A New Synthesis of *ortho*-Quinones by Transition-Metal-Mediated Oxygenation of Phenols with *tert*-Butylhydroperoxide and the Mimoun Oxodiperoxo Molybdenum Complex $[Mo(O_2)_2O] \cdot Py \cdot HMPT$

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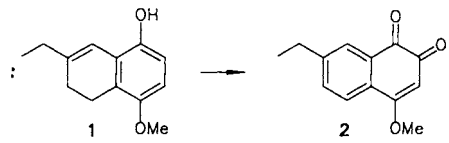
A specific oxygenation of phenols to *ortho*-quinones can be effected by a combination of the transition metal complexes $Ti(OiPr)_4$, $VO(acac)_2$, $Zr(acac)_4$, $Zr(OnPr)_4$ and *tert*-butylhydroperoxide (TBHP) or $[Mo(O_2)_2O] \cdot Py \cdot HMPT$. Naphthols, anthracenols, phenanthrols and donor substituted mononuclear phenols are readily converted into the corresponding 1,2-quinones. Unhindered *ortho*-naphthoquinones can yield binaphthyls with unreacted starting material by Michael addition.

Eine neue *ortho*-Chinon-Synthese durch Oxygenierung von Phenolen mit den Systemen *tert*-Butylhydroperoxid/Übergangsmetall-Komplex und dem Mimounschen Oxodiperoxo-Molybdän-Komplex $[Mo(O_2)_2O] \cdot Py \cdot HMPT$

Phenole können mit einer Kombination der Übergangsmetall-Komplexe $Ti(OiPr)_4$, $VO(acac)_2$, $Zr(acac)_4$, $Zr(OnPr)_4$ und *tert*-Butylhydroperoxid oder mit $[Mo(O_2)_2O] \cdot Py \cdot HMPT$ spezifisch zu *ortho*-Chinonen oxygeniert werden. Naphthole, Anthracenole, Phenanthrole und Donor-substituierte einkernige Phenole werden glatt in die entsprechenden 1,2-Chinone übergeführt. Ungehinderte *ortho*-Napthochinone können unter Michael-Addition mit nicht umgesetztem Ausgangsmaterial zu Biarylen abreagieren.

In an attempt to prepare an optically active building block for rhodomycinone synthesis, the Sharpless reaction[1] was tried with the phenolic olefin **1**. Instead of the expected epoxide, the *ortho*-quinone **2** was isolated in 70% yield.

Scheme 1



1 2

Mechanistic considerations indicated that this transition-metal-mediated oxygenation with *tert*-butylhydroperoxide (TBHP) that was followed by dehydrogenation had considerable potential as a highly selective *ortho*-quinone synthesis. No reagents for this transformation were known until now; in fact, the 1977 Houben-Weyl volume on quinones states: „Man kennt noch kein Oxydationsmittel, das spezifisch zu *o*-Chinonen führt"[2]. A few recent examples illustrate the increasing interest for *ortho*-quinones in ultrasound-promoted Diels-Alder reactions[3], in the preparation of tumorigenic benzo[*c*]phenanthrenes[4], benzofurandiones[5], or biologically active phenazines[6]. Furthermore, phenols as starting materials have become generally available by a new selenium-catalyzed variation of the Bayer-Villiger reaction[7]. We now report on the results of our investigations of the transition-metal-mediated specific transformation of phenols to *ortho*-quinones.

Two general methods of quinone synthesis are available (reviews[2,8-10]). A variety of reagents are available for dehydrogenation of hydroquinones (for example silver oxide, lead tetroxide, hypervalent iodine[11], hydrogen peroxide/iodine[12], bis(1,3-propanediamine)copper(II) chloride/oxygen[13], tetrachloro-*ortho*-quinone[14]; review[15]). Some reagents, such as silver(II) oxide/nitric acid[16] or ceric ammonium nitrate[17-19], are capable of converting hydroquinone di- or monomethyl ethers to the corresponding quinones. In the second, more difficult quinone synthesis at least one additional oxygen atom has to be introduced into the aromatic ring. As a rule, this oxygenation is not selective, and mixtures of *ortho*- and *para*-quinones result from the reaction of phenols with potassium nitrosodisulfonate[20,21], peracetic acid[22], potassium peroxydisulfate[23], or ceric ammonium nitrate[24] (compare also ref.[2]). In the oxidation of alkyl aryl ethers with more conventional oxidants such as lead tetraacetate, dibenzoyl peroxide, chromium(IV) oxide or nitric acid "no derivatives of benzo 1,2-quinones have been obtained from such reactions"[9]. However, high *ortho* selectivities are obtained in many cases in the oxydation of phenols with diphenyl seleninic anhydride introduced by Barton et al.[25], although the reagent sometimes also affords mixtures of *ortho*- and *para*-quinones[26]. Only few examples of the *ortho*-hydroxylation of phenols with the system CuCl/Cu(O)/oxygen are known[27,28].

Reaction of Naphthols, 1-Anthracenol, and 2-Phenanthrol

The *ortho* selectivity could not be checked with the example that led to the discovery of the reaction since the *para* position in **1** was blocked by a methoxy group. A variety of naphthols **3**–**13** and **30**–**32** were subsequently selected to elucidate the scope and limitation in the new *ortho*-quinone synthesis, and the results are summarized in Schemes 2–4 and Table 1. In the reaction of 5-methoxynaphthol (**3**) the oxygenation could take place in the *ortho* or *para* position. The starting material **3** was consumed in less than 1 h at −23°C with one equivalent of titanium isopropylate and three equivalents of TBHP in dichloromethane (Scheme 2). However, in addition to the orange-red quinone **14** (21%), a second, polar, pink product was isolated in comparable

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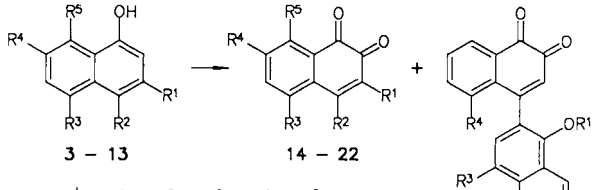
yield (22%). The spectral data indicated an "dimeric" structure **23**, which was presumably formed in a Michael addition of quinone **14** with unreacted starting material **3**. The coupling reaction can even be observed during TLC analysis if starting material and *ortho*-quinone are on the same spot. Evidently, the transition metal that served for the activation of TBHP for the *ortho*-selective oxygen transfer also catalyzed the Michael addition. Similar C–C couplings to form binaphthyl systems were observed in the autoxidation of naphthols[29,30] as well as in the copper-[31] or molybdenum-catalyzed[32] oxidations. The Michael addition to highly reactive intermediate *ortho*-quinones ("nascierende Chinone") is a general reaction as reviewed by Wanzlick[33]. In some cases, for example in the copper-catalyzed hydroxylation of a mononuclear phenol, the oxygen atom of the phenol can add to the intermediate *ortho*-quinone[27]. The $Ti(OiPr)_4$/TBHP reagent can be used to prepare specifically binaphthyl derivatives such as **23**–**26** or **33** – **36** (vide infra) starting from unhindered 1- or 2-naphthols. However, large substituents in *meta* position as in **4** or **5** or in *para* position as in **6** and **7** normally prevent the Michael addition, and good yields of the *ortho*-quinones **15**–**18** are isolated as shown in Table 1. We carefully looked for the formation of *para*-quinones in all relevant cases described in this paper, but they were never detected.

