Direct Synthesis of G-2N

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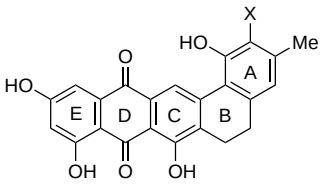
The synthesis of angularly fused quinone natural products has been achieved using a photoenolization reaction and a Diels−Alder reaction in the key carbon−carbon bond forming steps.

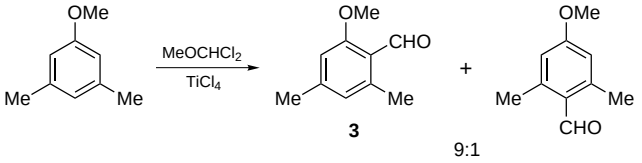
Linearly fused anthraquinone natural products such as aclacinomycin and daunomycin have been the subject of extensive synthetic and toxicological studies for over two decades.[1,2] Recent reports of the isolation of biologically active quinones that are angularly fused have provided the impetus for the creation of synthetic routes for angularly fused quinones. Some members of this quinone family exhibit phosphodiesterase inhibitory activity, significant antiretroviral activity, or inhibitory activity against funguses.[3] The structures of two members of this class, G-2N (**1**) and G-2A (**2**), are shown below.[4] A synthesis of G-2N and G-2A has been achieved



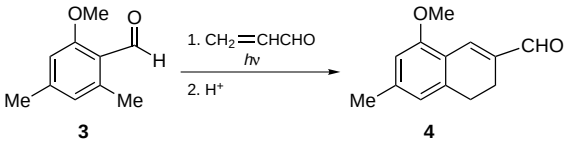
1: X = H
2: X = CO_2H

by Kelly using an innovative palladium-mediated intramolecular coupling of a bis-triflate.[5] We report herein a direct synthetic route to angularly fused anthraquinones exemplified by the preparation of G-2N, which is strategically distinct from the Kelly synthesis.

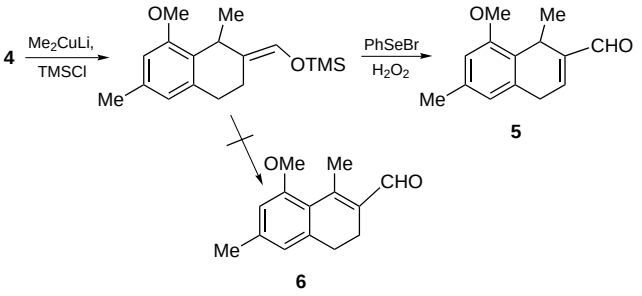
We envisioned the A ring of **1** coming from commercially available 3,5-dimethoxyphenol. The acylation of 3,5-dimethylanisole followed by an intermolecular photoenolization reaction would generate an AB ring system suitable for the appendage of rings D and E. The first compound that we studied was aldehyde **3**.[6] It could be synthesized by a Vilsmeier formylation reaction using DMF and phosphorus oxychloride; however, the isomer wherein the aldehyde was introduced para to the methoxyl group was co-produced in almost equal amounts. Fortunately, a variant of the Vilsmeier which employed dichloromethyl methyl ether and titanium tetrachloride proceded in 99% yield and generated a 9:1 ratio of **3** to the undesired para isomer.[7] The photoenolization reaction of **3** with acrolein produced the expected hydroxy



aldehyde, which could be readily dehydrated to the unsaturated aldehyde **4** in 85% overall yield.[8] The photoenolization reaction was slow, affording a 86% conversion over the course of 3 days. Efforts to increase the rate led to significant polymerization of the acrolein.



