The Vinylogous Michael Reaction – A Novel Perspective for Biaryl Synthesis

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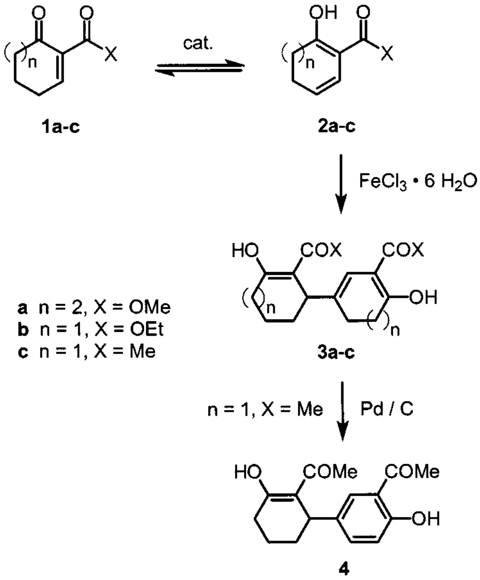
Dienol tautomers **2** of 2-acceptor-substituted cycloalkenones **1** undergo an iron(III)-catalyzed reaction sequence – formally a vinylogous Michael reaction – with benzoquinone derivatives **5** to yield products **6**, **7** and **9**, which are easily converted into highly functionalized biaryl compounds.

Biaryl compounds play an important role as atropisomeric subunits in chiral ligands and in natural products.[1] Synthetic access is commonly provided by a number of established methods such as the Ullmann coupling reaction[2] or palladium-catalyzed cross-coupling reactions.[3] We would like to report herein on a new reaction for the formation of a biaryl moiety.

In the course of our investigations on transition-metal-catalyzed Michael reactions[4] of 2-acceptor-substituted cycloalkenones **1**, we recently reported on the Fe^{III}-catalyzed formation of dimers **3** (Scheme 1).[5] This conversion is closely associated with the tautomerism of enones **1** and dienols **2** catalyzed by either Brönstedt acid or base.[6] This tautomerism is also observed with a catalytic amount of $FeCl_3 \cdot 6H_2O$, but now a subsequent reaction occurs yielding the dimeric products **3**. Formally, compounds **3** are the products of a vinylogous Michael reaction; dienol **2** reacts as a vinylogous donor in the γ-position, with enone **1** as the Michael acceptor, resulting in a 1,7-dioxo constitution of the product.[7] Such reactivity of Michael donors and acceptors, both in the vinylogous position, has been mentioned only once before in the literature, where compound **3c** was obtained as a by-product in low yield.[8] We propose that the reaction leading to **3** is a sequence of tautomerization, [4+2]-cycloaddition and retro-aldol reaction. This novel Fe^{III}-catalyzed sequence tolerates moisture and air. With a view to the synthesis of aromatic compounds, it is important that the dienol six-membered ring in compounds **3** can be oxidized to the aromatic system, which we demonstrated by the preparation of **4** from **3c** (Scheme 1: Pd/C in cyclohexene, yield 60%).

If the vinylogous donors **1** are converted with reactive dienophiles such as quinones **5** in the presence of a catalytic amount $FeCl_3 \cdot 6H_2O$, the formation of dimers is suppressed and the new cross-coupled products **6**, **7** and **9** are obtained which have the constitution of a biaryl precursor molecule, in which two carbocycles are connected by a new C−C single bond. Quinones are of particular interest in this reaction since many substituted derivatives are readily accessible. Moreover, an excess of the quinone can be utilized to directly oxidize the dienol moiety of the primary coupling product in situ to the biaryl target molecule in a one-pot protocol.[9]



Scheme 1. Enone-dienol tautomerism and iron(III)-catalyzed dimerization of 2-acceptor-substituted cycloalkenones; cat. = Brönstedt acid or base, $FeCl_3 \cdot 6H_2O$; yields: **3a**: 71%; **3b**: 83%; **3c**: 64%