Scheme 2



	R^1	R^2	R^3	R^4	R^5
3/14	H	H	OMe	H	H
4/15	t-Bu	H	OH	t-Bu	H
5/16	Ph	H	H	H	H
6/17	H	CPh_3	H	H	H
7/18	H	Et	H	H	H
8/19	H	OMe	H	H	H
9/20	H	Cl	H	H	H
10/21	H	OMe	H	H	OMe
11/-	H	H	H	H	H
12/22	H/H	H/H	H/H	OH/H	H/OH
13/-	H	Ac	H	H	H

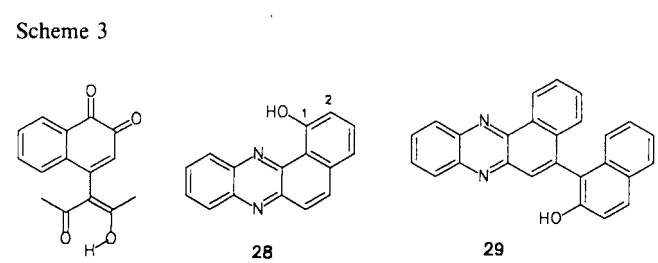
	R^1	R^2	R^3	R^4
23	H	OMe	H	OMe
24	H	H	Cl	H
25	Ac	H	Ac	H
26	H	H	H	H

For the purpose of *ortho*-quinone synthesis, the coupling reaction to form binaphthyls was undesirable. The ideal catalyst for the transformation to *ortho*-quinones should sufficiently activate the TBHP for oxygen transfer but not effectively catalyze the Michael addition. Subsequently, a number of commercially available transition-metal complexes such as $Cu(acac)_2$, $Zr(acac)_4$, $Zr(OnPr)_4$, $VO(acac)_2$, and the oxodiperoxo molybdenum complex of Mimoun[34] $[Mo(O_2)_2O] \cdot Py \cdot HMPT$ were tested. Aluminum triisopropylate leads to decomposition products, whereas the copper catalyst $Cu(acac)_2$ gave only low conversion rates even at prolonged reaction times. However, good results were obtained with the zirconium complexes $Zr(acac)_4$ and $Zr(O-nPr)_4$, as shown in Table 1. For example, 5-methoxynaphthol (**3**) and 4-methoxynaphthol (**8**) were converted into the *ortho*-quinones **14** and **19** in 57% and 89% yield, respectively, without formation of any coupling products. The reaction with $Zr(acac)_4$ can usually be conducted at room temperature by stirring the reaction components for a time depending on the reactivity of the substrate, followed by hydrolysis with 10% sulfuric acid (see Experimental for detailed procedures). However, by the use of $Zr(acac)_4$ the acetyl acetonate can be transferred as a Michael donor to sensitive *ortho*-quinones, as seen in the conversion of 1-naphthol (**11**) to the Michael adduct **27**. In such cases zirconium tetrapropylate (zirconium was discovered exactly 200 years ago by Klaproth) or the molybdenum catalyst (see below) have to be used.

Table 1. Yields and conditions in the conversion of phenols to *ortho*-quinones

Phenol, No.	Reagent	Conditions temp. [°C]	time [h]	No.	yield (%)	Product m.p.; ref. m.p. [°C]
1	$Ti(OiPr)_4$	–23	24	**2**	70	123
3	$Ti(OiPr)_4$	–23	1	**14**	21	203–205; 188–190[54]
3				**23**	22	250–252
3	$Zr(acac)_4$	20	12	**14**	57	
4	$Ti(OiPr)_4$	–23	3.5	**15**	44	302
4	$[Mo(O_2)_2O]L_2$	0	44	**15**	73	
5	$Ti(OiPr)_4$	–23	3.5	**16**	59	160; 156[55]
6	$Ti(OiPr)_4$	–23	5.5	**17**	85	258–259; 260–262[56]
7	$Ti(OiPr)_4$	–23	3	**18**	51	117
8	$Ti(OiPr)_4$	–23	3.5	**19**	83	188; 190[57]
8	$Cu(acac)_2$	20	19	**19**	11	
8	$Zr(acac)_4$	20	18	**19**	89	
9	$Ti(OiPr)_4$	–23	1	**24**	10	195
9	$Zr(acac)_4$	20	2.5	**20**	21	136; 134–135[58]
9				**24**	10	
10	$Ti(OiPr)_4$	20	6 d	**21**	15	202
11	$Zr(acac)_4$	0	14	**27**	11	175
11	$[Mo(O_2)_2O]L_2$	0	14	**26**	11	108
11				**36**	7	245; 246[29]
12	$[Mo(O_2)_2O]L_2$	–23	3	**28**	19	214
13	$[Mo(O_2)_2O]L_2$	20	5 d	**25**	49	178
13	$Ti(OiPr)_4$	–23	1.5	**25**	72	
13	$Zr(acac)_4$	20	18	**25**	16	
30	$[Mo(O_2)_2O]L_2$	20	20	**29**	91	291; 293–294[32]
30				**33**	34	162–164; 148–149[32]
31	$[Mo(O_2)_2O]L_2$	20	20	**34**	40	256
32	$[Mo(O_2)_2O]L_2$	20	18	**35**	13	>255
37	$[Mo(O_2)_2O]L_2$	–23	3	**39**	60	185; 202[20]
41	$[Mo(O_2)_2O]L_2$	–23	3	**42**	56	190; 195–216[59]
43	$Ti(OiPr)_4$	23	14	**47**	22	114; 114–115[60]
43	$[Mo(O_2)_2O]L_2$	20	18	**47**	32	
43	$VO(acac)_2$	–23	2	**47**	62	
44	$Ti(OiPr)_4$	20	3	**47**	35	
44	$[Mo(O_2)_2O]L_2$	20	16	**47**	15	
45	$Ti(OiPr)_4$	–23	3.5	**48**	31	138
45	$[Mo(O_2)_2O]L_2$	20	16	**48**	52	
46	$[Mo(O_2)_2O]L_2$	20	18	**49**	90	199; 200–202[61]

Scheme 3



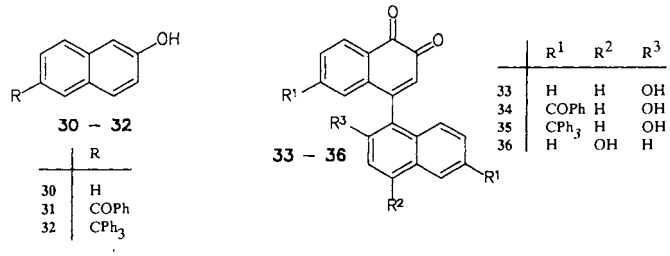
Not surprisingly, some very labile *ortho*-quinones were difficult to isolate in crystalline form (for a discussion of the stability of *ortho*-quinones see ref.[35]). 4-Chloro-1-naphthol (**9**) gave only a low yield of the Michael adduct **24** with the titanium catalyst, but the corresponding *ortho*-quinone **20**, a highly reactive vinylogous acid chloride, was obtained in 22% yield using $Zr(acac)_4$ (Table 1). Monitoring the reaction by TLC showed a slow conversion of 4,8-dimethoxy-1-naphthol (**10**) in the titanium-catalyzed reaction, and the product partly decomposed on concentration of the solution even at low temperatures. The slow conversion is attributed to the formation of a chelated complex of the neighboring oxygen functions with the transition metal. This behavior was also observed in other cases such as 2-methoxyphenol or 2-methoxycarbonyl-3-naphthol.

