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Studies on the chemistry of 2-(2-oxo-3-phenylpropyl)-benzaldehydes: novel total synthesis of 3-phenylnaphthalen-2-ols and 2-hydroxy-3-phenyl-1,4-naphthoquinones

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Abstract—We describe the first studies on the chemistry of 2-(2-oxo-3-phenylpropyl)benzaldehydes, which were converted into 3-benzylisochromen-1-ones via the corresponding 2-(2-oxo-3-phenylpropyl)benzoic acid. The 2-(2-oxo-3-phenylpropyl)benzaldehydes proved to be convenient starting materials for the synthesis of 3-phenyl-2-naphthols. Oxidation of the latter compounds resulted in a novel, efficient synthesis of 3-phenyl-1,2-naphthoquinones, which were efficiently transformed into 2-hydroxy-3-phenyl-1,4-naphthoquinones.

Molecules with the quinoid structure constitute one of the most interesting classes of compounds in organic chemistry. Their syntheses as well as their diverse chemical and physical properties have been compiled into two volumes of Patai's series 'The Chemistry of Functional Groups'.[1] The perennial chemical interest in naphthoquinones is due to their biological properties, their industrial applications and their potential as intermediates in the synthesis of heterocycles.[2]

Although a large number of 1,2-naphthoquinones have been described, 1,4-naphthoquinones are more abundant—particularly those that have one hydroxy group attached directly to the quinone moiety, a wide variety of which are found in nature. Most of these compounds exhibit interesting biological activity and this is reflected in the ever increasing number of publications concerning their isolation, characterization and synthesis in the laboratory.[3] Natural hydroxyquinones vary in structural complexity from the simple hydroxynaphthoquinones such as lawsone, the main component of a natural dye,[4] to hydroxyphenylnaphthoquinones[5] or complex structures such as the trimeric hydroxynaphthoquinone conocurvone, a potential anti-HIV agent.[6]

The common method for the synthesis of simple *o*-naphthoquinones consists of the oxidation of 2-naphthols,[6g,7] which are difficult to access, or the more problematic oxidation of the more readily available 1-naphthols.[8] Both approaches have been efficiently used in the synthesis of complex *o*-naphthoquinones.[9] Moreover, oxidation of simple *o*-naphthoquinones is a common method for the preparation of 2-hydroxy-1,4-naphthoquinones.[10] By contrast, similar chemistry for 3-phenyl-1,2-naphthoquinones **15** (Scheme 2) is very limited and, although some methods have been described for the preparation of such targets from 3-phenyl-1-naphthols,[11] to the best of our knowledge the preparation of quinones **15** from 3-phenyl-2-naphthols **14** (Scheme 2) has not been described.[12] On the other hand, only one example has been reported involving the oxidation of 3-phenyl-1,2-naphthoquinones **15** to 3-phenyl-2-hydroxy-1,4-naphthoquinones **2** (Scheme 1).[12a]

This paper represents a novel contribution to the chemistry of 3-phenyl-2-hydroxynaphthoquinones **2** and includes the first general method for the synthesis of 3-phenyl-2-naphthols **14**. A novel oxidation is described for the conversion of compounds **14** to the corresponding *o*-naphthoquinones **15**, which were further oxidized to 3-phenyl-2-hydroxy-1,4-naphthoquinones **2**.

The starting point for this work was the observation that a 2-phenyl-1,4-naphthoquinone subunit is present in the polycyclic ring system of a wide range of quinonoid compounds, including benzofuronaphthoquinones **4**,[13] benzopyronaphthoquinones **5**[14] and indolonaphthoquinones

Keywords: Quinones; Cyclization; Oxidation; Aldol reaction.
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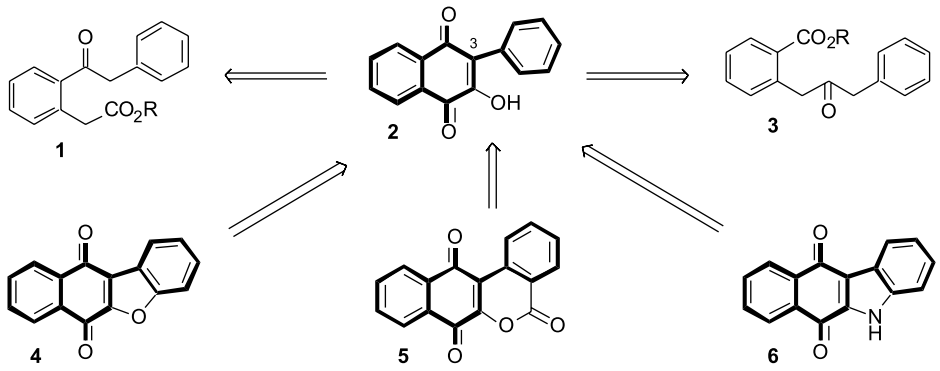
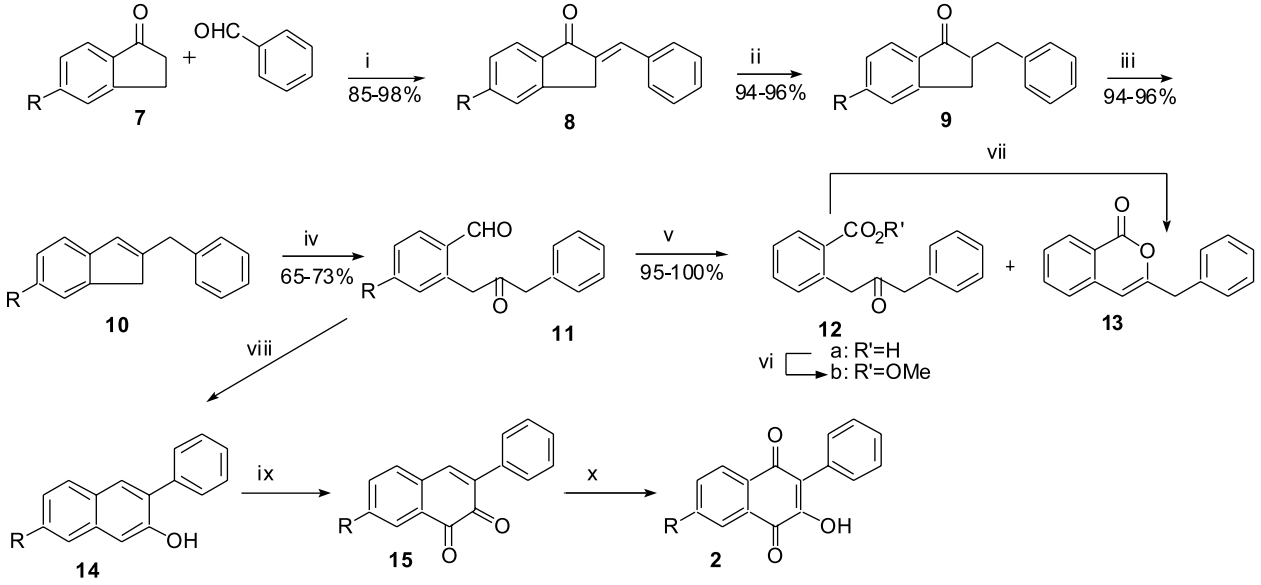


