of 6-(2-arylvinyl)-4-hydroxy-2*H*-pyran-2-ones **5a**–**5d** (Scheme 1). The deprotection of **4a** and **4b** was accompanied by partial or complete demethylation of the methoxy groups in the arylvinyl substituent.

The synthesis of 3-sulfanyl-4-hydroxy-2*H*-pyran-2-ones was described by Harris [24]. Some authors [25] prepared 3,6-substituted 4-hydroxy-2*H*-pyran-2-ones in a low yield (37%) in the presence of potassium carbonate by heating in *N*,*N*-dimethylformamide for 5 h at a bath temperature of 95°C.

We tried to find the best reaction conditions for the synthesis of 6-(arylvinyl)-4-hydroxy-3-(phenylsulfanyl)-2*H*-pyran-2-ones from 6-(arylvinyl)-4-hydroxy-2*H*-pyran-2-ones **5a**–**5d**. Initially, the reaction of pyranone **2** with *S*-phenyl benzenesulfonothioate was carried out in the presence of various bases in different solvents (25°C, 48 h). The results are collected in table. It is seen that the best yield of **6a** was achieved in water using potassium hydroxide as a base.

[1] The text was submitted by the authors in English.

Scheme 1.



4, Ar = 3,4,5-$(MeO)_3C_6H_2$ (**a**), 3,4-$(MeO)_2C_6H_3$ (**b**); **5**, Ar = 4-HO-3,5-$(MeO)_2C_6H_2$ (**a**), 3,4-$(HO)_2C_6H_3$ (**b**); **4**, **5**, Ar = Ph (**c**), furan-2-yl (**d**).

We then synthesized 6-(arylvinyl)-4-hydroxy-3-(phenylsulfanyl)-2*H*-pyran-2-ones **6b**–**6d** from hispidin (**5b**) and its analogs **5c** and **5d** in the presence of potassium hydroxide in water at room temperature (Scheme 2). The yields of **6a**–**6d** ranged from 62 to 78%.

In summary, we have developed a procedure for the synthesis of 6-(arylvinyl)-4-hydroxy-3-(phenylsulfanyl)-2*H*-pyran-2-ones by reaction of 6-(arylvinyl)-4-hydroxy-2*H*-pyran-2-ones with *S*-phenyl benzenesulfonothioate in aqueous medium in the presence of potassium hydroxide. The newly synthesized compounds, especially phenylsulfanyl derivatives, attract interest as potentially biologically active substances.

EXPERIMENTAL

Microwave-assisted reactions were carried out with a Whirlpool WMC10007AW commercial microwave oven (2450 MHz) equipped with a TEo13 resonance cavity connected to an MES 73-800 MW generator. The progress of reactions was monitored by TLC on commercial silica gel plates. The melting points were determined with a Kofler apparatus. The IR spectra were recorded as KBr discs on a JASCO FTIR-4100 spectrophotometer. The UV-Vis spectra were recorded on a T60U UV-Force spectrophotometer. The NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz) at 293 K using $CDCl_3$ as solvent and internal reference. The high resolution mass spectra (electrospray ionization) were recorded on an Orbitrap instrument.

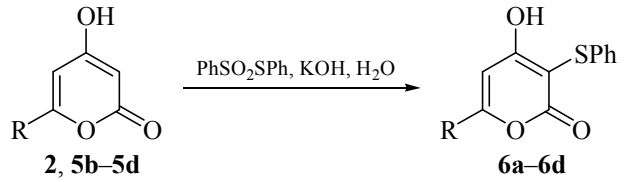
Reaction of 4-hydroxy-6-methyl-2*H*-pyran-2-one (**2**) with *S*-phenyl benzenesulfonothioate (25°C, 48 h)

Base	Solvent	Yield of **6a**, %
NaOH	DMSO	62
	H_2O	65
	EtOH	41
KOH	DMSO	72
	H_2O	78
	EtOH	40
t-BuOK	DMSO	40
	H_2O	42
	EtOH	30

Preparation of CaO–KF. Calcium oxide was added to a solution of potassium fluoride in 100 mL of distilled water (CaO–KF molar ratio 3 : 1). The mixture was stirred for 24 h at room temperature. The suspension was washed twice with distilled water, centrifuged, washed with methanol, and recentrifuged. The residue was dried for 24 h under reduced pressure and finely ground to obtain a clear beige powder.

4-Hyroxy-6-methyl-2*H*-pyran-2-one (2). Dehydroacetic acid (8.4 g, 50 mmol) was dissolved in 30 mL of

Scheme 2.



