The "Photo-Friedel–Crafts Acylation" of 1,4-Naphthoquinones

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Dedicated to Professor Hans J. Schäfer on the occasion of his 65th birthday

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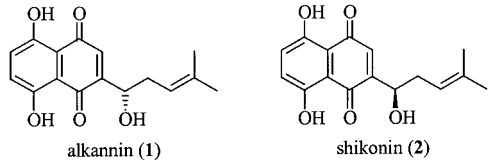
The photochemical reaction between 1,4-naphthoquinone (**3**) and several aliphatic and aromatic aldehydes **5a–f** resulted in the formation of acylated naphthohydroquinones **6a–f** in moderate to good yields of 42–79%. When benzaldehyde was used, the dibenzoylated product **7** was also isolated, in 14% yield. The regioselectivity was studied with the unsymmetrical substituted naphthoquinone **4** and butyraldehyde **5b** and benzaldehyde **5f**. With **5f**, the corresponding diaroylated compound **12** was again isolated as a minor product. Oxidation of selected photoproducts afforded the corresponding acylated naphthoquinones **8a**, **8b**, **8f**, and **13** in moderate to excellent yields of 53–94%.

Introduction

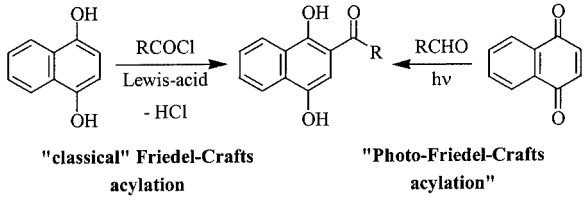
Acylated quinones and their derivatives are important natural products.[1] The enantiomeric naphthoquinones alkannin (**1**) and shikonin (**2**) (Scheme 1), for example, extracted from the roots of *Alkanna tinctoria* in Europe and *Lithospermum erythrorhizon* in the Orient, have been used for centuries as natural dyes or wound-healing drugs.[2] In addition, acylated hydroquinones and quinones serve as useful key intermediates for pharmaceuticals, and pathways to pyrano[2,3-*c*]naphthoquinones,[3] 1,4-benzodiazepines,[4] and lapachones[5] have been described in the literature.



Scheme 1. The structures of alkannin (**1**) and shikonin (**2**)

Acylated quinone derivatives have generally been prepared by Friedel–Crafts acylation in moderate to good yields.[6] Nevertheless, this classical method suffers from the use of equimolar amounts of corrosive acid chlorides and strong Lewis acids (usually $AlCl_3$), the formation of harmful by-products (especially volatile hydrochloric acid), and certain restrictions on functionalities in the starting materials. The photochemical reaction between a quinone and an aldehyde offers a mild and efficient alternative,[7] and for that reason is often referred to as the "photo-Friedel–Crafts acylation" in laboratory jargon (Scheme 2).

This extremely useful photochemical method was first reported in 1891 by Heinrich Klinger, who exposed the starting materials to natural sunlight over several months.[8] Over the following decades, however, the reaction found only little attention in organic synthesis. While most reported studies focused on 1,4-benzoquinone or *ortho*-quinone derivatives, publications on the related 1,4-naphthoquinones remained rare. We became interested in this application in the context of the photochemical bulk production of fine chemicals through the use of sunlight (as a modern version of Klinger's early experiments),[9] and investigated the scope and regiochemistry of the photoreaction, and the subsequent thermal oxidation to the corresponding acylated quinones in detail. An important aspect



Scheme 2. Possible pathways to acylated quinone precursors

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was a short and efficient alternative pathway to pyrano[2,3-*c*]naphthoquinone precursors, which were previously commonly synthesized in a six-step sequence from 1,5-dihydroxynaphthalene.[3b] The experiences from laboratory syntheses (using artificial light) were also used as the basis for a first solar-chemical field experiment.

Results and Discussion

Starting Materials

As a model system, the commercially available naphthoquinone (**3**), already incorporating the required annelated benzene ring of the desired products, was selected. For further regioselectivity studies of the acylation step, we chose 5-methoxynaphthoquinone (**4**), available in a two-step synthesis from 1,5-dihydroxynaphthalene. In the first step, the naphthalene derivative was transformed into 5-hydroxynaphthoquinone (juglone) either photochemically with singlet oxygen[10] in 55% yield or by Jones oxidation in 12% yield.[11] Methylation by a modified method described by Thompson and co-workers[12] gave the desired 5-methoxynaphthoquinone (**4**) in a high yield of 94%.

Photoreactions

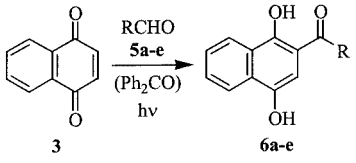
For the photochemical studies with naphthoquinone **3**, two different methods were applied: The aliphatic aldehydes **5a** and **5b** and the aromatic aldehydes **5d** and **5f** were irradiated under direct excitation conditions,[13a] whereas for the aromatic aldehydes **5c**, **5e**, and (again) **5f**, catalytic amounts of benzophenone (mediated conditions, vide infra) were added.[13b] In both cases, photolysis of **3** in the presence of 7−8 equiv. of aldehyde (to suppress competing photodimerizations of **3**[14]) in benzene or acetonitrile gave the acylated products **6a**−**f** in moderate to good yields (Scheme 3, Table 1). Since the quantum yield decreased with increasing conversion, due to quenching by the photoproduct (e.g. $\Phi = 0.51 \rightarrow 0.37$ for the **3**/**5a** pair[15]), prolonged irradiation was necessary to drive the reaction towards near completion. In sharp contrast to that of 1,4-benzoquinones,[21] the photoacylation proceeded highly chemoselectively, and no hydroquinone monoesters were found. Furthermore, no alkylation products arising from decarbonylation of the intermediately produced acyl radicals prior to C−C bond formation were detected.[16] The aromatic aldehydes **5c**−**e**, containing reactive substituents for further potential synthetic modifications, showed no negative influence on the efficiency of the photoreaction. Secondary acylation of the *p*-phthaloyl product **6e** to another quinone **3** was inhibited by the excess amount of aldehyde used. In most cases, the desired product precipitated during the irradiation, and so could easily be isolated by filtration and purified by simple recrystallization. In all other cases, isolation by column chromatography on silica gel was required. To perform large-scale solar-chemical outdoor experiments, an alternative to the toxic benzene or acetonitrile used as solvents had to be found. Toluene was used in one test experiment with **5b**, but the photoreaction became more sluggish and the isolated yield of **6b** dropped to 35%, possibly due to radical side reactions with the solvent.[14] Cheap and nontoxic *tert*-butyl alcohol was found to be a suitable alternative and, as one example, the photoproduct **6b** was obtained in 84% yield. Supercritical carbon dioxide has recently been used as an alternative solvent for the photo-induced addition of aldehydes to 1,4-benzoquinone or 2-cyclohexen-1-one, but this technique suffers from technical disadvantages (high pressure, small reactor volume), especially for large-scale experiments.[13c]

Table 1. Photoreaction between **3** and **5**

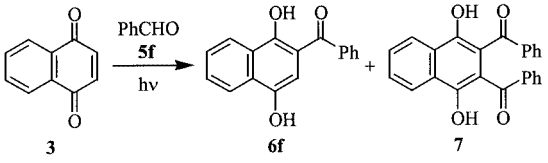
Aldehyde	R	Method[a]	Yield [%]
5a	Et	A	79
5b	Pr	A	78
5b	Pr	A[b]	35
5b	Pr	A[c]	84
5c	*p*-ClC_6H_4	B	58
5d	*p*-NCC_6H_4	A	63
5e	*p*-$OHCC_6H_4$	B[d]	42
5f	Ph	A	74 (**7**: 14)
5f	Ph	B	61 (**7**: 17)

[a] A: direct; B: Ph_2CO-mediated. [b] In toluene. [c] In *t*BuOH. [d] In MeCN (aldehyde insoluble in benzene).