Scheme 1.

6[15] (Scheme 1). This structural relationship was the basis for the development of a practical synthesis of these naphthoquinone targets from 2-hydroxy-3-phenyl-1,4-naphthoquinones (**2**), which were in turn prepared by attachment of a phenyl substituent to the C_3 position of 2-hydroxy-1,4-naphthoquinones and/or, more directly and efficiently, by mixed Claisen condensation of alkyl *o*-phenylethylphenylacetates **1**. However, this interesting methodology has not yet been fully exploited, probably due to the limited scope in terms of the availability of the necessary starting materials.

In the search for new routes for the preparation of 3-phenyl-2-hydroxy-1,4-naphthoquinones **2** without the above limitations, we reasoned that alkyl 3-phenyl-2-ketopropyl benzoates **3** should undergo a mixed Claisen condensation in a similar way to ketoacid esters **1** to give the naphthoquinones **2** on the basis that compounds **3** also have the necessary carbon skeleton and functionality for this transformation (Scheme 1). In order to confirm this hypothesis, we decided to explore the preparation of the practically unknown ketoacids **3** by the novel route outlined in Scheme 2, starting from 1-indanones.[16]

2-Benzylidene-1-indanone **8a**,[17] formed by the aldol condensation of 1-indanone **7a** and benzaldehyde, was subjected to controlled catalytic hydrogenation. The only process observed was the desired selective reduction of the double bond and this gave a quantitative yield of the previously obtained benzylindanone **9a**.[18] The IR spectrum of **9a** showed a band at 1708 cm^{-1} corresponding to the carbonyl group. The ^1H NMR spectrum included four doublet of doublets at 2.67, 2.86, 3.17 and 3.42 ppm, which are due to the two methylene groups, together with a multiplet at 3.01 ppm due to the proton in the α-position to the carbonyl. Subsequent treatment of compound **9a** with $NaBH_4$ in methanol led to complete transformation of this compound into a mixture of 2-benzyl-1-indanols,[19] which was heated under reflux with concentrated sulfuric acid in order to promote its dehydration.[20] The expected 2-benzylindene **10a** was obtained in 93% yield. The ^1H NMR spectrum of **10a** contained signals between 7.12 and 7.40 ppm for a total of nine aromatic protons, a singlet at 6.57 ppm corresponding to the proton of the double bond, and two singlets at 3.33 and 3.86 ppm, each due to two protons, which were assigned to the two methylene groups. The next step involved cleavage of the double bond in



Scheme 2. 2, **7**, **8**, **9**, **10**, **11**, **14**, **15**: (a) R=H; (b) R=OMe. Conditions. (i) NaMeO/MeOH, rt, 15–27 h. (ii) H_2, Pd/C, AcOEt, 1 atm, 1.5–3.5 h. (iii) (a) $NaBH_4$, MeOH, rt, 1–1.5 h; (b) H_2SO_4, reflux, 1–2 h. (iv) (a) O_3, −78 °C, 3–6 min; (b) Me_2S, −78 °C (4–7 h), rt (13 h). (v) CrO_3, H_2SO_4, H_2O, rt, 45 min. (vi) H_2SO_4, MeOH, reflux, 75 min. (vii) NaMeO, MeOH, reflux, 3 h. (viii) NaOH aq, rt, 1.5–2 h. (ix) Fremy's salt, K_2HPO_4, acetone, rt, 1–4 h. (x) H_2SO_4, MeOH, reflux, 29 h.

