°C: IR (Nujol) ν 1245, 1040, 845, 825, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00–7.03 (m, 2 H), 7.04–7.05 (m, 1 H), 7.07–7.09 (m, 1 H), 7.13–7.14 (m, 1 H), 7.20–7.21 (m, 1 H), 7.22 (s, 1 H), 7.24–7.26 (m, 1 H), 7.28–7.31 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.99, 136.46, 135.81, 134.67, 132.41, 130.45, 127.91, 127.72, 127.22, 127.12, 126.80, 126.74, 126.28, 125.69, 124.89, 124.10; MS m/z (relative intensity) 330.2 (M$^+$, 100), 331.1 (25), 332.2 (25), 329.2 (23); UV (MeOH) 287, 344 nm (log ϵ 4.26, 4.16). Anal. Calcd for $C_{16}H_{10}S_4$: C, 58.15; H, 3.05; S, 38.81. Found: C, 58.04; H, 3.10; S, 39.25.

5′-(2-Thienyl)-2,2′:3′,3″-terthiophene (3a). From 5.0 g of **11** was obtained 2.8 g (56%) of **3a**. Preparative HPLC and recrystallization from hexane gave white crystals, mp 78–79 °C; IR (Nujol) ν 1080, 840, 830, 790, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97–6.99 (m, 1 H), 7.02–7.07 (m, 3 H), 7.18 (s, 1 H), 7.19–7.21 (m, 1 H), 7.23–7.26 (m, 2 H), 7.28–7.32 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.73, 136.05, 135.58, 135.44, 134.38, 130.21, 128.19, 127.91, 127.24, 126.84, 126.43, 126.13, 125.38, 124.72, 123.93, 123.46; MS m/z (relative intensity) 330.2 (M$^+$, 100), 329.2 (33), 331.1 (25), 332.2 (24); UV (MeOH) 207, 262, 345 nm (log ϵ 4.16, 4.17, 4.21). Anal. Calcd as for **2a**. Found: C, 58.18; H, 3.13; S, 38.77.

5′-(3-Thienyl)-2,2′:4′,2″-terthiophene (4a). From 5.0 g of **12** was obtained 3.7 g (76%) of **4a**. Preparative HPLC and recrystallization from hexane gave pale yellow crystals, mp 82–83 °C: IR (Nujol) ν 1230, 1080, 850, 825, 780, 700, 630 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99–7.08 (m, 4 H), 7.20–7.22 (m, 1 H), 7.24–7.27 (m, 3 H), 7.29–7.32 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.66, 136.64, 135.14, 133.57, 132.29, 131.41, 128.13, 127.83, 127.12 126.18, 126.08, 125.67, 125.11, 124.64, 123.87; MS m/z (relative intensity) 330.2 (M$^+$, 100), 285.2 (39), 329.2 (36), 331.1 (26), 332.2 (25); UV (MeOH) 203, 242, 254, 286, 333 nm (log ϵ 4.23, 4.06, 4.05, 4.26, 4.16). Anal. Calcd as for **2a**. Found: C, 58.03; H, 3.02; S, 39.13.

5′-(3-Thienyl)-2,2′:4′,3″-terthiophene (5a). From 5.0 g of **13** was obtained 3.2 g (64%) of **5a**. Preparative HPLC and recrystallization from hexane gave white crystals, mp 90–91 °C; IR (Nujol) ν 1230, 1170, 840, 820, 785, 705, 690, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99–7.05 (m, 3 H), 7.19–7.20 (M, 1 H), 7.20 (m, 1 H), 7.22–7.24 (m, 3 H), 7.26–7.30 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.98, 136.60, 134.96, 134.21, 133.52, 132.05, 128.10, 127.98, 127.87, 126.38, 125.68, 125.37, 124.53, 123.75, 122.99, 122.72; MS m/z (relative intensity) 330.2 (M$^+$, 100), 329.2 (38), 285.2 (34), 331.1 (26), 332.2 (25); UV (MeOH) 207, 268, 334 nm (log ϵ 4.36, 4.15, 4.18). Anal. Calcd as for **2a**. Found: C, 57.94; H, 3.27; S, 39.19.