The mildest reaction conditions were possible with the molybdenum complex $[Mo(O_2)_2O] \cdot Py \cdot HMPT$, easily prepared in two steps from MoO_3[34]. The Mimoun oxodiperoxo molybdenum complex was used by Vedejs for α-hydroxylation of enolates[36]. The second oxygen atom of the complex was transferred rather slowly, and usually two equivalents of the reagent were used for the oxygenation and dehydrogenation processes in the conversion of phenols to *ortho*-quinones. Workup was possible either by hydrolysis with acid or, more conveniently, by filtration through a short column of silica gel, because the molybdenum formed less strongly bonded complexes with the *ortho*-quinones than titanium. This procedure was applied in the oxygenation of 1-naphthol (**11**). TLC control indicated the formation of *ortho*-naphthoquinone, but two more polar products were formed on prolonged reaction times. Both possible regioisomeric *ortho* and *para* Michael adducts **26** and **36** could be isolated in a ratio of approximately 3:2 (Table 1). The structures of **26** and **36** were confirmed by NOE showing the vicinity of 3′-H and 1′-OH in **26** and 2′-H and 8′-H in **36**. Cassebaum and Langenbeck[29] only described the isolation of the less soluble *para*-coupled product **36** in the acid-catalyzed coupling reaction of *ortho*-naphthoquinone with 1-naphthol. The reaction of 7-hydroxy-1-naphthol (**12**) was particularly interesting, because it contained partial structures of α- and β-naphthol competing for oxygenation, and the formation of two isomeric *ortho*-quinones was thus possible. A rapid conversion of the electron rich dinaphthol **12** was seen on TLC even at −23°C affording a major unpolar product as well as ca. 20% of a more polar component. Filtration through a short column of silica gel (dichloromethane) gave a yellow solution of the pure unpolar component. The diluted solution was stable for some time at room temperature, but the quinone could not be isolated in the solid state due to decomposition to a black precipitate on concentration, even at −23°C. The oxidation with $[Mo(O_2)_2O] \cdot Py \cdot HMPT$ was finally conducted in deuteriochloroform. The ^{1}H-NMR spectrum, run immediately after filtration of the reaction mixture demonstrated the formation of the yet unknown 8-hydroxy-1,2-naphthoquinone (**22**). The unstable quinone was further characterized by in situ conversion (see Experimental) with 1,2-phenylenediamine to the phenacetine **28**. The experiment demonstrated that 2-naphthols react faster than 1-naphthols and that unstable *ortho*-quinones can be prepared in dichloromethane or chloroform solution for physical measurements and further reactions.

4-Acetyl-1-naphthol (**13**) was selected as an example of acceptor-substituted naphthols. A clean conversion to an orange-red product was observed with titanium or molybdenum reagents (Table 1), but the spectral data indicated the formation of the unusual Michael adduct **25** in which the acetyl group was transferred from the carbon C-4 to the phenolic group of the Michael donor. The assignment of structure **25** was confirmed by nuclear Overhauser experiments, proving the vicinity of the protons 3-H and 3′-H and of 3-H with the *O*-acetyl group. A multistep reaction sequence is proposed to account for the remarkable formation of **25** from **13**. The reaction may be initiated by oxygenation and dehydrogenation to an intermediate 4-acetyl-*ortho*-naphthoquinone followed by Michael addition with acetyl transfer to the phenolic group. An initial Bayer-Villiger reaction is improbable since a number of acylated arenes (e.g. **31**) did not undergo the Bayer-Villiger reaction with $[Mo(O_2)_2O] \cdot Py \cdot HMPT$ readily. The examples **13** and **31** show that moderate electron acceptors on naphthols do not prevent the oxygenation to *ortho*-quinones.

In the next series the 2-naphthols **30**–**32** were treated with $[Mo(O_2)_2O] \cdot Py \cdot HMPT$ at room temperature. TLC analysis showed the rapid transformation of 2-naphthol (**30**) to the Michael adduct **33** which was characterized as the known phenazine **29**[32]. The electron-withdrawing benzoyl group in ring A of **31** prevented the reaction with the zirconium reagent at −23°C, but with $[Mo(O_2)_2O] \cdot Py \cdot HMPT$ a 40% yield of the Michael adduct **34** was isolated. A similar result was obtained in the conversion of **32** into **35**.

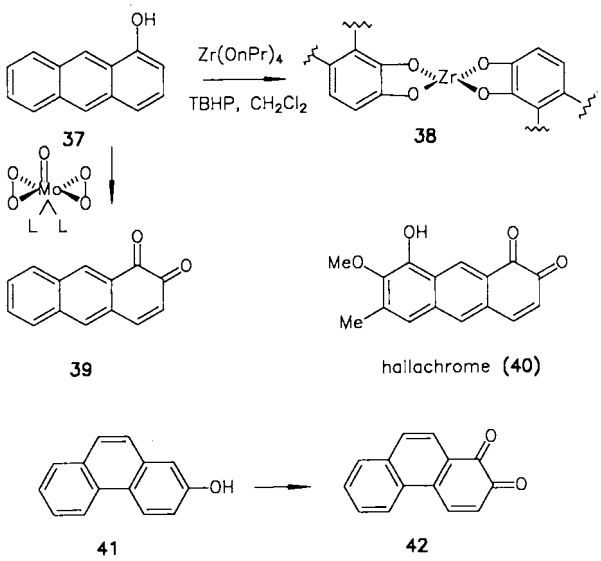
Scheme 4



The ready conversion of anthracene derivatives into 9,10- or 1,4-anthraquinones by a variety of oxidation reagents is well documented[37]. The oxygenation of 1-hydroxyanthracene (**37**) to 1,2-anthraquinone (**39**) is a rigorous test for the *ortho*-selectivity of the novel oxygenation procedure. Treatment of (**37**) with $Zr(acac)_4$ in dichloromethane gave an almost quantitative yield of an insoluble black precipitate. The mass spectrum confirmed the presence of a complex **38**, in which two 1,2-anthracenediol units are bound to zirconium as shown by peaks for all the isotopes of zirconium for the molecular ion. The formation of intermediate resorcinol complexes was not observed using the Mimoun molybde-

num complex, and the desired 1,2-anthraquinone (**39**) was isolated in 60% yield. Our *ortho*-quinone synthesis could prove useful in the synthesis of the structurally unique 1,2-anthraquinone hallachrome (**40**) isolated from marine worms[38]. Excellent yields were also obtained in the conversion of 2-phenanthrol[39] (**41**) to 1,2-phenanthrenequinone (**42**), and the reaction is presently beeing explored for the preparation of naturally occurring 1,2-phenanthrenequinones.

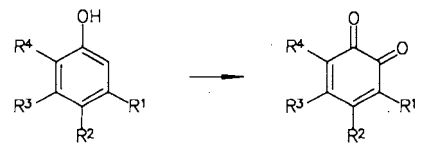
Scheme 5



Reaction of Phenols

A few examples of mononuclear phenols **43**–**46** were also included in our investigations, and the results are summarized in Scheme 6. Again, no *para*-quinones are formed, but the conversion to **47**–**49** was slower than with the corresponding polynuclear phenols. In contrast to the 1,2-naphthoquinones which easily undergo Michael additions, the *ortho*-benzoquinones dimerize preferentially by Diels-Alder reactions, and methylated *ortho*-benzoquinones in particular can be difficult to be isolated in the solid state. In these cases dilute dichloromethane solutions of the *ortho*-quinones can be prepared for further reactions, which may offer advantages over the aqueous conditions of the Teuber reaction[21]. If stable *ortho*-quinones are formed, the use of

Scheme 6



	R^1	R^2	R^3	R^4
43/47	H	$C(CH_3)_3$	H	$C(CH_3)_3$
44/47	$C(CH_3)_3$	H	$C(CH_3)_3$	H
45/48	OMe	OMe	OMe	H
46/49	H		$-OCH_2O-$	H

the more active titanium or vanadium catalysts is recommended. One example is the preparation of the Corey reagent[40,41] 2,4-di-*tert*-butyl-*ortho*-benzoquinone (**47**), which is used for oxidative deoxygenation reactions, from the cheap 2,4-di-*tert*-butylphenol (**43**) or from **44**. 4,5-Methylenedioxy-*ortho*-benzoquinone (**49**), described as fairly unstable[21], was regioselectively obtained in 90% yield from sesamol (**46**), as was the unknown 3,4,5-trimethoxy-1,2-benzoquinone (**48**) starting from the trimethoxyphenol **45** (Table 1).