indene **10a**, which was achieved by ozonolysis in dichloromethane at −78 °C, and subsequent reduction of the resulting ozonide with methylene sulfide.[21] In this way, ketoaldehyde **11a** was obtained in 71% yield and was easily identified from its analytical and spectroscopic data. The ^{1}H NMR spectrum showed a singlet at 9.98 ppm—corresponding to the aldehyde proton—and the ^{13}C NMR spectrum contained signals at 193.5 and 204.9 ppm corresponding to ketone and aldehyde carbonyls, respectively. Finally, oxidation of this ketoaldehyde under Jones conditions[22] (CrO_3, H_2O, H_2SO_4) led to a mixture of compounds. The major component (82% yield) was the expected ketoacid **12a**,[23] which showed in its IR spectrum an OH band at 2931–2856 cm^{-1} and carbonyl bands at 1714 and 1693 cm^{-1} corresponding to the carboxyl and the ketone functionalities, respectively. The ^{1}H NMR and ^{13}C NMR spectra of **12a** were very similar to those of the precursor **11a**, with the ^{13}C spectrum containing signals at 168.4 and 205 ppm due to the carboxyl and ketone carbonyls, respectively. The minor compound, isolated in 18% yield, was identified as lactone **13**[23] on the basis of its spectroscopic properties. For example, the IR spectrum contained a lactone carbonyl band at 1727 cm^{-1} and the ^{1}H NMR showed a singlet at 6.16 ppm due to the proton of the double bond and another singlet at 3.85 due to the methylene group. Additional confirmation of the structure of compound **13** was obtained from its ^{13}C NMR spectrum, which contained a highly deshielded signal at 162.8 ppm due to the lactone carbonyl together with a signal at 157 ppm, assigned to a carbon linked to oxygen, and a third signal at 39.8 ppm, corresponding to the methylene group.

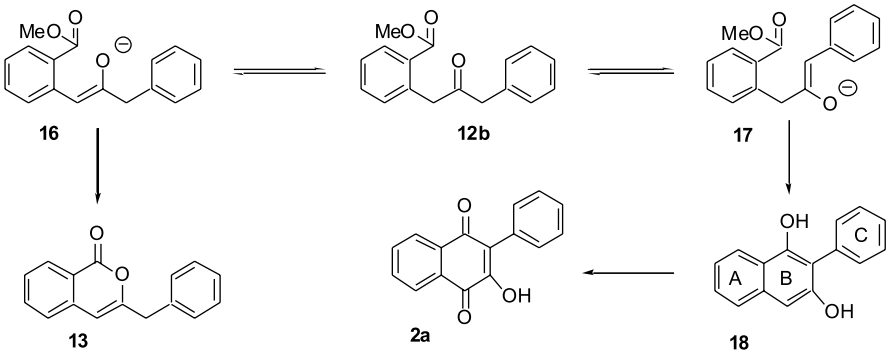
Benzylisochromanone **13** should result from the dehydration of ketoacid **12a** under the reaction conditions employed; in a separate experiment ketoacid **12a** was heated under reflux for 2 h in toluene containing H_2SO_4 to give isochromanone **13** in 92% yield.[24] Unfortunately, when ketoacid **12a** was esterified and a methanolic solution of the resulting ketoester **12b**[23] containing sodium methoxide was stirred at room temperature for 3 h, the expected naphthoquinone **2a** was not obtained. The only product in this reaction was the previously obtained benzylisochromanone **13**.[23]

The easy transformation of ketoester **12b** into benzylisochromanone **13** can be explained in terms of a competition between two irreversible processes (Scheme 3): cyclization of enolate **16** to compound **13** and transformation of enolate **17** into naphthol **18**, a possible precursor of naphthoquinone **2a**, would involve a mixed Claisen cyclization followed by aromatization of ring B. Formation of **13** as the only reaction product can be explained by assuming that enolate **16** is kinetically and thermodynamically more favoured than enolate **17**, due to interaction of the enolate moiety with the methoxycarbonyl group.

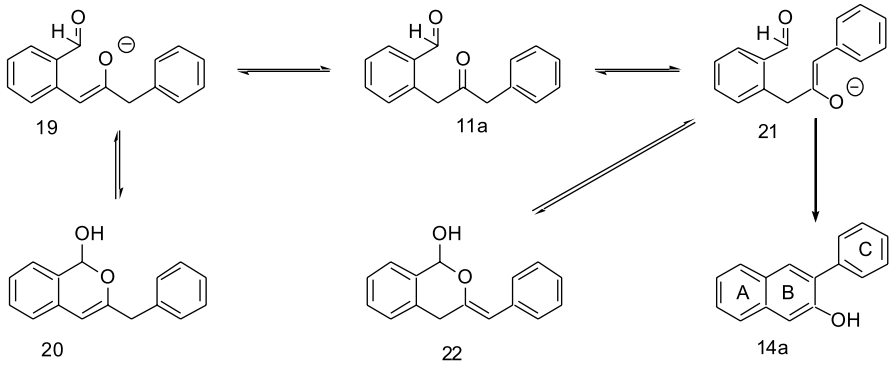
Although our initial route to prepare hydroxyphenylnaphthoquinone **2a** from ketoacid ester **12b** failed, satisfactory results were obtained on using its precursor, ketoaldehyde **11a**. Thus, when **11a** was subjected to basic conditions, a quantitative yield of 2-naphthol **14a** was obtained as a result of an intramolecular aldol condensation (Scheme 2). The IR spectrum of the product contained a typical band for a phenolic hydroxy group at 3457 cm^{-1}; the ^{1}H NMR spectrum showed a broad signal at 5.44 ppm, due to the hydroxy proton, and the ^{13}C NMR include a deshielded signal at 150.9 ppm, which was assigned to the carbon bearing the hydroxy group.

The different behaviour of ketoaldehyde **11a** with respect to its ketoester derivative **12b** can be explained in terms of a competition between three different processes (Scheme 4). The formation of hemiacetals **20** or **22** from ketoaldehyde **11a** via their respective enolates **19** and **21** should be reversible processes, but enolate **21** can also give naphthol **14a** by an intramolecular aldol reaction followed by enolization and dehydration to allow the aromatization of the B ring. The irreversible nature of this last transformation is the reason for the displacement of all the equilibria to the formation of compound **14a**.

