Synthesis of New Bicyclic Quinones: 2*H*-1-Benzopyran-5,8-quinones and Related Compounds

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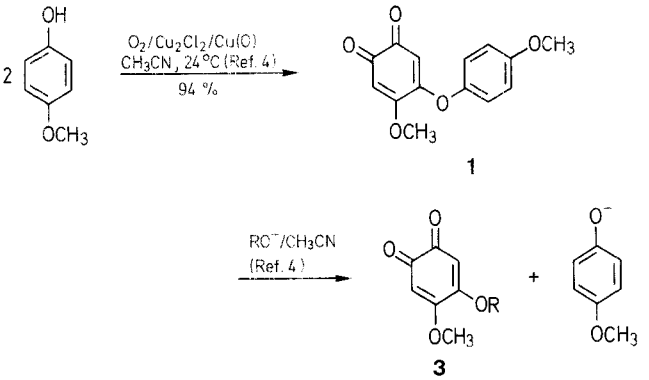
The synthesis of new 2*H*-1-benzopyran-5,8-quinones has been realized in three steps from *p*-methoxyphenol with 84–88% overall yield. It consists at first in a regioselective nucleophilic substitution of propargyl alcoholates on an appropriate 4,5-disubstituted *o*-quinone (obtained by copper-catalyzed oxidation of *p*-methoxyphenol) and subsequently in a thermal isomerization. Relative stabilities of title compounds are described, as well as several transformation products.

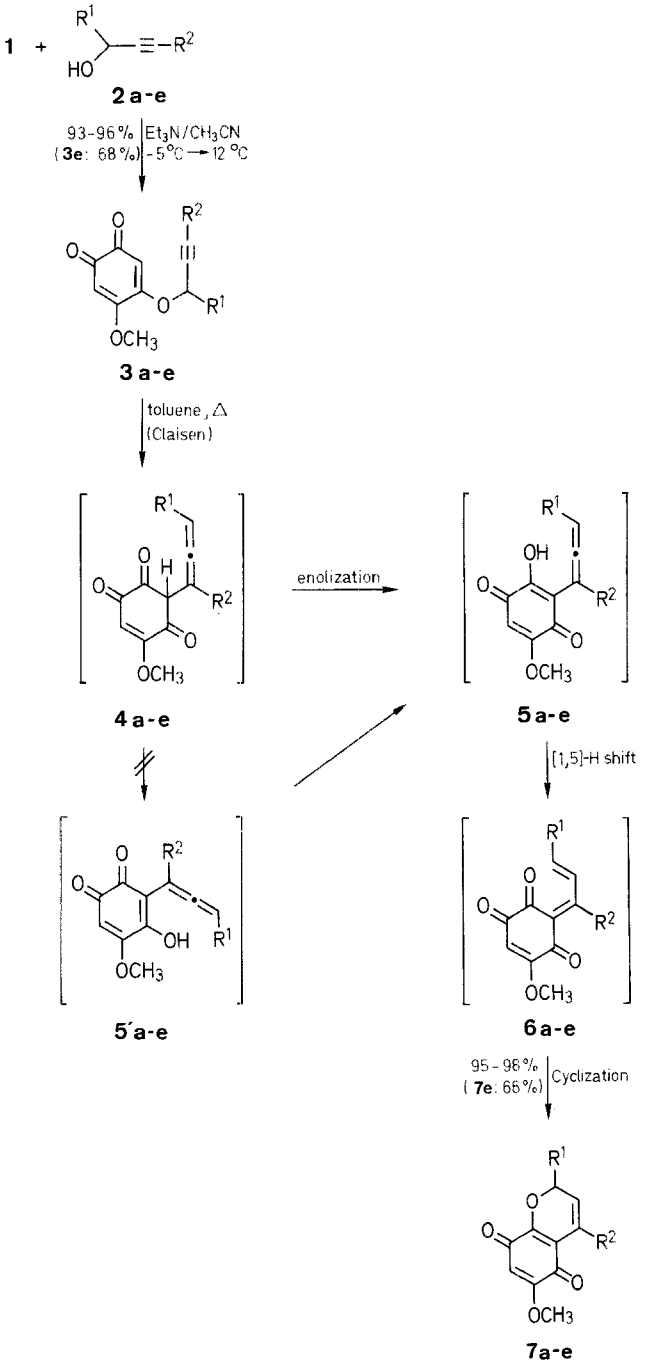
To our knowledge benzopyran quinones have never been synthesized, but a number of derivatives occur naturally: *in vivo*, prenyl quinones or quinols are cyclized into chromanols,[1,2] and phytylplastoquinone is possibly a natural precursor of γ-tocopherol.[1] In the course of studies on the mechanism of oxidation of vitamine E, the preparation of various 3,4-dihydro-2*H*-1-benzopyran-5,8-quinones have been reported.[3] It appeared to us of interest to develop a convenient synthesis of 2*H*-1-benzopyran-5,8-quinones: as precursors of analogs of vitamin E and as possible tool for the study of its metabolism. We report here a simple method of synthesizing these new products in three steps from *p*-methoxyphenol.