The next task was the transformation of **4** into aldehyde **6**. The addition of a cuprate reagent followed by trapping with trimethylchlorosilane afforded an enol silyl ether which could not be oxidized to **6**. The addition of phenylselenenyl chloride and subsequent oxidation produced the isomeric aldehyde **5** in 61% yield. The failure of the enol silyl ether to afford **6** might be attributed to $A^{1,3}$ strain, which forces the methyl group to adopt an axial conformation, thereby rendering the allylic methine proton less accessible. Treatment with palladium acetate in acetonitrile generated the corresponding naphthalene carboxaldehyde, a product of overoxidation.



Aldehyde **6** could be obtained from ketone **7**.[9] In this case the photoenolization reaction of **7** with acrolein afforded cyclobutenol **8** in 90% yield. However, the cyclobutenol could be induced to react with acrolein at 200 °C over 20 h. PTSA-mediated dehydration of the resulting hydroxy ketone provided aldehyde **6** in 80% yield over three steps.

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

(1) Liu, W.; Parker, W. L.; Slusarchyk, D. S.; Greenwood, G. L.; Graham, S. F.; Meyers, E. *J. Antibiot.* **1970**, *23*, 437.
(2) Bowie, J. H.; Johnson, A. W. *Tetrahedron Lett.* **1967**, *8*, 1499.
(3) Pradimicins: Tsunakawa, M.; Nishio, M.; Ohkuma, H.; Tsuno, T.; Konishi, M.; Naito, T.; Oki, T.; Kawaguchi, H. *J. Org. Chem.* **1989**, *54*, 2532.
(4) Isolation and structure determinations of G-2N and G-2A: Gerber, N. N.; Lechevalier, M. P. *Can. J. Chem.* **1984**, *62*, 2818. Rickards, R. W. *J. Antibiot.* **1989**, *42*, 336. Hauser, F. M.; Caringal, Y. *J. Org. Chem.* **1990**, *55*, 555.
(5) Kelly, T. R.; Xu, W.; Ma, Z.; Li, Q.; Bhushan, V. *J. Am. Chem. Soc.* **1993**, *115*, 5843.
(6) Saba, G.; Lai, A.; Monduzzi, M.; Gelli, G. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1569.
(7) Hassall, C.; Morgan, B. A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2853.
(8) Photoenolization review: Sammes, P. G. *Tetrahedron* **1976**, *32*, 405. Kraus, G. A.; Wu, Y. *J. Org. Chem.* **1992**, *57*, 2922.
(9) Prepared using acetyl chloride as in ref 6.

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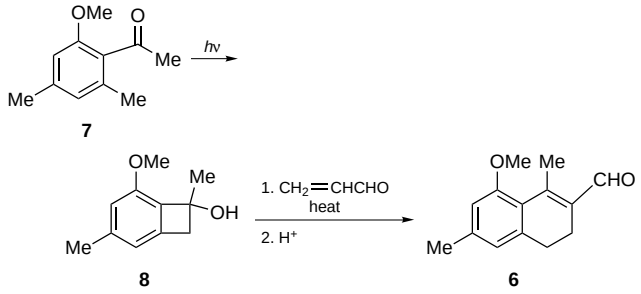
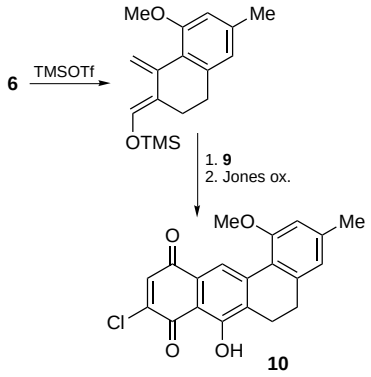
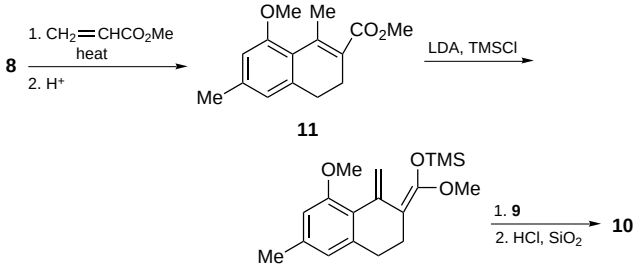