A special case was the irradiation of **3** in the presence of benzaldehyde (**5f**). Together with the monoaroylated product **6f** (74%), the dibenzoylated compound **7** was isolated in 14% yield (Scheme 4).[17] The total yield was slightly decreased in the benzophenone-mediated case, but, more significantly, the ratio of the two products changed in favor of the dibenzoylated product. Both compounds **6f** and **7** gave suitable crystals for X-ray structure analysis, and their structures are shown in Figure 1. In **6f**, the benzoyl carbonyl group lies within the naphthohydroquinone plane, and the benzoyl oxygen atom and the hydroxy group at C-1 form a hydrogen bond with a length of 1.80 Å. The incorporation of a second benzoyl group in **7** results in a deviation in planarity for the carbonyl groups and the hydroquinone ring (torsion angles: 30°). As a consequence, the

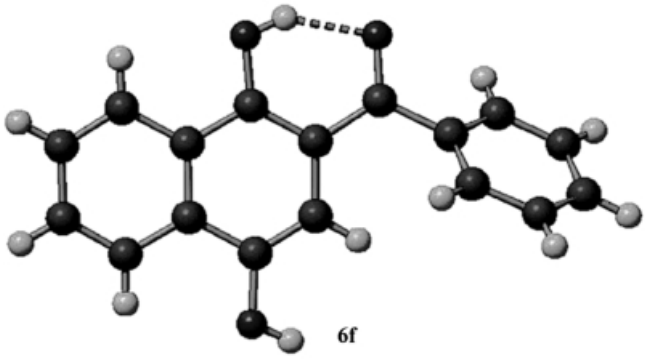


Scheme 3. Photoreactions with **3**



Scheme 4. Formation of mono- and dibenzoylated compounds in the case of **5f**

hydrogen bonds between the aroyl and the hydroxy groups are widened and were found to be 1.88 and 1.90 Å, respectively.



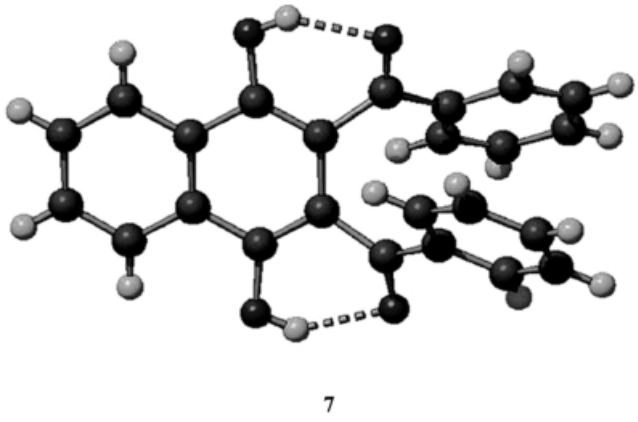
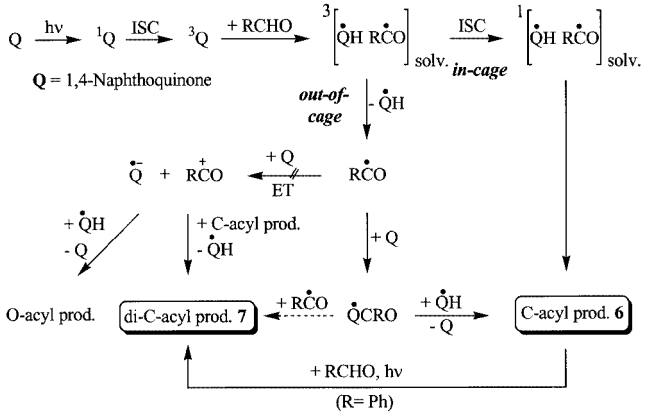


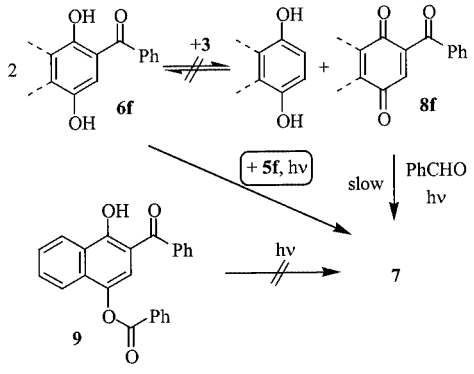
Figure 1. Molecular structures of **6f** and **7** as determined by X-ray diffraction

For the formation of the acylated photoproducts under direct excitation conditions, two limiting mechanisms have been discussed in the literature (Scheme 5). On the basis of CIDNP investigations, Maruyama and co-workers favored an *in-cage* scenario,[15,18] as first proposed by Schenck.[19] In contrast, a *free-radical* mechanism was suggested by Moore.[20] Bruce and co-workers confirmed the latter mechanism and supported it by trapping experiments with styrene and 1,1-diphenylethylene.[21] Finally, it was again Maruyama who showed that for the corresponding 1,2-naphthoquinone both *in-cage* and *out-of-cage* mechanism operated more or less simultaneously, depending on the specific reaction conditions (temperature, solvent, quinone or aldehyde applied) for each irradiation experiment.[22]

A striking difference to the 1,4-benzoquinone (**BQ**) case was the lack of formation of hydroquinone monoesters with 1,4-naphthoquinone **3**. These *O*-acylation products have been explained in terms of electron transfer (ET) from the acyl radical to a ground-state 1,4-benzoquinone, followed by addition of the corresponding electrophilic acyl cation to the quinone radical anion.[21] Since no monoesters were observed for 1,4-naphthoquinone, however, ET is unlikely. By the *out-of-cage* scenario, this is supported by the reduction potentials of the two quinones (**3**: $E_{1/2} = -0.71$ V; **BQ**: $E_{1/2} = -0.51$ V in MeCN vs. SCE).[23] In addition, the high chemoselectivity with **3** is in line with similar literature reports.[5] Several mechanistic pathways to the dibenzoylated compound **7** can be postulated (Scheme 6), and so were examined by us.



Scheme 5. Mechanistic scenarios based on literature precedence (see text)



Scheme 6. Possible pathways to **7**

(1) Diacylated compounds had already been described by Bruce and co-workers, and a thermal oxidation/reduction equilibrium between the monoacylated product and the initial quinone, followed by a rapid, secondary acylation of the intermediately generated acylated quinone, has been suggested to explain their formation.[24] Reasonable support for this explanation was provided by the isolation of similar amounts of unsubstituted hydroquinones and diacylated products for several acetaldehyde/1,4-benzoquinone pairs. The same authors also demonstrated secondary acylation with acetyl-1,4-benzoquinone and acetaldehyde, and isolated corresponding diacylated products in 20% total yield.[21b] However, final proof for this mechanism was absent. We were also hoping to adopt this scenario in our case, but when a 1:1 mixture of isolated product **6f** and quinone **3** was stirred (or irradiated) in benzene for 5 d, no reaction could be observed (within the detection limit of ^{1}H NMR). Furthermore, secondary benzoylation of independently prepared monoacylated quinone **8f** was found to proceed extremely slowly (vide infra), implying that **8f**, if

formed as an important intermediate, should have been isolated in significant amounts during the acylation reaction between **3** and **5f**. We therefore concluded that an in situ thermal or photochemical oxidation/reduction equilibrium should be ruled out, at least for the **3/5f** pair.

(2) Another reasonable pathway to **7** might be a rapid photo-Fries rearrangement of the intermediately formed benzoylated hydroquinone monobenzoate **9**.[25] To test this possibility, compound **9** (independently synthesized from **6f**) was irradiated under "photo-Friedel–Crafts" conditions. Since no reaction to give **7** was observed, the hydroquinone monoester **9** could not have been an important intermediate. In addition, Bruce and co-workers have already demonstrated that this mechanism does not operate for the monoacylation step.[21a]

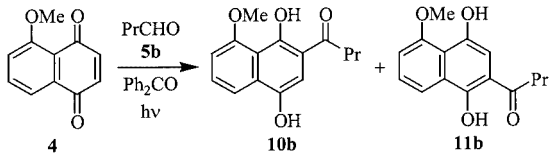
(3) Alternatively, the formation of **7** might be due to the addition of an acyl cation to a monoacylated hydroquinone **6f**, as known for "classical Friedel–Crafts" acylations,[6] but since ET did not occur (vide supra), the involvement of acyl cations and consequently of this possibility must be ruled out.

(4) When the monoacylated product **6f** was finally irradiated in the presence of benzaldehyde (**5f**), the dibenzoylated compound **7** was formed in 36% yield. Compound **6f**, similarly to benzophenone, had obviously acted as a mediator producing benzoyl radicals, which had added to **6f** through an *out-of-cage* mechanism to give **7**. In the presence of additional benzophenone, however, the reaction became more sluggish and larger amounts of polymeric by-products were obtained beside the desired **7**. This finding indicated that the monoacylated product **6f** or the alternative benzophenone had indeed acted as a mediator (rather than a sensitizer) initiating the radical chain mechanism (similar cases of pure benzophenone activations have been described[26]). Consequently, in the experiment involving benzophenone, the two mediators compete, and this might open alternative nonproductive reaction channels.

In summary, we have concluded that bis(acylation) proceeded (at least partly) by way of a secondary photoacylation from the monoadduct and the corresponding aldehyde. This was also supported by the increased amount of dibenzoylated product (based on product ratio) obtained in the benzophenone-mediated case. Furthermore, it can be speculated whether the stability[16] or polarity[31] of the intermediately formed acyl radical might play an additional role in the formation of **7**.