2, **6a**, R = Me; **5**, **6**, Ar = 3,4-$(HO)_2C_6H_3CH$=CH (**b**), PhCH=CH (**c**), 2-(furan-2-yl)ethenyl (**d**).

concentrated sulfuric acid. The mixture was heated at 120°C for 90 min, rapidly cooled down, and poured into ice water. The solid residue was collected by filtration, washed with water, and recrystallized from water. Yield 87%, white solid, mp 186–187°C [16]. IR spectrum, ν, cm^{-1}: 3321 (OH), 1719 (C=O), 1626 (C=C), 1543, 1307, 1252 (C–O–C), 870, 812. UV-Vis spectrum (EtOH), λ, nm (log ε): 390 (3.38), 279 (3.45), 215 (3.30). ^{1}H NMR spectrum, δ, ppm: 2.17 s (3H, CH_3), 5.23 s (1H, 3-H), 5.98 s (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 19.6, 88.3, 100.3, 163.4, 164, 170.7. Mass spectrum: *m*/*z* 126 (I_{rel} 33%) $[M]^+$. $C_6H_6O_3$. Calculated: *M* 126.12.

4-Methoxy-6-methyl-2*H*-pyran-2-one (3). A 200-mL flask was charged with 4-hydroxy-6-methyl-2*H*-pyran-2-one (3.78 g, 30 mmol), dimethyl sulfate (3.78 g, 30 mmol), K_2CO_3 (10 g), and butan-2-one (50 mL), and the mixture was refluxed for 20 h. The mixture was cooled and filtered, and the filtrate was evaporated under reduced pressure in a rotary evaporator. The product was recrystallized from petroleum ether. Yield 89 %, yellow solid, mp 86°C [26]. IR spectrum, ν, cm^{-1}: 1732, 1720 (C=O), 1649 (C=C), 1464, 1401, 1148 (C–O–C), 943, 545. ^{1}H NMR spectrum, δ, ppm: 2.21 s (3H, CH_3), 3.81 s (3H, CH_3O), 5.40 d (1H, 3-H), 5.79 d (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 19.7, 55.7, 87.2, 100.2, 161.8, 164.9, 171.2. Mass spectrum, *m*/*z* (I_{rel}, %): 140 (53) $[M]^+$, 132 (8.6), 125 (47), 113 (8), 112 (100), 69 (36), 59 (25), 53 (30), 43 (45). $C_7H_8O_3$. *M* 140.15.

6-(2-Arylvinyl)-4-methoxy-2*H*-pyran-2-ones 4a–4d *(general procedure).* The corresponding aromatic aldehyde (20 mmol) was dissolved in a minimum amount of methylene chloride, compound **3** (2.81 g, 20 mmol) and KF–CaO (4 g) were added, the solvent was evaporated at room temperature under reduced pressure, and the residue was activated by MWI in a microwave oven for 5–10 min. The mixture was acidified with 20% aqueous HCl (4 mmol), dissolved in 10 mL of of methylene chloride, and filtered, the filtrate was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was recrystallized from methanol.

4-Methoxy-6-[2-(3,4,5-trimethoxyphenyl)ethenyl)]-2*H*-pyran-2-one (4a) was synthesized from 3,4,5-trimethoxybenzaldehyde (3.92 g, 20 mmol), MW power 40W, irradiation time 10 min. Yield 90%, yellow solid, mp 201°C. IR spectrum, ν, cm^{-1}: 1707 (C=O), 1645, 1585, 1553, 1511, 1455, 1409, 1342, 1255, 1152, 1009, 842, 817. ^{1}H NMR spectrum, δ, ppm: 3.85 s (3H, OCH_3), 3.90 s (3H, OCH_3), 3.92 s (3H, OCH_3), 3.94 s (3H,OCH_3), 5.52 d (1H, 3-H), 5.98 d (1H, 5-H), 6.52 d (1H, α-H), 6.79 s (2H, 2′-H, 6′-H), 7.45 d (1H, β-H). ^{13}C NMR spectrum δ_C, ppm: 55.8 (4′-OCH_3), 56.1 (3′-OCH_3, 5′-OCH_3), 60.8 (4-OCH_3), 88.7 (C^3), 100.2 (C^5), 104.6 ($C^{2'}$, $C^{6'}$), 117.8 (C^{α}), 119.6 ($C^{4'}$),130.7 ($C^{1'}$), 135.7 (C^{β}),153.4 ($C^{3'}$, $C^{5'}$), 158.5 (C^6), 163.9 (C^2), 171.07 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 318 (64) $[M]^+$, 275 (9.4), 181 (4), 149 (27), 69 (100), 65 (47). $C_{17}H_{18}O_6$. Calculated: *M* 318.33.