In a previous paper,[4] we have shown how *p*-methoxyphenol is oxidized by molecular oxygen under copper catalysis to a 4-aryloxy-5-methoxy-*o*-benzoquinone **1**. Reaction of this particular dissymetric *o*-quinone **1** with an alcoholate in acetonitrile proceeded regioselectively by displacement of the better leaving group, i.e. *p*-methoxyphenolate rather than methanolate to give **3**.



Scheme **A**

Various 5-methoxy-4-propargyloxy-1,2-benzoquinones **3a–d** were prepared from quinone **1** with excellent yields (Table 1). Primary and secondary propargyl alcohols **2** are acidic enough to give alcoholates in the presence of a relatively weak base like triethylamine in contrast with allylic alcohols for which a much stronger base (e.g. 1,8-diazabicyclo[5.4.0]undec-7-ene, DBU) is needed.[4] This explains the total regioselectivity of the nucleophilic substitutions and the excellent yields following a quite simple procedure. Furthermore the new products **3a–d** are stable enough to be easily isolated by crystallization from the reaction medium.



2–7	R^1	R^2	2–7	R^1	R^2
a	H	H	**d**	n-C_5H_{11}	H
b	H	CH_3	**e**	C_6H_5	H
c	CH_3	H			

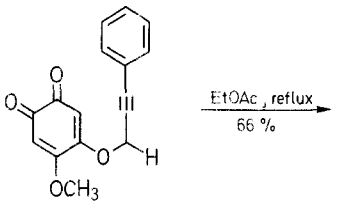
Scheme **B**

An exception is the quinone **3e** which is obtained in lower yield. The reason is probably the great mobility of the 1-phenylpropargyl group towards any nucleophile. So the reaction must be imperatively carried out at low temperature and great care must be taken during the work-up to keep the product away from moisture.

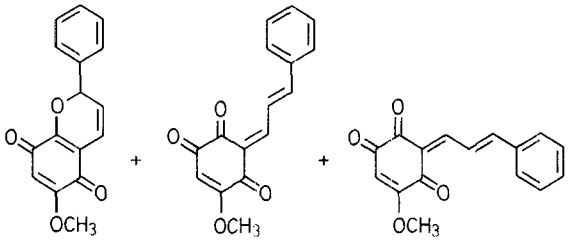
Tertiary alcohols, such as 1,1-dimethylpropargyl alcohol, do not provide the corresponding quinones **3**.

3-Quinones **3a–e** undergo a sequence of concerted thermal isomerizations to provide 2*H*-1-benzopyran-5,8-quinones **7a–e** with excellent yields (Table 2). Firstly, a [3,3]-Claisen-type sigmatropic rearrangement gives the allenyl ketones **4a–e** which enolize rapidly into 3-allenyl-2-hydroxy-5-methoxy-*p*-benzoquinones **5a–e** rather than less stable isomeric *o*-quinones **5'a–e**. Then a concerted [1,5]-hydride shift leads to dienic ketones **6a–e** whose exocyclic carbon-carbon double bond should be exclusively *cis* oriented. Further thermally "allowed" electrocyclization provides the 2*H*-1-benzopyran-5,8-quinone **7a–e** without any detectable trace of the *ortho* isomer. This reaction is new for quinonic substrates as well as in the naphthoquinonic series which is usually more easily accessible. A similar mechanism has been reported for the isomerization of aryl propargyl ethers into chromens,[5] but drastic conditions are required ($t_{\frac{1}{2}}$ = 12 h, 180 °C in dichlorobenzene[6] or silver(I) catalysis[7]) which account for lower yields and regioselectivity. Such an improvement has already been observed in the Claisen rearrangement of allyloxyquinones *versus* arylallylethers.[3,8]

2*H*-1-Benzopyran-5,8-quinones **7** are stable in neutral medium except if R^1 is a phenyl group: the pyran ring of **7e**, which is produced by isomerization of **3e**, spontaneously opens at room temperature to give two new products **6e**-(*Z,E*) and **6e**-(*E,E*), the last three compounds being in equilibrium.