Unsymmetrical Naphthoquinones

Juglone itself did not undergo the photochemical acylation,[21c] indicating a rapid *intramolecular* hydrogen transfer (phototautomerization) process.[27] The regioselectivity of the acylation step was therefore studied with the unsymmetrical methoxy-substituted quinone **4** and the two model aldehydes **5b** and **5f**. For **5b**, both regioisomers could be isolated after prolonged irradiation, in yields of 38% (2,8-isomer **10b**) and 23% (2,5-isomer **11b**), respectively (Scheme 7). The structure of the major 2,8-regioisomer **10b** was unambiguously established by crystal structure analysis (Figure 2). The methoxy oxygen atom and the hydroxy group at C-1 form a hydrogen bond with a length of 1.81 Å, whereas the carbonyl group undergoes intermolecular hydrogen bonding to the C-4 hydroxy group of a second molecule (distance: 1.86 Å; not shown). The intermolecular interaction results in an orientation of the acyl group different from that seen in the solid-state structures of **6f**, **7**, and **11f** (vide infra).



Scheme 7. Photoreaction between **4** and butyraldehyde **5b**

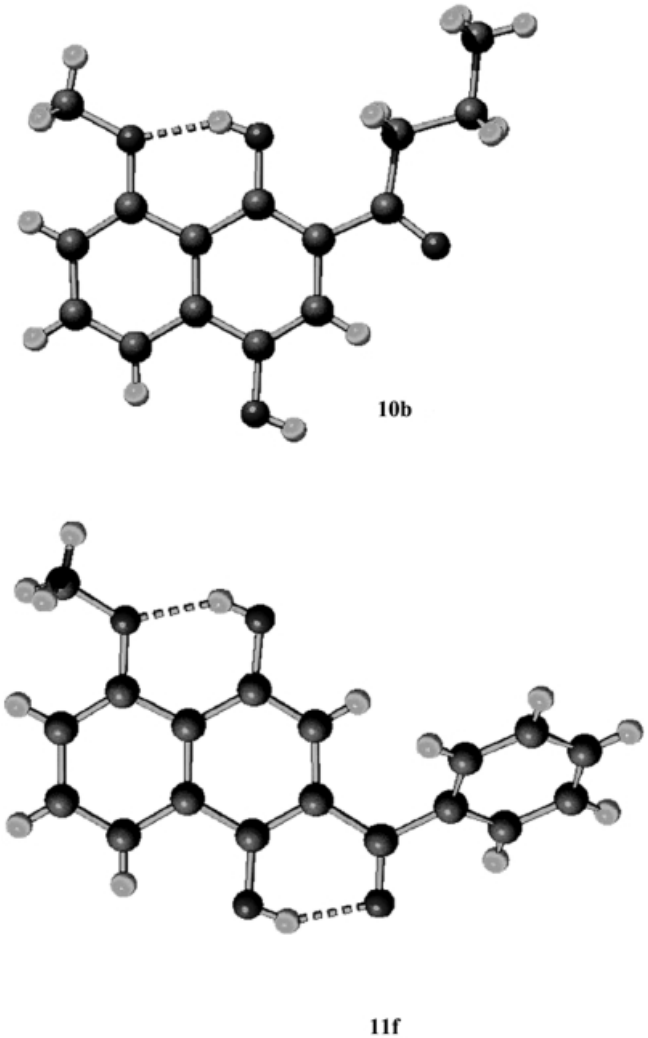
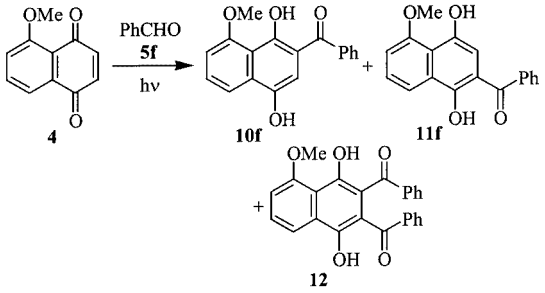


Figure 2. Molecular structures of **10b** and **11f** as determined by X-ray diffraction



Scheme 8. Photoreaction between **4** and benzaldehyde (**5f**)

In the case of benzaldehyde (Scheme 8), disubstitution was again observed, and the dibenzoylated compound **12** was obtained in 11% yield. Unlike in the butyraldehyde experiment, however, the regioselectivity switched, and the 2,5-isomer **11f** was formed as the main product (36%), together with the 2,8-isomer **10f** (14%).[28] The regioselectivity of **11f** was unambiguously confirmed by X-ray structure analysis (Figure 2). Intramolecular hydrogen bonds were found between the methoxy oxygen atom and the hydroxy group at C-4 (1.86 Å) and between the carbonyl group and the hydroxy group at C-1 (1.79 Å).

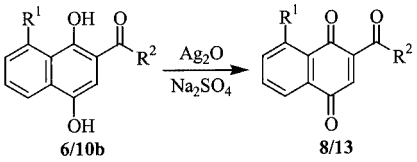
Since acyl radicals add more efficiently to alkenes with electron-withdrawing groups than to ordinary and electron-rich alkenes, they are regarded as nucleophilic radicals.[16b] According to FMO theory, they should therefore predominantly attack the C-2 double bond position bearing the larger LUMO coefficient in **4**. For aliphatic aldehydes, this scenario has been confirmed experimentally with other unsymmetrically substituted naphthoquinones,[29] and also theoretically by AM1 calculations.[30] Preliminary results on the scope and limitations of this concept also indicated that the regioselectivity could be controlled by use of additives (such as lithium perchlorate) that alter LUMO properties.[30a] Aroyl radicals are much more electrophilic,[31] and as a consequence the LUMO concept could no longer be applied. On the other hand, a significant contribution from the *in-cage* mechanism involving triplet excited **4** might additionally (or alternatively) be responsible for the diverse behavior of the **4**/**5b** pair.[30b]

Solar-Chemical Experiment

Since quinone absorption occurs at wavelengths above 350 nm, the "photo-Friedel–Crafts acylation" is suitable for *green* photochemistry with natural sunlight.[32] Although not all conditions from the laboratory study fitted with this concept (i.e., benzene as toxic solvent, 7–8 equiv. of aldehyde, long irradiation times), we did achieve a suitable and acceptable modification for an initial solar-chemical application by the use of *tert*-butyl alcohol/acetone (3:1) as solvent mixture. As a test system, the reaction between naphthoquinone (**3**) and butyraldehyde (**5b**) was subjected to solar irradiation conditions. In a sunlight-concentrating system (MAN-Helioman,[9a] concentration factor ca. 15 suns, 24 m^2 reflecting mirror area), **3** (500 g) in a *tert*-butyl alcohol/acetone mixture (80 l) was converted into the acylation product (**6b**) within 3 d (Germany, August 1996), and in 90% yield without appreciable amounts of by-products.[33] This result clearly demonstrated that the goal of *green* photochemistry with sunlight was achievable, although further modifications were desirable.

Oxidations and Secondary Acylation

Hydroquinones can be oxidized to the corresponding quinones by a variety of methods.[34] Because of its mild conditions and simple procedure, oxidation with Ag_2O in the presence of sodium sulfate was chosen (Scheme 9)[35] and applied to selected photoacylated products (Table 2). The acylated quinones **8a**, **8b**, **8f**, and **13** were readily produced in moderate to high yields of 53–94%, respectively. The solid-state structure of **8b** was additionally confirmed by crystal structure analysis (Figure 3).



Scheme 9. Oxidation reactions to **8** and **13**

Table 2. Oxidation of selected photoproducts to **8** and **13**

Hydroquinone	R^1	R^2	Yield (%)
6a	H	Et	94
6b	H	Pr	88
6f	H	Ph	53
10b	OMe	Pr	55

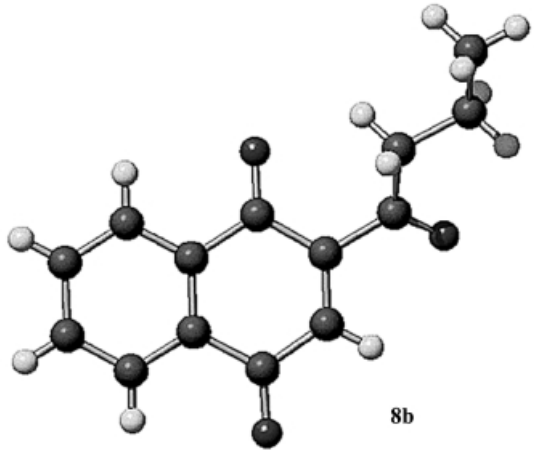


Figure 3. Molecular structure of **8b** as determined by X-ray diffraction

To test further whether monoacylated quinones were involved as intermediates in the production of the bis(acylated) products, compound **8f** was irradiated for 5 d in the presence of benzaldehyde (**5f**). Although the dibenzoylated product **7** could clearly be detected by TLC, careful inspection of the crude product mixture by ^1H NMR revealed

that the level of conversion into **7** was below 2%. This finding showed that secondary acylation occurred extremely slowly in comparison with the monoacylation. This was in agreement with an early report by Bogert and Howells,[36] these authors having failed to obtain dibenzoylated products from monobenzoylated 1,4-benzoquinone under solar-chemical conditions.