Acknowledgment. We are grateful for generous financial support from a Bristol-Myers Co. grant of Research Corporation (D.M.P., D.M.B.) and from the Loyola College Hauber Research Fund (D.M.B., E.P.K.). For insight into the accurate enumeration of the quaterthiophenes we are indebted to Professor Richard VandeVelde, S.J., of the mathematics department of Loyola University, Chicago.

Registry No. 2a, 134628-84-5; **3a**, 134628-85-6; **4a**, 134628-86-7; **5a**, 134628-87-8; **8**, 2309-48-0; **9**, 134628-88-9; **10**, 70314-42-0; **11**, 134628-89-0; **12**, 134628-90-3; **13**, 134704-87-3; 2-thiophenecarboxaldehyde, 98-03-3; 3-thiophenecarboxaldehyde, 498-62-4; 2-acetylthiophene, 88-15-3.

Supplementary Material Available: 2D COSY spectra for compounds **2a**, **3a**, **4a**, and **5a** (4 pages). Ordering information is given on any current masthead page.

Synthesis of 1,5- and 1,8-Dihydroxyanthraquinones from a Common Intermediate. A Direct Synthesis of Racemic 7-Deoxyaklavinone

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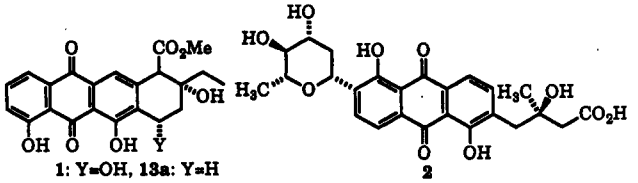
When quinone **6** was treated with diene **7** followed by oxidation, a 1,5-dihydroxyanthraquinone was obtained. When quinone **6** was subjected to a palladium-mediated aromatization, the resulting 5-hydroxy-1,4-naphthoquinone reacted with diene **7** followed by oxidation to produce a 1,8-dihydroxyanthraquinone, a key intermediate in a direct synthesis of 7-deoxyaklavinone, a known synthetic precursor of aklavinone.

In the past decade, a number of architecturally interesting and biologically active anthraquinones have been discovered. The anthracyclines, exemplified by aclacinomycinone (**1**), contain a 1,8-dihydroxyanthraquinone unit.[1] The vineomycins (**2**) have a 1,5-dihydroxyanthraquinone subunit.[2] Dynemicin, a recently discovered anticancer agent, contains a 1,4,5-trihydroxyanthraquinone subunit.[3] To date, synthetic routes to quinones **1** or **2** have been approached by quite different pathways.[4] We report herein that either the 1,5- or the 1,8-dihydroxyanthraquinone pattern can now be obtained from a common intermediate. In addition to these findings, we also describe a direct synthesis of aklavinone.



1: Y=OH, **13a**: Y=H **2**

Our approach to **1** was based on our previous studies of tandem photoenolization/intermolecular Diels–Alder reactions wherein the hydroxy diester **3** was obtained as a mixture of isomers.[5] This mixture could be converted into the keto diester **4** using the Jones oxidation. The reaction of **4** with ethyl vinyl ketone and Triton B in methanol produced diester **5** as a single stereoisomer (Scheme I). The selective transesterification of the less hindered ester was not planned; however, it was very welcome since it simplified the subsequent palladium chemistry. Oxidation of **5** by the method of Rapoport[6] afforded the unstable quinone **6**, which could not be purified by silica gel chro-

(1) Tone, H.; Nishida, H.; Takeuchi, T.; Umezawa, H. *Drugs Exp. Clin. Res.* **1985**, *11*, 9.

(2) For an excellent synthesis and leading references to the isolation of vineomycinone, see: Tius, M. A.; Gu, X.; Gomez-Galeno, J. *J. Am. Chem. Soc.* **1990**, *112*, 8188.

(3) Konishi, M.; Ohkuma, H.; Tsuno, T.; Oki, T. *J. Am. Chem. Soc.* **1990**, *112*, 3715.