Our synthetic plan continued with the transformation of naphthol **14a** into hydroxyphenylnaphthoquinone **2a** and this was achieved easily in two steps. Treatment of **14a** with Fremy's salt and potassium biphosphate in an aqueous acetone solution gave a 68% yield of *o*-naphthoquinone **15a**.[8f] The ^{1}H NMR spectrum of this compound showed a doublet for an aromatic proton at 8.03 ppm, a multiplet for an aromatic protons at 7.58 ppm and a multiplet due to seven aromatic protons and the proton of the double bond at 7.31–7.47 ppm. The ^{13}C NMR spectrum showed two very close signals at 180 and 179.1 ppm due to the carbonyl groups. Finally, aqueous sodium hydroxide was added to a methanolic solution of naphthoquinone **15a** and the mixture was stirred at room temperature for 15 min.[12a] This reaction gave 93% yield of the desired hydroxynaphthoquinone **2a**,[5a]



Scheme 3.



Scheme 4.

which was identified by direct comparison with an authentic sample of this compound.

The potential of this new synthetic route was confirmed by the successful preparation of hydroxyphenylnaphthoquinone **2b** from ketoaldehyde **11b** (Scheme 2). Compound **11b** was easily and efficiently obtained by aldol condensation of 1-indanone **7b** and benzaldehyde, followed by the regioselective hydrogenation of benzylideneindanone **8b**,[24] reduction of **9b** and dehydration of the resulting mixture of indanols and ozonolysis of benzylindene **10b**. As expected, the intramolecular aldol condensation of **11b** provided naphthol **14b**, which was easily oxidized to *o*-naphthoquinone **15b**. Finally, treatment of this compound with H_2SO_4 afforded the desired 2-hydroxynaphthoquinone **2b**.

In summary, we describe here the first total synthesis of phenylketopropylbenzaldehydes in a process that allowed us to develop novel chemistry in the field of quinones. Oxidation of these aldehydes constitutes a new and efficient method for the preparation of ketoacids **12**. Dehydration of the latter compounds constitutes a new and efficient method to obtain 3-benzylisochromanones **13**. Furthermore, the intramolecular aldol condensation of ketoaldehydes **11** constitutes the first general, efficient synthesis of 3-phenylnaphthalen-2-ols (**14**), which were oxidized to 3-phenyl-1,2-naphthoquinones (**15**) for the first time. Further oxidation of the latter compounds is the last step of a new, simple and efficient synthesis of 3-phenyl-2-hydroxy-1,4-naphthoquinones (**2**).

Work is now in progress to apply this synthetic route for naphthoquinones to the synthesis of complex naphthoquinones, including benzofuronaphthoquinones **4**, benzopyronaphthoquinones **5** and indolonaphthoquinones **6**.

1. Experimental

1.1. General

Melting points were determined on a Kofler Thermogerate apparatus and are uncorrected. Infrared spectra were recorded on a MIDAC FTIR spectrophotometer. Nuclear magnetic resonance spectra were recorded, unless otherwise specified, on a Bruker WM-250 apparatus, using deuterochloroform solutions containing tetramethylsilane as internal standard. Mass spectra were obtained on a Kratos MS 50 TC mass spectrometer. Thin layer chromatography (tlc) was performed using Merck GF-254 type 60 silica gel and dichloromethane/methanol mixtures as eluant; the tlc spots were visualized with ultraviolet light or iodine vapour. Column chromatography was carried out using Merck type 9385 silica gel. Solvents were purified as per Ref. 25. Solutions of extracts in organic solvents were dried with anhydrous sodium sulfate. Compounds **2a**, **8a**, **8b**, **9a**, **10a** and **12a**, **12b**, **13**, **15a** and **2a** have been previously prepared.

1.1.1. (*E*)-2-Benzylideneindan-1-one (8a). To a solution of benzaldehyde (2.44 mL, 24.06 mmol) in dry methanol was added a solution of sodium methoxide (prepared by addition of 66 mL of dry methanol to 157 mg of sodium) and a solution of 1-indanone (3 g, 22.70 mmol) in dry methanol (54 mL) dropwise at 0 °C under argon. The resulting mixture was stirred at rt for 13 h. The reaction mixture was then poured into water (100 mL) and the resulting suspension was acidified by the addition of 2 M HCl. The product was extracted into dichloromethane (3×100 mL). The combined organic extracts were dried with anhydrous sodium sulfate and concentrated to dryness in vacuo. Crystallisation of the solid residue with MeOH yielded the title compound (4.735 g, 95%) as white crystals. Mp 109–111 °C (MeOH). IR ($\bar{\nu}$, cm^{-1}, NaCl): 1697 (C=O). ^1H NMR (δ, ppm): 4.01 (s, 2H, $-CH_2-$), 7.38–7.67 (m, 9H, 8× Ar–H and CH=C), 7.90 (d, 1H, $J=7.5$ Hz, Ar–H). ^{13}C NMR (δ, ppm): 32.4 (CH_2), 124.5 (CH), 126.2 (CH), 127.7 (CH), 129.0 (2×CH), 129.7 (CH), 130.8 (2×CH), 134.0 (CH), 134.7 (CH), 134.8 (C), 135.5 (C), 138.1 (C), 149.7 (C), 194.4 (C=O). MS (*m*/*z*, %): 220 (M^+, 58), 219 [$(M-1)^+$, 100].

