Synthesis of 1,4-Phenanthrenequinones via Stannic Chloride-Induced Cyclizations

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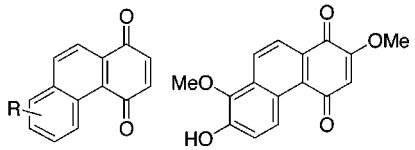
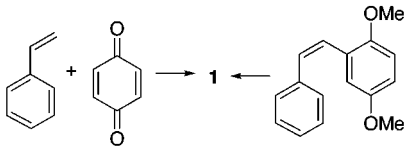
Substituted 1,4-phenanthrenequinones such as **1** are useful building blocks for the preparation of novel materials. Katz and others have shown that compounds such as **1** can be transformed into helicenes by Diels−Alder reactions.[1] Certain 1,4-phenanthrenequinones also have potential as synthetic intermediates for natural products synthesis. Additionally, some naturally occurring 1,4-phenanthrenequinones such as cypripedium (**2**) are biologically active.[2] Kraus and Carpenter have determined that some 1,4-phenanthrenequinones exhibit inhibitory activity in vitro against the equine infectious anemia virus.[3]

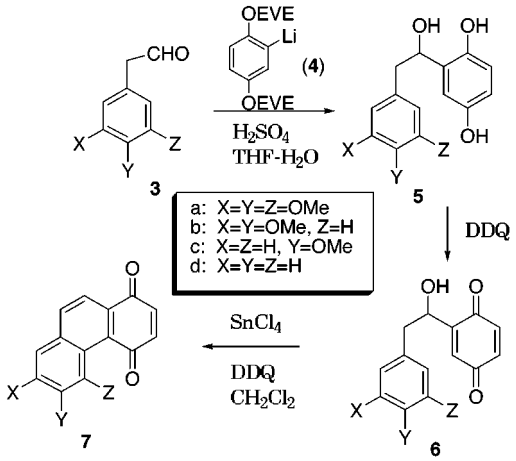


1 **2**

Most 1,4-phenanthrenequinones are prepared by photochemical cyclizations of stilbenes or Diels−Alder reactions involving styrenes and benzoquinones. Mallory and co-workers have demonstrated that certain stilbenes undergo photocyclization in the presence of oxidizing agents to afford hydroquinone dimethyl ethers that yield 1,4-phenanthrenequinone upon oxidation.[4] Rosen and Weber first demonstrated that benzoquinone reacted with styrenes to generate 1,4-phenanthrenequinones in 20−30% yield.[5] Subsequently, Manning and co-workers improved the reaction conditions.[6] Kelly and co-workers used this reaction to prepare a key intermediate for the synthesis of the aglycon of chartreusin.[7] Recently, Carreno and co-workers further improved the Diels−Alder cycloaddition route using arylsulfinyl benzoquinones as effective dienophiles.[8] Kita enhanced the diene component using an innovative silicon tether.[9] We describe herein a quinone-based route to 1,4-phenanthrenequinones featuring an intramolecular Lewis acid-mediated cyclization−dehydration sequence.



The route begins with known arylacetaldehydes **3a**−**d** that are readily available from substituted arylacetic acids through borane reduction followed by Dess−Martin oxidation.[10] In our experience, the Dess−Martin oxidation proved to be superior to the Swern oxidation (DMSO, $(COCl)_2$) and the PCC oxidation. The resulting arylacetaldehydes are reacted with aryllithium **4**[11] from −78 °C to ambient temperature followed by deprotection with a catalytic amount of 1 M sulfuric acid in 3:1 THF/water to afford hydroquinones **5a**−**d** in 70−76% yields. The use of the ethoxyethyl protecting group on the hydroquinone was crucial, since attempted removal of the methoxymethyl protecting group led to partial deprotection plus significant dehydration of the benzylic alcohol. DDQ oxidation of **5** provides the corresponding hydroxy benzoquinones **6a**−**d** in 90−95% yields.