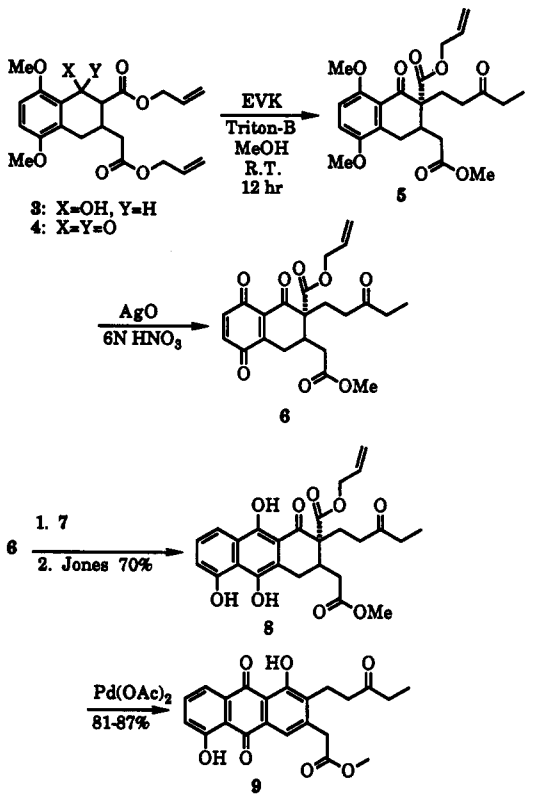
(4) Krohn, K. *Tetrahedron* **1990**, *46*, 291. Krohn, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 790.

(5) Kraus, G. A.; Chen, L. *Synlett* **1991**, 51.

(6) Snyder, C. D.; Rapoport, H. *J. Am. Chem. Soc.* **1972**, *94*, 227.

0022-3263/91/1956-5098$02.50/0

Scheme I



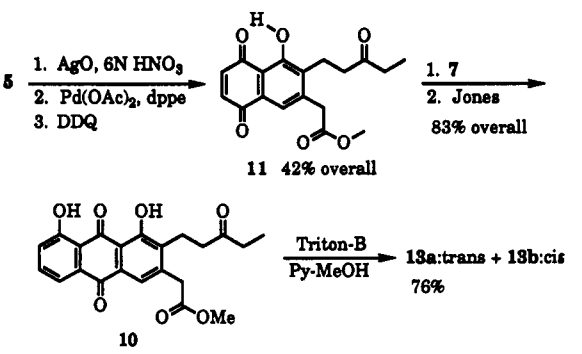
matography. Fortunately, **6** was the only organic product of the oxidation and could be used in subsequent Diels–Alder reactions without purification.

It is well-established that acyl quinones such as acetylbenzoquinone react with dienes at the double bond bearing the acyl group. The Diels–Alder reactions of quinones such as **6** that contain the acyl group as part of a ring have not been studied. We speculated that a Diels–Alder reaction might occur at the unsubstituted double bond. The regiochemistry of such an addition was also an open question. Interestingly, the cycloaddition of **6** with 1-[(trimethylsilyl)oxy]-1,3-butadiene (**7**) afforded two products (probably exo/endo isomers), which were converted into diketo diester **8** after Jones oxidation. As we had reported in a previous paper, the mixture of adducts could also be treated with palladium acetate in hot acetonitrile to produce a 1-hydroxyanthraquinone in a one-pot reaction.[5]

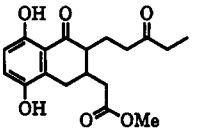
Palladium-mediated aromatization of **8** produced anthraquinone **9** in 87% yield.[7] This anthraquinone was not identical with Maruyama's intermediate **10** as evidenced by 300-MHz NMR.[8] However, anthraquinone **9** had the same molecular weight as **10** and the NMR of **9** did exhibit two sharp resonances at δ 12.65 and 13.11 that are indicative of an intramolecularly hydrogen-bonded hydroxy quinone unit.

In view of the classic studies by Boeckmann and coworkers,[9] it was expected that a 5-hydroxy-1,4-naphthoquinone unit would react with diene **7** to generate the desired regiochemistry. In order to synthesize the requisite dienophile, quinone **6** was treated with palladium acetate and 1,2-bis(diphenylphosphino)ethane (dppe) followed by DDQ oxidation to produce naphthoquinone **11**. The DDQ

Scheme II



step was necessary in order to convert the keto quinone byproduct **12** into **11**. In practice, the DDQ oxidation step



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could be conducted on the unpurified product from the palladium reaction without any decrease in the overall yield. Using this methodoloy, naphthoquinone **11** could be prepared from **5** in 42% overall yield (Scheme II). The reaction of **11** with diene **7** followed by Jones oxidation of the Diels–Alder adduct afforded anthraquinone **10** in 83% yield. The 300-MHz NMR spectrum of **10** correlated exactly with the spectral data published by Maruyama.