In our initial investigation we decided to focus on the quinone derivatives **5a−c** as acceptors (Scheme 2). Results are summarized in Table 1. All reactions 1 to 7 were performed in CH_2Cl_2 without exclusion of air or moisture. In all cases the biaryl precursors **6** and **9** were isolable by chromatography.[10] However, in some cases product mixtures were obtained: in reactions 1 and 3 the benzofuran derivatives **7a** and **7b** were isolated as the major products, in which, after tautomerization, a hydroquinone moiety was annulated to a dihydrofuran (Scheme 2). Subsequent oxidation of this five-membered ring to a furan prevents the reversion of this oxa-Michael addition.[11] Under the reaction conditions, a Fe^{II}/Fe^{III} redox pair as well as the hydroquinone/quinone system has to be considered, since the conversions were performed without exclusion of oxygen. As an example for the biaryl synthesis, we were able to oxidize the dienol moiety in compound **7b** with MnO_2 to the benzonaphthofuran **8** (after transformation into the bis-

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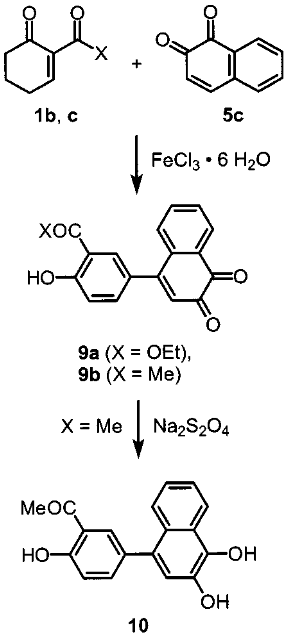
acetate, yield 56%). The alternative use of DDQ as oxidizing reagent did not give satisfactory results.

Table 1. Vinylogous Michael reactions of donors **1a**−**c** with acceptors **5a**−**c** catalyzed by FeCl$_3$·6H$_2$O; conditions: CH$_2$Cl$_2$, room temp., 12−16 h, no exclusion of air or moisture

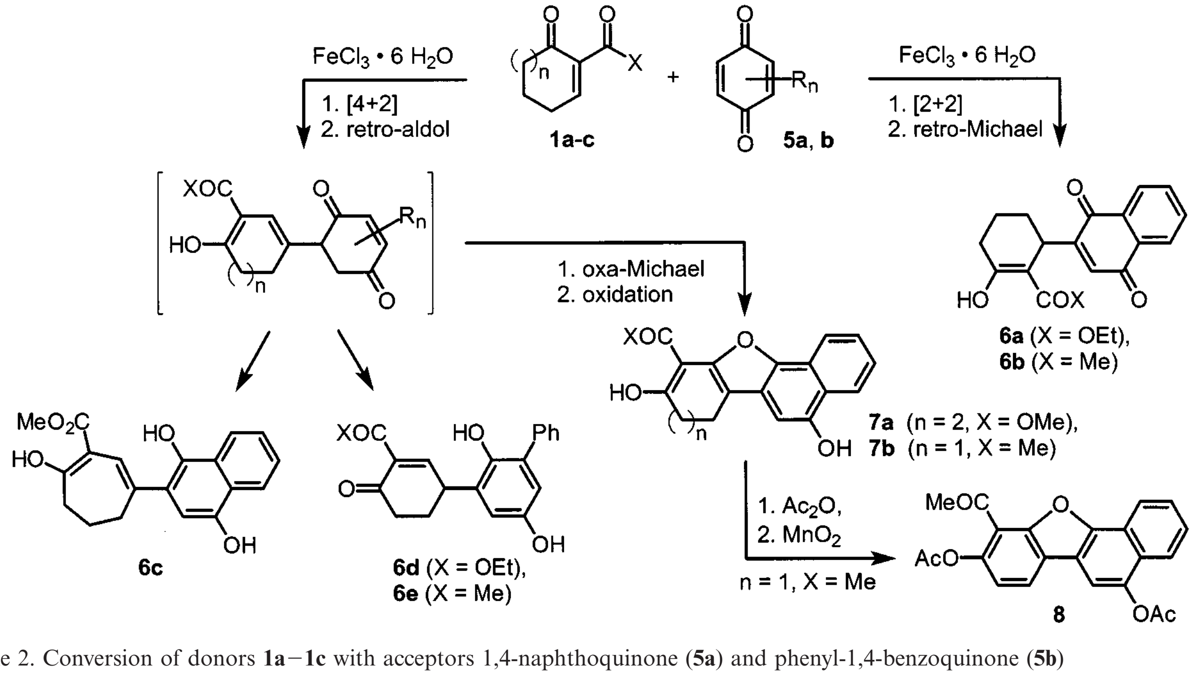
Reaction	Donor	Acceptor	Ratio acc./don.	FeCl$_3$·6H$_2$O (mol-%)	Products (yield%)
1	**1a**	**5a**	1:1	6	**6c** (14), **7a** (53)
2	**1b**	**5a**	1:1	5	**6a** (34)
3	**1c**	**5a**	2:1	5	**6b** (16), **7b** (33)
4	**1b**	**5b**	1:1	5	**6d** (49)
5	**1c**	**5b**	1:1	5	**6e** (37)
6	**1b**	**5c**	5:1	6	**9a** (43)
7	**1c**	**5c**	3:1	5	**9b** (39)