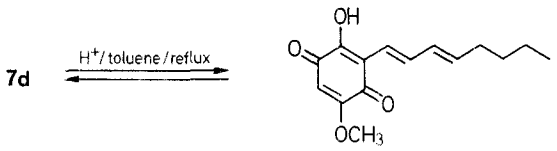
3e



7e **6e** (*Z,E*) **6e** (*E,E*)

The respective proportions of **7e**, **6e** (*Z,E*) and **6e** (*E,E*) are solvent-dependent, as shown by ^{1}H-NMR spectra (Table 3). Such a behavior of **7e** is not surprising and has already been noticed in the case of 6-arylpyrans.[9,10]

Acids catalyze the opening of pyran ring of quinones **7** and lead to an equilibrium between the two isomers **7** and **8** in inert solvent. The dienic quinone **8d** has been isolated but is fairly unstable.



8d

Table 1. 5-Methoxy-4-propargyloxy-1,2-benzoquinones **3** Prepared

Product	Reaction Conditions Time (h)/Temp. (°C)	Yield (%)	m.p. (°C)	Molecular Formula[a]	IR (KBr) ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)
3a[b]	24/−5	95	>250 (dec)	$C_{10}H_8O_4$ (192.2)	3200, 2130, 1665, 1650, 1585, 1580	2.89 (t, 1H, J = 1.2, ≡CH); 3.90 (s, 3H, OCH_3); 4.76 (d, 2H, J = 1.2, CH_2); 5.78 (s, 1H$_{quin}$); 5.91 (s, 1H$_{quin}$)
3b[c]	12/12	94	192	$C_{11}H_{10}O_4$ (206.2)	2250, 1665, 1645, 1580	1.85 (t, 3H, J = 2, CH_3); 3.85 (s, 3H, OCH_3); 4.7 (q, 2H, J = 2, CH_2); 5.75 (s, 1H$_{quin}$); 5.90 (s, 1H$_{quin}$)
3c	14/8	96	180	$C_{11}H_{10}O_4$ (206.2)	3220, 2115, 1665, 1650, 1585, 1575	1.75 (d, 3H, J = 7, CH_3); 2.65 (d, 1H, J = 2, ≡CH); 3.90 (s, 3H, OCH_3); 4.83 (dq, 1H, J = 2,7, $CHCH_3$); 5.75 (s, 1H$_{quin}$); 5.95 (s, 1H$_{quin}$)
3d[d]	20/10	93	112	$C_{15}H_{18}O_4$ (262.3)	3230, 2120, 1655, 1635, 1580 (br)	0.90 (t, 3H, J = 6, CH_3); 1.35 [m, 6H, $(CH_2)_3CH_3$]; 2.0 (m, 2H, $CHCH_2$); 2.65 (d, 1H, J = 2, ≡CH); 3.88 (s, 3H, OCH_3); 4.70 (td, 1H, J = 6,2, $CHCH_2$); 5.75 (s, 1H$_{quin}$); 5.95 (s, 1H$_{quin}$)
3e[e]	24/−5	68	>210 (dec)	$C_{16}H_{12}O_4$ (268.3)	3260, 2120, 1665, 1655, 1590, 1580	2.85 (d, 1H, J = 2, ≡CH); 3.85 (s, 3H, OCH_3); 5.75 (s, 1H$_{quin}$); 5.8 (d, 1H, J = 2, OCH); 6.05 (s, 1H$_{quin}$); 7.45 (m, 5H$_{arom}$)

The relative unstability of these intermediates do not allow the purification required for satisfactory microanalyses. They need to be transformed into **7** as soon as possible or kept at −20 °C in a dry nitrogen atmosphere.

[b] MS: *m/e* (rel. int. %) = 192 (M^+, 4); 164 (12); 69 (100).

[c] UV($CHCl_3$): λ_{max}(log ε) = 284 (4.1), 408 (2.84), 506 (sh) nm (1.63).

[d] UV($CHCl_3$): λ_{max}(log ε) = 286 (4.13), 408 (2.83), 506 (sh) nm (1.74).