Cyclization of **10** using Krohn's Triton B/pyridine conditions returned starting material.[10] The reason for the recovery of **10** using Krohn's conditions is unclear. It may be significant that Krohn has developed more than one recipe for cyclization and that conditions for conducting this reaction are very specific. In contrast, reaction of anthraquinone **10** with Triton B and pyridine in methanol, conditions also developed by Krohn, afforded 7-deoxyaklavinone **13a** along with the cis isomer **13b** in 76% yield as a 2:1 ratio of trans–cis isomers.[11] The melting point of **13a** was 217–219 °C, which compares very favorably with that reported by Kende (220–222 °C).[12] The NMR spectrum of **13a** was identical with that reported by Krohn. The melting point of isomer **13b** was 205–208 °C.

The use of quinone **6** as an intermediate for anthraquinones bearing either the 1,5- or 1,8-dihydroxyanthraquinone substitution pattern increases the utility of our photoenolization/Diels–Alder methodology. The synthesis of 7-deoxyaklavinone in seven steps from **4** demonstrates the efficiency of our approach. Since **13a** has been converted into **1** by several researchers, the synthesis of **13a** constitutes a formal total synthesis of **1**.

Experimental Section

H–EA refers to hexanes–ethyl acetate solvent mixtures for TLC and chromatography. The purity of all title compounds was determined to be >90% by 300-MHz proton NMR.

5,8-Dimethoxy-1,2,3,4-tetrahydro-4-oxo-3-(3-oxopentyl)-3-(2-oxa-1-oxo-4-pentenyl)-2-naphthaleneacetic Acid, Methyl Ester (5). To a solution of **3** (740 mg, 1.90 mmol) in 40 mL of acetone at 0 °C was added Jones reagent (1.0 mL). The reaction was stirred at 0 °C for 15 min and at 25 °C for 30 min. The excess

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(8) Uno, H.; Naruta, Y., Maruyama, K. *Tetrahedron* **1984**, *40*, 4725.
(9) Boeckman, R. K., Jr.; Dolak, T. M.; Culos, K. O. *J. Am. Chem. Soc.* **1978**, *100*, 7098.
(10) Krohn, K.; Priyono, W. *Liebigs Ann. Chem.* **1986**, 1506.
(11) Krohn, K.; Klimars, M.; Kohle, H.-J.; Ebeling, E. *Tetrahedron* **1984**, *40*, 3677.
(12) Kende, A. S.; Rizzi, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4247.

Jones reagent was quenched with 2-propanol. The acetone was diluted with brine and extracted with ethyl acetate. The organic layer was dried and concentrated in vacuo. To the crude residue was added 60 mL of MeOH, and the solution was cooled to 0 °C. To this solution were added ethyl vinyl ketone (2.0 mL) and 200 μL of Triton B. The solution was stirred at 25 °C for 12 h. The solvent was removed in vacuo. The residue was purified by SG chromatography using 3:1 H–EA to afford 446 mg (50% yield) of **5**.

3a: NMR ($CDCl_3$) δ 6.73 (d, J = 9.0 Hz, 1 H), 6.69 (d, J = 9.0 Hz, 1 H), 5.95 (m, 2 H), 5.30 (m, 5 H), 4.69 (dt, J_1 = 5.7 Hz, J_2 = 1.5 Hz, 2 H), 4.60 (dt, J_1 = 5.7 Hz, J_2 = 1.2 Hz, 2 H), 3.86 (s, 3 H), 3.76 (s, 4 H), 3.15 (dd, J_1 = 17.7 Hz, J_2 = 5.1 Hz, 1 H), 2.75 (m, 3 H), 2.55 (dd, J_1 = 8.8 Hz, J_2 = 15.3 Hz, 1 H), 2.28 (dd, J_1 = 11.1 Hz, J_2 = 17.7 Hz, 1 H); IR (neat) 3525, 1735, 1649 cm^{-1}; MS m/z 390 (M^+) 272; HRMS m/z for $C_{21}H_{26}O_7$ calcd 390.167 85, measured 390.167 77; TLC (3:1 H–EA) R_f = 0.2.