Initially, we evaluated the cyclization using **6a** and boron trifluoride etherate under a range of reaction conditions. Although the reaction provided a 35% isolated yield of quinone **7a** in methylene chloride, the reaction did not proceed in ether or THF. With stannic chloride in methylene chloride the yield of adduct **7a** was 41%. Presumably, dehydration of the benzylic alcohol occurred after cyclization but before oxidation to the phenanthrenequinone. Since the modest yield might be related to a redox process between the starting quinone and the initially formed phenanthrene hydroquinone, the reaction was conducted in the presence of oxidizing agents. DDQ proved to be more efficient than oxygen, affording **7d** in an isolated yield of 74% Using these conditions, quinones **6a**−**c** were then transformed into **7a**−**c** in 71%, 68%, and

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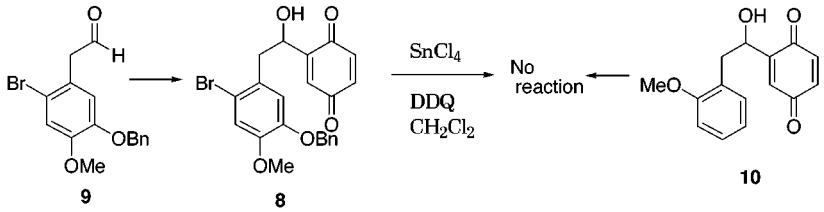

70% yields, respectively. It is interesting to note that the cyclization to quinone **7b** was regioselective.

Hydroxy quinone **8** was next prepared. The substituent pattern was designed to permit the synthesis of 5,6-disubstituted phenanthrenequinones that could not be prepared by cyclization of **6b**. Compound **8** was readily prepared from 6-bromo-4-methoxy-3-benzyloxyphenyl acetaldehyde (**9**), readily available by a reaction sequence recently employed by Overman in his synthesis of morphinans.[12] Unexpectedly, this quinone did not react using the stannic chloride conditions. Compound **10**, derived from 2-methoxyphenylacetaldehyde, also failed to cyclize. In view of the results with **6a**−**d**, the rationale for the failed cyclizations is unclear.

Phenanthrenequinones **7a**−**d** were prepared in five steps from commercially available phenylacetic acids. The mild reaction conditions employed in this sequence will undoubtedly permit access to a wide variety of functionalized quinones. The use of substituted benzoquinone precursors, combined with the regioselectivity of this procedure, further increases the scope of this chemistry. The biological activity of the phenanthrenequinones will be reported in due course.

Experimental Section

3,4,5-Trimethoxyphenylacetaldehyde (3a). To a stirred solution of 3,4,5-trimethoxyphenylacetic acid (1.13 g, 5 mmol) in dry THF (20 mL) at 0 °C under Ar was added a 1 M THF solution of BH_3·THF complex (10 mL, 10 mmol). After 4 h, water was carefully added with cooling, and the reaction mixture was diluted with ether, washed with $NaHCO_3$ solution, water, and brine, and dried. Solvents were removed, and the residue was dissolved in methylene chloride (20 mL) and added to a stirred solution of Dess−Martin reagent (2.54 g, 6 mmol) in CH_2Cl_2 (20 mL). After 1 h, the solution was diluted with ether and stirred for an additional 10 min with a mixture of saturated aqueous $NaHCO_3$ (20 mL) and 25% aqueous $Na_2S_2O_3$ (20 mL). The aqueous layer was separated and extracted with ether, and the combined organic fractions were washed with saturated $NaHCO_3$, water, and brine and dried. Evaporation of the solvents followed by SGC (20% EtOAc in hexanes) afforded pure aldehyde (0.90 g, 86%) as a clear oil that gave spectral data identical to that previously reported.[13]

3,4-Dimethoxyphenylacetaldehyde (3b). Following the general procedure described above and starting with (3,4-dimethoxyphenyl)acetic acid (0.98 g, 5 mmol), **3b** (0.76 g, 85%) was obtained as a clear oil that gave spectral data identical to that previously reported.[14]

