Synthesis of Biaryl Compounds by Vinylogous Michael Reactions

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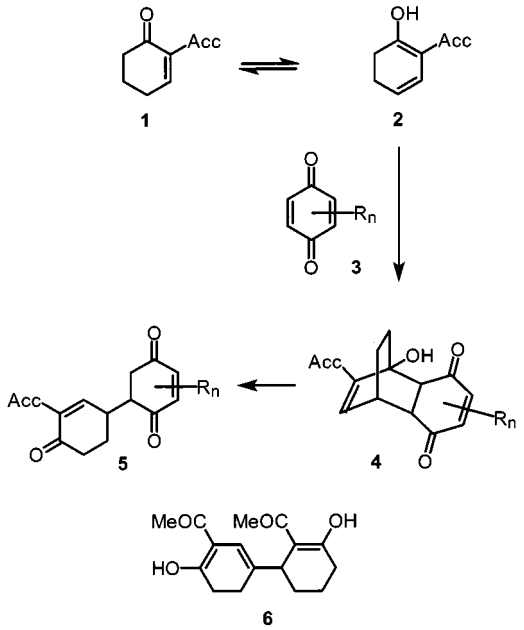
Acceptor-substituted cycloalkenones **1** undergo an iron(III)-catalyzed vinylogous Michael reaction – a sequence of enone–dienol tautomerism, [4+2]-cycloaddition, and retro-aldol reaction – with quinone derivatives **3**. A variety of products is obtained ranging from *meta*-terphenyl precursors **5** to dihydronaphthobenzofurans **7**. Reaction of 1,2-naphthoquinone (**3e**) with vinylogous donors **1** yields cross-coupled products **12**, which can be further converted into highly functionalized biaryl compounds **13** and **14**.

Introduction

Recently, we reported in short form on the iron(III)-catalyzed reaction of 2-acceptor-substituted cycloalkenones **1** with quinone derivatives **3** to give C−C-coupled products **5**, which can be converted by means of standard procedures to highly functionalized biaryl compounds.[1] Herein, we provide full experimental details and a complete discussion of the results presented in the earlier communication.

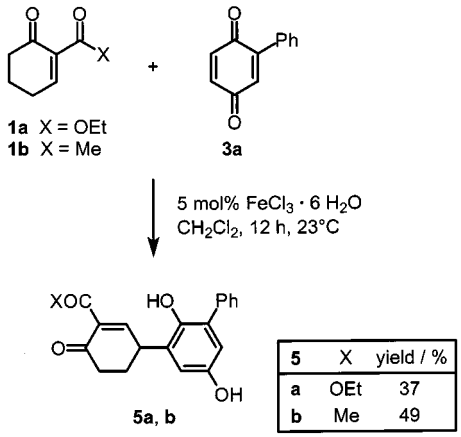


Scheme 1. Proposed mechanism for the vinylogous Michael reaction; Acc = acceptor group; structure of dimer **6**

Starting materials **1** show an unusual tautomerism with the dienol species **2** (Scheme 1).[2] The equilibrium between **1** and **2** can be catalyzed by $FeCl_3 \cdot 6H_2O$, and under these reaction conditions dienol tautomers **2** react as carbon nucleophiles at their γ-position with Michael acceptor molecules such as **3** to give C−C-coupled products **5** with a 1,7-dioxo constitution. In the absence of any acceptor akin to **3**, reaction of **2** with the enone tautomer **1** under the aforementioned conditions leads to dimeric products such as **6** (from **1b**, Acc = COMe).[2] We have named the conversion of **1** via **2** to **5** a vinylogous Michael reaction, since compound **2** is − compared to normal Michael donors,[3] which react as nucleophiles at their α-position − a vinylogous donor at its γ-position. Actually, we have some evidence that the vinylogous Michael reaction proceeds in a stepwise manner via a bicyclic intermediate **4**, which results from a [4+2]-cycloaddition between **2** and **3**.[4] Compound **4** has an aldol constitution, i.e. a hydroxy function vicinal to an acceptor group. Thus, under the reaction conditions, strained bicyclic intermediates **4** are readily converted in a retro-aldol reaction into the products **5** of a formally vinylogous Michael reaction.

Results and Discussion

In the presence of a catalytic amount of $FeCl_3 \cdot 6\,H_2O$, the vinylogous donors **1a** and **1b** tautomerize and then react with phenylbenzoquinone **3a** according to the vinylogous Michael reaction to give the cross-coupled products **5a** and **5b** (Scheme 2). The sequence of enone−dienol tautomeri-



5	X	yield / %
a	OEt	37
b	Me	49

Scheme 2. Reaction of vinylogous donors **1a**,**b** with phenylbenzoquinone **3a**

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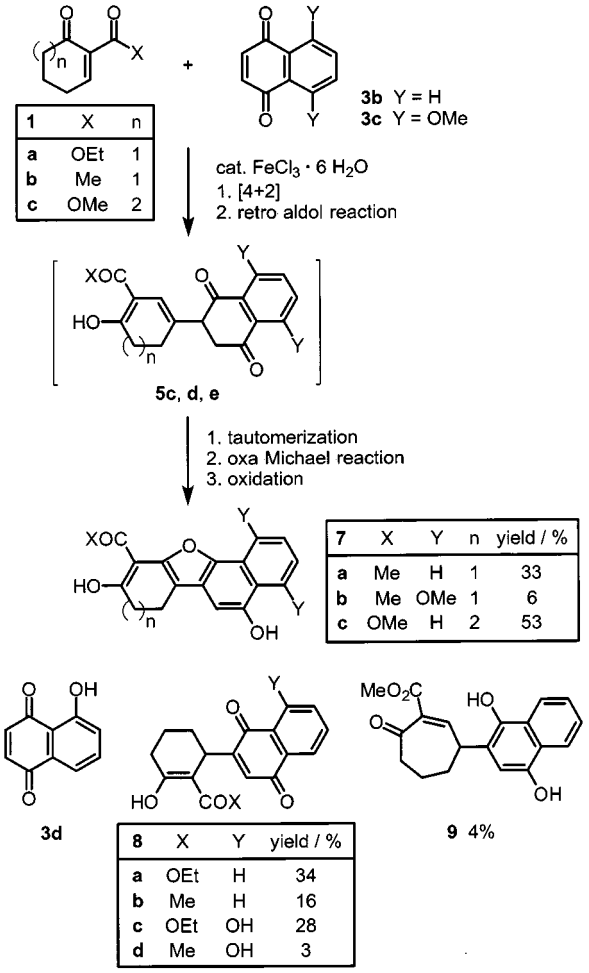