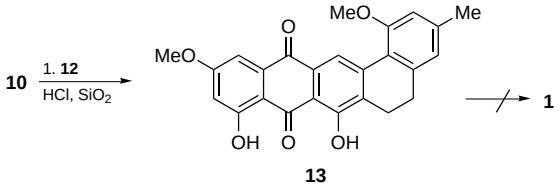
Attempted deprotonation of aldehyde **6** with lithium diisopropylamide (LDA) followed by trapping of the enolate with trimethylchlorosilane did not afford the desired enol silyl ether. However, aldehyde **6** did give the desired enol silyl ether when treated with trimethylsilyl triflate in the presence of diisopropylethylamine in methylene chloride at 0 °C. Reaction of the enol silyl ether with 2,6-dichlorobenzoquinone (**9**)[10] produced an unstable adduct which was not purified but was treated directly with Jones reagent. The resulting product, quinone **10**, was produced in only 6% yield.



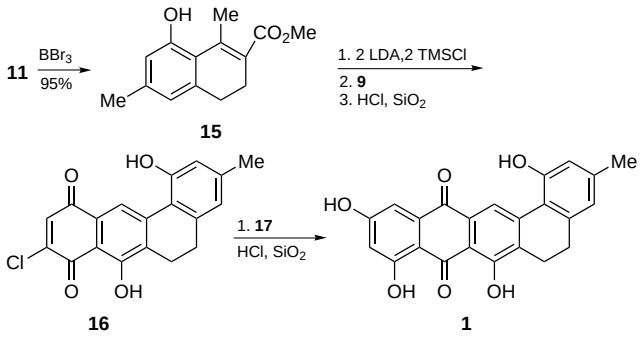
Since the lability of the Diels−Alder adduct appeared to be responsible for the poor yield, we elected to prepare the ester **11**. This compound could be generated from cyclobutenol **8** by thermolysis with methyl acrylate followed by PTSA-mediated dehydration. Ester **11** could readily be deprotonated using lithium diisopropylamide in THF at −78 °C. Trapping of the enolate with trimethylchlorosilane produced the desired enol silyl ether which was combined with quinone **9** and was allowed to slowly warm from −78 °C to ambient temperature. The resulting Diels−Alder adduct was treated with silica gel and aqueous HCl to afford quinone **10** in 95% yield from **11**.



The synthesis of anthraquinone **13**, the bis-methyl ether of **1**, was achieved by reacting quinone **10** with 1,3-dimethoxy-1-((trimethylsilyl)oxy)-1,3-butadiene (**12**) in THF at −30 °C. After the unpurified adduct was treated with silica gel and 6 N HCl, a 95% yield of **13** was obtained. Demethylation of **13** was attempted using a variety of reagents (BBr_3; BCl_3; $AlCl_3$, Me_2S; TMSI; pyr−HCl).[11] Unfortunately, these reagents either produced a mono-demethylated product or returned starting material.



In view of the problems encountered in the demethylation step, we studied deprotection at earlier stages of the synthesis. We found that ester **11** could be demethylated using BBr_3 at −78 °C in 95% yield. The reaction of phenol ester **15** with 2 equiv of LDA and 2 equiv of TMSCl afforded a diene which was converted into naphthoquinone **16** by reaction with 2,6-dichlorobenzoquinone (**9**) followed by aromatization using silica gel and 6 N HCl. Compound **16** reacted with 1-methoxy-1,3-bis-((trimethylsilyl)oxy)-1,3-butadiene (**17**)[12] to produce **1** in 83% yield. Our spectra of **1** were identical to data reported by Kelly.



The synthesis of G-2N from 3,5-dimethylanisole will make available quantities of this natural product for extensive biological testing. We intend to extend this successful synthetic route to the preparation of more functionalized quinones such as G-2A and KS-619-1.[13]

Experimental Section

Unless noted, materials were obtained from commercial suppliers and were used without purification. H:EA refers to hexanes:ethyl acetate solvent mixtures for TLC and silica gel flash chromatography (sgc). The purity of all title compounds was determined to be >95% by 300 MHz proton NMR and/or elemental analysis.