4-Methoxyphenylacetaldehyde (3c). Following the general procedure described above and starting with 4-methoxyphenylacetic acid (0.83 g, 5 mmol), **3c** (0.66 g, 88%) was obtained as a clear oil that gave spectral data identical to that previously reported.[14]

2-(3,4,5-Trimethoxyphenyl)-1-(2,5-dihydroxyphenyl)-ethanol (5a). To a stirred solution of 1,4-bis(1-ethoxyethoxy)-benzene (1.10 g, 4.31 mmol) in ether (20 mL) at 0 °C under Ar was added *t*-BuLi (1.65M in pentane, 2.50 mL, 4.12 mmol), and the resulting solution was stirred for 0.5 h. Then it was cooled to −78 °C, a solution of **3a** (824 mg, 3.92 mmol) in dry THF (5 mL) was added dropwise via a syringe pump, and the resulting mixture was allowed to slowly warm to room temperature. Saturated NH_4Cl was added, the aqueous layer was extracted with ether, and the combined organic fractions were washed with water. After concentration, the residue was dissolved in 4:1 THF−H_2O (50 mL) and treated with five drops of 1 M H_2SO_4. After complete deprotection (TLC control, ca. 4−6 h), ether was added, the aqueous layer was extracted with ether, and the combined organic fractions were washed with water and brine and dried. Removal of the solvent followed by SGC (30% EtOAc in hexanes) afforded **5a** (929 mg, 74%) as a slowly solidifying clear oil: ^{1}H NMR ($(CD_3)_2CO$) δ 2.88 (dd, J = 8.1, 13.5 Hz, 1 H), 3.01 (dd, J = 5.4, 13.5 Hz, 1 H), 3.68 (s, 3 H), 3.75 (s, 6 H), 4.71 (br d, J = 3.6 Hz, 1 H), 5.06−5.09 (m, 1 H), 6.50 (s, 2 H), 6.57 (dd, J = 3.0, 8.4 Hz, 1 H), 6.64−6.67 (m, 2 H), 7.62 (br s, 1 H), 8.02 (br s, 1 H); ^{13}C NMR ($(CD_3)_2CO$) δ 44.5, 55.4, 59.6, 72.8, 107.1, 113.8, 114.2, 116.3, 130.7, 134.8, 136.8, 147.7, 150.2, 153.1; IR (neat) cm^{-1} 3366, 1594, 1495; HRMS m/z M$^+$ calcd 320.1260, obsd 320.1265.

2-(3,4-Dimethoxyphenyl)-1-(2,5-dihydroxyphenyl)ethanol (5b). Following the general procedure described above and using **3b** (520 mg, 2.89 mmol) as a starting material, **5b** (636 mg, 76%) was obtained as a white foam: ^{1}H NMR ($(CD_3)_2CO$) δ 2.87 (dd, J = 8.1, 13.5 Hz, 1 H), 3.00 (dd, J = 4.8, 13.5 Hz, 1 H), 3.72 (s, 3 H), 3.75 (s, 3 H), 4.69 (d, J = 4.2 Hz, 1 H), 5.01−5.07 (m, 1 H), 6.56 (dd, J = 2.7, 8.4 Hz, 1 H), 6.63−6.66 (m, 2 H), 6.72−6.76 (m, 2 H), 6.81 (d, J = 7.8 Hz, 1 H), 7.65 (s, 1 H), 8.04 (s, 1 H); ^{13}C NMR ($(CD_3)_2CO$) δ 43.8, 55.1, 55.3, 73.0, 111.8, 113.7, 113.8, 114.1, 116.2, 121.7, 130.8, 131.8, 147.7, 148.0, 149.1, 150.2; IR (neat) cm^{-1} 3400, 1592, 1514.