1	X	n
a	OEt	1
b	Me	1
c	OMe	2

7	X	Y	n	yield / %
a	Me	H	1	33
b	Me	OMe	1	6
c	OMe	H	2	53

8	X	Y	yield / %
a	OEt	H	34
b	Me	H	16
c	OEt	OH	28
d	Me	OH	3

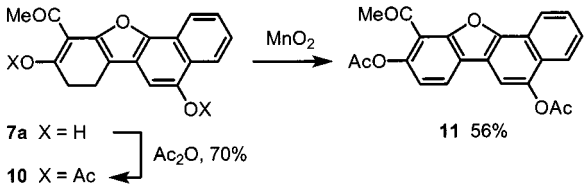
Scheme 3. Furan formation by reaction of vinylogous donors **1a**−**c** with 1,4-naphthoquinones **3b**−**d**; constitution of by-products **8a**−**d** and **9**

zation, [4+2]-cycloaddition, and retro-aldol reaction would formally lead to a species with an acceptor moiety having a cyclohexene-3,6-dione constitution. Under the reaction conditions, however, this moiety tautomerizes to the thermodynamically favoured hydroquinone system, as is found in compounds **5a** and **5b**. These products represent potential precursors for the synthesis of highly substituted *meta*-terphenyl compounds, since the cyclohexenone moiety can be oxidized to an aromatic system (vide infra).

Intermediates **5c**−**e** were generated in the iron(III)-catalyzed reactions of vinylogous donors **1b**−**c** with 1,4-naphthoquinone (**3b**) and its derivative **3c** (Scheme 3). Again, species **5c**−**e** tautomerized to the corresponding hydroquinones, which subsequently underwent an annulation reaction as a result of an oxa Michael addition to give dihydrofurans. These dihydrofurans were oxidized under the reaction conditions to the furan derivatives **7a**−**7c**, which were isolated as stable compounds by chromatography. The latter oxidation prevented a reversion of the oxa Michael reaction and can be explained by considering the aerobic reaction conditions together with the suitable catalytic system formed by the excess of quinone starting material in combination with the redox-active iron(II/III).[5] Compound **9** is the precursor of the oxa Michael addition leading to **7c** and was isolated as a by-product from the relevant reaction mixture.

The yields of **7a** and **7c** were moderate, while product **7b** was isolated only in very small amounts. In the case of **7a**, a side reaction led to by-product **8b**, which is formally the result of a reaction of **1b** in the β-position. This behavior can be rationalized in terms of a sequence of [2+2]-cycloaddition between donor **1b** and quinone **3b**, followed by retro Michael C−C bond cleavage.[6] Compounds with the same constitution pattern as **8b** were generated in the reactions of **1a** with **3b** and juglone (**3d**), as well as in the reaction of **1b** with juglone (**3d**). In these cases, products **8a**, **8c**, and **8d** were the only isolable materials in the reaction mixtures; no furan derivatives could be detected.[7] Quinones **3c** and **3d** are seemingly less active dienophiles in [4+2]-cycloadditions leading to furan derivatives **7**, possibly due to the deactivating influence of the donor substituents OH and OMe.

To exemplify the oxidation of a dienol moiety to an aromatic system, furan derivative **7b** was converted to the fully aromatic naphthobenzofuran **11** by treatment with MnO_2.[8] However, prior to oxidation, the phenolic OH groups were protected as acetates to prevent radical side reactions (Scheme 4).

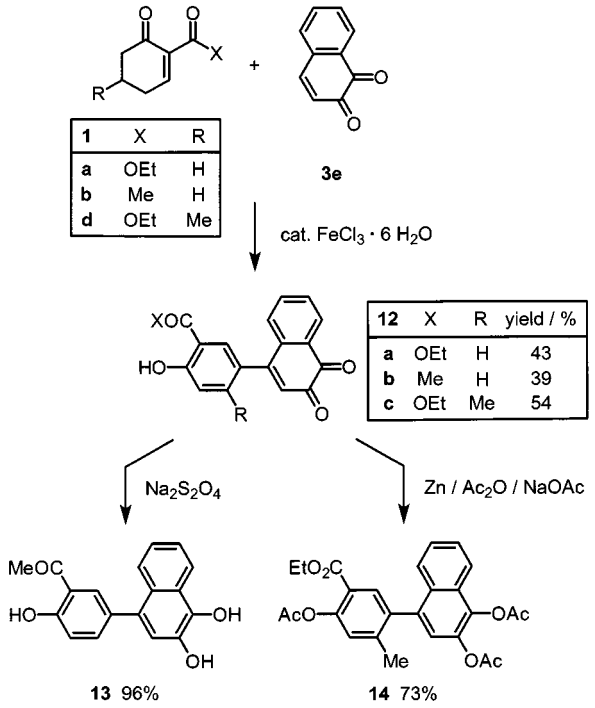


Scheme 4. Oxidative aromatization of furan derivative **7a**

The formation of compounds **7** and **8** illustrates that the oxidation state of the cross-coupled product cannot be predicted. In the context of biaryl synthesis, in situ oxidation of the donor (dienol) part of the product would be of particular interest. When vinylogous donors **1a**, **1b**, and **1d** were submitted to iron(III)-catalyzed reactions with 3- to 5-fold excesses of 1,2-naphthoquinone (**3e**), cross-coupled products **12a**−**c** were obtained in yields of 40−50% (Scheme 5). In compounds **12a**−**c**, the former donor and acceptor moieties are both fully oxidized. In such cases, biaryl synthesis is particularly simple since the 1,2-quinone moiety can be reduced very efficiently, as illustrated by the conversion of **12b** to **13** by treatment with aqueous $Na_2S_2O_4$ (Scheme 5).[9] Some unprotected 1,2-hydroquinones are sensitive to air. Compound **12c** was subjected to an alternative reduction protocol involving application of the system $Zn/Ac_2O/NaOAc$,[9] which led to the peracetylated product **14**. The preparation of **14** constitutes our first approach to compounds with an atropisomeric biaryl axis.[10]

Conclusion

Reactions of 2-acceptor-substituted cycloalkenones **1a**−**d** with quinone derivatives **3a**−**e** proceed in a vinylogous Michael fashion, involving a sequence of enone−dienol



Scheme 5. Biaryl synthesis by reaction of vinylogous donors **1a**,**b**,**d** with 1,2-naphthoquinone (**3e**); reductive aromatization of quinones **12a**,**c**

tautomerism, [4+2]-cycloaddition, and retro-aldol reaction. Only in a few cases can the primary coupling products **5a**,**b** be isolated. More typically, various other processes ensue, such as tautomerizations, annulation reactions, or oxidations, resulting in diverse final products such as dihydronaphthobenzofuran derivatives, for example, the precise natures of which are difficult to predict.