2-Methoxy-4,6-dimethylbenzaldehyde (3). To a solution of 3,5-dimethylanisole (8.00 g, 58.8 mmol) in 120 mL of dry CH_2Cl_2 was added titanium tetrachloride (12.9 mL, 117 mmol) at 0 °C. Dichloromethyl methyl ether (7.40 mL, 82.3 mmol) was added at −78 °C, and stirring was continued for 30 min. The resulting solution was warmed to 0 °C over 1 h, stirred for additional 15 min at 0 °C, poured into a mixture of 5 mL of concd HCl and 10 g of crushed ice, and shaken vigorously

(10) Savard, J.; Brassard, P. *Tetrahedron* **1984**, *40*, 3455.

(11) Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249. In our hands, the pyridinium hydrochloride conditions successfully employed by Kelly returned starting material.

(12) Brownbridge, P.; Chan, T. H.; Brook, M. A.; Kang, G. J. *Can. J. Chem.* **1983**, *61*, 688.

(13) KS-619-1: Matsuda, Y.; Kase, H. *J. Antibiot.* **1987**, *40*, 1104. Yasuzawa, T.; Yoshida, M.; Shirahata, K.; Sano, H. *J. Antibiot.* **1987**, *40*, 1111.

in a separatory funnel until the layers were clear. The organic phase was then separated, washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by sgc (H:EA = 50:1), to give 8.60 g (89% yield) of **3** and 0.96 g (10% yield) of 4-methoxy-2,6-dimethylbenzaldhyde.

3,4-Dihydro-8-methoxy-6-methyl-2-naphthalenecarboxaldehyde (4). To a solution of aldehyde **3** (4.00 g, 24.4 mmol) in 120 mL of dry benzene was added acrolein (2.74 g, 48.8 mmol). The resulting solution was degassed with argon at 5 °C for 20 min. It was irradiated in a Rayonet reactor (with a 3500 Å light source) for 3 days. PTSA (388 mg, 2.04 mmol) was added to the above solution. The solution was stirred for 48 h at rt, worked up with saturated sodium bicarbonate solution, and extracted with ether. The ether layer was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. After sgc (10:1 = H:EA), 4.18 g (85% yield) of **4** was obtained as a white solid (mp 96 °C): NMR ($CDCl_3$) δ 2.35 (s, 3H), 2.51 (t, J = 7.8 Hz, 2H), 2.78 (t, J = 7.8 Hz, 2H), 3.87 (s, 3H), 6.58 (s, 1H), 6.63 (s, 1H), 7.69 (s, 1H), 9.63 (s, 1H); IR ($CDCl_3$) cm^{-1} 2942, 2815, 1662, 1614, 1567, 1376, 1201, 1091, 909; MS *m/e* 100, 115, 128, 143, 159, 174, 181, 202; HRMS *m/e* for $C_{13}H_{14}O_2$ calcd 202.0988, measured 202.0988; ^{13}C NMR ($CDCl_3$) δ 18.7, 21.9, 27.2, 55.3, 109.5, 118.5, 121.0, 136.8, 139.4, 140.5, 142.4, 150.5, 192.6.