2-(4-Methoxyphenyl)-1-(2,5-dihydroxyphenyl)ethanol (5c). Following the general procedure described above and using **3c** (168 mg, 1.12 mmol) as a starting material, **5c** (204 mg, 70%) was obtained as a clear foam: ^{1}H NMR ($(CD_3)_2CO$) δ 2.85 (dd, J = 8.4, 13.5 Hz, 1 H), 2.99 (dd, J = 4.5, 13.5 Hz, 1 H), 3.75 (s, 3 H), 4.68 (d, J = 4.5 Hz, 1 H), 5.00−5.05 (m, 1 H), 6.55 (dd, J = 3.0, 9.3 Hz, 1 H), 6.64 (d, J = 9.3 Hz, 1 H), 6.68 (d, J = 3.0 Hz, 1 H), 6.80 (d, J = 8.7 Hz, 2 H), 7.14 (d, J = 8.7 Hz, 2 H), 7.73 (s, 1 H), 8.09 (s, 1 H); ^{13}C NMR ($(CD_3)_2CO$) δ 43.4, 54.6, 72.8, 113.4, 113.7, 114.1, 116.2, 130.6, 131.0, 131.3, 147.6, 150.2, 158.3; IR (neat) cm^{-1} 3370, 1601, 1490; HRMS m/z M$^+$ calcd 260.1049, obsd 260.1044.

2-Phenyl-1-(2,5-dihydroxyphenyl)ethanol (5d). Following the general procedure described above and using commercially available phenylacetaldehyde (335 mg, 2.79 mmol) as a starting material, **5d** (455 mg, 71%) was obtained as a white foam: ^{1}H NMR ($CDCl_3$) δ 3.01 (d, J = 6.3 Hz, 2 H), 3.78 (br s, 1 H), 4.87 (t, J = 6.3 Hz, 1 H), 6.39 (d, J = 3.6 Hz, 1 H), 6.58 (dd, J = 7.8, 3.6 Hz, 1 H), 6.63 (d, J = 7.8 Hz, 1 H), 6.73 (br s, 1 H), 7.11−7.24 (m, 5 H), 7.77 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 44.0, 75.9, 114.0, 115.5, 117.6, 126.8, 128.1, 128.6, 129.6, 137.8, 148.6, 149.2; IR (neat) cm^{-1} 3390, 1634, 1497.

2-(3,4,5-Trimethoxyphenyl)-1-(3,6-dioxo-1,4-cyclohexadienyl)ethanol (6a). To a chilled to ca. 10 °C solution of **5a** (880 mg, 2.75 mmol) in dioxane (15 mL) under Ar was added DDQ (655 mg, 2.89 mmol), and the resulting mixture was stirred for 0.5 h. Then it was filtered, the filtrate was concentrated, and the residue was purified by SGC (20% EtOAc in hexanes) to afford quinone **6a** (831 mg, 95%) as a brown semisolid: ^{1}H NMR ($CDCl_3$) δ 2.36 (br s, 1 H), 2.57 (dd, J = 9.3, 13.5 Hz, 1 H), 3.09 (dd, J = 3.3, 13.5 Hz, 1 H), 3.81 (s, 3 H), 3.84 (s, 6 H), 4.86−4.90 (m, 1 H), 6.46 (s, 2 H), 6.74−6.76 (m, 2 H), 6.83−6.85 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 44.0, 56.2, 60.9, 69.1, 106.3, 131.4, 133.0,

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136.5, 136.8, 137.0, 149.4, 153.4, 187.4, 187.7; IR (neat) cm^{-1} 3441, 1658, 1586; HRMS *m/z* M^+ calcd 318.1103, obsd 318.1109.

2-(3,4-Dimethoxyphenyl)-1-(3,6-dioxo-1,4-cyclohexadienyl)ethanol (6b). Oxidation of **5b** (330 mg, 1.14 mmol) under the same conditions provided **6b** (315 mg, 96%) as a light-brown foam: ^1H NMR ($CDCl_3$) δ 2.19 (d, J = 6.3 Hz, 1 H), 2.63 (dd, J = 8.7, 13.5 Hz, 1 H), 3.11 (dd, J = 3.6, 13.5 Hz, 1 H), 3.86 (s, 3 H), 3.88 (s, 3 H), 4.84−4.88 (m, 1 H), 6.75−6.81 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 43.2, 55.9, 56.0, 69.3, 11.4, 112.5, 121.6, 129.5, 131.5, 136.5, 136.8, 148.2, 149.2, 149.4, 187.4, 187.7; IR (neat) cm^{-1} 3505, 2937, 1659, 1516; HRMS *m/z* M^+ calcd 288.0998, obsd 288.1006.