Conclusion

The photochemical reaction between naphthoquinones and aliphatic and aromatic aldehydes is a versatile and chemoselective method for the preparation of acylated naphthohydroquinones. Oxidation of the photoproducts readily afforded the corresponding acylated naphthoquinones. All starting materials are commercially or synthetically easily available, which makes the reaction attractive as a short and efficient pathway to these target compounds. Since even double bonds were tolerated in the aldehyde,[5,13] a future alkannin and shikonin synthesis should be possible. Detailed studies on this synthetic application and on regioselectivity control are currently underway.

Experimental Section

General Remarks: All solvents were purified by standard procedures. The starting materials were obtained from commercial suppliers and were used without purification. Only benzaldehyde had to be distilled prior to usage. Ag_2O was freshly prepared according to Helferich and Klein.[37] 5-Hydroxy-1,4-naphthoquinone (juglone) was synthesized by methods described by Griffiths[11] and Jesaitis,[10] 5-methoxy-1,4-naphthoquinone by a method described by Garden.[12] Products were purified by recrystallization or column chromatography. Thin-layer chromatography (TLC): Merck F_{254} silica gel plates; detection by UV (254 and 366 nm). Preparative column chromatography: Merck 60 silica gel (0.063−0.200 mm) with cyclohexane (CH)/ethyl acetate (EA) solvent mixtures. M.p.: Büchi 510 or Wagner & Münz melting point apparatus; values uncorrected. IR: Perkin−Elmer 298 Infrared Spectrophotometer; KBr discs; $\tilde{\nu}$ in cm^{-1}. NMR: Bruker WM 300 (^1H NMR = 300 MHz. ^{13}C NMR = 75.5 MHz); δ in ppm, *J* in Hz; tetramethylsilane as internal standard. MS: Finnigan MAT 312 (EI, 70 eV, CI with NH_3) with SS 300 datasystem; values in *m/z* (%). GC-MS: Finnigan MAT 8230 (EI, 70 eV) with SS 300 datasystem or Varian Saturn 2 (ion-trap). Elemental analyses: Heraeus CHN-O-Rapid Elemental Analyzer. Photolyses: High-pressure mercury vapor lamps (Hanau TQ 150 or Philips HPK 125) or Rayonet photochemical reactor equipped with RPR-4190 lamps (λ = 419 ± 10 nm); Pyrex vessels; benzene from Baker (Baker analyzed grade), acetonitrile also from Baker (Baker grade).

3-Benzoyl-4-hydroxy-1-naphthyl Benzoate (9):[38] A mixture of **6f** (275 mg, 1.04 mmol), benzoic anhydride (215 mg, 0.95 mmol), and *p*-toluenesulfonic acid (30 mg) was heated under reflux for 2 h in 25 mL of benzene. The solution was stirred overnight at room temperature and directly chromatographed on silica gel, yielding 28 mg (7%) of **9** as a yellow/orange solid. M.p. 128−129 °C. ^1H NMR ($CDCl_3$): δ = 6.82 (s, 1 H, arom.), 7.41−7.44 (m, 2 H, arom.), 7.48−7.51 (m, 1 H, arom.), 7.55−7.60 (m, 1 H, arom.), 7.61−7.64 (m, 2 H, arom.), 7.66−7.69 (m, 1 H, arom.), 8.10 (d, *J* = 8.2 Hz, 1 H, arom.), 8.49 (d, *J* = 8.8 Hz, 1 H, arom.), 13.53 (s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 107.9 (CH, arom.), 111.4 (Cq, arom.), 121.7 (CH, arom.), 124.6 (CH, arom.), 126.0 (Cq, arom.), 126.6 (CH, arom.), 128.3 (CH, arom.), 128.8 (CH, arom.), 129.4 (Cq, arom.), 130.1 (CH, arom.), 131.5 (4 CH, arom.), 138.1 (Cq, arom.), 142.6 (Cq, arom.), 158.7 (Cq, COO), 200.9 (Cq, CO) ppm. MS (CI): *m/z* (%) = 386 $[M + NH_3]^+$ (59), 369 $[M]^+$ (100), 105 $[PhCO]^+$ (38). IR (KBr): $\tilde{\nu}$ = 3441 (OH), 2929 (CH), 1736 (COO), 1614 (CO), 1449 (C=C), 1264, 1085, 1024, 762, 703 cm^{-1}.

Photochemical Acylations. General Procedures. Method A: The quinone (45 mmol) and the aldehyde (345 mmol) were dissolved in 240 mL of benzene. The solution was carefully degassed, by passing a stream of argon through the solution (ca. 15 min), and irradiated at room temperature for 5 d. The reaction was monitored by TLC or GC. The solvent and excess aldehyde were removed under vacuum, and the residue was purified by column chromatography or by recrystallization from ethanol/*n*-hexane. **Method B:** A solution of the quinone (45 mmol), the aldehyde (345 mmol), and benzophenone (2.5 mmol) in 240 mL of benzene was carefully degassed with argon (ca. 15 min) and irradiated for 5 d at room temperature. After evaporation of the solvent and excess aldehyde, the residue was purified by column chromatography or by recrystallization from ethanol/*n*-hexane.

1-(1,4-Dihydroxy-2-naphthyl)-1-propanone (6a): Method A was used. Compounds **3** (7.00 g, 44.3 mmol) and **5a** (25.0 mL, 346.5 mmol) in 220 mL of benzene gave 7.60 g (79%) of **6a** as yellow crystals. R_f = 0.18 (CH/EA, 4:1). ^1H NMR ([D$_6$]DMSO): δ = 1.25 (t, *J* = 7.2 Hz, 3 H, CH_3), 3.04 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 7.09 (s, 1 H, arom.), 7.52 (t, *J* = 6.9 Hz, 1 H, arom.), 7.62 (t, *J* = 6.9 Hz, 1 H, arom.), 8.15 (d, *J* = 8.3 Hz, 1 H, arom.), 8.34 (d, *J* = 8.3 Hz, 1 H, arom.), 9.30 (s, 1 H, OH), 10.87 (s, 1 H, OH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 8.3 (CH_3), 31.8 (CH_2), 104.3 (CH, arom.), 112.0 (Cq, arom.), 122.3 (CH, arom.), 123.9 (CH, arom.), 125.7 (Cq, arom.), 126.0 (CH, arom.), 128.9 (CH, arom.), 129.9 (Cq, arom.), 144.8 (Cq, arom.), 155.2 (Cq, arom.), 206.5 (Cq, CO) ppm. MS (EI): *m/z* (%) = 216 $[M]^+$ (100), 198 $[M - H_2O]^+$ (25), 187 $[212 - C_2H_5]^+$ (67), 159 $[M - C_3H_5O]^+$ (5), 131 $[159 - CO]^+$ (15), 103 $[131 - CO]^+$ (15), 77 $[C_6H_5]^+$ (8), 51 $[C_4H_3]^+$ (6), 39 $[C_3H_3]^+$ (5). IR (KBr): $\tilde{\nu}$ = 3340 (OH), 2880−3080 (CH), 1630 (CO), 1590−1610 (C=C), 1470, 1460, 1400, 1310, 1210, 1140, 1070, 1040, 990, 850 (CH), 810 (CH), 770 (CH), 720 (CH) cm^{-1}. $C_{13}H_{12}O_3$ (216.24): calcd. C 72.21 H 5.59; found C 71.96, H 5.85.