Table 2. 2*H*-1-Benzopyran-5,8-quinones **7a–e** and Isomers **6e** Prepared

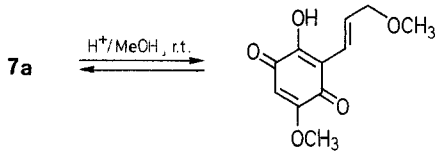
Product	Reaction Conditions: Time(h)/Temp.(°C)	Yield[a] (%)	m.p. (°C)	Molecular Formula[b]	IR (KBr) ν (cm^{-1})	UV ($CHCl_3$) λ_{max} (log ε) (nm)	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)	MS (70 eV) *m/e* (rel. inten. %)
7a	15/reflux	98	199	$C_{10}H_8O_4$ (192.2)	1665, 1635, 1615, 1585, 1250, 1210, 1035, 910, 860, 710, 700, 670	260 (3.89), 308 (4.08), 482 (2.84)	(250 MHz): 3.84 (s, 3H, OCH_3); 5.06 (dd, 2H, J = 2, 3.4, OCH_2); 5.74 (dt, 1H, J = 10, 3.4, =CHCH$_2$O); 5.81 (s, 1H$_{quin}$); 6.54 (dt, 1H, J = 10, 2, CH=CHCH$_2$O)	192 (M^+, 21); 179 (25); 121 (15); 69 (100)
7b	15/reflux	98	201	$C_{11}H_{10}O_4$ (206.2)	1665, 1640, 1615, 1570, 1250, 1215, 1175, 1045, 1010, 915, 855, 780	268 (4.05), 316 (3.86), 484 (2.83)	(90 MHz): 2.12 (m, 3H, CH_3); 3.83 (s, 3H, OCH_3); 4.83 (m, 2H, CH_2); 5.42 (m, 1H, =CH$_{pyran}$); 5.8 (s, 1H$_{quin}$)	206 (M^+, 19); 191 (17); 178 (28); 177 (24); 163 (38); 135 (13); 69 (100)
7c	3.5/reflux	97	148	$C_{11}H_{10}O_4$ (206.2)	1665, 1640, 1615, 1590, 1250, 1210, 1035, 910, 870, 745	260 (3.90), 308 (4.07), 484 (2.84)	(90 MHz): 1.5 (d, 3H, J = 7, CH_3); 3.83 (s, 3H, OCH_3); 5.25 (m, 1H, OCH); 5.65 (dd, 1H, J = 10, 4, =CHCHO); 5.8 (s, 1H$_{quin}$); 6.52 (dd, 1H, J = 10, 2, HC=CHCHO)	206 (M^+, 17); 191 (14); 178 (16); 163 (27); 135 (17); 69 (100)
7d[c]	4/80	95	95	$C_{15}H_{18}O_4$ (262.3)	1665, 1630, 1600, 1570, 1245, 1205, 1025, 905, 875, 730	260 (3.83), 308 (3.96), 488 (2.73)	(90 MHz): 0.87 (t, 3H, J = 6, CH_3); 1.32 [br s, 6H, $(CH_2)_3CH_3$]; 1.75 (m, 2H, $OCHCH_2$); 3.82 (s, 3H, OCH_3); 5.1 (dq, 1H, J = 2, 4, OCH); 5.63 (dd, 1H, J = 4, 10, =CHCHO); 5.77 (s, 1H$_{quin}$); 6.5 (dd, 1H, J = 2, 10, CH=CHCHO)	264 (M^+ + 2,7); 262 (M^+, 11); 191 (97); 163 (15); 28 (100)
7e	0.54/77[d]	66[d]	dec. >230[d]	$C_{16}H_{12}O_4$[d] (268.3)	1690, 1660 (br), 1610, 1590, 1570, 1540, 1250, 1200, 1175, 1070, 1015, 1000, 955, 910, 890, 845, 815, 750, 685[d]	262 (4.05), 288 (4.17), 420 (4.41)[d]	(200 MHz): 3.83 (s, 3H, OCH_3); 5.80 (s, 1H$_{quin}$); 5.83 (dd, 1H, J = 10, 3.7, =CHCHO); 6.12 (dd, 1H, J = 3.7, 1.6, OCH); 6.75 (dd, 1H, J = 10, 1.6, CH=CHCHO); 7.43 (m, 5H$_{arom}$)	268 (M^+ + 2,15); 266 (M^+, 17), 240 (43); 225 (20); 69 (100)[d]
6e (E, E) or (Z, E)							(200 MHz): 3.97 (s, 3H, OCH_3); 6.45 (s, 1H$_{quin}$); 7.43 (m, 5H$_{atom}$); 7.60 (dd, 1H, J = 15, 1, =CHPh); 8.20 (dd, 1H, J = 12, 1, =CHCH=CHPh); 8.59 (dd, 1H, J = 15, 12, CH=CHPh)	
6e (Z, E) or (E, E)							(200 MHz): 3.97 (s, 3H, OCH_3); 6.44 (s, 1H$_{quin}$); 7.43 (m, 5H$_{arom}$); 7.59 (dd, 1H, J = 15, 1, =CHPh); 8.13 (dd, 1H, J = 12, 1, =CHCH=CHPh); 8.60 (dd, 1H, J = 15, 12, CH=CHPh)	