6-[2-(3,4-Dimethoxyphenyl)ethenyl]-4-methoxy-2*H*-pyran-2-one (4b) was synthesized from 3,4-dimethoxybenzaldehyde (veratral, 3.32 g, 20 mmol), MW power 40 W, irradiation time 10 min. Yield 79%, yellow solid, mp 162–163°C. IR spectrum, ν, cm^{-1}: 2848 (C–H), 1718 (C=O), 1551, 1412, 1251, 1053, 843, 687. ^{1}H NMR spectrum, δ, ppm: 3.79 s (3H, 4-OCH_3), 3.88 s (3H, 4′-OCH_3), 3.90 s (3H, 3′-OCH_3), 5.44 d (1H, 3-H), 5.88 d (1H, 5-H), 6.43 d (1H, α-H), 6.84 d (1H, 5′-H), 7.00 d (1H, 2′-H), 7.05 d (1H, 6′-H), 7.42 d (1H, β-H). ^{13}C NMR spectrum, δ_C, ppm: 55.8, 55.9, 88.4, 100.5, 109.3, 111.2, 116.5, 121.6, 128.2, 135.6, 149.2, 150.4, 158.9, 164.1, 171.2. Mass spectrum: *m*/*z* 288 $[M]^+$. $C_{16}H_{16}O_5$. Calculated: *M* 288.29.

4-Methoxy-6-(2-phenylethenyl)-2*H*-pyran-2-one (4c) was synthesized from benzaldehyde (2.12 g, 20 mmol), MW power 40 W, irradiation time 9 min. Yield 88%, yellow solid, mp 136°C [27]. IR spectrum, ν, cm^{-1}: 3076, 1722 (C=O), 1639, 1549, 1446, 1251, 1154, 1006, 831, 686. ^{1}H NMR spectrum, δ, ppm: 3.56 s (3H, OCH_3), 5.51 d (1H, 3-H), 5.96 d (1H, 5-H), 6.61 d (1H, α-H), 7.31–7.41 m (3H, H_{arom}), 7.47–7.51 d (2H, H_{arom}), 7.50 d (1H, β-H). ^{13}C NMR spectrum, δ_C, ppm: 55.8, 88.7, 101.2, 118.6, 127.2, 128.8, 129.3, 135.2, 135.7, 158.5, 163.9, 171.2. Mass spectrum, *m*/*z* (I_{rel}, %): 229 (17), 228 (98) $[M]^+$, 211 (6), 210 (7), 200 (16), 199 (67), 198 (24), 183 (19), 182 (68), 168 (14), 167 (20), 157 (10), 141 (10), 115 (20). $C_{14}H_{12}O_3$. Calculated: *M* 228.25.

6-[2-(Furan-2-yl)ethenyl]-4-methoxy-2*H*-pyran-2-one (4d) was synthesized from furfural (2.35 g, 20 mmol), MW power 40 W, irradiation time 12 min. Yield 89%, yellow solid, mp 180°C [28]. IR spectrum, ν, cm^{-1}: 3179, 1700 (C=O), 1634, 1562, 1544, 1450, 1149, 1010, 946, 778. ^{1}H NMR spectrum, δ, ppm: 3.83 s (3H, OCH_3), 5.46 d (1H, 3-H), 5.92 d (1H, 5-H), 6.44–6.54 m (2H, furyl), 6.47 d (1H, α-H), 7.26 d (1H, β-H), 7.41–7.47 m (1H, furyl). ^{13}C NMR spectrum, δ_C, ppm:

55.8 (OCH_3), 88.6 (C^3), 101.2 (C^5), 112.3 ($C^{3'}$), 113.3 ($C^{4'}$), 116.5 (C^{α}) 122.5 (C^{β}), 143.9 ($C^{5'}$), 151.6 ($C^{2'}$), 158.4 (C^6), 163.8 (C^2), 171.3 (C^4). $C_{12}H_{10}O_4$. *M* 218.21.