The results summarized in Table 1 show that the oxidation state of the coupling product cannot be predicted and is highly dependent on individual substitution. In light of this it is of particular importance that the conversion of donors **1b** and **1c** with an excess of quinone **5c** yields the naphthoquinone derivatives **9a** and **9b** as single products (Scheme 3), in which both the hydroquinone and the dienol moiety were already completely oxidized. The transformation of these materials to biaryl compounds is particularly simple, as shown by the synthesis of compound **10** from **9b** with Na$_2$S$_2$O$_4$ (Et$_2$O/H$_2$O, yield 96%). These latter two examples are perfect examples of the high potential of the vinylogous Michael reaction for the synthesis of functionalized biaryl compounds.



Scheme 3. Conversion of **1b**, **1c** with 1,2-naphthoquinone (**5c**)

In summary, the vinylogous Michael reaction can be successfully applied to the conversion of quinone derivatives with 2-acceptor-substituted cycloalkenones although the yields are lower relative to the dimerization reaction. The catalyst is FeCl$_3$·6H$_2$O, which is optimal with regard to economic and ecological considerations. Moreover, no special reaction conditions are required, since air and moisture are tolerated. Coupling products are promising precursors for highly functionalized biaryl compounds, whose constitution is of significant interest with respect to the synthesis of natural products and biologically active compounds with quinone or hydroquinone substructures.[12] Although the moderate yields have to be taken in account, the vinylogous Michael reaction offers a valuable enrichment to established methods for biaryl synthesis and quinone functionalization.



Scheme 2. Conversion of donors **1a**−**1c** with acceptors 1,4-naphthoquinone (**5a**) and phenyl-1,4-benzoquinone (**5b**)

Experimental Section

Column chromatography was accomplished with Merck silica gel (Type 60, 0.063−0.200 mm). ^{1}H NMR spectra were recorded on a Bruker AM 400 (400 MHz) and DRX 500 (500 MHz). ^{13}C NMR spectra were recorded on a Bruker AC 200 (50 MHz) and DRX 500 (125 MHz). Assignments were made using H,H-COSY, DEPT, HMBC and HMQC experiments. MS spectra were obtained with Varian MAT 711 (EI, 70 eV) and MAT 955Q (high resolution, EI, 70 eV). IR spectra were recorded on a Nicolet Magna IR 750 (ATR). Elemental analyses were obtained with an Analytik Jena Vario EL. Melting points were measured with a Leica Galen III and are uncorrected.