[a] Yield of isolated products.
[b] Satisfactory microanalyses obtained: C ± 0.08, H ± 0.19 (Exceptions: **7e**, **6e**: C − 0.43).
[c] ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 13.6 (q, CH_3); 22.1, 23.4, 31.2, 35.3 [4t, $(CH_2)_4$]; 56.2 (q, OCH_3); 78.1 (d, OCH); 105.1 (d, =CH, quin); 114.3 (s, =CCH=quin); 115.8 (d, =CHCHO, pyran); 124.0 (d, −CH=CHCHO, pyran); 151.8 (s, =COCH$_3$, quin); 158.6 (s, =C−O−, quin); 178.1, 180.8 (2s, 2C=O, quin).
[d] These data are characteristic of the mixture **7e** + **6e** (*E*, *E*) + **6e** (*Z*, *E*)

Table 3. Solvent Dependent Equilibrium Between **7e** and **6e** (Determined by ^{1}H-NMR, 250 MHz)

Compound	Percentage Content in Solvents		
	$CDCl_3$	$CDCl_3$ (0.7) + C_6D_6 (0.3)	C_6D_6
7e	46	43	42
6e (Z, E) or (E, E)	12	22	24
6e (E, E) or (Z, E)	42	35	34

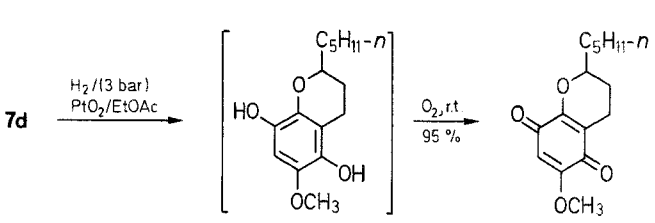
In nucleophilic solvent, e.g. methanol, benzopyranquinone **7** affords the open form **9**, in which the solvent has been incorporated. The impossibility to obtain complete disappearance of the starting material **7**, even with longer reaction time or increasing acid concentrations, suggests the existence of an equilibrium between both forms. The hydroxyquinone **9a** has only been identified by its ^{1}H-NMR spectrum due to its great unstability.



9a

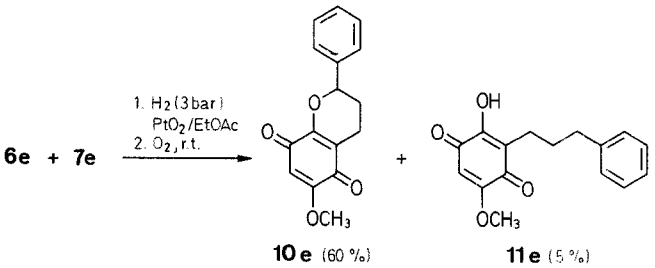
In both preceding experiments, quinones **7** are in equilibrium with hydroxymethoxyquinones **8** or **9**, whose cyclization must provide *p*-quinonic compounds. Furthermore, as it is well known that alkoxy-*o*-quinones readily isomerize in acidic medium into *p*-quinones,[11,12] the absence of any detectable bicyclic isomer of quinones **7** gives evidence for their *p*-quinonic structure.

Finally, benzopyranquinones **7** may be hydrogenated and subsequent aerial oxidation provides the dihydro derivatives **10**.



10d

The same procedure, effected on the mixture **7e–6e**, provides two separable products **10e** and **11e** with a 60% yield for the cyclic quinone **10e** which confirms the structures of these products **6e** and **7e**. The pale yellow colour of **10d, e** and their UV-visible spectra are consistent with a *p*-quinone structure.[1,11]



10e (60 %) **11e** (5 %)

All derivatives **8, 9, 10, 11** of quinones **7** were unknown compounds and this illustrate the large synthetic possibilities one can expect from their chemistry.

All reagents are commercially available. Acetonitrile was twice distilled from P_4O_{10} and kept under nitrogen atmosphere over molecular sieves (3 Å). Melting points were taken using a Kofler apparatus. IR Spectra were recorded on a Perkin-Elmer 298 infrared spectrophotometer. UV absorptions were measured using a Hewlett-Packard 8451 A UV spectrophotometer. ^{1}H-NMR spectra were obtained on Varian EM-390 (90 MHz), Bruker AM-200 SY (200 MHz) and AM-250 (250 MHz) spectrometers. ^{13}C-NMR spectra were obtained on Bruker AM-250 spectrometer.