1-(1,4-Dihydroxy-2-naphthyl)-1-butanone (6b): Method A was used. Compounds **3** (2.90 g, 18.3 mmol) and **5b** (8.30 mL, 143.9 mmol) in 100 mL of benzene gave 3.27 g (78%) of **6b** as yellow crystals. M.p. 142 °C (ethanol/*n*-hexane) (ref.[13a] 141−143 °C). R_f = 0.23 (CH/EA, 4:1). ^1H NMR ([D$_6$]DMSO): δ = 0.99 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.72 (qt, *J* = 7.4, 7.2 Hz, 2 H, CH_2CH_3), 3.03 (t, *J* = 7.2 Hz, 2 H, $COCH_2$), 7.15 (s, 1 H, arom.), 7.62 (ddd, *J* = 8.3, 6.0, 1.3 Hz, 1 H, arom.), 7.72 (ddd, *J* = 8.3, 6.0, 1.3 Hz, 1 H, arom.), 8.13 (ddd, *J* = 8.3, 0.5, 0.7 Hz, 1 H, arom.), 8.31 (ddd, *J* = 8.3, 0.5, 0.7 Hz, 1 H, arom.), 9.77 (s, 1 H, OH), 10.74 (s, 1 H, OH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 13.6 (CH_3), 17.3 (CH_2), 40.0 (br., CH_2), 104.4 (CH, arom.), 112.1 (Cq, arom.), 122.1 (CH, arom.), 123.6 (CH, arom.), 125.1 (Cq, arom.), 126.3 (CH, arom.), 129.2 (CH, arom.), 129.4 (Cq, arom.), 144.6 (Cq, arom.), 154.3 (Cq, arom.), 206.5 (Cq, CO) ppm. MS (EI): *m/z* (%) = 230 $[M]^+$ (83), 212 $[M - H_2O]^+$ (13), 197 $[212 - CH_3]^+$ (50), 187 $[M - C_3H_7]^+$ (100), 159 $[M - C_4H_7O]^+$ (12), 131 $[159 - CO]^+$ (25), 103 $[131 - CO]^+$ (22), 77 $[C_6H_5]^+$ (16), 51 $[C_4H_3]^+$ (5), 39 $[C_3H_3]^+$ (10). IR (KBr): $\tilde{\nu}$ = 3320 (OH), 2860−3040 (CH), 1620 (CO), 1590 (C=C), 1460, 1390, 1370, 1320, 1290, 1200, 1130, 1070, 1040, 870

(CH), 770 (CH), 710 (CH) cm^{-1}. $C_{14}H_{14}O_3$ (230.26): calcd. C 73.03, H 6.13; found C 73.01 H 6.27.

(4-Chlorophenyl)(1,4-dihydroxy-2-naphthyl)methanone (6c): Method B was used. Compound **3** (5.3 g, 33.3 mmol), benzophenone (340 mg, 1.9 mmol), and **5c** (36.6 g, 260.0 mmol) in 180 mL of benzene gave 5.8 g (58%) of **6c** as an orange solid. ^{1}H NMR ($CDCl_3$/[D_6]DMSO): δ = 6.85 (s, 1 H, arom.), 7.61−7.81 (m, 6 H, arom.), 8.15 (d, *J* = 8.1 Hz, 1 H, arom.), 8.36 (d, *J* = 8.1 Hz, 1 H, arom.), 9.77 (s, 1 H, OH), 11.58 (s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$/[D_6]DMSO): δ = 106.7 (CH, arom.), 113.2 (Cq, arom.), 122.6 (CH, arom.), 124.1 (CH, arom.), 127.0 (CH, arom.), 127.7 (Cq, arom.), 128.3 (Cq, arom.), 128.9 (2 CH, arom.), 129.6 (Cq, arom.), 129.9 (CH, arom.), 131.0 (2 CH, arom.), 137.0 (Cq, arom.), 145.1 (Cq, arom.), 154.8 (Cq, arom), 199.4 (Cq, CO) ppm. MS (EI): *m*/*z* (%) = 298 $[M]^+$ (62), 262 $[M - Cl]^+$ (32), 261 $[M - HCl]^+$ (47), 187 $[M - C_6H_4Cl]^+$ (51), 186 $[M - C_6H_5Cl]^+$ (73), 159 $[M - C_7H_4Cl]^+$ (46), 158 $[M - C_7H_5Cl]^+$ (70), 130 $[158 - H_3O]^+$ (80), 111 $[139 - CO]^+$ (100), 76 $[C_6H_4]^+$ (69). IR (KBr): ṽ = 3280 (OH), 3000−3100 (CH), 1920, 1620 (CO), 1570 (C=C), 1540, 1390, 1280, 1160, 1120, 1070 (CCl), 990, 750−840 (CH), 720 cm^{-1}. $C_{17}H_{11}ClO_3$ (298.73): calcd. C 68.35, H 3.71; found C 67.96, H 3.79.

4-[(1,4-Dihydroxy-2-naphthyl)carbonyl]benzonitrile (6d): Method A was used. Compounds **3** (2.63 g, 16.6 mmol) and **5d** (15.0 g, 114.4 mmol) in 90 mL of benzene gave 3.56 g (63%) of **6d** as red, cubic crystals. ^{1}H NMR ($CDCl_3$/[D_6]DMSO): δ = 6.78 (s, 1 H, arom.), 7.53−7.60 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1 H, arom.), 7.63−7.70 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1 H, arom.), 7.80−7.89 (m, 4 H, arom.), 8.17 (d, *J* = 8.3 Hz, 1 H, arom.), 8.42 (d, *J* = 8.3 Hz, 1 H, arom.), 11.85 (s, 1 H, OH), not observed (1 H, OH) ppm. ^{13}C NMR ($CDCl_3$/[D_6]DMSO): δ = 106.0 (CH, arom.), 111.5 (Cq, arom.), 114.4 (Cq, CN), 118.0 (Cq, arom.), 122.4 (CH, arom.), 124.2 (CH, arom.), 125.6 (Cq, arom.), 126.3 (CH, arom.), 129.4 (2 CH, arom.), 129.9 (CH, arom.), 130.3 (Cq, arom.), 131.9 (2 CH, arom.), 142.2 (Cq, arom.), 144.9 (Cq, arom.), 157.6 (Cq, arom.), 198.7 (Cq, CO) ppm. MS (EI): *m*/*z* (%) = 289 $[M]^+$ (100), 187 $[M - C_7H_4N]^+$ (67), 158 $[187 - CHO]^+$ (61), 130 $[158 - CO]^+$ (96), 102 $[130 - CO]^+$ (90), 76 $[C_6H_4]^+$ (83), 51 $[C_4H_3]^+$ (92). IR (KBr): ṽ = 3380 (OH), 3080 (CH), 2220 (C≡N), 1630 (CO), 1590 (C=C), 1560, 1470, 1390, 1300, 1250, 1120, 1020, 990, 760−850 (CH), 720 cm^{-1}. $C_{18}H_{11}NO_3$ (289.29): calcd. C 74.73, H 3.83, N 4.84; found C 74.38, H 3.86, N 4.73.

4-[(1,4-Dihydroxy-2-naphthyl)carbonyl]benzaldehyde (6e): Method B was used. Compound **3** (3.80 g, 24 mmol), benzophenone (260 mg, 1.4 mmol), and **5e** (16.0 g, 119.3 mmol) in 120 mL acetonitrile gave 2.95 g (42%) of **6e** as an orange solid. ^{1}H NMR ([D_6]DMSO): δ = 6.80 (s, 1 H, arom.), 7.65 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1 H, arom.), 7.75 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1 H, arom.), 7.89−8.18 (m, 5 H, arom.), 8.38 (d, *J* = 8.3 Hz, 1 H, arom.), 9.77 (s, 1 H, OH), 10.17 (s, 1 H, CHO), 11.45 (s, 1 H, OH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 106.1 (CH, arom.), 112.3 (Cq, arom.), 122.1 (CH, arom.), 123.7 (CH, arom.), 125.1 (Cq, arom.), 126.9 (CH, arom.), 129.1 (2 CH, arom.), 129.3 (Cq, arom.), 129.5 (2 CH, arom.), 130.0 (CH, arom.), 137.7 (Cq, arom.), 142.7 (Cq, arom.), 144.5 (Cq, arom.), 154.8 (Cq, arom.), 193.2 (Cq, CHO), 199.7 (Cq, CO) ppm. MS (EI): *m*/*z* (%) = 292 $[M]^+$ (100), 263 $[M - CHO]^+$ (21), 235 $[263 - CO]^+$ (2), 207 $[235 - CO]^+$ (3), 186 $[M - C_7H_6O]^+$ (52), 158 $[M - C_8H_6O_2]^+$ (17), 130 $[158 - CO]^+$ (32), 102 $[130 - CO]^+$ (24), 77 $[C_6H_5]^+$ (34), 51 $[C_4H_3]^+$ (17), 39 $[C_3H_3]^+$ (3). IR (KBr): ṽ = 3300 (OH), 2740−3050 (CH), 1670 and 1630 (CO), 1560−1600 (C=C), 1490, 1460, 1390, 1300−1350, 1250, 1200, 1160, 1110, 1100, 1070, 1020, 990, 840, 750−800 (CH), 720, 710 cm^{-1}. $C_{18}H_{12}O_4$ (292.29): calcd. C 73.97, H 4.14; found C 73.81, H 4.16.