2-Acetyl-3-(3-acetyl-4-hydroxyphenyl)cyclohexan-1-one (4): A mixture of dimer **3c** (30 mg, 0.11 mmol) and Pd/C (10%, 90 mg) in toluene (2 mL) was stirred at 130°C for 3.5 h in a tightly closed reaction flask (reaction control was accomplished by TLC). The solvent was removed and the residue chromatographed on silica gel [hexane/*tert*-butyl methyl ether (MTB) 2:1, $R_f = 0.24$]. Compound **4** was obtained as a colorless resin (18 mg, 0.065 mmol, 60%). By NMR spectroscopy, the diketone moiety exists completely as the the enol-tautomer. − ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.47{-}1.66$ (m, 2 H, CH_2), 1.75−1.82 (m, 1 H, CH*H*), 1.89 (s, 3 H, CH_3), 1.94−2.03 (m, 1 H, C*H*H), 2.43−2.48 (m, 2 H, CH_2), 2.61 (s, 3 H, CH_3), 3.91 (dd, $J = 5.2, 3.3$ Hz, 1 H, 3-H), 6.95 (d, $J = 8.6$ Hz, 1 H, 5′-H), 7.32 (dd, $J = 8.6, 2.3$ Hz, 1 H, 6′-H), 7.47 (d, $J = 2.2$ Hz, 1 H, 2′-H), 12.16 (s, 1 H, OH), 16.33 (s, 1 H, OH). − ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): $\delta = 16.39$ (CH_2), 25.33 (CH_3), 26.68 (CH_3), 30.87 (CH_2), 32.10 (CH_2), 39.36 (CH), 108.78 (C), 118.68 (CH), 119.51 (C), 129.17 (CH), 135.81 (C), 136.00 (CH), 161.01 (C), 183.00 (C), 200.79 (C=O), 204.35 (C=O). − IR (ATR): $1/\lambda = 3009$ (w), 2939 (m), 2872 (w), 1720 (w), 1703 (w), 1642 (vs), 1613 (s), 1482 (s), 1414 (m), 1366 (s), 1300 (s), 1285 (m), 1240 (m), 1216 (s), 1189 (m), 1174 (m), 1023 (w), 961 (m), 908 (w), 834 (m), 784 (m) cm^{-1}. − MS (EI, 70 eV), *m*/*z* (%): 274 (40) [M^+], 256 (100) [$M^+ - H_2O$], 241 (16) [$M^+ - H_2O - CH_3$], 231 (33) [$M^+ - CH_3 - CO$], 228 (13) [$M^+ - CH_3 - CH_2O$], 213 (49) [$M^+ - H_2O - CH_3 - CO$], 200 (20), 185 (21), 171 (9), 152 (10), 137 (12), 122 (10), 97 (8), 84 (12), 69 (11). − $C_{16}H_{18}O_4$: calcd. 274.1205; found 274.1210 (HRMS).

2-Acetyl-6-(2,5-dihydroxy-3-phenylphenyl)-1-cyclohexen-3-one (6e): A mixture of compound **1c** (100 mg, 0.72 mmol), quinone **5b** (133 mg, 0.72 mmol) and $FeCl_3 \cdot 6H_2O$ (9.8 mg, 0.036 mmol) in CH_2Cl_2 (1.5 mL) was stirred for 12 h at room temperature. After removal of the solvent and purification by chromatography on silica gel (hexanes/MTB 2:1, $R_f = 0.10$) **6e** was obtained as a colorless solid (87 mg, 0.27 mmol, 37%). − M.p. 159−161°C. − ^{1}H NMR (500 MHz, [D_6]-acetone): $\delta = 1.76{-}1.85$ (m, 1 H, 6-CH*H*), 1.95−2.01 (m, 1 H, 6-C*H*H), 2.29−2.46 (m, 2 H, 5-CH_2), 2.37 (s, 3 H, CH_3), 3.45−3.51 (m, 1 H, 4-CH), 5.55 (d, $J = 7.4$ Hz, 1 H, 3-CH), 6.77 (d, $J = 2.4$ Hz, 1 H, 6′-CH), 6.84 (d, $J = 2.5$ Hz, 1 H, 4′-CH), 7.23−7.28 (m, 1 H, 4′′-H), 7.35−7.40 (m, 2 H, 3′′-H), 7.67−7.71 (m, 2 H, 2′′-H), 7.96 (s, 1 H, 5′-OH), 11.71 (s, 1 H, 2′-OH). − ^{13}C{^{1}H} NMR (125 MHz, [D_6]-acetone): $\delta = 25.35$ (5-CH_2), 25.48 (CH_3), 30.44 (6-CH_2), 41.57 (4-CH), 80.92 (3-CH), 107.81 (2-C), 111.84 (6′-CH), 114.61 (4′-CH), 124.46 (3′-C), 128.07 (4′′-CH), 129.11 (2′′-CH), 129.87 (3′′-CH), 134.30 (1′-C), 138.39 (1′′-C), 150.13 (2′-C), 153.28 (5′-C), 187.39 (1-C), 202.03 (C=O). − IR (ATR): $1/\lambda = 3340$ (m), 2935 (w), 2883 (w), 1700 (w), 1601 (s), 1576 (m), 1505 (w), 1459 (m), 1419 (vs), 1363 (m), 1321 (m), 1301 (m), 1280 (m), 1261 (m), 1239 (m), 1198 (s), 1163 (m), 991 (w), 899 (m), 874 (m), 855 (m), 814 (w), 769 (m), 698 (m) cm^{-1}. − MS (EI, 70 eV), *m*/*z* (%): 322 (100) [M^+], 305 (10) [$M^+ - OH$], 289 (9), 279 (19), 261 (9), 199 (14), 186 (16), 165 (8), 91 (8), 77 (7), 69 (10). − $C_{20}H_{18}O_4$ (322.36): calcd. C 74.52, H 5.63; found C 74.10, H 5.80. − Mol. mass. calcd. 322.1205, found 322.1208 (HRMS).