Only the reactions of 1,2-naphthoquinone (**3e**) with donors **1** lead to significant yields of the cross-coupled products **12**. The latter result is, however, of particular importance with respect to the synthesis of highly functionalized biaryl compounds, since species **12** can be reduced in one step to the respective hydroquinone derivatives **13** and **14**. This new approach to such materials, which are classically synthesized by, e.g., Pd-, Ni-, or Cu-mediated reactions,[11] is particularly simple. No special inert or anhydrous reaction conditions are required and the catalyst $FeCl_3 \cdot 6\,H_2O$ is a cheap and non-toxic material. Yields in the range 40−50% for the formation of compounds **12** (in a cascade of six single steps) are acceptable in view of the highly interesting constitutions of these materials.[12]

Experimental Section

General: Column chromatography was carried out on Merck silica gel (Type 60, 0.063−0.200 mm) with *tert*-butyl methyl ether (MTB) and hexanes (PE) as eluents. − ^{1}H NMR: Bruker DRX 500 (500 MHz), AM 400 (400 MHz), and AC 200 (200 MHz). − ^{13}C NMR: Bruker DRX 500 (125 MHz) and AC 200 (50 MHz). ^{1}H and ^{13}C resonances were assigned by means of DEPT, HMBC, HMQC, and H,H-COSY experiments. − MS: Varian MAT 711 and MAT 955Q (high resolution). − IR: Nicolet Magna IR 750. − Starting materials **3a**, **3b**, **3d**, and **3e** are commercially available and were used as purchased. Compounds **1a**,[13] **1b**,[14] **1c**,[4] and **3c**[15] were prepared according to literature procedures. Donor **1d** was synthesized according to an established procedure.[16] The syntheses and analytical data of compounds **5b**, **7a**, **11**, **12b**, and **13** were reported in our preliminary communication.[1]

Ethyl 4-Methyl-6-oxocyclohex-1-ene-1-carboxylate (1d): A solution of ethyl 4-methyl-2-oxocyclohexane-1-carboxylate (1.00 g, 5.43 mmol) in THF (1 mL) was added to a suspension of NaH (60% in mineral oil, 326 mg, 8.14 mmol; washed with pentane) in THF (14 mL) at 0 °C over a period of 15 min. PhSeCl (905 mg, 5.97 mmol) was then added in one portion and the mixture was stirred for 2 min. The resulting solution was carefully added to a mixture of MTB, hexane, and saturated aqueous $NaHCO_3$ solution (15 mL of each) at 0 °C. The organic layer was separated and the aqueous layer was extracted with MTB. The combined organic phases were washed with brine and dried with Na_2SO_4. Removal of all volatile materials left the crude selenide as a colorless resin. − ^{1}H NMR (200 MHz, $CDCl_3$) (mixture of two diastereoisomers): δ = 0.98 (d, *J* = 7.0 Hz, 3 H), 1.17−1.28 (m, 3 H), 1.54−1.78 (m, 2 H), 1.81−2.09 (m, 2 H), 2.07−2.22 (m, 1 H), 2.30−2.42 (m, 1 H), 2.51−2.63 (m, 1 H), 4.09−4.22 (m, 2 H), 7.23−7.42 (m, 3 H), 7.53−7.62 (m, 2 H). − An aqueous solution of hydrogen peroxide (35%, 1.05 g, 10.9 mmol) was added dropwise to a solution of the crude selenide in CH_2Cl_2 (15 mL). The resulting mixture was stirred at room temp. for 10 min and then poured into a mixture of aqueous Na_2CO_3 solution (10%, 5 mL) and CH_2Cl_2 (15 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by kugelrohr distillation (1 mbar, oven temp. 130 °C) to yield the title compound **1d** as a colorless oil (849 mg, 5.66 mmol, 86%) (mixture of dienol and keto tautomer, ratio 4:1 by ^{1}H NMR analysis). − ^{1}H NMR (200 MHz, $CDCl_3$): keto tautomer: δ = 1.08 (d, *J* = 6.5 Hz, 3 H), 1.31 (t, *J* = 7.5 Hz, 3 H), 2.08−2.35 (m, 3 H), 2.48−2.68 (m, 2 H), 4.25 (q, *J* = 7.5 Hz, 2 H), 7.63 (dd, *J* = 5.6 Hz, *J* = 2.7 Hz, 1 H); dienol tautomer: δ = 1.03−1.10 (d, *J* = 7.0 Hz, 3 H), 1.32 (t, *J* = 7.0 Hz, 3 H), 2.12−2.31 (m, 2 H), 2.55−2.61 (m, 1 H), 4.23 (q, *J* = 7.0 Hz, 2 H), 5.53 (dd, *J* = 9.6 Hz, *J* = 3.6 Hz, 1 H), 6.19 (dd, *J* = 9.6 Hz, *J* = 1.8 Hz, 1 H), 12.46 (s, 1 H).

Ethyl 3-(2,5-Dihydroxybiphenyl-3-yl)-6-oxocyclohex-1-ene-1-carboxylate (5a): A mixture of compound **1a** (100 mg, 0.600 mmol), 2-phenyl-1,4-benzoquinone (**3a**) (110 mg, 0.600 mmol), and $FeCl_3 \cdot 6H_2O$ (8.0 mg, 0.030 mmol) in CH_2Cl_2 (1.5 mL) was stirred for 12 h at room temp. After removal of the solvent and purification of the residue by twofold chromatography on SiO_2 [(i) PE/MTB, 2:1, R_f = 0.14; (ii) PE/EtOAc, 4:1, R_f = 0.17], **5a** was obtained as a yellowish resin (103 mg, 0.29 mmol, 49%). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.84−1.99 (m, 2 H, 5-H_2), 2.25−2.43 (m, 2 H, 4-H_2), 4.21 (td, *J* = 8.0 Hz, *J* = 5.2 Hz, 1 H, 3-H), 4.17−4.26 (m, 1 H, OC*H*H), 4.41−4.49 (m, 1 H, OCH*H*), 4.86 (br. s, 1 H, OH), 5.55 (d, *J* = 7.5 Hz, 1 H, 2-H), 6.66 (d, *J* = 2.4 Hz, 1 H, 4′-H or 6′-H), 6.83 (d, *J* = 2.5 Hz, 1 H, 4′-H or 6′-H), 7.26−7.30 (m, 1 H), 7.36−7.40 (m, 2 H), 7.72−7.76 (m, 2 H), 12.76 (s, 1 H, OH). − ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 14.3 (CH_3), 24.4 (CH_2), 27.3 (CH_2), 40.1 (CH), 60.7 (CH_2), 78.8 (CH), 97.6 (C), 110.4 (CH), 114.0 (CH), 123.7 (CH), 127.2 (CH), 128.1 (2 CH), 128.2 (2 CH), 132.6 (C), 136.6 (C), 150.0 (C), 150.3 (C), 172.4 (C), 177.1 (C). − IR (ATR): $\tilde{\nu}$ = 3427 cm^{-1} (m, br.), 1723 (m), 1646 (s), 1608 (m), 1576 (m), 1463 (m), 1420 (s), 1369 (m), 1323 (m), 1285 (s), 1249 (vs), 1237 (vs), 1204 (s), 1181 (s), 1076 (m), 1039 (m), 908 (m), 847 (m), 770