3,4-Dihydro-8-methoxy-1,6-dimethyl-2-naphthalenecarboxaldehyde (6). To a solution of benzocyclobutanol **8** (2.00 g, 11.2 mmol) in benzene in a sealable tube was added acrolein (3.14 g, 56.1 mmol). The resulting solution was degassed with argon for 15 min at 0 °C and heated to 200 °C for 20 h. PTSA (213 mg, 1.12 mmol) was added to the solution. The mixture was stirred for 48 h at rt, worked up with saturated sodium bicarbonate solution, and extracted with ether. The ether layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by sgc (H:E = 30:1) to afford 2.16 g (89% yield) of **6** as a white solid (mp 74−75 °C): NMR ($CDCl_3$) δ 2.32 (s, 3H), 2.34−2.37 (m, 2H), 2.52−2.57 (m, 2H), 2.60 (t, J = 1.3 Hz, 3H), 3.83 (s, 3H), 6.63 (s, 2H), 10.31 (s, 1H); IR ($CDCl_3$) cm^{-1} 2939, 1650, 1593, 1195, 1111, 1031, 834; MS *m/e* 43, 63, 77, 91, 115, 128, 172, 187, 201, 216; HRMS *m/e* for $C_{14}H_{16}O_2$ calcd 216.1150, measured 216.1153; ^{13}C NMR ($CDCl_3$) δ 16.4, 19.6, 21.4, 28.9, 55.1, 110.9, 120.9, 122.3, 134.2, 141.0, 141.5, 150.4, 157.9, 190.1.

6-Methoxy-1,4-dimethylbenzocyclobutenol (8). A solution of **7** (3.00 g, 16.8 mmol) in 150 mL of acetone was degassed with argon for 20 min and irradiated in a Hanovia apparatus (450 medium pressure lamp in a quartz immersion vessel) for 5 days. The solvent was removed in vacuo. The residue was purified by sgc (H:EA = 5:1), giving 2.70 g (90% yield) of **8** and 0.29 g of **7**. The product **8** was a white solid (mp 79 °C): NMR ($CDCl_3$) δ 1.69 (s, 3H), 2.29 (s, 3H), 2.64 (s, 1H), 3.24 (d, J = 14.1 Hz, 1H), 3.10 (d, J = 14.1 Hz, 1H), 3.88 (s, 3H), 6.49 (s, 1H), 6.56 (s, 1H); IR ($CDCl_3$) cm^{-1} 3593, 3412, 2973, 1607, 1576, 1226, 908, 835; MS *m/e* 43, 51, 65, 77, 91, 105, 120, 148, 163, 178; HRMS *m/e* for $C_{11}H_{14}O_2$ calcd 178.0994, measured 178.0995; ^{13}C NMR ($CDCl_3$) δ 20.8, 26.0, 27.7, 47.3, 55.7, 114.9, 117.7, 131.3, 140.8, 142.5, 153.2; TLC (H:EA = 5:1) R_f = 0.4.

Methyl 3,4-Dihydro-8-methoxy-1,6-dimethyl-2-naphthalenecarboxylate (11). To a solution of benzocyclobutenol **8** (1.00 g, 5.61 mmol) in 20 mL of benzene in a sealable tube was added methyl acrylate (3.86 g, 44.9 mmol). The resulting solution was degassed with argon for 15 min at 0 °C and heated to 200 °C for 20 h. PTSA (107 mg, 0.561 mmol) was added to the above solution. The mixture was stirred for 48 h at rt, worked up with saturated sodium bicarbonate solution, and extracted with ether. The ether layer was washed with brine, dried, and concentrated in vacuo. The residue was purified by sgc (H:EA = 50:1) to give 1.19 g (86% yield) of **11** as a colorless oil: NMR ($CDCl_3$) δ 2.33 (s, 3H), 2.40−2.45 (m, 2H), 2.47 (br s, 3H), 2.57−2.62 (m, 2H), 3.79 (s, 3H), 3.87 (s, 3H), 6.63 (s, 2H); IR ($CDCl_3$) cm^{-1} 2946, 1707, 1609, 1352, 1278; MS *m/e* 51, 70, 91, 115, 128, 156, 172, 187, 199, 215, 231, 246; HRMS *m/e* for $C_{15}H_{18}O_3$ calcd 246.1256, measured 246.1255; ^{13}C NMR ($CDCl_3$) δ 20.3, 21.5, 24.5, 29.6, 51.3, 55.3, 111.1, 120.5, 123.3, 126.3, 139.4, 140.5, 143.5, 157.4, 169.2.