1.1.2. 2-Benzylindan-1-one (9a). 10% Pd/C (32.5 mg) was added to a deoxygenated solution of benzylideneindanone **8a** (4.802 g, 21.80 mmol) in ethyl acetate (480 mL) and the mixture was stirred under a hydrogen atmosphere (1 atm) at rt for 75 min. After removal of the excess of hydrogen in vacuo, the reaction mixture was filtered though celite, which was eluted with ethyl acetate. The filtrate was concentrated to dryness in vacuo to give a quantitative yield of the title compound (4.62 g) as a transparent oil. IR ($\bar{\nu}$, cm^{-1}, NaCl): 1708 (C=O). ^1H NMR (δ, ppm): 2.67 (dd, 1H, $J=13.8$, 10.4 Hz, $-CH_2-$), 2.86 (dd, 1H, $J=16.9$, 3.3 Hz, $-CH_2-$), 3.01 (m, 1H, –CH–), 3.17 (dd, 1H, $J=16.9$, 7.5 Hz, $-CH_2-$), 3.42 (dd, 1H, $J=13.8$, 3.8 Hz, $-CH_2-$), 7.26–7.42 (m, 7H, 7×Ar–H), 7.58 (t, 1H, $J=7.4$ Hz, Ar–H), 7.80 (d, 1H, $J=$

7.4 Hz, Ar–H). ^{13}C NMR (δ, ppm): 32.2 (CH_2), 37.0 (CH_2), 48.9 (CH), 124.1 (CH), 126.4 (CH), 126.7 (CH), 127.5 (CH), 128.6 (2×CH), 129.0 (2×CH), 134.9 (CH), 136.7 (C), 139.7 (C), 153.7 (C), 207.9 (C=O). MS (*m/z*, %): 222 (M^+, 51), 131 (100).

1.1.3. 2-Benzyl-1*H*-indene (10a). Small portions of $NaBH_4$ (1.607 g, 42.50 mmol) were added every 15 min during 1 h to a solution of benzylindanone **9a** (1.18 g, 5.31 mmol) in methanol (80 mL). The mixture was stirred at rt for 30 min and poured into water (50 mL). The methanol was evaporated in vacuo and the remaining suspension was extracted with dichloromethane (3×100 mL). The combined organic extracts were dried and concentrated to dryness in vacuo. The resulting solid was immediately mixed with 9 M H_2SO_4 (100 mL) and the stirred suspension was heated under reflux in a dry atmosphere for 30 min. 20% aqueous NaOH was added to give a basic pH and the suspension was extracted with dichloromethane (3× 100 mL). The combined organic extracts were dried and concentrated to dryness in vacuo to give a 93% yield of the title compound (4.13 g) as a transparent oil ^{1}H NMR (δ, ppm): 3.33 (s, 2H, CH_2), 3.86 (s, 2H, CH_2), 6.57 (s, 1H, HC=C), 7.12–7.40 (m, 9H, 9×Ar–H). ^{13}C NMR (δ, ppm): 38.1 (CH_2), 40.9 (CH_2), 120.4 (CH), 123.7 (CH), 124.1 (CH), 126.4 (CH), 126.5 (CH), 128.0 (CH), 128.7 (2×CH), 129.1 (2×CH), 140.2 (C), 143.6 (C), 145.5 (C), 149.5 (C). MS (*m/z*, %): 206 (M^+, 30), 91 (100).

1.1.4. 2-(2-Oxo-3-phenylpropyl)benzaldehyde (11a). N_2, O_2 and O_3 were bubbled consecutively for 10, 10 and 2 min, respectively, through a solution of indene **10a** (200 mg, 0.97 mmol) in dichloromethane (30 mL) at −78 °C until the persistent presence of a blue color due to the ozonide was detected. O_2 was then bubbled through for a further 10 min to destroy excess O_3 and finally N_2 was bubbled for 5 min. Dimethyl sulfide was added and the mixture was stirred at −78 °C under argon for 4 h 30 min and at rt for 25 h. The solvent was removed in vacuo and the solid residue was submitted to column chromatography (eluent: AcOEt/hexane, 1:9) to yield 71% of the target compound (164 mg) as a yellow oil. IR ($\bar{\nu}$, cm^{-1}, NaCl): 1706 (CHO, C=O). ^{1}H NMR (δ, ppm): 3.95 (s, 2H, $-CH_2-$), 4.14 (s, 2H, $-CH_2-$), 7.14 (d, 1H, J=6.9 Hz, Ar–H), 7.30–7.55 (m, 7H, 7×Ar–H), 7.79 (m, 1H, Ar–H), 9.98 (s, 1H, –CHO). ^{13}C NMR (δ, ppm): 46.9 (CH_2), 50.1 (CH_2), 127.1 (CH), 127.8 (CH), 128.8 (2×CH), 129.9 (2×CH), 132.8 (CH), 133.8 (CH), 134.3 (C), 134.5 (C), 135.2 (CH), 136.0 (C), 193.5 (C=O), 204.9 (CHO). MS (*m/z*, %): 238 (M^+, 1), 91 (100). HRMS: $C_{16}H_{14}O_2$ (M^+), calcd 238.0994; found 238.0989.

1.1.5. 2-(2-Oxo-3-phenylpropyl)benzoic acid (12a) and 3-benzylisochromen-1-one (13). 1.5 mL of the Jones reagent (500 mg of CrO_3, 1 mL H_2O, 0.5 mL H_2SO_4) was added to solution of ketoaldehyde **11a** in acetone (12 mL) under a dry atmosphere. The mixture was stirred at rt for 45 min, isopropyl alcohol (1 mL) was added and the acetone was evaporated in vacuo. The resulting suspension was extracted with dichloromethane (3×75 mL) and the combined organic layers were washed with 10% aq NaOH (3× 75 mL) and concentrated to dryness in vacuo. Isochromanone **13** was obtained in 18% yield as a yellow liquid. IR ($\bar{\nu}$, cm^{-1}, NaCl): 1727 (C=O). ^{1}H NMR (δ, ppm): 3.85 (s, 2H, $-CH_2-$), 6.16 (s, 1H, –CH=C–), 7.29–7.48 (m, 6H, 6×Ar–H), 7.45 (m, 1H, Ar–H), 7.65 (m, 1H, Ar–H), 8.24 (m, 1H, Ar–H). ^{13}C NMR (δ, ppm): 39.8 ($-CH_2-$), 103.9 (–CH–), 120.1 (C), 125.2 (CH), 127.2 (CH), 127.8 (CH), 128.7 (2×CH), 129.3 (2×CH), 129.5 (CH), 134.7 (CH), 135.7 (C), 137.3 (C), 157.0 (C–O), 162.8 (C=O). MS (*m/z*, %): 236 (M^+, 44), 89 (11).