(m), 697 (m). − MS (EI, 70 eV): *m*/*z* (%) = 352 (6) [M$^+$], 306 (100) [M$^+$ − EtOH], 280 (8), 264 (15), 250 (8), 237 (15), 223 (24), 178 (11), 165 (14), 152 (8), 115 (8), 102 (8), 91 (7), 77 (9), 69 (17). − $C_{21}H_{20}O_5$: calcd. 352.1311; found 352.1311 (HRMS).

2-Acetyl-4-(2-acetyl-3-hydroxycyclohex-2-en-1-yl)cyclohexa-1,3-dien-1-ol (6): A mixture of **1b** (200 mg, 1.45 mmol) and $FeCl_3{\cdot}6H_2O$ (20 mg, 0.072 mmol) in CH_2Cl_2 (2.5 mL) was stirred for 14 h at room temp. After removal of the solvent, the residue was chromatographed on silica gel (PE/MTB, 5:1, R_f = 0.12) to give **6** as a colorless solid (128 mg, 0.928 mmol, 64%); m.p. 114−115 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.55−1.67 (m, 2 H), 1.67−1.72 (m, 1 H), 1.77−1.83 (m, 1 H), 2.04 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.21−2.31 (m, 1 H), 2.34−2.38 (m, 2 H), 2.38−2.44 (m, 1 H), 2.48−2.59 (m, 2 H), 3.25 (br. s, 1 H), 5.78 (s, 1 H, 3-CH), 15.59 (s, 1 H, OH), 16.26 (s, 1 H, OH). − $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 18.9 (CH_2), 19.7 (CH_3), 24.6 (CH_3), 26.2 (CH_2), 26.7 (CH_2), 30.9 (CH_2), 35.4 (CH_2), 40.9 (CH), 108.2 (C), 108.6 (C), 119.4 (CH), 134.7 (C), 178.8 (C), 182.8 (C), 199.3 (C=O), 200.6 (C=O). − IR (ATR): $\tilde{\nu}$ = 2941 cm^{-1} (m), 1651 (sh), 1605 (s), 1448 (m), 1410 (m), 1363 (m), 1328 (m), 1316 (m), 1271 (m), 1242 (m), 1218 (m), 951 (m). − MS (EI, 70 eV): *m*/*z* (%) = 276 (28) [M$^+$], 258 (100) [M$^+$ − OH], 243 (27) [M$^+$ − OH − Me], 215 (35) [M$^+$ − OH − Me − CO], 202 (21), 187 (11), 139 (13), 91 (11), 77 (8). − $C_{16}H_{20}O_4$ (276.3): calcd. C 69.55, H 7.30; found C 69.15, H 6.90; calcd. 276.1362; found 276.1365 (HRMS).

10-Acetyl-7,8-dihydro-1,4-dimethoxynaphtho[1,2-*b*]benzofuran-5,9-diol (7b): A mixture of 2-acetylcyclohex-2-en-1-one (**1b**) (150 mg, 1.09 mmol), 5,8-dimethoxy-1,4-naphthoquinone (**3c**) (237 mg, 1.09 mmol), and $FeCl_3{\cdot}6H_2O$ (14.7 mg, 0.0540 mmol) in CH_2Cl_2 (3 mL) was stirred for 12 h at room temp. After removal of the solvent, chromatography of the residue on SiO_2 (PE/MTB, 2:1, R_f = 0.13) afforded the title compound **7b** (23 mg, 0.065 mmol, 6%) as a yellow solid, which crystallized as yellow needles from PE/MTB (2:1); m.p. 214 °C (dec.). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.71 (s, 3 H, CH_3), 2.84 (t, *J* = 6.9 Hz, 2 H, 8-H_2), 2.92 (t, *J* = 6.8 Hz, 2 H, 7-H_2), 3.99 (s, 3 H, 1-OMe), 4.05 (s, 3 H, 4-OMe), 6.71 (d, *J* = 8.5 Hz, 1 H, 3-H), 6.79 (d, *J* = 8.5 Hz, 1 H, 2-H), 6.92 (s, 1 H, 6-H), 9.52 (s, 1 H, 5-OH), 15.75 (s, 1 H, OH). − $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 16.8 (C-7), 21.6 (C-2′), 36.3 (C-8), 56.2 (1-OMe), 56.6 (4-OMe), 101.1 (C-6), 103.2 (C-3), 104.9 (C-10), 105.2 (C-2), 107.7 (C-6b), 112.9 (C-4a), 115.3 (C-11b), 125.6 (C-6a), 143.0 (C-5), 149.4 (C-1), 150.0 (C-10a), 150.5 (C-4), 150.8 (C-11a), 177.4 (C-1′), 202.0 (C-9). − IR (ATR): $\tilde{\nu}$ = 3368 cm^{-1} (m), 2957 (m), 2926 (m), 2853 (m), 1651 (m), 1612 (m), 1592 (m), 1454 (m), 1442 (m), 1400 (m), 1377 (m), 1352 (m), 1278 (m), 1255 (s), 1223 (m), 1181 (m), 1148 (m), 1043 (s), 795 (s). − MS (EI, 70 eV): *m*/*z* (%) = 354 (100) [M$^+$], 339 (44) [M$^+$ − Me], 324 (18) [M$^+$ − 2 Me], 306 (6), 264 (6), 177 (7). − $C_{20}H_{18}O_6$: calcd. 354.1103; found 354.1106 (HRMS).