9-Chloro-5,6-dihydro-7-hydroxy-1-methoxy-3-methylbenz[*a*]anthracene-8,11-dione (10). From 6. To a solution of aldehyde **6** (240 mg, 1.11 mmol) and triethylamine (2.49 mL, 17.8 mmol) in 20 mL of THF was added trimethylsilyl triflate (1.72 mL, 8.88 mmol) dropwise at −78 °C. After 5 min, the mixture was put in an ice bath and then allowed to warm to rt over 3 h. The THF was replaced with 50 mL of pentane, and the mixture was flushed through a short Celite pad. The pentane solution was concentrated in vacuo to afford a yellowish unstable oil. The oil was dissolved in 6 mL of THF and was added to a solution of 2,6-dichlorobenzoquinone (216 mg, 1.22 mmol) in 6 mL of THF at rt. The resulting solution was boiled for 10 h. The THF was replaced with acetone (12 mL). Jones reagent (0.82 mL, 2.2 mmol) was added to the acetone solution at 0 °C. After 30 min, the mixture was diluted with water and extracted with ether. The ether layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by sgc (H:E = 30:1) to give 24 mg of **10** (6% yield) as a dark red solid (mp ∼230 °C with decomposition).

From 11. To a solution of LDA (0.15 mmol) in 1 mL of THF (prepared from diisopropylamine (0.021 mL, 0.15 mmol) and *n*-butyllithium (0.06 mL, 0.15 mmol)) was added a solution of ester **11** (38 mg, 0.15 mmol) in 1 mL of THF at −78 °C. The resulting solution was stirred for 40 min. TMSCl (0.024 mL, 0.18 mmol) was added to the solution. After 30 min, the solution was slowly warmed to rt (1.5 h). The THF was replaced with pentane. The resulting suspension was quickly flushed through a short Celite pad. The solution was concentrated in vacuo. A labile yellowish oil was obtained. The oil was dissolved in 1 mL of THF and was added to a solution of 2,6-dichloroquinone (28 mg, 0.15 mmol) in 1 mL of THF at −78 °C. The resulting solution was slowly warmed to rt and stirred overnight. Several drops of 6 N HCl were added to the solution followed by the addition of 1 g of silica gel. The THF was removed in vacuo, and the residue was allowed to stand overnight. The residue was then washed with ether. The ether solution was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by sgc (H:EA = 30:1) to afford 52 mg (95% yield) of **10** as a red solid (mp ∼230 °C with decomposition): NMR ($CDCl_3$) δ 2.39 (s, 3H), 2.74−2.78 (m, 2H), 2.89−2.92 (m, 2H), 3.94 (s, 3H), 6.74 (s, 2H), 7.17 (s, 1H), 8.61 (s, 1H), 12.13 (s, 1H); IR ($CDCl_3$) cm^{-1} 3415, 1654, 1626, 1596, 1280, 1033; MS *m/e* 45, 77, 101, 145, 170, 189, 219, 251, 275, 339, 354; HRMS *m/e* for $C_{20}H_{15}O_4Cl$ calcd 354.0659, measured 354.0657; ^{13}C NMR ($CDCl_3$) δ 20.7, 21.8, 28.8, 55.7, 109.1, 111.1, 111.9, 120.9, 121.5, 128.9, 133.4, 136.8, 141.0, 141.4, 142.2, 145.8, 157.9, 159.1, 182.3, 182.5; TLC (H:E = 30:1) R_f = 0.11.