(1,4-Dihydroxy-2-naphthyl)(phenyl)methanone (6f): Method A was used. Compounds **3** (2.34 g, 14.8 mmol) and **5f** (12.9 mL, 127.6 mmol) in 70 mL of benzene gave 2.9 g (74%) of **6f** as red crystals (after further sublimation as yellow needles). M.p. 125 °C (ethanol/*n*-hexane) (ref.[13a] 124−126 °C). R_f = 0.26 (CH/EA, 4:1). ^{1}H NMR ([D_6]DMSO): δ = 6.94 (s, 1 H, arom.), 7.50−7.90 (m, 7 H, arom.), 8.17 (d, *J* = 8.2 Hz, 1 H, arom.), 8.39 (d, *J* = 8.2 Hz, 1 H, arom.), 9.76 (s, 1 H, OH), 11.26 (s, 1 H, OH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 106.6 (CH, arom.), 112.5 (Cq, arom.), 122.2 (CH, arom.), 123.7 (CH, arom.), 125.3 (Cq, arom.), 126.5 (CH, arom.), 128.4 (2 CH, arom.), 128.7 (2 CH, arom.), 129.3 (Cq, arom.), 129.5 (CH, arom.), 131.7 (CH, arom.), 137.9 (Cq, arom.), 144.6 (Cq, arom.), 154.9 (Cq, arom.), 200.5 (Cq, CO) ppm. MS (EI): *m*/*z* (%) = 264 $[M]^+$ (100), 186 $[M - C_6H_6]^+$ (56), 158 $[186 - CO]^+$ (14), 130 $[158 - CO]^+$ (32), 102 $[130 - CO]^+$ (27), 77 $[C_6H_5]^+$ (50), 51 $[C_4H_3]^+$ (23), 39 $[C_3H_3]^+$ (3). IR (KBr): ṽ = 3260 (OH), 3040 (CH), 1620 (CO), 1540−1570 (C=C), 1540, 1450, 1380, 1290, 1240, 1150, 1060, 650−810 (CH) cm^{-1}. $C_{17}H_{12}O_3$ (264.27): calcd. C 77.26, H 4.58; found C 77.68, H 4.62.

(3-Benzoyl-1,4-dihydroxy-2-naphthyl)(phenyl)methanone (7): This compound was obtained as a side product of **6f**, as 785 mg (14%) of light yellow needles. Compound **7** (40 mg, 36%) was independently obtained after irradiation of **6f** (82 mg, 0.28 mmol) and **5f** (1.0 mL, 9.9 mmol) in 5 mL of benzene. M.p. 144−145 °C. R_f = 0.44 (CH/EA, 4:1). ^{1}H NMR ([D_6]DMSO): δ = 7.30−7.80 (m, 12 H, arom.), 8.26 (dd, *J* = 6.3, 3.2 Hz, 2 H, arom.), 9.55 (s, 2 H, OH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 121.3 (2 Cq, arom.), 122.9 (2 CH, arom.), 127.2 (2 Cq, arom.), 127.3 (2 CH, arom.), 128.2 (4 CH, arom.), 129.1 (4 CH, arom.), 132.6 (2 CH, arom.), 138.2 (2 Cq, arom.), 144.6 (2 Cq, arom.), 196.3 (2 Cq, CO) ppm. MS (EI): *m*/*z* (%) = 368 $[M]^+$ (95), 350 $[M - H_2O]^+$ (100), 289 (7), 263 $[289 - C_2H_2]^+$ (2), 233 (2), 205 $[233 - CO]^+$ (3), 178 $[205 - C_2H_3]^+$ (5), 152 $[178 - C_2H_2]^+$ (2), 105 $[C_7H_5O]^+$ (27), 77 $[C_6H_5]^+$ (51), 51 $[C_4H_3]^+$ (18), 39 $[C_3H_3]^+$ (2). IR (KBr): ṽ = 3300 (OH), 3060 (CH), 1730, 1620 (CO), 1570−1610 (C=C), 1490, 1440, 1240, 1160−1180, 1030, 1010, 990, 830, 720−770 (CH), 690 cm^{-1}. $C_{24}H_{16}O_4$ (368.37): calcd. C 78.25, H 4.38; found C 77.95, H 4.60.

1-(1,4-Dihydroxy-8-methoxy-2-naphthyl)-1-butanone (10b): Method B was used. Compound **4** (1.72 g, 9.2 mmol), benzophenone (35 mg, 0.2 mmol), and **5b** (4.1 mL, 71.3 mmol) in 50 mL of benzene gave 900 mg (38%) of **10b** as dark yellow crystals. R_f = 0.18 (CH/EA 4:1). ^{1}H NMR ($CDCl_3$): δ = 1.02 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.79 (qt, *J* = 7.3 Hz, 2 H, CH_2CH_3), 2.98 (t, *J* = 7.3 Hz, 2 H, $COCH_2$), 4.03 (s, 3 H, OCH_3), 6.92 (dd, *J* = 7.9, 1.0 Hz, 1 H, arom.), 7.16 (s, 1 H, arom.), 7.51 (dd, *J* = 7.9, 8.4 Hz, 1 H, arom.), 7.81 (dd, *J* = 8.4, 1.0 Hz, 1 H, arom.), not observed (2 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.9 (CH_3), 18.2 (CH_2), 41.7 ($COCH_2$), 56.3 (OCH_3), 106.4 (CH, arom.), 106.9 (CH, arom.), 113.6 (Cq, arom.), 115.1 (CH, arom.), 116.7 (Cq, arom.), 129.3 (CH, arom.), 132.3 (Cq, arom.), 144.2 (Cq, arom.), 157.0 (Cq, arom.), 159.2 (Cq, arom.), 205.14 (Cq, CO) ppm. MS (EI): *m*/*z* (%) = 260 $[M]^+$ (30), 243 $[M - OH]^+$ (4), 227 $[M - CH_5O]^+$ (4), 217 $[M - C_2H_3O]^+$ (100), 202 $[217 - CH_3]^+$ (13), 174 $[202 - CO]$ (4), 161 $[202 - C_3H_5]$ (3), 146 $[174 - CO]^+$ (4), 131 $[174 - C_2H_3O]$ (4), 118 $[146 - CO]$ (9), 103 $[131 - CO]$ (4), 89 $[118 - CHO]$ (4), 77 $[C_6H_5]^+$ (4), 51 $[C_4H_3]^+$ (2), 39 $[C_3H_3]^+$ (7). IR (KBr): ṽ = 3300 (OH), 2860−3100 (CH), 1620−1640 (CO), 1600 (C=C), 1510, 1480, 1430, 1390, 1340, 1300, 1250, 1230, 1190, 1160, 1080, 1040, 1010, 890, 870, 810 (CH), 750 (CH), 730 (CH), 690 cm^{-1}. $C_{15}H_{16}O_4$ (260.29): calcd. C 69.22, H 6.20; found C 69.05, H 6.31.

1-(1,4-Dihydroxy-5-methoxy-2-naphthyl)-1-butanone (11b): Minor regioisomer; 551 mg (23%) as a yellow solid. R_f = 0.23 (CH/EA, 4:1). ^{1}H NMR ($CDCl_3$): δ = 1.04 (t, J = 7.4 Hz, 3 H, CH_3), 1.91 (qt, J = 7.4 Hz, 2 H, CH_2CH_3), 2.98 (t, J = 7.4 Hz, 2 H, $COCH_2$), 4.07 (s, 3 H, OCH_3), 6.99 (dd, J = 7.9, 0.7 Hz, 1 H, arom.), 7.05 (s, 1 H, arom.), 7.41 (dd, J = 7.9, 8.3 Hz, 1 H, arom.), 8.08 (dd, J = 8.3, 0.7 Hz, 1 H, arom.), 8.81 (s, 1 H, OH), 10.84 (s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.9 (CH_3), 17.9 (CH_2), 40.8 ($COCH_2$), 56.3 (OCH_3), 106.4 (CH, arom.), 108.1 (CH, arom.), 113.4 (Cq, arom.), 118.2 (CH, arom.), 119.1 (Cq, arom.), 126.0 (CH, arom.), 127.8 (Cq, arom.), 145.5 (Cq, arom.), 154.6 (Cq, arom.), 155.6 (Cq, arom.), 206.6 (Cq, CO) ppm. MS (EI): *m/z* (%) = 260 $[M]^+$ (100), 242 $[M - H_2O]^+$ (37), 227 $[M - CH_5O]^+$ (50), 217 $[M - C_2H_3O]^+$ (38), 199 $[217 - H_2O]^+$ (5), 189 $[M - C_4H_7O]^+$ (16), 174 $[189 - CH_3]^+$ (8), 161 $[189 - CO]^+$ (5), 131 $[174 - C_2H_3O]^+$ (4), 121 (13), 102 $[131 - CHO]^+$ (4), 89 (9), 63 (3), 53 (2), 39 $[C_3H_3]^+$ (10). IR (KBr): ṽ = 3380 (OH), 2820−3060 (CH), 1640 (CO), 1590 (C=C), 1570, 1460, 1430, 1380, 1230−1250, 1170, 1060, 880, 810 (CH), 750 (CH), 700 (CH) cm^{-1}. $C_{15}H_{16}O_4$ (260.29): calcd. C 69.22, H 6.20; found C 69.16, H 6.20.