3b: NMR ($CDCl_3$) δ 6.70 (s, 2 H), 5.93 (m, 2 H), 5.23 (m, 5 H), 4.84 (d, J = 5.4 Hz, 2 H), 4.60 (d, J = 5.7 Hz, 2 H), 4.18 (d, J = 1.2, 1 H), 3.84 (s, 3 H), 3.76 (s, 1 H), 3.05 (dd, J_1 = 16.8 Hz, J_2 = 3.3 Hz, 1 H), 2.71 (dd, J_1 = 10.2 Hz, J_2 = 9.3 Hz, 1 H), 2.45 (m, 4 H); IR (neat) 3541, 1730, 1649 cm^{-1}; MS m/z 390 (M^+), 272, 257, 232; HRMS m/z for $C_{21}H_{26}O_7$ calcd 390.167 85, measured 390.167 77; TLC (3:1 H–EA) R_f = 0.3.

4: NMR ($CDCl_3$) δ 13.03 (0.5 H, s), 6.96 (m, 1 H), 6.82 (m, 1 H), 5.93 (m, 2 H), 5.28 (m, 4 H), 4.64 (m, 4 H), 3.87 + 3.85 (s, 3 H), 3.81 + 3.78 (s, 3 H), 3.39 (m, 1 H), 3.24 (m, 1 H), 2.57 (m, 2 H), 2.26 (m, 1 H), 2.95 (m, 1 H); IR (neat) 3454, 1738, 1688 cm^{-1}; TLC (3:2 H–EA) R_f = 0.25.

5: NMR ($CDCl_3$) δ 6.95 (d, J = 9.0 Hz, 1 H), 6.79 (d, J = 9.0 Hz, 1 H), 5.71 (m, 1 H), 5.11 (m, 2 H), 4.49 (m, 2 H), 3.83 (s, 3 H), 3.78 (s, 3 H), 3.70 (s, 3 H), 3.18 (dd, J_1 = 16.5 Hz, J_2 = 13.5 Hz, 1 H), 2.78 (dd, J_1 = 16.5 Hz, J_2 = 13.8 Hz, 1 H), 2.55 (m, 6 H), 2.41 (q, J = 7.5 Hz, 2 H), 2.08 (m, 1 H), 1.02 (t, 7.5 Hz); IR (neat) 1738, 1683 cm^{-1}; HRMS m/z for $C_{24}H_{30}O_8$ calcd 446.193 66, measured 446.193 66; ^{13}C NMR ($CDCl_3$) δ 210.42, 193,59, 172,50, 170.66, 153.91, 149.82, 132.01, 131.22, 122.69, 118.49, 115.35, 110.29, 65.61, 60.34, 56.38, 55.91, 51.87, 37.05, 35.92, 35.66, 26.83, 25.88; TLC (1:1 H–EA) R_f = 0.5.

8,9,10-Trihydroxy-4-oxo-1,2,3,4-tetrahydro-3-(3-oxopentyl)-3-(2-oxa-1-oxo-4-pentenyl)anthracene-2-acetic Acid, Methyl Ester (8). To a suspension of **5** (100 mg, 0.22 mmol) and AgO (200 mg, 1.61 mmol) in 8 mL of THF at 25 °C was added 300 μL of HNO_3. After 15 min, the suspension was diluted with 10 mL of 4:1 $CHCl_3$–H_2O. The organic layer was dried and concentrated. The unstable quinone was dissolved in 6 mL of CH_2Cl_2, and the solution was cooled to −15 °C. To this solution was added 1-[(trimethylsilyl)oxy]butadiene (0.5 mL). The solution was stirred at −15 °C for 1 h and was allowed to warm to 25 °C over 5 h. The mixture was treated with excess of Jones reagent in 1 mL of acetone at 0 °C for 15 min. 2-Propanol was added to destroy excess Jones reagent. The crude product was purified by SG chromatography using 2:1 H–EA to afford **8**.