Methyl 5,10-Dihydroxycyclohepteno[3,4-*a*]naphtho[2,1-*d*]furan-11-carboxylate (7c): A mixture of ester **1c** (298 mg, 1.77 mmol), quinone **3b** (280 mg, 1.77 mmol), and $FeCl_3{\cdot}6H_2O$ (48 mg, 0.18 mmol) in CH_2Cl_2 (2 mL) was stirred at room temp. for 12 h. After dilution with MTB (2 mL), the mixture was directly chromatographed on SiO_2 (PE/MTB, 2:1). A first fraction (R_f = 0.33) contained the dimer of **1c** (colorless oil, 67 mg, 0.20 mmol, 22%). From a second brown band (R_f = 0.28), the title compound **7c** (131 mg, 0.400 mmol, 23%) was obtained as a brown solid. Finally, a polar, yellow fraction (R_f = 0.25−0.05) was obtained, from which compound **9** could be isolated after two subsequent chromatographic purifications (R_f = 0.17, 24 mg, 0.074 mmol, 4%, yellow solid). However, the remaining material collected from the third, polar fraction (156 mg) was redissolved in MeOH (2 mL), $FeCl_3 \cdot 6\,H_2O$ (270 mg, 1.00 mmol) was added, and the resulting mixture was stirred overnight at room temp. Subsequent chromatography on SiO_2 (PE/MTB, 2:1) yielded another portion of the title compound **7c** (116 mg, 0.357 mmol, 20%; total yield 43%). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.23−2.31 (m, 2 H, CH_2), 2.49−2.52 (m, 2 H, CH_2), 2.83 (t, *J* = 7.3 Hz, 2 H, CH_2), 3.94 (s, 3 H, OMe), 5.39 (br. s, 1 H, OH), 6.85 (s, 1 H, 3-H), 7.45−7.49 (m, 1 H), 7.56−7.61 (m, 1 H), 8.21−8.24 (m, 2 H), 13.29 (s, 1 H, OH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz): δ = 22.5 (CH_2), 27.0 (CH_2), 33.6 (CH_2), 52.1 (CH_3), 95.8 (C), 99.2 (CH), 116.2 (C), 119.9 (CH), 121.5 (C), 122.6 (C), 122.7 (CH), 124.0 (CH), 124.3 (C), 126.6 (CH), 144.1 (C), 145.7 (C), 147.5 (C), 172.1 (C), 180.9 (C). − IR (ATR): $\tilde{\nu}$ = 3437 cm^{-1} (s, br.), 2951 (m), 1733 (m), 1711 (m), 1641 (s), 1591 (s), 1448 (s), 1373 (m), 1339 (m), 1242 (s), 1174 (m), 1156 (m), 1103 (m), 1068 (s), 834 (m), 754 (s). − MS (EI, 70 eV): *m*/*z* (%) = 324 (76) [M$^+$], 292 (100) [M$^+$ − MeOH], 268 (18), 236 (62), 152 (20). − $C_{19}H_{16}O_5$: calcd. 324.0998; found 324.0996 (HRMS).

2-[2-(Ethoxycarbonyl)-3-oxocyclohex-1-yl]-1,4-naphthoquinone (8a): A mixture of compound **1a** (100 mg, 0.600 mmol), 1,4-naphthoquinone (**3b**) (94 mg, 0.60 mmol), and $FeCl_3{\cdot}6H_2O$ (8.1 mg, 0.030 mmol) in CH_2Cl_2 (1.5 mL) was stirred for 12 h at room temp. After removal of the solvent and purification of the residue by chromatography on SiO_2 (PE/MTB, 7:1, R_f = 0.23), **8a** was obtained as a yellow solid (66 mg, 0.20 mmol, 34%; m.p. 104−105 °C), in which the oxo ester moiety was shown to exist completely in the enol form. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.48−1.62 (m, 1 H, 5′-*H*H), 1.64−1.73 (m, 2 H, 5′-H*H*, 6′-*H*H), 1.84−1.95 (m, 1 H, 6′-H*H*), 2.33−2.39 (m, 2 H, 4′-H), 4.03−4.11 (m, 2 H, OCH_2), 4.27−4.32 (m, 1 H, 1′-H), 6.65 (s, 1 H, 3-H), 7.72−7.79 (m, 2 H, 6-H, 7-H), 8.04−8.10 (m, 1 H, 5-H), 8.12−8.17 (m, 1 H, 8-H), 12.56 (s, 1 H, OH). − $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 14.0 (CH_3), 17.1 (C-5′), 27.2 (C-6′), 28.9 (C-4′), 31.7 (C-1′), 60.5 (OCH_2), 97.7 (C-2′), 126.1 (C-5), 126.7 (C-8), 132.1 (C-4a), 132.4 (C-8a), 133.7 (C-6 and C-7), 134.7 (C-3), 154.7 (C-2), 171.5 (C=O), 175.0 (C-3′), 184.6 (C-1), 186.0 (C-4). − IR (ATR): $\tilde{\nu}$ = 1662 cm^{-1} (vs), 1614 (m), 1595 (m), 1330 (m), 1313 (m), 1302 (m), 1269 (m), 1256 (m), 1243 (m), 1222 (s), 1177 (m), 1084 (m). − MS (EI, 70 eV): *m*/*z* (%) = 326 (3) [M$^+$], 308 (22) [M$^+$ − H_2O], 293 (36) [M$^+$ − H_2O − Me], 280 (100) [M$^+$ − EtOH], 252 (86) [M$^+$ − EtOH − CO], 224 (81) [M$^+$ − EtOH − 2 CO], 210 (23), 196 (67), 181 (17), 168 (19), 152 (18), 139 (19), 123 (14), 115 (14), 105 (17), 77 (17). − $C_{19}H_{18}O_5$: calcd. 326.1154; found 326.1155 (HRMS).

2-(2-Acetyl-3-oxocyclohex-1-yl)-1,4-naphthoquinone (8b): A mixture of diketone **1b** (100 mg, 0.720 mmol), quinone **3b** (229 mg, 1.45 mmol), and $FeCl_3{\cdot}6H_2O$ (9.8 mg, 0.036 mmol) in CH_2Cl_2 (2.5 mL) was stirred for 12 h at room temp. After removal of the solvent, chromatography of the residue on SiO_2 (PE/MTB, 2:1, R_f = 0.28) afforded **8b** (34 mg, 0.12 mmol, 16%) as a yellow solid in a first fraction and **7a** (R_f = 0.16) in a second fraction. NMR analysis showed **8b** to exist completely in the enol form. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47−1.58 (m, 1 H, CH*H*), 1.64−1.73 (m, C*H*H), 1.75−1.82 (m, 1 H, CH*H*), 1.89−1.96 (m, 1 H, C*H*H), 1.97 (s, 3 H, CH_3), 2.40−2.45 (m, 2 H, CH_2), 4.34−4.39 (m, 1 H, 1′-H), 6.67 (d, *J* = 0.7 Hz, 1 H, 3-H), 7.74−7.80 (m, 2 H, 6-H and 7-H), 8.06−8.11 (m, 1 H, 5-H), 8.13−8.17 (m, 1 H, 8-H), 16.30 (s, 1 H, OH). − $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 16.5 (CH_2), 24.8 (CH_3), 27.4 (CH_2), 30.5 (CH_2), 33.3 (CH), 106.9 (C-3), 126.3 (CH), 126.8 (CH), 132.1 (C), 132.3 (C), 133.9 (CH), 134.1 (CH), 136.1 (CH), 153.7 (C), 183.6 (C), 184.6 (C), 184.8 (C), 199.9 (C=O). − MS (EI, 70 eV): *m*/*z*