6-(2-Arylvinyl)-4-hydroxy-2*H*-pyran-2-ones 5a–5d *(general procedure).* A solution of ethanethiol (0.06 g, 1 mmol) in DMF (3 mL) was added in a nitrogen atmosphere to a suspension of sodium hydride (100 mg, 60% oil dispersion) in anhydrous dimethylformamide (2 mL). The mixture was stirred for 6 min, and a solution of 6-(2-arylvinyl)-4-methoxy-2*H*-pyran-2-one **4a**–**4d** (37 mmol) in DMF (3 mL) was added. The mixture was refluxed for 2 h with stirring, cooled to room temperature, acidified with 10% aqueous HCl to pH 5–6, and extracted with ethyl acetate (10 mL). The extract was dried over $MgSO_4$, the solvent was removed, and the brown solid residue was recrystallized from methanol.

4-Hydroxy-6-[2-(4-hydroxy-3,5-dimethoxy)ethenyl)]-2*H*-pyran-2-one (5a). Yield 67%, mp 225-226°C. IR spectrum, ν, cm^{-1}: 3250–3600 (OH), 1689 (C=O), 1683, 1634, 1549, 1516, 1343, 1215, 972, 830, 819. ^{1}H NMR spectrum, δ, ppm: 3.80 s (3H, OCH_3), 3.83 s (3H, OCH_3), 5.33 d (1H, 3-H), 6.15 d (1H, 5-H), 6.95 d (1H, α-H), 7.05 s (2H, 2′-H, 6′-H), 7.30 d (1H, β-H), 8.70 s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 56.3 (OCH_3), 90.1 (C^3), 100.12 (C^5), 105.9 ($C^{2'}$, $C^{6'}$), 117.27 (C^{α}), 126.1 ($C^{4'}$), 135.3 (C^{β}), 137.7 ($C^{1'}$), 148.4 ($C^{3'}$, $C^{5'}$), 160 (C^6), 163.3 (C^2), 170.5 (C^5). Mass spectrum, *m*/*z* (I_{rel}, %): 290 (71.5) $[M]^+$, 220 (18.6), 162 (8.5), 86 (65.3), 84 (80.8), 49 (100). $C_{15}H_{14}O_6$. Calculated: *M* 290.28.

6-[2-(3,4-Dihydroxyphenyl)ethenyl]-4-hydroxy-2*H*-pyran-2-one (5b). Yield 70%, mp 259°C. IR spectrum, ν, cm^{-1}: 3100–3588 (OH), 1660 (C=O), 1645 (C=C), 1608, 1601, 1542, 1449, 1281, 1158, 1110, 971, 823. UV-Vis spectrum (MeOH), λ_{max}, nm (log ε): 221 (4.34), 252 (4.10), 368 (4.33). ^{1}H NMR spectrum, δ, ppm: 5.32 d (1H, 3-H), 6.12 d (1H, 5-H), 6.59 d (1H, α-H), 6.75 d (1H, 5′-H), 6.90 d (1H, 6′-H), 7.04–7.26 m (3H, H_{arom}).^{13}C NMR spectrum, δ_C, ppm: 89.52 (C^3), 100.75 (C^5), 114.31 ($C^{2'}$), 116.31 ($C^{5'}$), 116.57 (C^{β}), 120.59 ($C^{6'}$), 126.99 ($C^{1'}$), 134.85 (C^{α}), 145.801 ($C^{3'}$), 147.61 ($C^{4'}$), 160.00 (C^6), 163.28 (C^2), 170.58 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 246 (34) $[M]^+$, 220 (4.8), 202 (7.09), 192 (3.1), 187 (8.3), 178 (10.1), 163 (12.2), 145 (7.01), 136 (34), 183 (9.9), 123 (11.4), 117 (10), 110 (17.5), 85 (25.4), 84 (26.6), 83 (22), 69 (18.7), 58 (43), 43 (100). $C_{13}H_{10}O_5$. Calculated: *M* 246.22.

4-Hydroxy-6-(2-phenylethenyl)-2*H*-pyran-2-one (5c). Yield 79 %, mp 254°C. IR spectrum, ν, cm^{-1}: 3198–3647 (OH), 1660 (C=O), 1645 (C=C), 1608, 1601, 1542, 1449, 1281, 1158, 1110, 971, 823. UV spectrum (MeOH), λ_{max}, nm (log ε): 221 (4.34), 252 (4.10), 368 (4.33). ^{1}H NMR spectrum, δ, ppm: 5.32 d (1H, 3-H), 6.22 d (1H, 5-H), 6.99 d (1H, α-H), 7.33 d (1H, β-H), 7.33–7.45 m (5H, H_{arom}), 11.9 s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 90.1 (C^3), 100.1 (C^5), 120.3 (C^{α}), 127.98 ($C^{3'}$, $C^{5'}$), 131.85 ($C^{4'}$), 134.2 (C^{β}), 135.3 ($C^{1'}$), 160.00 (C^6), 163.1 (C^2), 170.3 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 214 (47) $[M]^+$, 210 (21), 209 (51), 184 (23), 169 (26), 115 (33), 114 (29), 55 (63), 43 (100). $C_{13}H_{10}O_3$. Calculated: *M* 214.24.