The basic organic extracts were neutralized with concentrated HCl and the resulting suspension was extracted with dichloromethane (3×100 mL). The combined organic extracts were washed with water (2×100 mL), dried and concentrated to dryness in vacuo to give 82% yield of the ketoacid **12a** (108 mg) as white crystals. Mp 133–135 °C (MeOH). IR ($\bar{\nu}$, cm^{-1}, NaCl): 2931–2856 (OH), 1714 (COOH) 1693 (C=O). ^{1}H NMR (δ, ppm, $CDCl_3$): 3.83 (s, 2H, CH_2), 4.14 (s, 2H, CH_2), 7.20–7.38 (m, 7H, 7×Ar–H), 7.49 (t, 1H, J=7.1 Hz, Ar–H), 7.92 (dd, 1H, J=7.6, 1.1 Hz, Ar–H). ^{13}C NMR (δ, ppm, DMSO): 48.2 (CH_2), 48.8 (CH_2), 126.7 (CH), 127.2 (2×CH), 128.4 (2×CH), 130.1 (CH), 130.6 (CH), 132.3 (CH), 132.7 (CH), 135.2 (C), 136.1 (C), 137.2 (C), 168.4 ($-CO_2H$), 205.0 (C=O). MS (*m/z*, %): 236 [$(M-18)^+$, 19], 135 (100).

1.1.6. 2-(2-Oxo-3-phenylpropyl)benzoic acid methyl ester (12b). A solution of ketoacid **12a** (160 mg, 0.63 mmol) and concentrated sulfuric acid (1 mL) in methanol (20 mL) was heated under reflux in a dry atmosphere for 75 min. The methanol was evaporated in vacuo and the residue was poured into saturated sodium bicarbonate (50 mL). The suspension was extracted with dichloromethane (3×50 mL). The combined organic layers were dried and concentrated to dryness in vacuo. The solid residue was submitted to column chromatography (eluent AcOEt/hexane, 1:9) to give isochormanone **13** (0.09 mmol, 14% yield) and ketoester **12b** (0.43 mmol, 68% yield) as a yellow oil. IR ($\bar{\nu}$, cm^{-1}, NaCl): 1726 (C=O), 1655 (C=O). ^{1}H NMR (δ, ppm): 3.83 (s, 3H, OCH_3), 3.87 (s, 2H, CH_2), 4.11 (s, 2H, CH_2), 7.11 (d, 1H, J=7.5 Hz, Ar–H), 7.25–7.37 (m, 6H, 6×Ar–H), 7.45 (m, 1H, Ar–H), 8.03 (dd, 1H, J= 7.8, 1.4 Hz, Ar–H). ^{13}C NMR (δ, ppm): 48.2 (CH_2), 49.8 (CH_2), 51.9 (OCH_3), 126.9 (CH), 127.2 (CH), 128.6 (2×CH), 129.2 (C), 129.7 (2×CH), 131.0 (CH), 132.3 (CH), 132.5 (CH), 134.4 (C), 136.7 (C), 167.4 (C=O), 205.2 (C=O). MS (*m/z*, %): 268 (M^+, 1), 91 (100).

1.1.7. 3-Benzyl-isochromen-1-one (13). A mixture of sodium methoxide (10.8 mg, 0.2 mmol) and ketoester **12b** (300 mg, 1.12 mmol) in dry methanol (10 mL) was heated under reflux during 3 h. The reaction mixture was acidified by adding 10% aq HCl and the resulting suspension was extracted with dichloromethane (3×25 mL). The combined organic extracts were washed with water (25 mL), dried and concentrated to dryness in vacuo to give quantitative yield of the title compound as a yellow oil.

1.1.8. 3-Phenylnaphthalen-2-ol (14a). A solution of ketoaldehyde **11a** (86 mg, 0.36 mmol) in 5% aq NaOH (5 mL) was stirred under a dry atmosphere at rt for 2 h. The reaction mixture was acidified by adding 10% aq HCl and the resulting suspension was extracted with dichloromethane (3×25 mL). The combined organic extracts were washed with water (25 mL), dried and concentrated to

dryness in vacuo to give a quantitative yield of the target compound as a white solid. Mp 87–89 °C (MeOH). IR ($\bar{\nu}$, cm^{-1}, NaCl): 3457 (–OH). ^1H NMR (δ, ppm): 5.44 (br s, 1H, –OH), 7.35–7.68 (m, 8H, 8×Ar–H), 7.74–7.83 (m, 3H, 3×Ar–H). ^{13}C NMR (δ, ppm): 110.3 (CH), 124.0 (CH), 126.3 (CH), 126.6 (CH), 127.9 (CH), 128.2 (CH), 129.3 (CH), 129.4 (2×CH), 129.7 (2×CH), 130.6 (C), 134.4 (C), 137.0 (C), 150.9 (C–OH). MS (*m/z*, %): 220 (M^+, 100). Anal. Calcd for $C_{16}H_{12}O$, C: 87.25; H: 5.49. Found C: 87.14; H: 5.51.