10-Acetyl-5,9-dihydroxy-7,8-dihydrobenzo[b]naphtho[2,1-d]furan (7b): A mixture of diketone **1c** (100 mg, 0.72 mmol), quinone **5a** (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 temperature. After removal of the solvent chromatography on SiO_2 (hexanes/MTB 2:1, $R_f = 0.28$) afforded **6c** (34 mg, 0.12 mmol, 16%) as a yellow solid in a first fraction and **7b** ($R_f = 0.16$) in a second fraction, which was purified by a second chromatographic step on SiO_2 (hexanes/MTB 4:1, $R_f = 0.11$) to give a yellow solid (70 mg, 0.24 mmol, 33%). − **7b**: M.p. 165−168°C. − ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.67$ (s, 3 H, CH_3), 2.82−2.87 (m, 2 H, 7-CH_2), 2.89−2.94 (m, 2 H, 8-CH_2), 5.29 (s, 1 H, OH), 6.85 (s, 1 H, 6-CH), 7.46 (ddd, $J = 8.0, 7.2, 0.9$ Hz, 1 H, 3-CH), 7.59 (ddd, $J = 7.9, 7.3, 0.8$ Hz, 1 H, 2-CH), 8.14 (d, $J = 8.2$ Hz, 1 H, 1-CH), 8.22 (d, $J = 8.3$ Hz, 1 H, 4-CH), 15.79 (s, 1 H, OH). − ^{13}C{^{1}H} NMR (50 MHz): $\delta = 16.90$ (7-CH_2), 22.11 (CH_3), 36.25 (8-CH_2), 99.24 (6-CH), 104.94 (10-C), 108.91 (6b-C), 119.50 (1-CH), 121.50 (10c-C), 121.97 (6a-C), 122.63 (4b-C), 122.79 (4-CH), 123.95 (3-CH), 127.00 (2-CH), 144.89 (10b-C), 147.93 (5-C), 149.41 (10a-C), 177.25 (9-C), 210.77 (C=O). − IR (ATR): $1/\lambda = 3369$ (m), 2960 (w), 2927 (w), 2855 (w), 1629 (s), 1591 (s), 1446 (m), 1398 (m), 1385 (m), 1346 (m), 1321 (m), 1261 (m), 1233 (m), 1192 (w), 1154 (w), 1114 (w), 1061 (m), 929 (m), 820 (m), 761 (m), 755 (m) cm^{-1}. − MS (EI, 70 eV), *m*/*z* (%): 294 (100) [M^+], 276 (27) [$M^+ - H_2O$], 247 (7), 234 (11), 165 (9), 152 (5), 69 (12). − $C_{18}H_{14}O_4$: calcd. 294.0892; found 294.0892 (HRMS).