8: NMR ($CDCl_3$) δ 13.30 (s, 1 H), 8.51 (s, 1 H), 8.43 (s, 1 H), 7.85 (d, J = 7.8 Hz, 1 H), 7.21 (t, J = 7.8 Hz, 1 H), 6.88 (d, J = 7.8 Hz, 1 H), 5.79 (m, 1 H), 5.17 (m, 2 H), 4.56 (m, 2 H), 3.75 (s, 3 H), 3.30 (m, 1 H), 2.55 (m, 9 H), 2.30 (m, 1 H), 1.07 (t, J = 7.5 Hz, 3 H); IR (CH_2Cl_2) 3600, 3460, 1735, 1715, 1670 cm^{-1}; MS m/z CI MS (M^+ + 1) 485; TLC (2:1 H–EA) R_f = 0.36.

4,8-Dihydroxy-9,10-dioxo-3-(3-oxopentyl)-2-anthraceneacetic Acid, Methyl Ester (9). A solution of **8** (11 mg, 0.023 mmol), palladium acetate (3 mg), and 6 mg of dppe in 3 mL of acetonitrile was heated at reflux for 40 min. The solvent was removed in vacuo and the residue purified by SG chromatography using 4:1 H–EA to afford 7.3 mg (81% yield) of **9**.

9: NMR ($CDCl_3$) δ 13.11 (s, 1 H), 12.65 (s, 1 H), 7.83 (dd, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1 H), 7.70 (s, 1 H), 7.67 (dd, J_1 = 7.5 Hz, J_2 = 7.8 Hz, 1 H), 7.31 (dd, J_1 = 7.8, J_2 = 1.2 Hz, 1 H), 3.92 (s, 2 H), 3.72 (s, 3 H), 3.03 (t, J = 7.5 Hz, 2 H), 2.80 (t, J = 7.5 Hz, 2 H), 2.44 (q, J = 7.5 Hz, 2 H), 1.06 (t, J = 7.5 Hz, 3 H); IR (CH_2Cl_2) 3050, 1735, 1715, 1630 cm^{-1}; MS m/z CI MS (NH_3) 397; HRMS m/z for $C_{22}H_{20}O_7$ calcd 396.120 90, measured 396.121 11; TLC (4:1 H–EA) R_f = 0.38; mp 170–172 °C.

4-Hydroxy-5,8-dihydro-5,8-dioxo-3-(3-oxopentyl)-naphthaleneacetic Acid, Methyl Ester (11). To a suspension of ester **5** (100 mg, 0.22 mmol) and AgO (200 mg, 1.61 mmol) in 10 mL of THF was added 300 μL of 6 N HNO_3. After 15 min, the reaction was quenched by the addition of 4:1 $CHCl_3$–H_2O. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried and concentrated in vacuo. The residue was used directly in the next step.

A solution of $Pd(OAc)_2$ (17 mg, 0.075 mmol) and 30 mg of dppe in 10 mL of CH_3CN was heated at reflux under argon for 2 min. The solution was cooled, and the crude quinone was added. The solution was heated at reflux for 50 min, cooled to 25 °C, diluted with CH_2Cl_2, and filtered through Florisil. The solvent was removed in vacuo. To the residue was added 10 mL of toluene and DDQ (50 mg, 0.22 mmol). The solution was heated at 110 °C for 5 h. Purification by SG chromatography afforded 30.5 mg (42% yield) of **11**.

11: NMR ($CDCl_3$) δ 12.36 (s, 1 H), 7.48 (s, 1 H), 6.92 (s, 2 H), 3.88 (s, 2 H), 3.71 (s, 2 H), 2.99 (t, J = 7.5 Hz, 2 H), 2.77 (t, J = 7.5 Hz, 2 H), 2.43 (q, J = 7.2 Hz, 2 H), 1.05 (t, J = 7.2 Hz, 3 H); IR (CH_2Cl_2) 3025, 1738, 1715, 1670 cm^{-1}; MS m/z 330 (M^+) 274.1; HRMS m/z for $C_{18}H_{18}O_6$ calcd 330.110 34, measured 330.109 99; TLC (3:1 H–EA) R_f = 0.375.