6-[2-(Furan-2-yl)ethenyl]-4-hydroxy-2*H*-pyran-2-one (5d). Yield 73%, mp 233°C. IR spectrum, ν, cm^{-1}: 2700–3210 (OH), 1715, 1638 (C=O), 1659 (C=C), 1555, 1490, 1301, 1158, 1010, 961, 823. ^{1}H NMR spectrum, δ, ppm: 5.32 d (1H, 3-H), 6.27 d (1H, 5-H), 6.59 d (1H, 4′-H), 6.67 d (1H, α-H), 6.90 d (1H, 3′-H), 7.13 d (1H, β-H), 7.78 d (1H, 5′-H), 11,68 s (OH). ^{13}C NMR spectrum, δ_C, ppm: 90.1 (C^3), 102 (C^5), 112.9 ($C^{3'}$), 113.9 ($C^{4'}$), 117.2 (C^{α}), 121.5 (C^{β}), 145 ($C^{5'}$), 151.5 ($C^{2'}$), 158.9 (C^6), 163.1 (C^2), 17.3 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 204 (100) $[M]^+$, 199 (21), 187 (7), 176 (13), 161 (33), 121 (34), 110 (15), 95 (30), 69 (18), 65 (13). $C_{11}H_8O_4$. Calculated: *M* 204.21.

***S*-Phenyl benzenesulfonothioate** was synthesized according to the procedure described in [30] by oxidation of diphenyl disulfide (12 g, 50 mmol) in 20 mL of acetic acid with 30% aqueous and hydrogen peroxide (10 g, 100 mmol). Yield 85%, white solid, mp 44°C (from MeOH) [29]. IR spectrum, ν, cm^{-1}: 3070, 1590, 1145, 1000, 600, 380. ^{1}H NMR spectrum, δ, ppm: 7.21–7.37 m (5H, H_{arom}), 7.58–7.81 m (5H, H_{arom}). Mass spectrum: *m*/*z* 250 (I_{rel} 100%). $C_{12}H_{10}O_2S_2$. Calculated: *M* 250.22.

6-(2-Arylvinyl)-4-hydroxy-3-(phenylsulfanyl)-2*H*-pyran-2-ones 6a–6d *(general procedure).* A mixture of 6-substituted 4-hydroxy-2*H*-pyran-2-one **2** or **5b**–**5d** (4 mmol), potassium hydroxide (5 mmol), and 1.20 mL of water was stirred for 5 min, *S*-phenyl benzenesulfonothioate (1.02 g, 4 mmol) was added, and the mixture was stirred for 48 h at room temperature with a magnetic stirrer. The mixture was then acidified with 20% aqueous HCl to pH 2 and extracted with methylene chloride (3 × 20 mL). The combined extracts were dried over magnesium sulfate and evaporated, and the residue was purified by

chromatography on silica gel using methylene chloride–ethanol (95/5) as eluent.

4-Hydroxy-6-methyl-3-(phenylsulfanyl)-2*H*-pyran-2-one (6a). Yield 78%, white solid, mp 166°C. IR spectrum, ν, cm^{-1}: 3000–3400 (OH), 2634, 2570, 1724, 1652 (C=O), 1556, 1482, 1444, 1406, 1388, 1348, 1348, 1290, 1170, 1066, 946, 832, 762, 736, 688. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.26 s (3H, CH_3), 6.20 s (1H, 5-H), 7.07–7.15 m (3H, *o*-H, *p*-H), 7.27 t (2H, *m*-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.75 (CH_3), 90.57 (C^3), 100.15 (C^5), 125.13 (C^4), 125.79 ($C^{2'}$), 128.84 (C^3), 129.06 ($C^{3'}$), 137.01 ($C^{1'}$), 163.36 (C^6), 164.45 (C^2), 173.10 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 236 (6), 235 (11), 234 (100) $[M]^+$, 229 (49), 177 (8), 149 (58), 133 (7), 121 (60), 120 (77), 113 (16), 108 (48), 107 (8), 105 (6). $C_{12}H_{10}O_3S$. Calculated: *M* 234.27.