10-Acetyl-5,9-diacetoxybenzo[b]naphtho[2,1-d]furan (8): A mixture of 10-acetyl-5,9-diacetoxy-7,8-dihydrobenzo[b]naphtho[2,1-d]furan (6.0 mg, 0.016 mmol) and activated MnO_2 (100 mg) in benzene (0.5 mL) was stirred at 50°C for 45 min and thereafter at room temperature for 12 h. After removal of the solvent the residue was chromatographed on SiO_2 (hexanes/MTB 2:1, $R_f = 0.14$) to give the product as a colorless solid (3.3 mg, 0.0088 mmol, 56%). − M.p. 152°C (decomposition). − ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.38$ (s, 3 H, CH_3), 2.53 (s, 3 H, CH_3), 2.99 (s, 3 H, CH_3), 7.17 (d, $J = 8.2$ Hz, 1 H, 8-H), 7.65 (ddd, $J = 8.2, 6.8, 1.0$ Hz, 1 H, 3-H), 7.73 (ddd, $J = 8.2, 7.1, 1.1$ Hz, 1 H, 2-H), 7.80 (s, 1 H, 6-H), 8.01 (d, $J = 8.5$ Hz, 1 H, 1-H), 8.04 (d, $J = 8.4$ Hz, 1 H, 7-H), 8.42 (d, $J = 8.1$ Hz, 1 H, 4-H). − ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): $\delta = 21.06$ ($2 \times CH_3$), 32.45 (CH_3), 110.51 (6-CH), 117.47 (6a-C), 117.76 (10-C), 119.01 (8-CH), 121.10 (4-CH), 121.53 (10c-C), 122.43 (1-CH), 123.48 (7-CH), 123.94 (6b-C), 126.42 (4a-C), 127.09 (3-CH), 127.58 (2-CH), 143.29 (10b-C), 147.37 (9-C), 150.41 (5-C), 154.21 (10a-C), 169.65 (C=O), 169.88 (C=O), 196.02 (C=O). − IR (ATR): $1/\lambda = 2967$ (w), 2856 (w), 1759 (s), 1705 (m), 1640 (w), 1622 (w), 1597 (w), 1446 (w), 1421 (w), 1367 (m), 1205 (vs), 1179 (s), 1169 (s), 1110 (m), 1059 (m), 1022 (m), 962 (w), 904 (w), 863 (w), 764 (m) cm^{-1}. − MS (EI, 70 eV), *m*/*z* (%): 376 (16) [M^+], 334 (29) [$M^+ - CH_2CO$], 292 (100), 274 (6), 249 (10), 163 (6), 97 (7), 71 (10). − $C_{22}H_{16}O_6$ (376.37): calcd. 376.0947; found 376.0950 (HRMS).

4-(3-Acetyl-4-hydroxyphenyl)-1,2-naphthoquinone (9b): A mixture of diketone **1c** (100 mg, 0.72 mmol), quinone **5c** (344 mg, 2.17 mmol), and $FeCl_3 \cdot 6H_2O$ (9.8 mg, 0.036 mmol) in CH_2Cl_2 (3 mL) was stirred for 10 h at room temperature. After removal of all volatile materials in vacuo two chromatographic steps on SiO_2 (1. hexanes/MTB 1:1, $R_f = 0.21$; 2. toluene/MTB 20:1, $R_f = 0.19$) yielded compound **9b** (82 mg, 0.28 mmol, 39%) as a red solid. −

M.p. 225−226°C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.68 (s, 3 H, CH_3), 6.43 (s, 1 H, 3-CH), 7.14 (d, J = 8.6 Hz, 1 H, 5′-CH), 7.29 (dd, J = 7.7, 1.0 Hz, 1 H, 5-CH), 7.56 (dd, J = 8.6, 2.3 Hz, 1 H, 6′-CH), 7.57 (td, J = 7.4, 1.3 Hz, 1 H, 7-CH), 7.62 (td, J = 7.6, 1.7 Hz, 1 H, 6-CH), 7.84 (d, J = 2.2 Hz, 1 H, 2′-CH), 8.23 (dd, J = 7.4, 1.5 Hz, 1 H, 8-CH), 12.50 (s, 1 H, OH). − $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 26.74 (CH_3), 119.21 (5′-CH), 119.78 (3′-C), 127.19 (1′-C), 127.51 (3-CH), 129.15 (5-CH), 130.63 (2′-CH), 130.84 (8-CH), 131.08 (7-CH), 131.78 (8a-C), 134.89 (4a-C), 135.26 (6-CH), 136.01 (6′-CH), 155.64 (4-C), 163.57 (4′-C), 179.34 (1-C), 180.42 (2-C), 204.13 (C=O). − IR (ATR): 1/λ = 3373 (w), 2962 (w), 2929 (w), 1722 (w), 1697 (m), 1642 (vs), 1599 (m), 1586 (m), 1561 (w), 1478 (m), 1364 (m), 1313 (m), 1293 (s), 1250 (m), 1214 (m), 966 (w), 755 (m) cm^{-1}. − MS (EI, 70 eV), m/z (%): 294 (21) [M^+ + 2 H], 264 (100) [M^+ − CO], 249 (74) [M^+ − CO − CH_3], 221 (26), 189 (14), 165 (64), 139 (20), 111 (12), 97 (19), 85 (20), 83 (23), 81 (24), 71 (27). − $C_{18}H_{12}O_4$: calcd. 294.0892; found 294.0894 (M^+ + 2 H, HRMS).