2-(4-Methoxyphenyl)-1-(3,6-dioxo-1,4-cyclohexadienyl)-ethanol (6c). Oxidation of **5c** (242 mg, 0.93 mmol) under the same conditions provided **6c** (232 mg, 97%) as a yellow oil: ^1H NMR ($CDCl_3$) δ 2.14 (br s, 1 H), 2.65 (dd, J = 8.7, 13.5 Hz, 1 H), 3.10 (dd, J = 3.6, 13.5 Hz, 1 H), 3.80 (s, 3 H), 4.82−4.86 (m, 1 H), 6.71−6.79 (m, 3 H), 6.86 (d, J = 8.7 Hz, 2 H), 7.15 (d, J = 8.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 42.6, 55.4, 69.5, 114.3, 128.8, 130.6, 131.6, 136.5, 136.8, 149.3, 158.8, 187.4, 187.7; IR (neat) cm^{-1} 3480, 1657, 1612.

2-Phenyl-1-(3,6-dioxo-1,4-cyclohexadienyl)ethanol (6d). Oxidation of **5d** (141 mg, 1.08 mmol) under the same conditions provided **6d** (127 mg, 92%) as a brown foam: ^1H NMR ($CDCl_3$) δ 2.24 (br s, 1 H), 2.71 (dd, J = 7.8, 13.5 Hz, 1 H), 3.15 (dd, J = 3.3, 13.5 Hz, 1 H), 4.88−4.91 (m, 1 H), 6.74−6.78 (m, 3 H), 7.23−7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 43.5, 69.4, 127.2, 127.3, 128.9, 129.5, 131.6, 136.5, 136.8, 137.0, 187.4, 187.7; IR (neat) cm^{-1} 3210, 1666, 1635.

5,6,7-Trimethoxy-1,4-phenanthrenequinone (7a). To a solution of hydroxyquinone **6a** (76 mg, 0.24 mmol) in dry methylene chloride (5 mL) at −78 °C under Ar was added a 1 M solution of $SnCl_4$ in CH_2Cl_2 (0.24 mL, 0.24 mmol) followed by DDQ (54 mg, 0.24 mmol), and the resulting mixture was allowed to slowly warm to room temperature. Then it was diluted with ether washed with aqueous NH_4Cl and brine and dried. Concentration followed by SGC (15% EtOAc in hexanes) afforded **7a** (51 mg, 71%) as a bright orange solid: mp 141 °C; ^1H NMR ($CDCl_3$) δ 3.91 (s, 3 H), 3.97 (s, 3 H), 3.99 (s, 3 H), 6.77 (d, J = 9 Hz, 1 H), 6.93 (s, 1 H), 7.02 (d, J = 9 Hz, 1 H), 7.82 (d, J = 7 Hz, 1 H), 7.92 (d, J = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 56.1, 60.9, 61.2, 102.8, 120.2, 121.5, 130.8, 131.8, 133.4, 134.8, 135.2, 140.4, 143.9, 150.4, 155.8, 184.9, 186.8; IR (neat) cm^{-1} 1680, 1655, 1620; MS *m/z* (CI) 298 (100); HRMS *m/z* (M^+) calcd 298.08412, obsd 298.08411. Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.39, H, 5.13.