5-Methoxy-4-(4-methoxyphenoxy)-1,2-benzoquinone (1):
A mixture of *p*-methoxyphenol (1 g, 8 mmol), powdered copper (255 mg, 4 mmol) and Cu_2Cl_2 (70 mg, 0.7 mmol) in CH_3CN (15 mL) is stirred under oxygen at 20 °C. After 10 min, the exothermic reaction begins and the mixture is maintained for 4.5 h at 24 °C in a thermostated bath. The solvent is removed under vacuum, the oily yellow-brownish residue is taken up in CH_2Cl_2 (1 mL) and purified by flash-chromatography on silica gel (15–40 µm, 10 g, ∅ = 2.5 cm, h ≃ 4 cm, eluent: cyclohexane/EtOAc, 70 : 30). Unreacted phenol (350 mg) is recovered by evaporation of the first colorless fractions and washing with cyclohexane (2 × 5 mL). The orange-colored fractions are concentrated to yield orange crystals. Washing with ether (2 × 3 mL) provides pure **1**; yield: 645 mg, 95% based on consumed phenol); m.p. 132 °C (Lit.[4] m.p. 132 °C).

UV ($CHCl_3$): λ_{max} (log ε) = 280 (4.09), 352 (3.14), 512 nm (sh) (1.7).

MS (70 eV): *m/e* (rel. inten. %): 262 (M^+ + 2, 100); 260 (M^+, 10), 247 (14), 232 (55), 219 (16), 187 (15), 149 (25), 135 (20), 124 (26), 109 (82), 77 (22), 69 (66), 43 (50).

4-(2-Butyn-1-yloxy)-5-methoxy-1,2-benzoquinone (3b); Typical Procedure:
A suspension of 4-(4-methoxyphenoxy)-5-methoxy-1,2-benzoquinone (**1**; 500 mg, 1.9 mmol) and 2-butyn-1-ol (**2b**, 0.15 mL, 1.96 mmol) is stirred in dry CH_3CN (5 mL) at − 5 °C under nitrogen. Triethylamine (0.27 mL, 1.9 mmol) is added and the mixture is allowed to warm up to + 12 °C. After 1 h, the solution becomes brown and homogeneous, and is left until starting quinone **1** has completely reacted (TLC or HPLC). Orthoquinone **3b** (230 mg), which has partially crystallized, is isolated by suction and washed with ether (2 × 5 mL). Mother liquors are evaporated under reduced pressure and recrystallized from dry ether to give a second crop (140 mg) of quinone (**3b**); total yield: 370 mg (94%); m.p. 192 °C.

5-Methoxy-4-(1-phenyl-2-propyn-1-yloxy)-1,2-benzoquinone (3e):
To a stirred suspension of 4-(4-methoxyphenoxy)-5-methoxy-1,2-benzoquinone (**1**; 880 mg, 3.4 mmol), and 1-phenyl-2-propynol (**2e**; 450 mg, 3.4 mmol), in dry CH_3CN (9 mL) at − 5 °C under nitrogen, triethylamine is added (0.47 mL, 3.4 mmol). After 4 h, the mixture becomes dark and homogeneous. After 16 more h, the *o*-quinone **3e** has partially crystallized. Solvent is evaporated, substituted by dry EtOAc (3 mL) under vacuum and the solution is left under nitrogen at − 30 °C for 4 h to provide orange crystals of quinone **3e** which are carefully washed with dry ether (2 × 3 mL); yield: 620 mg (68%); m.p. > 210 °C (dec).

6-Methoxy-2*H*-1-benzopyran-5,8-quinones (7a–d), General Procedure:
A suspension of 4-propargyloxy-5-methoxy-1,2-benzoquinone (**3**; 1 mmol) in toluene (40 mL) is heated with stirring at 80–110 °C until the starting quinone **3** has completely disappeared (TLC). The solvent is removed under vacuum to provide **7** as red crystals. Further purification can be carried out by filtration on silica gel or crystallization from $CHCl_3$/ether.

6-Methoxy-2-phenyl-2*H*-1-benzopyran-5,8-quinone (7e) and Isomers 6e (*E,E*) + (*Z,E*):
A suspension of 5-methoxy-4-(1-phenyl-2-propyn-1-yloxy)-1,2-benzoquinone (**3e**; 590 mg, 2.2 mmol) in dry EtOAc (15 mL) is rapidly brought to reflux with stirring. After 2 min, the material becomes homogeneous and, after 3 more min, orange crystals of **7e** + **6e** appear. The mixture is left 30 min at reflux, then cooled to − 30 °C, filtered, and washed with ether (2 × 5 mL) to afford **7e** + **6e**; yield: 390 mg.