4-(3-Acetyl-4-hydroxyphenyl)-1,2-dihydroxynaphthalene (10): A mixture of quinone **9b** (10 mg, 0.034 mmol) in Et_2O (3 mL) and $Na_2S_2O_4$ (saturated solution in H_2O, 1.5 mL) was stirred at room temperature for 25 min. The organic layer was separated and the aqueous extracted twice with Et_2O. The combined organic layers were dried over Na_2SO_4. The solvent was evaporated to give pure **10** as a colorless solid (9.6 mg, 0.033 mmol, 96%). − M.p. 164−165°C. − ^{1}H NMR (500 MHz, [D_6]-acetone): δ = 2.71 (s, 3 H, CH_3), 7.06 (d, J = 8.5 Hz, 1 H, 5′-H), 7.17 (s, 1 H, 3-H), 7.27 (ddd, J = 8.2, 6.9, 1.1 Hz, 1 H, 6-H), 7.43 (ddd, J = 8.2, 6.8, 1.0 Hz, 1 H, 7-H), 7.60 (dd, J = 8.5, 2.2 Hz, 1 H, 6′-H), 7.70 (dd, J = 8.3, 0.9 Hz, 1 H, 5-H), 7.90 (s, br., 1 H, OH), 7.95 (d, J = 2.1 Hz, 1 H, 2′-H), 8.21 (dd, J = 8.2, 1.3 Hz, 1 H, 8-H), 8.46 (s, br., 1 H, OH), 12.34 (s, 1 H, OH). − $^{13}C\{^1H\}$ NMR (125 MHz, [D_6]-acetone): δ = 26.19 (CH_3), 117.75 (5′-CH), 119.11 (3-CH), 119.60 (3′-C), 121.28 (8-CH), 123.52 (7-CH), 124.93 (6-CH), 125.27 (5-CH), 126.09 (8a-C), 127.22 (4a-C), 130.66 (4-C), 131.54 (1′-C), 132.45 (2′-CH), 132.48 (2-C), 138.15 (1-C), 138.19 (6′-CH), 161.36 (4′-C), 205.50 (C=O). − IR (ATR): 1/λ = 3398 (m), 2956 (w), 2926 (w), 1702 (w), 1638 (vs), 1606 (m), 1586 (m), 1514 (w), 1475 (m), 1441 (w), 1367 (s), 1311 (s), 1292 (vs), 1243 (m), 1213 (s), 1169 (m), 1095 (w), 964 (m), 763 (m) cm^{-1}. − MS (EI, 70 eV), m/z (%): 294 (100) [M^+], 280 (8) [M^+ − H − CH_3], 265 (4) [M^+ − H − CO], 251 (7) [M^+ − CO − CH_3], 205 (8), 176 (6), 165 (6), 149 (7), 140 (8), 97 (6), 83 (6), 71 (7), 69 (13). − $C_{18}H_{14}O_4$ (294.31): Mol. mass calcd. 294.0892, found 294.0892 (HRMS).

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[10] In contrast to **6c**−**6e**, compounds **6a** and **6b** show an unexpected substitution pattern in the cyclohexanone ring which is connected at the β-position to the quinone system. We presume **6a** and **6b** to be the result of a side reaction of a [2+2]-cycloaddition followed by a retro-Michael reaction.

[11] As other by-products we were able to identify charge-transfer complexes. Moreover, we presume formation of radical coupling by-products which, however, we have not been able to detect as yet.

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