1-(1,4-Dihydroxy-8-methoxy-2-naphthyl)(phenyl)methanone (10f): Method A was used. Compounds **4** (192 mg, 1.0 mmol) and **5f** (2.0 mL, 19.8 mmol) in 22 mL benzene gave 42 mg (14%) of **10f** as a dark orange solid. M.p. 158−160 °C. ^{1}H NMR ($CDCl_3$): δ = 4.03 (s, 3 H, OCH_3), 6.91 (s, 1 H, arom.), 6.93 (d, J = 7.5 Hz, 1 H, arom.), 7.44 (d, J = 7.5 Hz, 2 H, arom.), 7.53 (d, J = 8.2 Hz, 2 H, arom.), 7.75 (d, J = 7.5 Hz, 2 H, arom.), 7.77 (d, J = 8.2 Hz, 1 H, arom.), 12.17 (br, 1 H, OH), not observed (1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 56.3 (CH_3), 106.7 (CH, arom.), 109.6 (CH, arom.), 115.0 (CH, arom.), 116.3 (Cq, arom.), 128.8 (CH, arom.), 129.2 (CH, arom.), 129.5 (CH, arom.), 131.9 (Cq, arom.), 133.2 (CH, arom.), 134.3 (CH, arom.), 135.0 (CH, arom.), 138.5 (Cq, arom.), 142.7 (Cq, arom.), 155.1 (Cq, arom.), 158.5 (Cq, arom.), 198.9 (Cq, CO) ppm. MS (CI): *m/z* (%) = 294 $[M]^+$ − IR (KBr): ṽ = 3360 (OH), 1625 (CO), 1416, 1254, 1045, 890, 727, 685 cm^{-1}.

1-(1,4-Dihydroxy-5-methoxy-2-naphthyl)(phenyl)methanone (11f): Major regioisomer; 108 mg (36%) as red crystals. R_f = 0.37 (CH/EA 7:3). ^{1}H NMR ($CDCl_3$): δ = 4.04 (s, 3 H, OCH_3), 6.93 (s, 1 H, arom.), 6.99 (dd, J = 7.9, 0.7 Hz, 1 H, arom.), 7.42 (dd, J = 7.9, 8.3 Hz, 1 H, arom.), 7.45−7.60 (m, 3 H, arom.), 7.69−7.74 (m, 2 H, arom.), 8.14 (dd, J = 8.3, 0.9 Hz), 8.74 (s, 1 H, OH), 11.03 (s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 56.3 (CH_3), 109.0 (CH, arom.), 109.2 (CH, arom.), 113.2 (Cq, arom.), 118.3 (CH, arom.), 119.3 (Cq, arom.), 126.0 (CH, arom.), 127.8 (Cq, arom.), 128.3 (2 CH, arom.), 129.0 (2 CH, arom.), 131.6 (CH, arom.), 138.2 (Cq, arom.), 145.2 (Cq, arom.), 155.7 (Cq, arom.), 155.9 (Cq, arom.), 201.2 (Cq, CO) ppm. MS (EI): *m/z* (%) = 294 $[M]^+$ (100), 279 $[M - CH_3]^+$ (12), 261 $[279 - H_2O]^+$ (1), 233 $[261 - CO]^+$ (7), 216 $[M - C_6H_6]^+$ (72), 205 $[233 - CO]^+$ (3), 188 $[216 - CO]^+$ (23), 173 $[216 - C_2H_3O]^+$ (15), 160 $[188 - CO]^+$ (39), 145 $[160 - CH_3]^+$ (12), 131 $[160 - CHO]^+$ (9), 118 $[145 - C_2H_3]^+$ (8), 105 $[C_7H_5O]^+$ (13), 89 $[118 - CHO]^+$ (13), 77 $[C_6H_5]^+$ (47), 51 $[C_4H_3]^+$ (17), 39 $[C_3H_3]^+$ (5). IR (KBr): ṽ = 3400 (OH), 2830−3080 (CH), 1640 (CO), 1570−1600 (C=C), 1570, 1460, 1440, 1390, 1330, 1220−1260, 1170, 1070, 1010, 890 (CH), 800−820 (CH), 750 (CH), 690−710 (CH) cm^{-1}. $C_{18}H_{14}O_4$ (294.31): calcd. C 73.46, H 4.79; found C 73.44, H 4.94.

(3-Benzoyl-1,4-dihydroxy-8-methoxy-2-naphthyl)(phenyl)methanone (12): This compound was obtained as a side product of **10f** and **11f**; 45 mg (11%), as orange cubes. R_f = 0.25 (CH/EA, 7:3). ^{1}H NMR ($CDCl_3$): δ = 4.06 (s, 3 H, OCH_3), 7.08−7.62 (m, 12 H, arom.), 8.07 (dd, J = 8.5, 0.9 Hz, 1 H, arom.), 9.94 (s, 1 H, OH), not observed (1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 56.5 (CH_3), 109.1 (CH, arom.), 116.8 (Cq, arom.), 117.3 (Cq, arom.), 117.4 (CH, arom.), 117.6 (Cq, arom.), 127.8 (2 CH, arom.), 127.9 (2 CH, arom.), 128.4 (2 CH, arom.), 128.9 (2 CH, arom.), 129.2 (Cq, arom.), 129.3 (CH, arom.), 132.1 (2 CH, arom.), 132.5 (2 CH, arom.), 138.6 (Cq, arom.), 139.0 (Cq, arom.), 147.3 (Cq, arom.), 149.8 (Cq, arom.), 156.9 (Cq, arom.), 195.4 (Cq, CO), 196.2 (Cq, CO) ppm. MS (EI): *m/z* (%) = 398 $[M]^+$ (37), 381 $[M - OH]^+$ (42), 380 $[M - H_2O]^+$ (53), 363 $[380 - OH]^+$ (46), 349 $[380 - OCH_3]^+$ (39), 334 $[363 - CHO]^+$ (41), 305 $[334 - CHO]^+$ (47), 275 $[305 - OCH_2]^+$ (47), 274 $[305 - OCH_3]^+$ (39), 189 $[M - C_6H_4CO]^+$ (48), 105 $[C_7H_5O]^+$ (83), 77 $[C_6H_5]^+$ (100). IR (KBr): ṽ = 3340 (OH), 2820−3080 (CH), 1620−1640 (CO), 1570−1600 (C=C), 1450, 1390, 1320, 1240, 1170, 1070, 1030, 990, 930, 890, 840, 700−770 (CH), 670 cm^{-1}. $C_{25}H_{18}O_5$ (398.41): calcd. C 75.36, H 4.56; found C 75.23, H 4.71.

Oxidation. General Procedure: The acylated photoproduct (15 mmol) was dissolved in 150 mL of dry ether. Anhydrous sodium sulfate (10.0 g, 70 mmol) was added, followed in small portions by freshly prepared Ag_2O[37] (4.0 g, 17 mmol). The suspension was stirred for 1 h at room temperature, filtered, and concentrated to a smaller volume. On cooling, the acylated quinone crystallized, was filtered off, and dried under vacuum.

2-Propionyl-1,4-naphthoquinone (8a): The General Procedure was used. Compound **6a** (2.1 g, 9.7 mmol), sodium sulfate (10.6 g), and Ag_2O (3.9 g) in 125 mL of ether gave 1.96 g (94%) of **8a** as a yellow solid. M.p. 84−85 °C. ^{1}H NMR ($CDCl_3$): δ = 1.19 (t, J = 7.2 Hz, 3 H, CH_3), 2.97 (q, J = 7.2 Hz, 2 H, CH_2CH_3), 7.09 (s, 1 H, olefin.), 7.77−7.82 (m, 2 H, arom.), 8.06−8.14 (m, 2 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 7.6 (CH_3), 36.9 (CH_2), 126.3 (CH, arom.), 126.9 (CH, arom.), 131.8 (2 Cq, arom.), 134.3 (CH, arom.), 134.5 (CH, arom.), 136.7 (CH, olefin.), 145.9 (Cq, olefin.), 183.4 (Cq, CO), 184.9 (Cq, CO), 201.2 (Cq, CO) ppm. MS (EI): *m/z* (%) = 215 $[M + 1]^+$ (80), 196 $[M - H_2O - 1]^+$ (46), 187 $[215 - CO]^+$ (34), 168 $[187 - H_2O - 1]^+$ (14), 157 $[M - C_3H_5O]^+$ (100), 129 $[157 - CO]^+$ (81), 101 $[129 - CO]^+$ (47), 76 $[C_6H_4]^+$ (19), 50 $[C_4H_2]^+$ (15), 39 $[C_3H_3]^+$ (7). IR (KBr): ṽ = 2850−3060 (CH), 1660−1680 (CO), 1590 (C=C), 1450, 1400, 1350, 1300, 1255, 1220, 1160, 1110, 940, 850, 775 (CH), 700 (CH) cm^{-1}. $C_{13}H_{10}O_3$ (214.22): calcd. C 72.89, H 4.71; found C 72.92, H 4.90.