Mechanism

The oxygen transfer in the extensively studied Sharpless reaction[42–45] (compare also ref.[46]) is known to occur in a nonradical fashion, in contrast to the epoxidation mediated by metal(III) porphyrins, which involves radicals[47]. From the investigations on the Sharpless reaction the rapid ligand exchange at the transition metal was known [for instance of O*i*Pr in $Ti(OiPr)_4$ by allyl alcohol and TBHP]. The absence of *ortho*/*para* mixtures observed in our investigation also suggests a nonradical oxygenation. The oxygen transfer must be followed by a dehydrogenation step to produce *ortho*-quinones. However, the system transition metal/TBHP was very sluggish in dehydrogenating *para*-hydroquinones to *para*-quinones, in contrast to $[Mo(O_2)_2O] \cdot Py \cdot HMPT$. With the exception of $[Mo(O_2)_2O] \cdot Py \cdot HMPT$, all transition-metal complexes used form readily sparingly soluble precipitates with *ortho*-hydroquinones that are only very slowly converted into *ortho*-quinones. Thus, the dehydrogenation must occur at an intermediate prior to the isomerization to hydroquinones. In fact, such hydroquinone complexes may be a dead end on the way to *ortho*-quinones, as seen in the formation of the 1,2-anthracenol complex **38**.

The results can be summarized in a number of statements:

1. The oxygenation of phenols with TBHP mediated by transition-metal complexes is *ortho*-specific.

2. The conversion of phenols to *ortho*-quinones proceeds by a nonradical oxygen transfer and a subsequent dehydrogenation to the final quinones.

3. Sensitive *ortho*-naphthoquinones tend to form Michael adducts with unreacted phenols, especially in the presence of titanium catalysts but less so when using $[Mo(O_2)_2O] \cdot Py \cdot HMPT$.

4. Unstable *ortho*-quinones can be prepared in dilute dichloromethane solution.

Experimental

Melting points were determined with a Dr. Tottoli apparatus (Büchi) and are uncorrected. – Infrared (IR) spectra were obtained with a Perkin-Elmer spectral photometer 157G and a Nicolet 320 FT-IR spectrometer, and the carbonyl bands of the *ortho*-quinones were in the range of 1700–1680 and 1600–1635 cm^{-1} (KBr). – Nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded with a Bruker AM 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm (δ) downfield relative to tetramethylsilane as standard (in $CDCl_3$). The degree of substitution on carbon atoms was determined by DEPT. – Ultraviolet/visible (UV/VIS) spectra were recorded with a Beckman UV 5230 spectral photometer in methanol; λ_{max} in nm (lg ε). – Mass spectra were obtained with a

Finnigan MAT 8430 mass spectrometer (70 eV). – Analytical TLC was performed on silica gel plates (0.25 mm; Merck), preparative TLC on silica gel plates (1 mm; Schleicher & Schüll or PF 254/366; Merck), and column chromatography with silica gel 60 (230 – 400 mesh, Merck). – Elemental analyses were performed by the microanalytical laboratory of the Institut für Pharmazeutische Chemie, Technische Universität Braunschweig. – Phenols that were not commercially available were prepared according to literature procedures (**1**[48], **3**[49], **4**[35], **5**[50], **6**[51], **7**[49], **10**[49], **13**[52], **32**[53], **37**[37], **41**[39]. – The ratio of the M^+ to the $M^+ + 2$ peaks in the mass spectra were dependent on the evaporation temp. High temp. increased the $M^+ + 2$ peak; at very low temperatures the $M^+ + 2$ could not be observed (compare ref.[35]).

General Procedure for the Oxygenation of Phenols to ortho-Quinones: A solution of 1 mmol of phenol in 10 ml of dry dichloromethane (alternatively acetone or tetrahydrofuran) was treated at −23°C under nitrogen with 1 mmol of the transition-metal complex per phenolic hydroxy group as indicated in Table 1 [(Ti(O*i*Pr)$_4$; VO(acac)$_2$, Zr(acac)$_4$, Zr(O*n*Pr)$_4$]. The mixture was stirred for 0.5 h at that temp. to complete ligand exchange, detectable by the dissolution of the sparingly soluble phenols and by formation of an orange-brown colour. Then 0.67 ml of a 4.5 M solution of *tert*-butylhydroperoxide (TBHP) (3.0 mmol)[1] was added. Alternatively (see Table 1) 2 mmol of the Mimoun complex [Mo(O$_2$)$_2$O] · Py · HMPT[34] was added without TBHP. The mixture was stirred at the temp. and for the times indicated in Table 1 (TLC monitoring). Hydrolysis was effected by addition of 10 ml of 10% sulfuric acid and stirring at 0°C until a good separation of the phases was visible (0.5–3h). The organic phase was dried (MgSO$_4$), evaporated to dryness (at low temp. if required) and the product crystallized from dichloromethane/ether. Reaction mixtures were separated by column chromatography on silica gel (dichloromethane/5–10% ether) or by preparative TLC. In reactions with [Mo(O$_2$)$_2$O] · Py · HMPT as oxidant insoluble molybdenum salts precipitated, and the reaction mixture could be worked up by acidic hydrolysis or by filtration through a short column of silica gel and elution with dichloromethane/5% ether. The colour of the *ortho*-benzoquinones was yellow to orange, those of the *ortho*-naphthoquinones yellow to red and the binaphthyl-*ortho*-quinones were dark red to violet on TLC with dark red to black crystals. For yields and melting points see Table 1. The reaction was run on a 2- or 5-mmol scale for commercially available phenols without change in yield.

In situ Transformation of ortho-Quinones to Phenazines: A solution of 0.5 mmol of 2-naphthol (**30**) or 1,7-dihydroxynaphthalene (**12**) in 10 ml of dichloromethane was treated with 1 mmol of [Mo(O$_2$)$_2$O] · Py · HMPT and stirred for the times and the temp. indicated in Table 1. Then 2 ml of acetic acid and 4 mmol of 1,2-phenylenediamine were added, and stirring was continued for 12 h at 20°C. The solution was filtered through a short column of silica gel and eluted with dichloromethane to remove excess of phenylenediamine. The unpolar fractions were further purified by preparative TLC (dichloromethane/5% diethyl ether) to afford 85 mg (91%) of **29**, m.p. 291°C; (ref.[32] 293–294°C) and 23 mg (19%) of **28**, m.p. 214°C.

1-Hydroxybenzo[a]phenazine (**28**): UV: λ_{max} (lg ε) = 212 nm (4.29), 223 (4.36), 262 (4.63), 283 (4.23), 360 (3.44), 441 (4.01). – ^{1}H NMR: δ = 7.34 (dd, *J* = 8, *J* = 0.9 Hz; 1H, 2-H), 7.43 (dd, *J* = 7.1, *J* = 0.9 Hz; 1H, 4-H), 7.70 (t, *J* = 7.9 Hz; 1H, 34-H), 7.87 to 7.90 (m, 3H, 5,- 8-, 11-H), 7.98 (d, *J* = 9.4 Hz; 1H, 6-H), 7.98–8.24 (m, 2H; 9-, 10-H), 14.40 (s, 1H, OH). – ^{13}C NMR: δ = 114.21 (s), 116.19 (d), 119.42 (d), 126.56 (d), 127.35 (d), 129.35 (d), 129.97 (d), 130.57 (d), 131.73 (d), 134.37 (s), 134.62 (d), 137.97 (s), 141.98 (s), 144.33 (s), 144.54 (s), 160.76 (s.). – MS (130°C): *m/z* (%) = 246 (100) [M^+], 218 (28), 190 (1).