Dimethyl Ether of G-2N (13). To a solution of **10** (50 mg, 0.14 mmol) in 1 mL of THF was added a solution of 1,3-dimethoxy-1-((trimethylsilyl)oxy)butadiene (**12**) (57 mg, 0.28 mmol) in 1 mL of THF at −30 °C. The resulting solution was slowly warmed to rt and stirred overnight. Several drops of 6 N HCl were added to the above solution followed by the addition of 1.0 g of silica gel. The THF was removed, and the residue was allowed to stand overnight. The solid was washed with ether, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by sgc (H:E = 20:1) to give 53 mg (91% yield) of **13** as an orange solid (mp >300 °C): NMR ($CDCl_3$) δ 2.39 (s, 3H), 2.75−2.80 (m, 2H), 2.90−2.95 (m, 2H), 3.94 (s, 3H), 3.96 (s, 3H), 6.69 (d, J = 2.3 Hz, 1H), 6.75 (s, 2H), 7.40 (d, J = 2.3 Hz, 1H), 8.79 (s, 1H), 12.43 (s, 1H), 12.56 (s, 1H); IR (KBr) cm^{-1} 3358, 1629, 1596, 1333, 1266, 1156, 1037; MS *m/e* 45, 91, 158, 208, 232, 285, 332, 416; HRMS *m/e* for $C_{25}H_{20}O_6$ calcd 416.1260, measured 416.1260; ^{13}C NMR ($CDCl_3$) δ 20.7, 21.7, 28.8, 55.6, 56.0, 106.5, 107.9, 110.6, 111.0, 113.2, 119.1, 120.9, 121.4, 130.5, 133.5, 135.7, 140.8, 141.0, 141.4, 157.8, 159.0, 165.1, 166.4, 182.3, 190.7; TLC (H:EA = 5:1) R_f = 0.32. Anal. Calcd for $C_{25}H_{20}O_6$: C, 72.11; H, 4.84. Found: C, 72.36; H, 4.47.

Methyl 3,4-Dihydro-8-hydroxy-1,6-dimethyl-2-naphthalenecarboxylate (15). To a solution of ester **11** (0.100 g, 0.41 mmol) in 4 mL of dry CH_2Cl_2 was added BBr_3 (0.16 mL, 1.64 mmol) at −78 °C dropwise. The mixture was stirred for 0.5 h at −78 °C, warmed up to −20 °C slowly, and stirred for

1 h. The mixture was warmed to 0 °C and stirred for 2 h, and the reaction was quenched with Et_2O followed by the addition of a saturated $NaHCO_3$ solution. The resulting solution was stirred for 2 h and then extracted with ether. The ether layer was dried and concentrated in vacuo. The residue was purified by sgc (H:EA = 10:1) to give 90 mg (95% yield) of **15** as white solid (mp 156−157 °C): NMR ($CDCl_3$) δ 2.26 (s, 3H), 2.41−2.46 (m, 2H), 2.54 (t, J = 1.5 Hz, 3H), 2.58−2.63 (m, 2H), 3.79 (s, 3H), 4.98 (s, 1H), 6.46 (s, 1H), 6.60 (s, 1H); IR ($CDCl_3$) cm^{-1} 3379, 2982, 1693, 1615, 1205, 1166, 1086, 903, 758; MS m/e 51, 77, 103, 115, 128, 145, 158, 173, 185, 201, 217, 232; HRMS m/e for $C_{14}H_{16}O_3$ calcd 232.1099, measured 232.1103; ^{13}C NMR ($CDCl_3$) δ 20.0, 21.0, 24.6, 29.5, 51.5, 116.1, 120.8, 121.4, 126.6, 139.7, 140.8, 142.7, 153.5, 169.3; TLC (H:E = 10:1), R_f = 0.17.