2-Butyryl-1,4-naphthoquinone (8b): The General Procedure was used. Compound **6b** (1.6 g, 6.9 mmol), sodium sulfate (7.6 g), and Ag_2O (2.8 g) in 80 mL of ether gave 1.38 g (88%) of **8b** as dark yellow needles. M.p. 64−66 °C. ^{1}H NMR ($CDCl_3$): δ = 0.99 (t, J = 7.3 Hz, 3 H, CH_3), 1.72 (qt, J = 7.3 Hz, 2 H, CH_2CH_3), 2.92 (t, J = 7.3 Hz, 2 H, $COCH_2$), 7.07 (s, 1 H, olefin.), 7.77−7.82 (m, 2 H, arom.), 8.06−8.14 (m, 2 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.6 (CH_3), 17.1 (CH_2), 45.3 ($COCH_2$), 126.3 (CH, arom.), 126.8 (CH, arom.), 131.8 (2 Cq, arom.), 134.3 (CH, arom.), 134.5 (CH, arom.), 136.5 (CH, olefin.), 146.1 (Cq, olefin.), 183.4 (Cq, CO), 184.9 (Cq, CO), 200.7 (Cq, CO) ppm. MS (EI): *m/z* (%) = 229 $[M + 1]^+$ (92), 210 $[M - H_2O]^+$ (44), 200 $[M - CO]^+$ (26), 185 $[M - C_3H_7]^+$ (41), 157 $[M - C_4H_7O]^+$ (100), 129 $[157 - CO]^+$ (76), 101 $[129 - CO]^+$ (51), 76 $[C_6H_4]^+$ (22), 50 $[C_4H_2]^+$ (15), 39 $[C_3H_3]^+$ (40). IR (KBr): ṽ = 2800−3060 (CH), 1650 (CO), 1580 (C=C), 1440, 1390, 1340, 1285, 1240, 1150, 1100, 920, 770 (CH), 735 (CH), 700, 680 cm^{-1}. $C_{14}H_{12}O_3$ (228.25): calcd. C 73.67, H 5.30; found C 73.74, H 5.40.

2-Benzoyl-1,4-naphthoquinone (8f): The General Procedure was used. Compound **6f** (3.3 g, 12.5 mmol), sodium sulfate (10.0 g), and Ag_2O (3.36 g) in 100 mL of ether gave 2.0 g (53%) of **8f** as a yellow

Table 3. Crystal structure data for compounds **6f**, **7**, **10b**, **11f**, and **8b**

Compound	**6f**	**7**	**10b**	**11f**	**8b**
Empirical formula	$C_{17}H_{12}O_3$	$C_{24}H_{16}O_4$	$C_{15}H_{16}O_4$	$C_{18}H_{14}O_4$	$C_{14}H_{12}O_3$
Formula mass	264.27	368.37	260.28	294.29	228.24
Color	red	yellow	dark yellow	red	yellow
Size [mm]	0.3 × 0.2 × 0.1	0.2 × 0.1 × 0.1	0.5 × 0.4 × 0.2	0.6 × 0.2 × 0.5	0.5 × 0.2 × 0.1
T [K]	223(2)	293(2)	223(2)	223(2)	223(2)
a [Å]	9.607(2)	8.219(1)	7.627(1)	17.732(3)	4.823(1)
b [Å]	11.477(2)	8.971(1)	7.872(1)	7.245(1)	11.167(3)
c [Å]	13.582(2)	12.601(1)	11.641(1)	22.038(4)	11.271(2)
α [°]	114.61(1)	96.94(1)	71.29(1)	90	106.43(2)
β [°]	101.13(1)	98.97(1)	78.16(1)	90	98.17(2)
γ [°]	100.21(4)	92.96(1)	74.95(1)	90	95.81(2)
V [Å^3]	1279.0(4)	908.7(2)	633.58(13)	2831.2(8)	569.9(2)
Z	4	2	2	8	2
$d_{calcd.}$ [g/cm^3]	1.372	1.346	1.364	1.381	1.330
Crystal system	triclinic	triclinic	triclinic	orthorhombic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	*Pbca* (no. 61)	$P\bar{1}$ (no. 2)
No. refl. meas.	5468	3979	2838	2887	2597
No. uni. refl.	5194	3707	2594	2887	2310
No. obs. refl.[a]	3702	2908	2354	2017	1939
R	0.074	0.044	0.056	0.045	0.049
R_w	0.197	0.138	0.141	0.118	0.139
Largest diff. peak/hole [e/Å^3]	0.43/−0.41	0.22/−0.18	0.38/−0.35	0.21/−0.23	0.27/−0.29

[a] For $I > 2\sigma(I)$.

solid. M.p. 157–160 °C. ^{1}H NMR ($CDCl_3$): δ = 6.99 (s, 1 H, olefin.), 7.45–7.53 (m, 2 H, arom.), 7.60–7.67 (m, 1 H, arom.), 7.79–7.92 (m, 4 H, arom.), 8.08–8.16 (m, 2 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 126.5 (CH, arom.), 126.9 (CH, arom.), 128.9 (2 CH, arom.), 129.6 (2 CH, arom.), 131.9 (Cq, arom.), 134.4 (2 CH, arom.), 134.5 (CH, arom.), 135.6 (CH, olefin.), 147.2 (Cq, olefin.), 184.4 (Cq, CO), 191.9 (Cq, CO), 192.4 (Cq, C-11) ppm. MS (EI): *m*/*z* (%) = 262 $[M]^+$ (73), 246 $[M - H_2O]^+$ (2), 234 $[M - CO]^+$ (13), 206 $[234 - CO]^+$ (4), 186 $[M - C_6H_5]^+$ (9), 178 $[206 - CO]^+$ (3), 157 $[M - C_7H_5O]^+$ (3), 129 $[157 - CO]^+$ (7), 105 $[C_7H_5O]^+$ (100), 89 $[105 - H_2O]$ (2), 77 $[C_6H_5]^+$ (32), 51 $[C_4H_3]^+$ (17), 39 $[C_3H_3]^+$ (3). IR (KBr): $\tilde{\nu}$ = 3000–3080 (CH), 1650 (CO), 1560 (C=C), 1440, 1340, 1290, 1270, 1250, 1170, 1130, 1070, 975, 910, 895, 820, 795, 780 (CH), 770 (CH), 720 (CH), 695, 680, 670 cm^{-1}. $C_{17}H_{10}O_3$ (262.26): calcd. C 77.86, H 3.84; found C 77.84, H 3.83.

2-Butyryl-8-methoxy-1,4-naphthoquinone (13): The General Procedure was used. Compound **10b** (447 mg, 1.73 mmol), sodium sulfate (1.5 g) and Ag_2O (0.6 g) in 40 mL of ether gave 271 mg (55%) of **13** as a dark yellow solid. M.p. 100–102 °C. ^{1}H NMR ($CDCl_3$): δ = 0.97 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.72 (tq, J = 7.2, 7.4 Hz, 2 H, CH_2CH_3), 2.90 (t, J = 7.2, 7.4 Hz, 2 H, $COCH_2$), 4.03 (s, 3 H, OCH_3), 6.99 (s, 1 H, olefin.), 7.36 (dd, J = 6.2, 3.1 Hz, 1 H, arom.), 7.70–7.73 (m, 2 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.6 (CH_3), 17.1 (CH_2), 45.3 ($COCH_2$), 56.3 (OCH_3), 118.5 (CH, arom.), 119.0 (CH, arom.), 119.3 (Cq, arom.), 133.7 (CH, arom.), 133.8 (Cq, arom.), 135.5 (CH, olefin.), 148.4 (Cq, olefin.), 160.0 (Cq, arom.), 182.8 (Cq, CO), 185.1 (Cq, CO), 201.7 (Cq, CO) ppm.

X-ray Crystallographic Studies:[39] All data sets were collected with an Enraf Nonius CAD-4 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86,[40] structure refinement SHELX-93,[41] depiction SCHAKAL97.[42] Hydrogen atoms were calculated and refined as riding atoms. Crystal structure data and details are listed in Table 3.

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