6,7-Dimethoxy-1,4-phenanthrenequinone (7b). Cyclization of **6b** (69 mg, 0.24 mmol) afforded **7b** (44 mg, 68%) as an orange solid: mp 234 °C (lit.[5] mp 236 °C); ^1H NMR ($CDCl_3$) δ 4.04 (s, 3 H), 4.10 (s, 3 H), 6.90 (s, 2 H), 7.11 (s, 1 H), 7.97 (d, J = 7.5 Hz, 1 H), 8.02 (d, J = 7.5 Hz, 1 H), 9.06 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 56.0, 56.2, 106.1, 106.7, 121.0, 125.3, 126.5, 130.8, 133.1, 134.0, 136.1, 140.5, 151.4, 153.2, 186.0, 188.7; IR (neat) cm^{-1} 1670, 1650, 1620.

6-Methoxy-1,4-phenanthrenequinone (7c): Cyclization of **6c** (28 mg, 0.11 mmol) afforded **7c** (18 mg, 70%) as an orange solid: mp 192 °C (lit.[5] mp 195 °C); ^1H NMR ($CDCl_3$) δ 4.01 (s, 3 H), 6.90 (d, J = 10.2 Hz, 1 H), 6.94 (d, J = 10.2 Hz, 1 H), 7.28 (dd, J = 2.8, 9.0 Hz, 1 H), 7.76 (d, J = 9.0 Hz, 1 H), 8.00 (d, J = 8.4 Hz, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 9.02 (d, J = 2.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.6, 105.5, 120.0, 121.9, 125.4, 130.2, 132.0, 132.6, 132.8, 135.0, 135.9, 140.8, 161.6, 186.2, 188.5; IR (neat) cm^{-1} 1660, 1620. Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.80, H, 4.34.

1,4-Phenanthrenequinone (7d). Cyclization of **6d** (77 mg, 0.34 mol) afforded **7d** (52 mg, 74%) as a light-yellow solid: mp 146 °C (lit.[5] mp 145 °C); ^1H NMR ($CDCl_3$) δ 6.94 (d, J = 11.4 Hz, 1 H), 6.99 (d, J = 11.4 Hz, 1 H), 7.64−7.78 (m, 2 H), 7.89−7.92 (m, 1 H), 8.16 (d, J = 9.0 Hz, 1 H), 8.20 (d, J = 9.0 Hz, 1 H) 9.54 (d, J = 3.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 122.0, 127.2, 128.0, 128.8, 130.0, 130.3, 132.3, 135.3, 135.9, 136.6, 140.6, 142.3, 186.1, 188.4; IR (neat) cm^{-1} 1670, 1660, 1620.

(5-Benzyloxy-2-bromo-4-methoxyphenyl)acetaldehyde (9). To a solution of 5-benzyloxy-2-bromo-4-methoxybenzaldehyde[15] (321 mg, 1 mmol) in CH_2Cl_2 (4 mL) were added trimethylsulfonium methylsulfate (245 mg, 1.3 mmol) and 50% aqueous NaOH (0.5 mL), and the resulting mixture was vigorously stirred for 3 h at room temperature. Water (5 mL) and ether (10 mL) were added, and the organic phase was separated. The aqueous phase was extracted with ether (10 mL), and the combined organic fractions were washed with water and brine and dried. After removal of the solvents, the residue was dissolved in dry THF (10 mL) and treated with $BF_3{\cdot}Et_2O$ (13 μL, 0.1 mmol). After 0.5 h, the solution was diluted with ether, washed with water and brine, and dried. Concentration followed by SGC purification of the residue (15% EtOAc in hexanes) afforded **9** (275 mg, 82%) as a clear oil: ^1H NMR ($CDCl_3$) δ 3.72 (d, J = 1.8 Hz, 2 H), 3.87 (s, 3 H), 5.10 (s, 2 H), 6.74 (s, 1 H) 7.10 (s 1 H), 7.30−7.42 (m, 5 H), 9.67 (t, J = 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 50.1, 56.3, 71.4, 115.7, 116.2, 116.9, 124.2, 127.5, 128.2, 128.7, 136.5, 147.9, 149.9, 198.7; IR (neat) cm^{-1} 2950, 1735, 1533.