(%) = 296 (3) [M^+], 278 (100) [$M^+ - H_2O$], 256 (4), 253 (15), 250 (23), 235 (5), 222 (5), 207 (5), 197 (9), 165 (7), 158 (11), 149 (8), 137 (17), 123 (11), 111 (11), 95 (20), 81 (59), 69 (86). − $C_{18}H_{16}O_4$: calcd. 278.0943; found 278.0944 [$M^+ - H_2O$] (HRMS).

2-(2-Ethoxycarbonyl-3-oxocyclohex-1-yl)-8-hydroxy-1,4-naphthoquinone (8c): A mixture of ethyl 6-oxocyclohex-1-ene-1-carboxylate (**1a**) (100 mg, 0.595 mmol), 5-hydroxy-1,4-naphthoquinone (**3c**) (104 mg, 0.595 mmol), and $FeCl_3 \cdot 6H_2O$ (4.8 mg, 0.018 mmol) in CH_2Cl_2 (2 mL) was stirred for 12 h at room temp. After removal of the solvent, twofold chromatography of the residue on SiO_2 [(i) PE/MTB, 6:1, R_f = 0.26; (ii) PE/MTB, 8:1, R_f = 0.17] afforded the title compound **8c** (57 mg, 0.17 mmol, 28%) as an orange solid, which crystallized as yellow-orange needles from PE/MTB (2:1); m.p. 138−139 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (t, J = 7.1 Hz, 3 H, CH_3), 1.47−1.60 (m, 1 H, 5′-*H*H), 1.66−1.74 (m, 2 H, 5′-H*H*, 6′-*H*H), 1.86−1.96 (m, 1 H, 6′-H*H*), 2.32−2.39 (m, 2 H, 4′-H_2), 4.04−4.13 (m, 2 H, OCH_2), 4.25−4.30 (m, 1 H, 1′-H), 6.62 (s, 1 H, 3-H), 7.27 (dd, J = 8.0 Hz, J = 1.9 Hz, 1 H, 5-H), 7.58−7.64 (m, 2 H, 6-H, 7-H), 12.15 (s, 1 H, OH), 12.56 (s, 1 H, OH). − ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 14.1 (CH_3), 17.1 (C-5′), 27.2 (C-6′), 28.9 (C-3′), 31.2 (C-1′), 60.5 (OCH_2), 97.5 (C-2′), 115.2 (C-8a), 118.7 (C-8), 124.3 (C-5), 132.1 (C-4a), 135.5 (C-3), 136.5 (C-6), 154.6 (C-2), 161.7 (C-8), 171.3 (C=O), 175.1 (C-3′), 184.4 (C-4), 190.0 (C-1). − IR (ATR): $\tilde{\nu}$ = 1663 cm^{-1} (s), 1637 (vs), 1610 (s), 1457 (m), 1361 (m), 1308 (m), 1291 (s), 1263 (s), 1221 (vs), 1176 (m), 1168 (m), 1084 (m), 836 (m). − MS (EI, 70 eV): *m*/*z* (%) = 342 (6) [M^+], 324 (2), [$M^+ - H_2O$], 296 (100) [M^+ − EtOH], 268 (20) [M^+ − EtOH − CO], 240 (51) [M^+ − EtOH − 2 CO], 226 (10), 212 (17), 197 (6), 184 (8), 165 (9), 128 (6), 115 (5), 77 (4). − $C_{19}H_{18}O_6 \cdot 0.5\,H_2O$ (351.4): calcd. C 64.95, H 5.45; found C 65.10, H 5.41. − $C_{19}H_{18}O_6$: calcd. 342.1103; found 342.1110 (HRMS).

2-(2-Acetyl-3-oxocyclohex-1-yl)-8-hydroxy-1,4-naphthoquinone (8d): A mixture of 2-acetylcyclohex-2-en-1-one (**1b**) (80.0 mg, 0.579 mmol), 5-hydroxy-1,4-naphthoquinone (**3c**) (101 mg, 0.579 mmol), and $FeCl_3 \cdot 6H_2O$ (7.8 mg, 0.029 mmol) in CH_2Cl_2 (1 mL) was stirred for 12 h at room temp. After removal of the solvent, chromatography of the residue on SiO_2 (PE/MTB, 6:1, R_f = 0.19) afforded the title compound **8d** (15 mg, 0.017 mmol, 3%) as a red-orange solid; m.p. 179 °C (dec.). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.47−1.56 (m, 1 H), 1.67−1.74 (m, 1 H), 1.79−1.86 (m, 1 H), 1.91−1.98 (m, 1 H), 1.99 (s, 3 H, CH_3), 2.41−2.45 (m, 2 H, 4-H), 4.34−4.37 (m, 1 H, 1′-H), 6.65 (s, 1 H, 3-H), 7.29 (dd, J = 8.0 Hz, J = 1.3 Hz, 1 H, 5-H), 7.61−7.67 (m, 2 H, 6-H, 7-H), 12.07 (s, 1 H, OH), 16.30 (s, 1 H, OH). − ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 16.5 (CH_2), 24.8 (CH_3), 27.4 (CH_2), 30.5 (CH_2), 32.8 (C-1′), 106.7 (C-2′), 115.2 (C-8a), 119.0 (C-7), 124.5 (C-5), 132.1 (C-4a), 136.8 (CH), 136.9 (CH), 153.7 (C-2), 161.9 (C-8), 183.7 (C), 184.0 (C), 189.9 (C=O), 199.8 (C=O). − IR (ATR): $\tilde{\nu}$ = 1662 cm^{-1} (m), 1637 (s), 1608 (s), 1456 (m), 1413 (m), 1362 (m), 1292 (s), 1272 (m), 1243 (m), 1217 (m), 1168 (m). − MS (EI, 70 eV): *m*/*z* (%) = 312 (1) [M^+], 294 (100) [$M^+ - H_2O$], 269 (10) [M^+ − Me − CO], 266 (12) [$M^+ - H_2O$ − CO], 251 (4) [$M^+ - H_2O$ − Me − CO], 241 (6) [M^+ − Me − 2 CO], 213 (4) [M^+ − Me − 2 CO − C_2H_4], 186 (3), 97 (6), 81 (6). − $C_{18}H_{16}O_5$: calcd. 312.0998; found 312.0997 (HRMS).