1.1.9. 3-Phenyl-1,2-naphthoquinone (15a). A solution of Fremy's salt (682 mg, 2.54 mmol) and potassium biphosphate (120 mg, 0.88 mmol) in water (18 mL) was added to a solution of naphthol **14a** (80 mg, 0.34 mmol) in acetone (10 mL). The suspension was stirred in a dry atmosphere at rt for 1 h and the acetone was evaporated in vacuo. The pink suspension was extracted with dichloromethane (3× 25 mL) and the combined organic layers were washed with water (25 mL), dried and concentrated to dryness in vacuo. The remaining solid residue was submitted to flash column chromatography (eluent: AcOEt/hexane, 1:9) and the target compound **15a** was isolated (57 mg, 68% yield) as a pink solid. Mp 125–127 °C (MeOH). IR ($\bar{\nu}$, cm^{-1}, NaCl): 1663 (C=O). ^1H NMR (δ, ppm): 7.31–7.47 (m, 8H, 7×Ar–H and –CH=C–), 7.58 (m, 1H, Ar–H), 8.03 (d, 1H, J= 7.6 Hz, Ar–H). ^{13}C NMR (δ, ppm): 128.4 (2×CH), 128.5 (2×CH), 128.9 (CH), 130.0 (CH), 130.1 (CH), 130.4 (CH), 130.8 (C), 134.1 (C), 135.3 (C), 136.0 (CH), 138.8 (C), 141.9 (CH), 179.1 (C=O), 180.0 (C=O). MS (*m/z*, %): 234 (M^+, 4), 206 (100).

1.1.10. 2-Hydroxy-3-phenyl-[1,4]naphthoquinone (2a). A suspension of quinone **14a** (27 mg, 0.12 mmol), MeOH (2 mL) and 20% aq NaOH (2 mL) was stirred under a dry atmosphere at rt for 15 min. The mixture was acidified with 2 M HCl and extracted with dichloromethane (3×25 mL). The combined organic extracts were washed with water (25 mL), dried and concentrated to dryness in vacuo to yield the target quinone **2a** (0.11 g, 93% yield) as a red solid. Mp 47–49 °C (MeOH). IR ($\bar{\nu}$, cm^{-1}, NaCl): 3425 (–OH), 1710 (C=O), 1650 (C=O). ^1H NMR (δ ppm): 7.40–7.54 (m, 5H, 5×Ar–H), 7.72–7.85 (m, 2H, 2×Ar–H), 8.15–8.23 (m, 2H, 2×Ar–H). ^{13}C NMR (δ, ppm): 126.2 (CH), 127.3 (CH), 128.0 (2×CH), 128.7 (CH), 129.3 (C), 129.9 (C), 130.6 (2×CH), 133.0 (C), 133.2 (CH), 135.3 (CH), 152.2 (C–OH), 181.9 (C=O), 183.1 (C=O). MS (*m/z*, %): 250 (M^+, 5), 149 (100).

1.1.11. (*E*)-2-Benzylidene-5-methoxy-indan-1-one (8b). In a similar way to **8a**, reaction of methoxyindanone **7b** (4.0 g, 24.66 mmol) and benzaldehyde (2.7 mL, 26.17 mmol) gave 81% yield of the title compound as white crystals. Mp 171–173 °C (MeOH). IR ($\bar{\nu}$, cm^{-1}, KBr): 1686 (C=O). ^1H NMR (δ, ppm): 3.90 (s, 3H, OMe), 3.98 (d, J=1.0 Hz, 2H, CH_2), 6.92–6.97 (m, 2H, HC=C and ArH), 7.38–7.48 (m, 3H, 3×ArH), 7.59–7.66 (m, 3H, 3×ArH), 7.84 (d, J=8.4 Hz, 1H, ArH). ^{13}C NMR (δ, ppm): 32.4 (CH_2), 55.6 (OMe), 109.6 (CH), 115.2 (CH), 126.1 (CH), 128.8 (2×CH), 129.3 (C), 130.5 (2×CH), 131.4 (C), 132.6 (CH), 135.2 (C), 135.5 (C), 152.5 (C), 165.2 (C), 192.7 (C=O). MS (*m/z*, %, CI): (251 [(M^++1), 100].

1.1.12. 2-Benzyl-5-methoxyindan-1-one (9b). Benzylydeneindanone **8b** was submitted to catalytic hydrogenation under the same conditions as for **8a** to give a quantitative yield of the title compound as white crystals. Mp 102–104 °C (MeOH). IR ($\bar{\nu}$, cm^{-1}, KBr): 1689 (C=O). ^1H NMR (δ, ppm): 2.61–2.83 (m, 2H, –CH_2–), 2.94–3.14 (m, 2H, –CH_2–), 3.38 (dd, J=4.1, 13.9 Hz, 1H, –CH–), 3.85 (s, 3H, –OMe), 6.82–6.91 (m, 2H, 2×ArH), 7.19–7.32 (m, 5H, 5×ArH), 7.71 (d, J=8.5 Hz, 1H, ArH). ^{13}C NMR (δ, ppm): 32.1 (CH_2), 37.1 (CH_2), 49.0 (CH), 55.5 (OMe), 109.6 (CH), 115.3 (CH), 125.6 (CH), 126.2 (CH), 128.4 (2×CH), 128.9 (2×CH), 129.7 (C), 139.7 (C), 156.5 (C), 165.4 (C), 205.9 (C=O). MS (*m/z*, %): 252 (M^+, 33), 161 (100). Anal. Calcd for $C_{17}H_{16}O_2$, C: 80.93; H: 6.39. Found C: 81.09; H: 6.12.

1.1.13. 2-Benzyl-5-methoxy-1*H*-indene (10b). Reaction of benzylmethoxyindanone **9b** (2.84 g, 11.27 mmol) with $NaBH_4$ and then with H_2SO_4, in a similar way to **10a**, gave 76% yield of the title compound (1.39 g) as a white solid. Mp 64–66 °C (MeOH/Et_2O). ^1H NMR (δ, ppm): 3.27 (s, 2H, CH_2), 3.81 (s, 2H, CH_2), 3.82 (s, 3H, OMe), 6.47 (s, 1H, =CH), 6.81 (dd, J=8.2 Hz, J'=2.3 Hz, 1H, ArH), 6.98 (d, J=1.3 Hz, 1H, ArH), 7.17–7.36 (m, 6H, 6×ArH). ^{13}C NMR (δ, ppm): 37.9 (CH_2), 40.8 (CH_2), 55.5 (OMe), 110.4 (CH), 111.6 (CH), 120.3 (CH), 126.1 (CH), 127.1 (CH), 128.4 (2×CH), 128.8 (2×CH), 138.4 (C), 140.2 (C), 145.2 (C), 146.9 (C), 157.3 (C). MS (*m/z*, %): 236 (M^+, 38), 145 (100). Anal. Calcd for $C_{17}H_{16}O$, C: 86.40; H: 6.82. Found C: 86.67; H: 6.69.