$C_{16}H_{10}N_2O$ (246.3) Calcd. C 78.03 H 4.09 N 11.37
Found C 77.98 H 4.06 N 11.39

7-Ethyl-4-methoxy-1,2-naphthoquinone (**2**): UV: λ_{max} (lg ε) = 211 nm (4.21), 254 (4.49), 260 (4.47), 283 (3.96), 336 (3.29), 418 (3.36). – ^{1}H NMR: δ = 1.28 (t, *J* = 7.6 Hz; 3H, CH$_3$), 2.74 (q, *J* = 7.6 Hz; 2H, C*H*$_2$CH$_3$), 4.01 (s; 3H, OCH$_3$), 5.93 (s; 1H, 3-H), 7.51 (dd, $J_{5,6}$ = 8.0, $J_{6,8}$ = 1.6 Hz; 1H, 6-H), 7.76 (d, $J_{5,6}$ = 8.0 Hz; 1H, 5-H), 7.95 (d, $J_{6,8}$ = 1.6 Hz; 1H, 8-H). – ^{13}C NMR: δ = 15.67 (q), 29.37 (t), 57.49 (q), 103.09 (d), 125.66 (d), 129.28 (d), 130.33 (s), 131.12 (s), 135.21 (d), 149.25 (s), 169.90 (s), 180.35 (s), 180.60 (s). – MS: *m/z* (%) = 216 (4) [M^+], 201 (5) [$M^+ - CH_3$], 188 (100) [$M^+ - CO$], 173 (61) [$M^+ - CH_3 - CO$], 159 (24), 145 (7), 131 (9), 130 (15), 117 (10), 115 (16), 102 (5), 91 (3).

$C_{13}H_{12}O_3$ (216.2) Calcd. C 72.21 H 5.59
Found C 71.45 H 5.44

5-Methoxy-1,2-naphthoquinone (**14**): UV: λ_{max} (lg ε) = 214 nm (4.27), 254 (4.19), 357 (sh), 453 (3.56). – ^{1}H NMR (DMSO): δ = 3.96 (s; 3H, OCH$_3$), 6.35 (d, $J_{3,4}$ = 10.4 Hz; 1H, 3-H), 7.20 (d, $J_{6,7}$ = 8.2 Hz; 1H, 6-H), 7.49 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 7.5 Hz; 1H, 7-H), 7.66 (d, $J_{7,8}$ = 7.5 Hz; 1H, 8-H), 8.02 (d, $J_{3,4}$ = 10.4 Hz; 1H, 4-H). – ^{13}C NMR (DMSO): δ = 56.21 (q), 118.13 (d), 122.27 (d), 123.04 (s), 126.00 (d), 132.22 (d), 132.81 (s), 139.33 (d), 156.69 (s), 179.39 (s), 180.99 (s). – MS: *m/z* (%) = 190 (2) [$M^+ + 2H$], 188 (4) [M^+], 173 (1) [$M^+ - CH_3$], 160 (100) [$M^+ - CO$], 132 (8), 131 (21), 117 (24), 102 (19).

3,7-Di-tert-butyl-5-hydroxy-1,2-naphthoquinone (**15**): UV: λ_{max} (lg ε) = 214 nm (sh), 218 (4.48), 264 (4.30), 365 (3.32), 485 (3.66). – ^{1}H NMR (DMSO): δ = 1.25 [s; 9H, C(CH$_3$)$_3$], 1.27 [s; 9H, C(CH$_3$)$_3$], 7.23 (d, $J_{6,8}$ = 1.8 Hz; 1H, 6-H), 7.43 (d, $J_{6,8}$ = 1.8 Hz; 1H, 8-H), 7.64 (s; 1H, 4-H), 10.55 (s; 1H, OH). – ^{13}C NMR (DMSO): δ = 28.38 (q), 29.90 (q), 33.94 (s), 34.00 (s), 116.86 (d), 117.96 (s), 119.28 (d), 130.89 (s), 131.87 (d), 142.76 (s), 153.53 (s), 154.55 (s), 179.01 (s), 179.91 (s). – MS: *m/z* (%) = 288 (40) [$M^+ + 2H$], 286 (2) [M^+], 273 (46) [$M^+ + 2H - CH_3$], 259 (20), 258 (48) [$M^+ - CO$], 243 (100) [$M^+ - CO - CH_3$], 228 (14), 201 (11), 199 (16), 187 (25), 185 (11), 149 (15), 128 (14), 115 (20), 109 (13).

$C_{18}H_{22}O_3$ (286.4) Calcd. C 75.50 H 7.74
Found C 75.63 H 7.71

3-Phenyl-1,2-naphthoquinone (**16**): UV: λ_{max} (lg ε) = 209 nm (4.42), 260 (4.47), 339 (3.37), 432 (3.40). – ^{1}H NMR: δ = 7.38–7.54 (m; 7H, Ar-, Ph-H), 7.50 (s; 1H, 4-H), 7.64–7.68 (m; 1H, Ar-H), 8.10 (d, *J* = 8.2 Hz; 1H, 8-H). – ^{13}C NMR: δ = 128.48 (d), 128.55 (d), 128.94 (d), 130.09 (d), 130.13 (d), 130.41 (d), 130.83 (s), 134.13 (s), 135.34 (s), 136.03 (d), 138.79 (s), 141.90 (d), 179.08 (s), 180.06 (s). – MS: *m/z* (%) = 236 (21) [$M^+ + 2H$], 234 (4) [M^+], 206 (100) [$M^+ - CO$], 178 (39), 176 (42), 152 (22), 102 (9), 88 (11), 76 (25).

4-Triphenylmethyl-1,2-naphthoquinone (**17**): UV: λ_{max} (lg ε) = 211 nm (4.77), 254 (4.34), 321 (3.51), 390 (3.29). – ^{1}H NMR: δ = 6.48 (s; 1H, 3-H), 7.08–7.17 (m; 2H, Ar-H), 7.21–7.27 (m; 16 H, Ph-, Ar-H), 8.10 (dd, $J_{7,8}$ = 7.7, $J_{6,8}$ = 1.4 Hz; 1H, 8-H). – ^{13}C NMR: δ = (d), 128.13 (d), 129.48 (d), 129.84 (d), 131.00 (d), 131.11 (d), 131.55 (s), 132.82 (d), 133.78 (d), 135.26 (s), 160.91 (s), 179.81 (s), 181.80 (s). – MS: *m/z* (%) = 400 (44) [M^+], 372 (90) [$M^+ - CO$], 371 (23), 354 (16), 295 (47) [$M^+ - CO - C_6H_5$], 294 (56), 265 (100), 252 (34), 189 (25), 165 (75).

4-Ethyl-1,2-naphthoquinone (**18**): UV: λ_{max} (lg ε) = 207 nm (4.20), 255 (4.37), 342 (3.33), 399 (3.24). – ^{1}H NMR: δ = 1.34 (t, *J* = 7.4 Hz; 3H, CH$_2$C*H*$_3$), 2.78 (qd, J_1 = 7.4, J_2 = 1.3 Hz; 2H, C*H*$_2$CH$_3$), 6.41 (d, *J* = 1.3 Hz; 1H, 3-H), 7.53 (td, J_1 = 7.6, J_2 = 1.0 Hz; 1H,

7-H), 7.59 (dd, J_1 = 7.6, J_2 = 1.0 Hz; 1H, 5-H), 7.69 (td, J_1 = 7.6, J_2 = 1.4 Hz; 1H, 6-H), 8.16 (dd, J_1 = 7.6, J_2 = 1.4 Hz; 1H, 8-H). – ^{13}C NMR: δ = 12.29 (q), 26.18 (t), 125.45 (d), 125.88 (d), 130.15 (d), 130.59 (d), 131.42 (s), 135.08 (s), 135.52 (d), 158.71 (s), 179.80 (s), 180.75 (s). – MS: *m/z* (%) = 186 (7) [M$^+$], 158 (100) [M$^+$ – CO], 157 (19), 143 (5), 130 (18), 129 (39), 128 (16), 127 (7), 116 (37).