2-(5-Benzyloxy-2-bromo-4-methoxyphenyl)-1-(3,6-dioxo-1,4-cyclohexadienyl)ethanol (8). Following the protocol described for **6** and starting with **9** (101 mg, 0.30 mmol), **8** (99 mg, 74% over two steps) was prepared as a brown foam: ^1H NMR ($CDCl_3$) δ 2.45 (d J = 6 Hz, 1 H), 2.87 (dd, J = 7.8, 13.8 Hz, 1 H), 3.11 (dd, J = 4.8, 13.8 Hz, 1 H), 3.83 (s, 3 H), 4.80−4.84 (m, 1 H), 5.10 (s, 2 H), 6.55 (s, 1 H), 6.68 (d, J = 9.9 Hz, 1 H), 6.72 (d, J = 9.9 Hz, 1 H), 6.80 (s, 1 H), 6.98 (s, 1 H), 7.28−7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 42.5, 56.3, 69.0, 71.3, 115.7, 116.1, 117.4, 127.6, 128.1, 128.2, 128.7, 131.6, 136.3, 136.6, 136.9, 147.3, 148.7, 149.4, 187.5, 187.6; IR (neat) cm^{-1} 3425, 1656, 1590; HRMS *m/z* M^+ calcd 442.0417, obsrd 442.0409.

2-(2-Methoxyphenyl)-1-(3,6-dioxo-1,4-cyclohexadienyl)-ethanol (10). Following the general procedure described for **3a** and starting with 2-methoxyphenylacetic acid (0.83 g, 5 mmol), 2-methoxyphenylacetaldehyde (0.64 g, 85%) was obtained as a clear oil that gave spectral data identical to that previously reported.[14]

The addition of aryllithium **4** to 2-methoxyphenylacetaldehyde (110 mg, 0.73 mmol) was conducted following the general procedure described for **5a**, affording 2-(2-methoxyphenyl)-1-(2,5-dihydroxyphenyl)ethanol (116 mg, 61%) as a clear semisolid: ^1H NMR ($(CD_3)_2CO$) δ 2.96−3.11 (m, 2 H), 3.82 (s, 3 H), 4.81 (br s, 1 H), 5.06−5.10 (m, 1 H), 6.54−6.57 (m, 2 H), 6.63 (d, J = 7.2 Hz, 1 H), 6.82 (t, J = 7.5 Hz, 1 H), 6.93 (d, J = 7.5 Hz, 1 H), 7.10−7.20 (m, 2 H), 7.64 (br s, 1 H), 8.10 (br s, 1 H); ^{13}C NMR ($(CD_3)_2CO$) δ 38.8, 54.9, 72.4, 110.4, 113.7, 114.2, 116.4, 120.2, 127.2, 127.5, 130.5, 131.3, 148.2, 150.0, 157.9; IR (neat) cm^{-1} 3395, 1605, 1520.

Oxidation of 2-(2-methoxyphenyl)-1-(2,5-dihydroxyphenyl)-ethanol (184 mg, 0.71 mmol) under the same conditions as described for **6a** provided **10** (173 mg, 95%) as a light-brown oil: ^1H NMR ($CDCl_3$) δ 3.00 (dd, J = 6.8, 13.5 Hz, 1 H), 3.17 (dd, J = 4.5, 13.5 Hz, 1 H), 3.80 (s, 3 H), 4.92−4.96 (m, 1 H), 6.56 (s, 1 H), 6.68 (dd, J = 2.4, 9.9 Hz, 1 H), 6.75 (d, J = 9.9 Hz, 1 H), 6.84−6.93 (m, 2 H), 7.06 (dd, J = 7.5, 1.6 Hz, 1 H), 7.22 (td, J = 7.5, 1.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 37.8, 55.6, 69.4, 110.7, 121.2, 125.0, 128.7, 131.2, 131.7, 136.3, 136.9, 149.7, 157.3, 187.6, 187.8; IR (neat) cm^{-1} 2936, 1658, 1520.

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Supporting Information Available: NMR spectra for obtained compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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