6-[2-(3,4-Dihydroxyphenyl)ethenyl]-4-hydroxy-3-(phenylsulfanyl)-2*H*-pyran-2-one (6b). Yield 62%, black solid, mp 259°C. IR spectrum, ν, cm^{-1}: 3600–3350 (OH), 1762, 1626 (C=O), 1502, 1444, 1406, 1300, 1210, 1176, 1137, 1044, 1018, 976, 738, 690. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.41 (1H, 5-H), 6.82 d (1H, α-H), 7.19 d (2H, *o*-H), 7.22–7.32 m (3H, *m*-H, *p*-H), 7.59 d (1H, 5′-H), 7.67 s (1H, 2′-H), 7.86 d (1H, 6′-H), 8.02 d (1H, β-H), 10.42 s (OH)). Mass spectrum, *m*/*z* (I_{rel}, %): 354 (0.31) $[M]^+$, 281 (0.86), 231 (0.31), 218 (9.11), 207 (8.9), 168 (8.5), 185 (9.5), 154 (9.6), 110 (62.3), 109 (24.3), 84 (17.5), 78 (74.1), 66 (28.5), 64 (44.9), 51 (27.7), 44 (100). $C_{19}H_{14}O_5S$. Calculated: *M* 354.38.

4-Hydroxy-6-(2-phenylethenyl)-3-(phenylsulfanyl)-2*H*-pyran-2-one (6c). Yield 68%, brown solid, mp 238°C. IR spectrum, ν, cm^{-1}: 3600–3350 (OH), 1634 (C=O), 1604, 1548, 1416, 1364, 1208, 1174, 970, 732, 689. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.25 (1H, 5-H), 6.64 d (1H, α-H), 7.07–7.26 m (5H, H_{arom}), 7.26–7.45 m (2H, H_{arom}), 7.41 d (1H, β-H), 7.46–7.60 m (3H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 92.51 (C^3), 102.39 (C^5), 118.60 (C^{α}), 124.89 ($C^{4''}$), 126.12 ($C^{2'}$,$C^{6'}$), 127.11 ($C^{3'}$,$C^{5'}$), 128.41 ($C^{3''}$, $C^{5''}$), 128.53 ($C^{4'}$), 129.11 ($C^{2''}$, $C^{6''}$) 134.83 ($C^{1''}$), 135.68 (C^{β}), 136.50 ($C^{1'}$), 158.71 (C^2), 160.42 (C^6), 163.63 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 324, 322 (100) $[M]^+$, 213 (8.0), 174 (5.7), 173 (21.4), 150 (3.6), 131 (6.6), 121 (11.0), 109 (4.5), 103 (6.0), 69 (5.4), 51 (40.0), 43 (9.5). $C_{19}H_{14}O_3S$. Calculated: *M* 322.38.

6-[2-(Furan-2-yl)ethenyl]-4-hydroxy-3-(phenylsulfanyl)-2*H*-pyran-2-one (6d). Yield 65%, brown solid, mp 210°C (from MeOH). IR spectrum, ν, cm^{-1}: 3650–3200 (OH), 1620 (C=O), 1581, 1534, 1475, 1411, 1353, 1275, 1219, 1016, 964, 736, 689. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.49 s (1H, 5-H), 6.67 d.d (1H, furyl), 6.82 d (1H, α-H), 6.93 d (1H, 3′-H), 7.14–7.19 m (3H, H_{arom}), 7.28 d (1H, β-H), 7.27–7.38 m (2H, H_{arom}), 7.85 (1H, furyl), 12.44 s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 92.4 (C^3), 101.24 (C^5), 112.99 ($C^{3'}$), 114.65 ($C^{4'}$), 116.74 (C^{α}), 122.74 (C^{β}), 125.22 (C^{p}), 125.95 (C^{m}), 129.09 (C^{o}), 136.93 (C^{i}), 145.43 ($C^{5'}$), 151.36 ($C^{2'}$), 159.11 (C^6), 162.1 (C^2), 172.55 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 314 (8.5), 313 (12.2), 312 (100) $[M]^+$, 203 (4.9), 202 (4.9), 163 (39.0), 140 (6.1), 122 (4.9), 121 (72.0), 107 (12.2), 69 (9.8), 49 (8.5). $C_{17}H_{12}O_3S$. Calculated: *M* 312.34.

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