$C_{12}H_{10}O_2$ (186.2) Calcd. C 77.40 H 5.41
Found C 77.10 H 5.48

4-Methoxy-1,2-naphthoquinone (**19**): UV: λ_{max} (lg ε) = 212 nm (4.17), 249 (4.39), 253 (sh), 275 (3.99), 334 (3.31), 401 (3.32). – ^{1}H NMR: δ = 4.03 (s; 3H, OCH_3), 5.98 (s; 1H, 3-H), 7.58 (ddd, $J_{5,6}$ = 7.6, $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.3 Hz; 1H, 6-H), 7.70 (ddd, $J_{6,7}$ = 7.6, $J_{7,8}$ = 7.6, $J_{5,7}$ = 0.9 Hz; 1H, 7-H), 7.87 (dd, $J_{5,6}$ = 7.6, $J_{5,7}$ = 0.9 Hz; 1H, 5-H), 8.11 (dd, $J_{7,8}$ = 7.6, $J_{6,8}$ = 1.3 Hz; 1H, 8-H). – ^{13}C NMR: δ = 55.82 (q), 102.06 (d), 123.75 (d), 128.03 (d), 129.36 (s), 130.52 (d), 130.97 (s), 133.97 (d), 167.69 (s), 178.40 (s), 178.51 (s). – MS: *m/z* (%) = 188 (4) [M$^+$], 175 (3) [M$^+$ + 2H – CH_3], 173 (9) [M$^+$ – CH_3], 160 (73) [M$^+$ – CO], 159 (24), 131 (11), 129 (7), 102 (11).

4-Chloro-1,2-naphthoquinone (**20**): UV: λ_{max} (lg ε) = 212 nm (4.17), 224 (sh), 253 (4.25), 338 (3.25), 422 (3.07). – ^{1}H NMR: δ = 6.77 (s; 1H, 3-H), 7.64 (td, J_1 = 7.7, J_2 = 0.9 Hz; 1H, 7-H), 7.78 (td, J_1 = 7.7, J_2 = 1.3 Hz; 1H, 6-H), 7.92 (dd, J_1 = 7.7, J_2 = 0.9 Hz; 1H, 5-H), 8.18 (dd, J_1 = 7.7, J_2 = 1.3 Hz; 1H, 8-H). – ^{13}C NMR: δ = 127.66 (d), 127.94 (d), 130.10 (d), 130.58 (s), 132.05 (d), 132.71 (s), 135.74 (d), 152.68 (s), 178.05 (s), 178.32 (s). – MS: *m/z* (%) = 194 (3) [M$^+$, M$^+$ + 2H], 192 (1) [M$^+$], 166 (18) [M$^+$ – CO], 164 (58) [M$^+$ – CO], 129 (100), 101 (39).

4,8-Dimethoxy-1,2-naphthoquinone (**21**): UV: λ_{max} (lg ε) = 214 nm (4.36), 239 (4.25), 274 (3.88), 398 (3.78). – ^{1}H NMR: δ = 3.98 (s; 3H, OCH_3), 4.00 (s; 3H, OCH_3), 5.95 (s; 1H, 3-H), 7.17 (d, $J_{6,7}$ = 8.4 Hz; 1H, 7-H), 7.52 (d, $J_{5,6}$ = 7.9 Hz; 1H, 5-H), 7.62 (dd, $J_{6,7}$ = 8.4, $J_{5,6}$ = 7.9 Hz; 1H, 6-H). – ^{13}C NMR: δ = 56.38 (q), 56.74 (q), 102.71 (d), 104.06 (s), 115.83 (d), 117.32 (d), 134.00 (s), 136.05 (d), 161.89 (s), 168.17 (s), 178.53 (s), 179.63 (s). – MS: *m/z* (%) = 220 (49) [M$^+$ + 2H], 218 (4) [M$^+$], 205 (76) [M$^+$ + 2H – CH_3], 190 (100) [M$^+$ – CO], 177 (28) [M$^+$ + 2H – CH_3 – CO], 175 (78) [M$^+$ – CH_3 – CO], 161 (51), 133 (38).

$C_{12}H_{10}O_4$ (218.2) Calcd. C 66.05 H 4.62
Found C 66.14 H 4.68

8-Hydroxy-1,2-naphthoquinone (**22**): ^{1}H NMR: δ = 6.45 (d, J = 10.1 Hz; 1H, 3-H), 6.91 (d, J = 7.3 Hz; 1H), 7.09 (d, J = 8.5 Hz; 1H), 7.40 (d, J = 10.1 Hz; 1H, 4-H), 7.56 (dd, J_1 = 8.5, J_2 = 7.3 Hz; 1H, 6-H), 12.03 (s; 1H, OH).

4-[4-Chloro-1-hydroxy-2-naphthyl]-1,2-naphthoquinone (**24**): UV: λ_{max} (lg ε) = 216 nm (4.63), 245 (4.57), 302 (3.90), 322 (sh), 337 (sh), 413 (sh). – ^{1}H NMR (DMSO): δ = 6.50 (s; 1H, 3-H), 7.04 (dd, J_1 = 7.8, J_2 = 0.9 Hz; 1H), 7.51 (s; 1H), 7.59 – 7.71 (m; 3H), 7.78 (m; 1H), 8.08 (dd, J_1 = 7.3, J_2 = 1.7 Hz; 1H), 8.18 (d, J = 8.4 Hz; 1H), 8.37 (d, J = 8.4 Hz; 1H), 10.01 (s; 1H, OH). – ^{13}C NMR (DMSO): δ = 117.61 (s), 120.92 (s), 123.33 (d), 123.64 (d), 126.14 (s), 126.33 (d), 126.50 (d), 128.42 (d), 128.62 (d), 128.96 (d), 129.64 (d), 130.48 (d), 131.67 (s), 134.94 (s), 135.28 (d), 148.95 (s), 151.65 (s), 179.04 (s), 179.95 (s). – MS: *m/z* (%) = 338 (3) [M$^+$ + 2H], 336 (12) [M$^+$, M$^+$ + 2H], 334 (8) [M$^+$], 306 (25) [M$^+$ – CO], 278 (21), 271 (18), 243 (33), 226 (14), 215 (61), 213 (52), 113 (12), 107 (17).