Methyl 3-(1,4-Dihydroxynaphth-2-yl)-7-oxocyclohept-1-ene-1-carboxylate (9): Prepared analogously to compound **7c**. Yellow solid, R_f = 0.17 (SiO_2, PE/MTB, 2:1). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.51−1.66 (m, 3 H), 1.79−1.87 (m, 2 H), 2.16−2.20 (m, 1 H), 3.83 (s, 3 H, OMe), 4.09 (dt, J = 6.8 Hz, J = 4.0 Hz, 1 H, 6-H), 6.48 (s, 1 H, 3′-H), 6.91 (d, J = 6.8 Hz, 1 H, 7-H), 7.75−7.77 (m, 2 H, 5′-H, 8′-H), 8.08−8.11 (m, 2 H, 6′-H, 7′-H), 10.31 (br. s, 2 H, OH). − ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 19.5 (CH_2), 22.2 (CH_2), 31.8 (CH), 32.5 (CH_2), 52.1 (CH_3), 126.4 (CH), 126.6 (CH), 130.9 (C), 131.4 (C), 132.7 (C), 134.1 (CH), 134.2 (CH), 136.1 (2 CH), 140.6 (C), 145.8 (C), 147.8 (C), 166.2 (C), 186.3 (C). − IR (ATR): $\tilde{\nu}$ = 3429 cm^{-1} (s), 3305 (m), 2948 (m), 1729 (vs), 1656 (vs), 1637 (sh), 1591 (s), 1441 (s), 1327 (s), 1291 (vs), 1261 (vs), 1237 (s), 1208 (m), 1112 (s), 1067 (m), 763 (m), 718 (s). − MS (EI, 70 eV): *m*/*z* (%) = 326 (24) [M^+], 294 (100) [M^+ − MeOH], 265 (26), 251 (14), 238 (10), 210 (8), 139 (12). − $C_{19}H_{18}O_5$: calcd. 326.1154; found 326.1152 (HRMS).

10-Acetyl-5,9-diacetoxy-7,8-dihydronaphtho[1,2-*b*]benzofuran (10): Dihydrobenzonaphthofuran **7a** (45 mg, 0.15 mmol) was dissolved in pyridine (1.5 mL), Ac_2O (0.8 mL) and DMAP (1.9 mg, 0.016 mmol) were added, and the mixture was stirred overnight at room temp. Saturated aqueous NH_4Cl solution (5 mL) was then added and the mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ solution and brine, and dried with $MgSO_4$. The solvent was evaporated and the crude product was purified by chromatography on SiO_2 (PE/MTB, 2:1, R_f = 0.15) to give the title compound **10** as a colorless solid (40 mg, 0.11 mmol, 70%); m.p. 137−139 °C. Further conversion to compound **11** has been reported previously.[1] − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 2.53 (s, 3 H, CH_3), 2.89 (t, J = 6.5 Hz, 2 H, 8-H), 3.05 (t, J = 6.6 Hz, 2 H, 7-H), 7.36 (s, 1 H, 6-H), 7.54 (ddd, J = 8.2 Hz, J = 6.8 Hz, J = 1.1 Hz, 1 H, 3-H), 7.63 (ddd, J = 8.1 Hz, J = 7.1 Hz, J = 0.8 Hz, 1 H, 2-H), 7.92 (d, J = 8.3 Hz, 1 H, 4-H), 8.17 (d, J = 8.2 Hz, 1 H, 1-H). − ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 18.0 (C-7), 20.6 (CH_3), 21.0 (CH_3), 21.6 (CH_3), 40.0 (C-8), 109.9 (C-6), 117.3 (C-6b), 117.8 (C-10), 120.0 (C-1), 121.5 (C-11b), 121.8 (C-6a), 122.5 (C-4), 125.1 (C-4a), 125.8 (C-3), 127.2 (C-2), 143.0 (C-5), 148.4 (C-11a), 149.4 (C-10a), 153.1 (C-9), 168.2 (C=O), 169.7 (C=O), 198.4 (C=O). − IR (ATR): $\tilde{\nu}$ = 1759 cm^{-1} (s), 1705 (m), 1367 (s), 1205 (vs), 1179 (s), 1169 (s), 1110 (m), 1059 (m), 1022 (m), 764 (m). − MS (EI, 70 eV): *m*/*z* (%) = 378 (3) [M^+], 376 (64) [M^+ − 2 H], 334 (80) [M^+ − H − Me − CO], 292 (100) [M^+ − 2 Me − 2 CO], 277 (32), 274 (30), 249 (49), 221 (13), 192 (7), 189 (9), 165 (18), 163 (24), 91 (8). − $C_{22}H_{18}O_6$: calcd. 376.0947; found 376.0945 [M^+ − 2 H] (HRMS).

4-[3-(Ethoxycarbonyl)-4-hydroxyphenyl]-1,2-naphthoquinone (12a): A mixture of 1,2-naphthoquinone (**3e**) (229 mg, 1.45 mmol), oxo ester **1a** (50 mg, 0.30 mmol), and $FeCl_3 \cdot 6H_2O$ (2.9 mg, 0.018 mmol) in CH_2Cl_2 (2.5 mL) was stirred overnight at room temp. After removal of the solvent, the residue was chromatographed on silica gel (PE/MTB, 1:1) to give a red fraction (R_f = 0.29) containing **12a**, which was further purified by a second chromatographic separation (SiO_2, PE/MTB, 4:1, R_f = 0.14). Product **12a** was obtained as a microcrystalline red solid (41 mg, 0.13 mmol, 43%); m.p. 158−159 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (t, J = 7.1 Hz, 3 H, CH_3), 4.45 (q, J = 7.1 Hz, 2 H, CH_2), 6.43 (s, 1 H, 3-H), 7.14 (d, J = 8.6 Hz, 1 H, 5′-H), 7.30 (dd, J = 7.7 Hz, J = 1.1 Hz, 1 H, 5-H), 7.54 (dd, J = 8.6 Hz, J = 2.4 Hz, 1 H, 6′-H), 7.56 (td, J = 8.4 Hz, J = 1.2 Hz, 1 H, 6-H), 7.62 (td, J = 7.5 Hz, J = 1.7 Hz, 1 H, 7-CH), 7.97 (d, J = 2.3 Hz, 1 H, 2′-CH), 8.22 (dd, J = 7.4 Hz, J = 1.4 Hz, 1 H, 8-H), 11.13 (s, 1 H, OH). − ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 14.2 (CH_3), 62.0 (CH_2), 113.1 (C-3′), 118.3 (C-5′), 127.4 (C-1′), 127.5 (C-3), 129.3 (C-5), 130.0 (C-2′), 130.7 (C-8), 130.9 (C-6), 131.7 (C-8a), 134.9 (C-4a), 135.2 (C-7 and C-6′), 155.8 (C-4), 162.8 (C-4′), 169.5 (C=O), 179.5 (C-1), 180.5 (C-2). − IR (ATR): $\tilde{\nu}$ = 1700 cm^{-1} (m), 1674 (vs), 1662 (vs), 1611 (m), 1601 (m), 1587 (m), 1489 (m), 1402 (m), 1374 (m), 1346 (m),