9-Chloro-5,6-dihydro-1,7-dihydroxy-3-methylbenz[*a*]-anthracene-8,11-dione (16). To a solution of LDA (0.80 mmol) in 2 mL of THF (prepared from disopropylamine (0.11 mL, 0.84 mmol) and *n*-butyllithium (0.32 mL, 0.80 mmol)) was added a solution of ester **15** (90 mg, 0.39 mmol) in 2 mL of THF at −78 °C. The resulting solution was stirred for 40 min. TMSCl (0.10 mL, 0.79 mmol) was added to the solution. After 30 min, the solution was slowly warmed to rt over 1.5 h. The THF was replaced with pentane. The resulting suspension was quickly flushed through a short Celite pad. The solution was concentrated. The ketene acetal was obtained as a yellowish unstable oil. The oil was dissolved in 2 mL of THF and was added to a solution of 2,6-dichlorobenzoquinone (124 mg, 0.70 mmol) in 2 mL of THF at −78 °C. The resulting solution was slowly warmed to rt and stirred overnight. Several drops of 6 N HCl were added into the solution followed by the addition of 2 g of silica gel. The THF was removed in vacuo, and the residue was allowed to stand overnight. The residue was then washed with ether. The ether solution was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by sgc (H:E = 5:1), giving 115 mg (93% yield) of **16** as red dark solid (mp ∼240 °C with decomposition): NMR ($CDCl_3$) δ 2.32 (s, 3H), 2.75−2.79 (m, 2H), 2.90−2.95 (m, 2H), 3.75 (s, 1H), 6.58 (s, 1H), 6.72 (s, 1H), 7.18 (s, 1H), 8.65 (s, 1H), 12.13 (s, 1H); IR (KBr) cm^{-1} 3424, 2917, 1657, 1628, 1256, 952; MS m/e 49, 88, 138, 152, 189, 219, 259, 277, 322, 340; HRMS m/e for $C_{19}H_{13}O_4Cl$ calcd 340.0502, measured 340.0505; ^{13}C NMR ($CDCl_3$) δ 20.4, 20.9, 28.0, 111.8, 115.8, 116.4, 119.4, 120.1, 128.9, 131.5, 136.6, 140.2, 140.5, 141.7, 144.7, 155.9, 157.5, 181.8, 182.3; TLC (H:EA = 5:1) R_f = 0.15. Anal. Calcd for $C_{19}H_{13}O_4Cl$: C, 66.97; H, 3.84. Found: C, 66.83; H, 3.83.

G-2N (1). To a solution of the chloro quinone **16** (20 mg, 0.059 mmol) in THF (0.5 mL) was added a solution of 1,3-dimethoxy((trimethylsilyl)oxy)butadiene (30 mg, 0.12 mmol) in 0.5 mL of THF at −30 °C. The resulting solution was slowly warmed to rt and stirred overnight. Several drops of **6** N HCl were added to the solution followed by the addition of 1.0 g of silica gel. The THF was removed. The residue was allowed to stand overnight and then washed with ether. The ether solution was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by sgc (H:E = 5:1) to give 19 mg (yield 83%) of G-2N as a dark red solid (mp >300 °C): UV (EtOH) 266, 310, 470 nm; NMR (DMSO-d_6) δ 2.24 (s, 3H), 2.69−2.72 (m, 2H), 2.78−2.81 (m, 2H), 6.60 (d, J = 2.4 Hz, 1H), 6.62 (s, 1H), 6.70 (s, 1H), 7.15 (d, J = 2.4 Hz, 1H), 8.81 (s, 1H), 10.17 (s, 1H), 12.15 (s, 1H), 12.53 (s, 1H); IR (KBr) cm^{-1} 3389, 2948, 1616, 1594, 1311, 1263, 1168, 1026, 840; MS m/e 70, 84, 165, 205, 251, 306, 370, 388; HRMS m/e for $C_{23}H_{16}O_6$ calcd 388.0947, measured 388.0958; ^{13}C NMR (DMSO-d_6) δ 20.9, 25.1, 28.1, 107.8, 108.8, 109.2, 112.7, 115.2, 116.5, 119.8, 120.1, 130.2, 132.0, 135.5, 140.2, 140.3, 141.2, 155.9, 158.0, 164.4, 165.6, 181.6, 189.6; TLC (H:E = 5:1) R_f = 0.15.

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Supporting Information Available: Copies of ^1H NMR spectra of all title compounds (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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