$C_{20}H_{11}ClO_3$ (334.8) Calcd. C 71.76 H 3.31 Cl 10.59
Found C 70.67 H 3.18 Cl 12.52
$C_{20}H_{11}{}^{35}ClO_3$ Calcd. 334.039674 Found 334.039 (MS)
$C_{20}H_{11}{}^{37}ClO_3$ Calcd. 336.037517 Found 336.037 (MS)

4-[1-Acetoxy-4-acetyl-2-naphthyl]-1,2-naphthoquinone (**25**): UV: λ_{max} (lg ε) = 217 nm (4.70), 220 (sh), 233 (4.68), 305 (4.01), 352 (sh). – ^{1}H NMR: δ = 2.27 (s; 3H, $OCOCH_3$), 2.75 (s; 3H, $COCH_3$), 6.52 (s; 1H, 3-H), 7.09 – 7.12 (m; 1H), 7.55 – 7.60 (m; 2H), 7.66 – 7.70 (m; 1H), 7.73 – 7.75 (m; 1H), 7.86 (s; 1H, 3′-H), 7.94 (dd, J_1 = 7.6, J_2 = 0.8 Hz; 1H), 8.22 – 8.24 (m; 1H), 8.81 (d, J = 8.5 Hz; 1H). – ^{13}C NMR: δ = 20.59 (q), 30.08 (q), 122.15 (d), 124.70 (s), 126.59 (d), 127.82 (s), 128.07 (d), 128.42 (d), 128.85 (d), 129.41 (d), 129.60 (d), 130.60 (d), 131.22 (d), 131.58 (s), 131.74 (s), 134.34 (s), 134.39 (s), 135.63 (d), 147.10 (s), 152.41 (s), 168.42 (s), 179.02 (s), 180.25 (s), 200.39 (s). – MS: *m/z* (%) = 386 (3) [M$^+$ + 2H], 384 (2) [M$^+$], 342 (100) [M$^+$ – CH_2CO], 314 (28) [M$^+$ – CH_2CO – CO], 299 (39) [M$^+$ – CH_2CO – CO – CH_3], 271 (19) [M$^+$ – CH_2CO – 2 CO – CH_3], 243 (14), 215 (19), 213 (19).

$C_{24}H_{16}O_5$ (384.4) Calcd. C 74.99 H 4.20
Found C 74.28 H 4.28

4-[1-Hydroxy-2-naphthyl]-1,2-naphthoquinone (**26**): UV: λ_{max} (lg ε) = 217 nm (4.62), 237 (4.67), 255 (sh), 297 (3.87), 334 (sh), 409 (3.33). – ^{1}H NMR (DMSO): δ = 6.44 (s; 1H, 3-H), 7.04 (dd, J_1 = 7.3, J_2 = 1.3 Hz; 1H), 7.32 (d, J = 8.4 Hz; 1H), 7.54 – 7.66 (m; 5H), 7.94 (dd, J_1 = 8.8, J_2 = 1.5 Hz; 1H), 8.07 (dd, J_1 = 7.3, J_2 = 1.5 Hz; 1H), 8.28 (d, J = 7.7 Hz; 1H), 9.66 (s; 1H, OH).

$C_{20}H_{12}O_3$ + 1/2 H_2O (309.3) Calcd. C 77.66 H 4.24
Found C 77.39 H 4.07

4-(1-Hydroxyethylen)-2-oxopropyl-1,2-naphthoquinone (**27**): UV: λ_{max} (lg ε) = 208 nm (4.14), 225 (4.39), 286 (4.03), 334 (sh), 388 (sh). – ^{1}H NMR: δ = 2.06 (s; 6 H, $COCH_3$), 6.43 (s; 1H, 3-H), 7.38 (dd, $J_{5,6}$ = 7.6, $J_{5,7}$ = 0.9 Hz; 1H, 5-H), 7.60 (td, $J_{6,7}$ = $J_{7,8}$ = 7.6, $J_{5,7}$ = 0.9 Hz; 1H, 7-H), 7.70 (td, $J_{5,6}$ = $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.3 Hz; 1H, 6-H), 8.22 (dd, $J_{7,8}$ = 7.6, $J_{6,8}$ = 1.3 Hz; 1H, 8-H), 16.79 (s; 1H, enol-H). – ^{13}C NMR: δ = 23.92 (q), 109.68 (s), 127.98 (d), 130.83 (d), 130.88 (d), 131.51 (d), 131.64 (s), 135.40 (s), 136.08 (d), 152.16 (s), 179.04 (s), 180.67 (s), 190.49 (s). – MS: *m/z* (%) = 258 (40) [M$^+$ + 2H], 256 (4) [M$^+$], 228 (37) [M$^+$ – CO], 215 (48), 213 (100) [M$^+$ – $COCH_3$], 199 (18), 197 (24), 185 (70), 171 (38), 169 (19).

$C_{15}H_{12}O_4$ (256.3) Calcd. C 70.31 H 4.72
Found C 70.35 H 4.70

6-Benzoyl-4-[6-benzoyl-2-hydroxy-1-naphthyl]-1,2-naphthoquinone (**34**): UV: λ_{max} (lg ε) = 213 nm (sh), 227 (4.72), 267 (4.76), 322 (4.13), 377 (sh). – ^{1}H NMR (DMSO): δ = 6.54 (s; 1H, 3-H), 7.11 (s; 1H), 7.39 – 7.44 (m; 3H), 7.58 – 7.63 (m; 5 H), 7.68 – 7.72 (m; 1H), 7.81 (d, J = 7.3 Hz; 3H), 7.93 (d, J = 7.9 Hz; 1H), 8.00 (d, J = 8.8 Hz; 1H), 8.11 (d, J = 9.0 Hz; 1H), 8.26 – 8.29 (m; 2H), 10.56 (s; 1H, OH). – ^{13}C NMR (DMSO): δ = 115.13 (s), 119.00 (d), 124.43 (d), 126.23 (d), 128.35 (d), 128.42 (d), 128.72 (d), 128.79 (d), 129.44 (d), 131.04 (d), 131.26 (d), 131.42 (s), 132.00 (d), 132.28 (d), 132.42 (d), 133.04 (d), 133.37 (s), 133.49 (s), 135.03 (s), 135.44 (s), 137.31 (s), 141.06 (s), 149.63 (s), 154.28 (s), 178.13 (s), 179.19 (s), 193.88 (s), 195.20 (s). – MS: *m/z* (%) = 510 (56) [M$^+$ + 2H], 508 (21) [M$^+$], 480 (100) [M$^+$ – CO], 478 (45), 401 (13), 375 (29) [M$^+$ – CO – C_6H_5CO], 347 (22), 329 (13), 289 (7), 213 (10), 211 (3), 162 (2), 145 (2), 105 (71).

$C_{34}H_{20}O_5$ (508.5) Calcd. C 80.31 H 3.96
Found C 80.00 H 4.15

4-[2-Hydroxy-1-naphthyl-6-triphenylmethyl]-6-triphenylmethyl-1,2-naphthoquinone (**35**): UV: λ_{max} (lg ε) = 212 nm (4.96), 242 (4.88), 254 (sh), 266 (sh), 285 (sh), 339 (3.78), 364 (3.74). – ^{1}H NMR (DMSO): δ = 6.36 (s; 1H, 3-H), 6.73 (d, J = 1.8 Hz; 1H), 6.87 – 6.90 (m; 4 H), 6.99 (dd, J_1 = 9.0, J_2 = 1.9 Hz; 1H), 7.06-7.10 (m; 10 H), 7.12 – 7.21 (m; 10 H), 7.23 – 7.29 (m; 8 H), 7.50 (d, J = 9.0 Hz; 1H), 7.59 – 7.61 (m; 2H), 7.98 (d, J = 8.2 Hz; 1H), 9.73 (s; 1H, OH). – ^{13}C NMR (DMSO): δ = 64.77 (s), 65.08 (s), 115.36 (d), 123.62 (d), 126.59 (d), 126.64 (d), 127.39 (s), 128.25 (d), 128.67 (d), 130.18 (s),

130.54 (d), 130.64 (s), 130.73 (d), 130.84 (d), 131.04 (d), 133.53 (d), 135.54 (s), 141.28 (s), 145.63 (s), 146.79 (s), 152.21 (s), 154.05 (s), 179.12 (s), 180.41 (s). – MS: *m/z* (%) = 786 (100) [M^+ + 2H], 784 (28) [M^+], 756 (56) [M^+ – CO], 709 (41) [M^+ + 2H – C_6H_5], 679 (39) [M^+ – CO – C_6H_5], 513 (21) [M^+ – CO – CPh_3], 387 (12), 309 (17), 300 (8), 243 (24, $CPh_3^{+\cdot}$), 165 (24).