2-Hydroxy-5-methoxy-3-[1,3-(*E,E*)-octadien-1-yl]-1,4-benzoquinone (8d):
Method A: A suspension of 5-methoxy-4-(1-octyn-3-yloxy)-1,2-benzoquinone (**3d**; 920 mg, 3.5 mmol) in toluene (30 mL) and AcOH (0.1 mL)

is rapidly brought to reflux with stirring. After 1 h, the material becomes homogeneous. When no more **3d** remains (TLC), solvents are removed under vacuum. ^{1}H-NMR of crude product shows a 60/40 mixture of respectively **8d** and benzopyranquinone **7d**. Flash chromatography on silica gel (elution mixture: cyclohexane/EtOAc/AcOH, 30:70:1) affords **7d** (yield: 360 mg, 39%), and then **8d** (yield: 190 mg, 21%).

8d: Dark violet crystals; m.p.: 113 °C (ether/*n*-hexane): degree of purity: 90% determined by ^{1}H-NMR (fairly unstable).

IR (KBr): ν = 3310, 1655, 1625 (br), 1640 (sh), 1600 (br), 985, 900, 840 cm^{-1}.

^{1}H-NMR (250 MHz, $CDCl_3$/TMS): δ = 0.91 (t, 3H, CH_3); 1.38 [m, 4H, $(CH_2)_2CH_3$]; 2.16 (q, 2H, J = 7 Hz, =$CHCH_2$); 3.87 (s, 3H, OCH_3); 5.88 (s, 1 H_{quin}); 5.93 (dt, 1H, J = 15.2, 7 Hz, =$CHCH_2$); 6.22 (dd, 1H, J = 10.6, 15.2 Hz, CH=$CHCH_2$); 6.46 (d, 1H, J = 16 Hz, CH=$CHCH$=$CHCH_2$); 7.36 (dd, 1H, J = 16, 10.6 Hz, =$CHCH$=$CHCH_2$); 7.80 (s, 1H, OH).

Method B: A solution of **7d** (100 mg, 0.38 mmol) in toluene (5 mL) and acetic acid (0.2 mL) or *p*-toluenesulfonic acid (5 mg) heated for 1 h provides a mixture of **7d** and **8d** (TLC); yield: 10 mg. Reversely, a solution of **8d**, under the same conditions provides a mixture of **7d** and **8d** (TLC).

2-Hydroxy-5-methoxy-3-(1-methoxy-2-propen-1-yl)-1,4-benzoquinone (9a):

A solution of 6-methoxy-2*H*-1-benzopyran-5,8-quinone (**7a**; 100 mg, 0.45 mmol) in methanol (5 mL) and conc. H_2SO_4 (0.1 mL) is left for 24 h at room temperature. The solution is concentrated (1 mL) and then diluted with ether (30 mL), washed with water (3 × 5 mL), dried ($MgSO_4$) and evaporated. ^{1}H-NMR of the crude orange oily product shows a mixture 75:25 of **9a** and **7a** respectively.

9a: ^{1}H-NMR (90 MHz, $CDCl_3$/TMS): δ = 3.38 (s, 3H, CH_2OCH_3); 3.87 (s, 3H, =$COCH_3$); 4.08 (d, 2H, J = 5 Hz, CH_2); 5.87 (s, 1 H_{quin}); 6.55 (d, 1H, J = 16 Hz, HC=$CHCH_2$); 6.9 (dt, 1H, J = 16, 5 Hz, =$CHCH_2$); 7.6 (s, 1H, OH).

6-Methoxy-2-pentyl-3,4-dihydro-2*H*-1-benzopyran-5,8-quinone (10d):

A solution of 6-methoxy-2-pentyl-5,8-dihydro-2*H*-1-benzopyran-5,8-dione (**7d**; 100 mg, 0.38 mmol) in EtOAc (10 mL) is stirred with PtO_2 (4.4 mg, 0.02 mmol, 0.05 equiv) for 3 h under hydrogen at a pressure of 3 bar in a glass-coated pressure reactor. The colorless solution is then stirred in the air at room temperature for 14 h, filtered on silica gel and evaporated under reduced pressure to provide pure **10d** as pale lemon-yellow crystals yield: 96 mg (95%); m.p. 144 °C.