1.1.14. 2-(4-Methoxy-2-oxo-3-phenylpropyl)benzaldehyde (11b). Ozonolysis of compound **10b** under the same conditions as for **10a** gave a 72% yield of the title compound as a white solid. Mp 164–166 °C (MeOH). IR ($\bar{\nu}$, cm^{-1}, KBr): 1705 (C=O), 1718 (–CHO). ^1H NMR (δ, ppm): 3.83 (s, 3H, –OMe), 3.93 (s, 2H, CH_2), 4.09 (s, 2H, CH_2), 6.64 (d, J=2.5 Hz, 1H, ArH), 6.92 (m, 1H, ArH), 7.26–7.36 (m, 5H, 5×ArH), 7.71 (d, J=8.5 Hz, 1H, ArH), 9.84 (s, 1H, CHO). ^{13}C NMR (δ, ppm): 47.0 (CH_2), 50.0 (CH_2), 55.4 (OMe), 112.1 (CH), 118.7 (CH), 126.9 (–CH), 127.6 (C), 128.5 (2×CH), 129.7 (2×CH), 134.3 (C), 137.9 (CH), 138.3 (C), 163.5 (C), 191.6 (CHO), 204.6 (C=O). MS (*m/z*, %): 268 (M^+, 5), 91 (100). Anal. Calcd for $C_{17}H_{16}O_3$, C: 76.10; H: 6.01. Found C: 69.91; H: 6.27.

1.1.15. 7-Methoxy-3-phenyl-naphthalen-2-ol (14b). In a similar way to **14a**, reaction of the ketoaldehyde **11b** (559 mg, 2.08 mmol) with 5% aq NaOH provided the title compound (502 mg, 97%) as a white solid. Mp 164–166 °C (MeOH). IR ($\bar{\nu}$, cm^{-1}, KBr): 3405 (OH). ^1H NMR (δ, ppm): 3.94 (s, 3H, –OMe), 5.67 (s, 1H, OH), 7.05–7.10 (m, 2H, 2×ArH), 7.45–7.73 (m, 7H, 8×ArH). ^{13}C NMR (δ, ppm): 55.2 (OMe), 104.2 (CH), 109.4 (CH), 116.5 (CH), 124.2 (C), 127.6 (CH), 127.8 (C), 128.9 (2×CH), 129.1 (2×CH), 129.2 (CH), 129.2 (CH), 135.4 (C), 136.9 (C), 151.2 (C), 157.9 (C). MS (*m/z*, %): 250 (M^+, 100). Anal. Calcd for $C_{17}H_{14}O_2$, C: 81.58; H: 5.64. Found C: 81.29; H: 6.47.

1.1.16. 7-Metoxy-3-phenyl-1,2-naphthoquinone (15b). Reaction of naphthol **14b** (194 mg, 0.78 mmol) with Fremy's salt (1.46 mg, 5.43 mmol) and potassium biphosphate (256 mg, 1.88 mmol) under the same conditions as for

the oxidation of **14a**, gave 63% yield of the title compound (123 mg) as a pink solid. Mp 167–169 °C (MeOH). IR ($\bar{\nu}$, cm^{-1}, KBr): 1662 (C=O), 1648 (C=O). ^1H NMR (δ, ppm): 3.88 (s, 3H, OMe), 7.11 (m, 2H, =CH and ArH), 7.29–7.55 (m, 7H, 7×ArH). ^{13}C NMR (δ, ppm): 55.8 (OMe), 114.3 (CH), 121.9 (CH), 128.2 (C), 128.2 (4×CH), 128.4 (CH), 131.7 (CH), 132.0 (C), 134.2 (C), 135.7 (C), 142.1 (CH), 161.3 (C), 178.7 (C=O), 179.6 (C=O). MS (*m*/*z*, %): 264 (M^+, 19), 236 (100). Anal. Calcd for $C_{17}H_{12}O_3$, C: 77.26; H: 4.58. Found C: 76.91; H: 4.60.

1.1.17. 2-Hydroxy-7-methoxy-3-phenyl-[1,4]naphthoquinone (2b). Reaction of *o*-naphthoquinone **14b** with 20% aq NaOH under the same conditions as for the preparation of **14a** gave 90% yield of the title compound as a red solid. Mp 164–166 °C (MeOH/Benzene). IR ($\bar{\nu}$, cm^{-1}, KBr): 3327 (OH), 1660 (C=O), 1596 (C=O). ^1H NMR (δ, ppm): 3.94 (s, 3H, –OMe), 7.21–7.25 (m, 1H, ArH), 7.37–7.55 (m, 6H, 6×ArH), 8.10 (d, J=8.8 Hz, 1H, ArH). ^{13}C NMR (δ, ppm): 56.0 (OMe), 109.6 (CH), 121.2 (CH), 121.7 (C), 125.9 (C), 127.7 (2×CH), 128.5 (CH), 129.4 (CH), 129.9 (C), 130.6 (2×CH), 130.8 (C), 151.8 (C), 163.3 (C), 181.8 (C=O), 182.9 (C=O). MS (*m*/*z*, %): 280 (M^+, 100). Anal. Calcd for $C_{17}H_{12}O_3$, C: 72.85; H: 4.32. Found C: 73.12; H: 3.97.

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