$C_{58}H_{40}O_3$ (785.0) Calcd. C 88.75 H 5.14
Found C 88.81 H 5.41

4-[4-Hydroxy-1-naphthyl]-1,2-naphthoquinone (**36**): UV: λ_{max} (lg ε) = 215 nm (4.68), 237 (4.60), 249 (sh), 301 (3.93), 325 (sh), 408 (3.44). – ^{1}H NMR (DMSO): δ = 6.38 (s; 1H, 3-H), 6.74 (dd, J_1 = 7.5, J_2 = 1.1 Hz; 1H), 7.00 (d, J = 7.7 Hz; 1H), 7.35 (d, J = 7.7 Hz; 1H), 7.43 (ddd, J_1 = 8.3, J_2 = 6.8, J_3 = 1.3 Hz; 1H), 7.48–7.57 (m; 3H), 7.76 (d, J = 8.2 Hz; 1H), 8.06 (dd, J_1 = 7.4, J_2 = 1.6 Hz; 1H), 8.24 (d, J = 7.6 Hz; 1H), 10.56 (s; 1H, OH).

1,2-Anthraquinone (**39**): UV: λ_{max} (lg ε) = 217 nm (4.24), 234 (4.27), 300 (4.31), 451 (3.40). – ^{1}H NMR: δ = 6.56 (d, $J_{3,4}$ = 9.9 Hz; 1H, 3-H), 7.64 (d, $J_{3,4}$ = 9.9 Hz; 1H, 4-H), 7.67–7.75 (m; 2H, 6,7-H), 7.85 (s; 1H, 10-H), 7.94 (d, J = 8.1 Hz; 1H), 8.04 (d, J = 8.0 Hz; 1H), 8.73 (s; 1H, 9-H). – ^{13}C NMR: δ = 128.23 (d), 128.92 (s), 129.06 (d), 130.46 (s), 130.65 (d), 130.81 (d), 130.84 (d), 133.08 (s), 133.88 (d), 136.13 (d), 146.04 (d), 179.35 (s), 181.39 (s). – MS: *m/z* (%) = 210 (5) [M^+ + 2H], 208 (11) [M^+], 180 (100) [M^+ – CO], 152 (44), 126 (11), 97 (5).

1,2-Phenanthrenequinone (**42**): ^{1}H NMR: δ = 6.58 (d; J = 10.6 Hz; 1H, 3-H), 7.68–7.70 (m, 2H, 6-, 7-H), 7.90–7.92 (m, 1H, 8-H), 8.16 (d, J = 8.5 Hz; 1H, 9-H), 8.29 (dd, J = 9.7, J = 3.3 Hz; 1H, 5-H), 8.33 (d, J = 10.6 Hz; 1H, 4-H). – ^{13}C NMR: δ = 123.68 (d), 124.35 (d), 127.68 (d), 128.53 (d), 129.34 (d), 129.58 (d), 129.77 (s), 131.36 (d), 131.93 (s), 137.22 (s), 139.50 (d), 179.41 (s), 180.72 (s).

3,5-Di-tert-butyl-1,2-benzoquinone (**47**): UV: λ_{max} (lg ε) = 208 nm (3.93), 245 (sh), 403 (3.09). – ^{1}H NMR: δ = 1.23 [s; 9 H, $C(CH_3)_3$], 1.27 [s; 9 H, $C(CH_3)_3$], 6.22 (d, J = 2.3 Hz; 1H, 6-H), 6.94 (d, J = 2.3 Hz; 1H, 4-H). – ^{13}C NMR: δ = 27.89 (q), 29.22 (q), 35.49 (s), 36.04 (s), 122.10 (d), 133.48 (d), 149.96 (s), 163.33 (s), 180.06 (s), 181.15 (s). – MS: *m/z* (%) = 220 (4) [M^+], 207 (8), 192 (49) [M^+ – CO], 177 (23) [M^+ – CO – CH_3], 164 (43), 149 (100), 136 (8), 108 (21), 93 (4), 91 (5), 57 (8).

3,4,5-Trimethoxy-1,2-benzoquinone (**48**): UV: λ_{max} (lg ε) = 210 nm (4.00), 250 (3.97), 293 (3.62), 334 (sh), 462 (sh). – ^{1}H NMR: δ = 3.86 (s; 3H, OCH_3), 3.88 (s; 3H, OCH_3), 4.19 (s; 3H, OCH_3), 5.63 (s; 1H, 6-H). – ^{13}C NMR: δ = 57.36 (q), 61.30 (q), 61.60 (q), 99.85 (d), 138.95 (s), 150.54 (s), 166.30 (s), 171.01 (s), 177.40 (s). – MS: *m/z* (%) = 200 (5) [M^+ + 2H], 198 (21) [M^+], 170 (100) [M^+ – CO], 155 (30) [M^+ – CO – CH_3], 141 (5), 127 (84), 99 (70), 69 (36), 53 (12).

$C_9H_{10}O_5$ (198.2) Calcd. C 54.55 H 5.09
Found C 54.11 H 5.15

4,5-Methylendioxy-1,2-benzoquinone (**49**): UV: λ_{max} (lg ε) = 209 nm (3.90), 254 (3.78), 288 (4.00), 392 (2.82), 450 (sh). – ^{1}H NMR: δ = 6.04 (s; 2H), 6.11 (s; 2H). – ^{13}C NMR: δ = 101.37 (d), 104.13 (t), 160.87 (s), 177.39 (s). – MS: *m/z* (%) = 151 (3), 149 (3), 136 (4), 132 (1), 118 (100), 116 (5), 104 (1), 100 (3), 88 (6), 86 (4), 75 (2), 74 (36), 70 (4).

CAS Registry Numbers

1: 121732-83-0 / **2**: 121732-84-1 / **3**: 3588-80-5 / **4**: 61357-48-0 / **5**: 30069-65-9 / **6**: 58378-11-3 / **7**: 10240-09-2 / **8**: 84-85-5 / **9**: 604-44-4 / **10**: 3843-55-8 / **11**: 90-15-3 / **12**: 575-38-2 / **13**: 3669-52-1 / **14**: 61539-67-1 / **15**: 121732-85-2 / **16**: 51670-51-0 / **17**: 58378-10-2 / **18**: 121732-86-3 / **19**: 18916-57-9 / **20**: 6655-90-9 / **21**: 32358-82-0 / **22**: 50614-69-2 / **23**: 121732-87-4 / **24**: 121732-88-525 / **25**: 121732-89-6 / **26**: 121732-90-9 / **27**: 121732-91-0 / **28**: 28825-09-4 / **29**: 116079-82-4 / **30**: 135-19-3 / **31**: 52222-87-4 / **32**: 115915-20-3 / **33**: 104746-25-0 / **34**: 121732-92-1 / **35**: 121732-93-2 / **36**: 112553-60-3 / **37**: 610-50-4 / **39**: 655-04-9 / **41**: 605-55-0 / **42**: 573-12-6 / **43**: 96-76-4 / **44**: 1138-52-9 / **45**: 642-71-7 / **46**: 533-31-3 / **47**: 3383-21-9 / **48**: 121732-94-3 / **49**: 21505-19-1 / $VO(acac)_2$: 3153-26-2 / $Zr(acac)_4$: 17501-44-9 / $Mo(O_2)_2O \cdot Py \cdot HMPT$: 23319-63-3 / $Ti(OiPr)_4$: 546-68-9 / $Zr(OnPr)_4$: 23519-77-9 / $Cu(acac)_2$: 46369-53-3 / *tert*-butylhydroperoxide: 75-91-2 / 1,2-phenylenediamine: 95-54-5

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[161/89]