$C_{15}H_{20}O_4$	calc.	C 68.16	H 7.63
(264.3)	found	68.11	7.54

IR (KBr): ν = 1670, 1660, 1630, 1605, 900, 870 cm^{-1}.

UV ($CDCl_3$): λ_{max} (log ε) = 292 (4.35), 404 nm (2.60).

^{1}H-NMR (90 MHz, $CDCl_3$/TMS): δ = 0.87 (t, 3H, J = 7 Hz, CH_3); 1.1–2.5 (m, 12H, 6CH_2); 3.8 (s, 3H, OCH_3); 4.05 (m, 1H, OCH); 5.75 (s, 1 H_{quin}).

^{13}C-NMR (62.9 MHz, $CDCl_3$/TMS): δ = 13.9 (q, CH_3); 17.5, 22.4, 24.8, 25.3, 31.6, 34.2 (6t, 6CH_2); 56.3 (q, OCH_3); 78.4 (d, OCH); 104.7 (d, =CH); 116.5 (s, =C); 154.2 (s, =$COCH_3$); 159.4 (s, =CO); 181.1, 181.6 (2s, 2C=O).

6-Methoxy-2-phenyl-3,4-dihydro-2*H*-1-benzopyran-5,8-quinone (10e):

A suspension of 6-methoxy-2-phenyl-2*H*-1-benzopyran-5,8-quinone **7e** and isomers **6e** (200 mg, 0.75 mmol) and PtO_2 (8 mg, 0.05 equiv) in EtOAc (30 mL) is stirred for 3 h under hydrogen at a pressure of 3 bar in a glass-coated pressure reactor. The homogeneous, colorless solution is then stirred under air for 14 h, filtered and concentrated (5 mL). The pale lemon-yellow crystals of **10e** (60 mg) are isolated by vacuum filtration and washed with ether (2 × 5 mL). The mother liquor is evaporated and a second crop (36 mg) is obtained from ether. The mother liquor from the second crystallization is concentrated again and flash chromatographed (elution mixture : cyclohexane/ EtOAc/ AcOH, 70:30:1) to afford **10e** (yield: 25 mg, 60%), and 2-hydroxy-5-methoxy-3-(1-phenylpropan-3-yl)-1,4-benzoquinone (**11e**; yield: 11 mg, 5%). **10e**: m.p. 244 °C.

$C_{16}H_{14}O_4$	calc.	C 71.10	H 5.22
(270.3)	found	70.66	5.24

IR (KBr): ν = 1660 (br); 1630, 1620, 1595 (br), 1495, 1045, 1010, 910, 845, 775, 765, 710 cm^{-1}.

UV ($CHCl_3$): λ_{max} (log ε) = 290 (4.33), 400 nm (2.59).

^{1}H-NMR (90 MHz, $CDCl_3$/TMS): δ = 2.1 (m, 1H, CH_2CH_2CHO); 2.5 (dd, 2H, J = 8, 6 Hz, CH_2CH_2CHO); 3.8 (s, 3H, OCH_3); 5.1 (dd, 1H, J = 9, 3.5 Hz, CHO); 5.77 (s, 1 H_{quin}); 7.35 (s, 5 H_{arom}).

^{13}C-NMR (62.9 MHz, $CDCl_3$/TMS): δ = 17.9 (t, CH_2CH_2-CHO); 27.9 (t, CH_2CH_2CHO); 56.4 (q, OCH_3); 79.3 (d, OCH); 104.9 (d, =CH, quinone); 116.7 (s, OC=C, quinone); 125.9 (d, 2 × 2′-C_{arom}); 128.4 (d, 4′-C_{arom}); 128.7 (d, 2 × 3′-C_{arom}); 154.2 (s, =$COCH_3$, quinone); 159.4 (s, =C–O, quinone); 181.1, 181.3 (2 s, 2 × C=O, quinone).

11e: m.p. = 133 °C.

IR (KBr): ν = 3340, 1660, 1635, 1600 (br), 1495, 1080, 1040, 910, 840, 750, 705 cm^{-1}.

^{1}H-NMR (200 MHz, $CDCl_3$/TMS): δ = 1.82 (m, 2H, $CH_2CH_2C_6H_5$); 2.52 [t, 2H, J = 7 Hz, $CH_2(CH_2)_2C_6H_5$]; 2.66 (t, 2H, J = 7 Hz, $CH_2C_6H_5$); 3.87 (s, 3H, OCH_3); 5.83 (s, 1 H_{quin}); 7.1–7.3 (m, 6H, 5 H_{arom} and OH).

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