1314 (m), 1291 (s), 1234 (s), 1209 (s), 1089 (m), 1017 (m), 796 (m), 777 (m). − MS (EI, 70 eV): *m/z* (%) = 324 (16) [M^+ + 2 H], 294 (28) [M^+ − CO], 278 (18) [M^+ + 2 H − EtOH], 248 (75), 220 (11), 192 (26), 176 (14), 163 (100), 152 (10), 139 (18), 115 (9), 87 (9), 75 (10). − $C_{19}H_{14}O_5$: calcd. 324.0998; found 324.0993 [M^+ + 2 H] (HRMS).

4-[5-(Ethoxycarbonyl)-4-hydroxy-2-methylphenyl]-1,2-naphthoquinone (12c): A mixture of ethyl 4-methyl-6-oxocyclohex-1-ene-1-carboxylate (**1d**) (500 mg, 2.74 mmol), 1,2-naphthoquinone (**3e**) (1.52 g, 9.60 mmol), and $FeCl_3{\cdot}6H_2O$ (37.1 mg, 0.137 mmol) in CH_2Cl_2 (14 mL) was stirred for 12 h at room temp. After removal of the solvent, the residue was chromatographed on SiO_2 (PE/MTB, 5:1, R_f = 0.07) to yield the title compound **12c** (498 mg, 1.48 mmol, 54%) as a red solid; m.p. 49 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 4.35−4.45 (m, 2 H, CH_2), 6.36 (s, 1 H, 3-H), 6.92−6.95 (m, 1 H, 5-H), 6.96 (s, 1 H, 3′-H), 7.50−7.59 (m, 2 H, 6-H and 7-H), 7.70 (s, 1 H, 6′-H), 8.17−8.21 (m, 1 H, 8-H), 10.93 (s, 1 H, OH). − $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 14.1 (CH_3), 20.5 (CH_3), 61.7 (CH_2), 110.8 (C-5′), 119.4 (C-3′), 127.6 (C-1′), 128.4 (C-3), 129.0 (C-5), 129.6 (C-6′), 130.4 (C-8), 130.9 (C-7), 131.4 (C-8a), 135.4 (C-4a), 135.5 (C-6), 144.1 (C-2′), 156.2 (C-4), 162.0 (C-4′), 169.6 (C=O), 179.3 (C-1), 180.7 (C-2). − IR (ATR): $\tilde{\nu}$ = 1700 cm^{-1} (m), 1673 (vs), 1617 (m), 1585 (m), 1376 (m), 1338 (m), 1320 (m), 1286 (m), 1255 (s), 1220 (s), 795 (m). − MS (EI, 70 eV): *m/z* (%) = 338 (100) [M^+ + 2 H], 311 (19) [M^+ + 2 H − C_2H_3], 308 (24) [M^+ − C_2H_4], 292 (58) [M^+ + 2 H − EtOH], 280 (11), 262 (12), 234 (38), 189 (9), 178 (32), 165 (12), 152 (9), 91 (8). − $C_{20}H_{18}O_5{\cdot}0.5\ H_2O$ (347.4): calcd. C 69.15, H 5.51; found C 69.70, H 5.06. − $C_{20}H_{18}O_5$: calcd. 338.1154; found 338.1154 [M^+ + 2 H] (HRMS).

Ethyl 2-Acetoxy-5-(3,4-diacetoxynaphth-1-yl)-4-methylbenzoate (14): A mixture of 4-[5-(ethoxycarbonyl)-4-hydroxy-2-methylphenyl]-1,2-naphthoquinone (**12c**) (25 mg, 0.074 mmol), anhydrous NaOAc (24 mg, 0.30 mmol), and zinc dust (73 mg, 1.1 mmol) in acetic anhydride (2 mL) was stirred for 1.5 min at 60 °C and thereafter for 12 h at room temp. The reaction mixture was then poured into ice and water, and the aqueous layer was extracted with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$ and concentrated. The residue was chromatographed on SiO_2 (PE/MTB, 2:1, R_f = 0.10) to yield the title compound **14** (19 mg, 0.040 mmol, 54%) as a colorless resin. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 4.29 (q, *J* = 7.1 Hz, 2 H, OCH_2), 7.08 (s, 1 H), 7.22 (s, 1 H), 7.41−7.43 (m, 2 H), 7.52−7.57 (m, 1 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.95 (s, 1 H). − $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 14.2 (CH_3), 20.3 (CH_3), 20.5 (CH_3), 20.7 (CH_3), 21.1 (CH_3), 61.0 (CH_2), 120.7 (C), 121.6 (CH), 122.8 (CH), 125.1 (CH), 126.1 (CH), 126.6 (CH), 127.1 (CH), 127.9 (C), 130.8 (C), 133.6 (CH), 136.5 (C), 136.66 (C), 136.68 (C), 138.5 (C), 144.0 (C), 150.3 (C), 164.2 (C=O), 168.1 (C=O), 168.3 (C=O), 169.8 (C=O). − MS (EI, 70 eV): *m/z* (%) = 464 (6) [M^+], 422 (26) [M^+ − CH_2CO], 419 (8) [M^+ − EtO], 380 (53) [M^+ − 2 CH_2CO], 338 (100) [M^+ − 3 CH_2CO], 292 (41) [M^+ − 3 CH_2CO − EtOH], 263 (13), 235 (10), 219 (8), 189 (14), 178 (21). − $C_{26}H_{24}O_8{\cdot}H_2O$ (482.5): calcd. C 64.72, H 5.43; found C 64.12, H 5.22. − $C_{26}H_{24}O_8$: calcd. 464.1471; found 464.1476 (HRMS).

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