4,5-Dihydroxy-9,10-dioxo-3-(3-oxopentyl)anthracene-2-acetic Acid, Methyl Ester (10). To a solution of **11** (12 mg, 0.036 mmol) in 1.5 mL of CH_2Cl_2 at −30 °C was added 1-[(trimethylsilyl)oxy]butadiene (0.5 mL). The solution was stirred at −30 °C for 20 h and at 25 °C for 9 h. The solvent was removed in vacuo. To a solution of the unpurified product in 5 mL of acetone was added Jones reagent (0.3 mL). The excess Jones reagent was destroyed with 2-propanol. The product was purified by SG chromatography using 5:1 H–EA to afford 12.1 mg (83% yield) of **10**. Compound **10** was a yellow solid with mp 178–179 °C. In addition, 1.3 mg (9% yield) of **9** was produced.

10: NMR ($CDCl_3$) δ 12.53 (s, 1 H), 12.07 (s, 1 H), 7.83 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1 H), 7.70 (s, 1 H), 7.69 (t, J = 7.8 Hz, 1 H), 7.30 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1 H), 3.92 (s, 2 H), 3.72 (s, 3 H), 3.03 (t, J = 7.5 Hz, 2 H), 2.80 (t, J = 7.5 Hz, 2 H), 2.44 (q, J = 7.2 Hz, 2 H), 1.07 (t, J = 7.2 Hz, 3 H); IR (CH_2Cl_2) 3050, 1740, 1715, 1670 cm^{-1}; MS m/z 396.1 (M^+) 340, 307, 279, 265; HRMS m/z for $C_{22}H_{20}O_7$ calcd 396.1290, measured 396.120 54; TLC (3:1 H–EA) R_f = 0.458; mp 178–179 °C.

7-Deoxyaklavinone (13a). To a solution of **10** (10 mg, 0.025 mmol) in 6 mL of MeOH at −15 °C was added 1 mL of pyridine followed by 300 μL of Triton B. After 3 h at −15 °C, the reaction was allowed to warm slowly to 8 °C. The solution was poured into cold 2 N HCl, and the aqueous layer was extracted twice with CH_2Cl_2. The organic layer was washed with brine, dried, and concentrated. The residue was purified by SG chromatography using 6:1 H–EA to afford 5.0 mg (50% yield) of **13a** and 2.6 mg (26% yield) of **13b**.

13a: NMR ($CDCl_3$) δ 12.50 (s, 1 H), 12.10 (s, 1 H), 7.82 (dd, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1 H), 7.67 (dd, J_1 = 8.1 Hz, J_2 = 7.5 Hz, 1 H), 7.66 (s, 1 H), 7.29 (dd, J_1 = 8.1 Hz, J_2 = 1.2 Hz, 1 H), 3.94 (s, 1 H), 3.73 (s, 3 H), 3.07 (ddd, J_1 = 19.2 Hz, J_2 = 6.9 Hz, J_3 = 2.1 Hz, 1 H), 2.85 (ddd, J_1 = 19.2 Hz, J_2 = 10.5 Hz, J_3 = 6.9 Hz, 1 H), 2.31 (ddd, J_1 = 14.1 Hz, J_2 = 10.5 Hz, J_3 = 6.9 Hz, 1 H), 1.94 (ddt, J_1 = 14.1 Hz, J_2 = 6.9 Hz, J_3 = 2.1 Hz, 1 H), 1.72 (dq, J_1 = 14.7 Hz, J_2 = 7.2 Hz, 1 H), 1.60 (dq, J_1 = 14.7 Hz, J_2 = 7.2 Hz, 1 H), 1.08 (t, J = 7.5 Hz, 3 H); IR (CH_2Cl_2) 3590, 3055, 2928, 2855, 1734, 1622, 1471, 1419, 1384, 1289, 1249, 1160, 909 cm^{-1}; MS m/z 396 (M^+), 378, 340, 319, 307, 279; HRMS m/z for $C_{22}H_{20}O_7$ calcd 396.120 90, measured 396.120 99; TLC (2:1 H–EA) R_f = 0.58; mp 217–219 °C.

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Supplementary Material Available: Proton NMR data for compounds **4**, **5**, **8**, and **11** (6 pages). Ordering information is given on any current masthead page.