1080, 1030, 910, 790, 770, 750, 700; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (dd, J = 3.5, 3.8 Hz, 4 H), 4.37 (dd, J = 3.5, 3.8 Hz, 4 H), 2.98 (s, 6 H), 2.19 (br s, 4 H), 1.61 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 158.43, 129.75, 61.07, 36.61, 33.29, 25.52, 23.33; MS m/z (M^+) calcd 410.1702, obsd 410.1754.

Anal. Calcd for $C_{20}H_{22}N_6O_4$: C, 58.53; H, 5.40. Found: C, 58.07; H, 5.49.

Photocyclization of 47. A solution of **47** (16 mg, 0.04 mmol) in acetone (16 mL) and dichloromethane (10 mL) was placed in a Pyrex text tube, stoppered with a rubber septum, and deoxygenated with argon for 3 min. Following irradiation with a 450-W Hanovia lamp housed in a Pyrex well for 3.5 h, TLC analysis showed no **47** remaining. The solvent was evaporated and the residue was purified by flash chromatography (silica gel, elution with the four-component solvent system used for **47**). There was isolated 13 mg (81%) of **48** as colorless crystals, mp > 300 °C (from dichloromethane–pentane): IR (KBr, cm^{-1}) 2950, 2920, 1745, 1680, 1460, 1390, 1255, 755, 740; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (br s, 4 H), 3.11 (s, 6 H), 3.01 (br s, 4 H), 2.02–1.50 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 152.83, 56.41, 45.86, 35.14, 26.46, 25.40, 17.27; MS m/z (M^+) calcd 410.1702, obsd 410.1687.

Anal. Calcd for $C_{20}H_{22}H_6O_4$: C, 58.53; H, 5.40. Found: C, 57.92; H, 5.53.

MTAD Addition to 5. A solution of **5** (45 mg, 0.25 mmol) in dry dichloromethane (2.5 mL) was treated dropwise with a solution of MTAD (1.0 mmol) in the same solvent (2.5 mL). The red color of the dienophile was instantaneously consumed as it came into contact with the hexaene. The solvent was evaporated and the solid residue was recrystallized from ethyl acetate to give 48 mg of **49**. Chromatography of the mother liquor on silica gel returned an additional 22 mg of **49** (total yield of 69%), a colorless crystalline solid, mp 247 °C dec (from dichloromethane–pentane): IR (KBr, cm^{-1}) 3050, 3000, 2940, 2910, 1760, 1690, 1455, 1390, 1190, 1035, 775, 730; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (dd, J = 3.3, 3.7 Hz, 2 H), 6.28 (dd, J = 3.4, 3.9 Hz, 2 H), 5.95 (dd, J = 2.8, 7.6 Hz, 2 H), 5.51 (dd, J = 2.8, 7.6 Hz, 2 H), 4.68 (dd, J = 3.4, 3.9 Hz, 2 H), 4.57 (dd, J = 3.3, 3.7 Hz, 2 H), 2.97 (s, 3 H), 2.95 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 158.04, 156.60, 129.53, 126.62, 125.19, 124.89, 56.96, 53.71, 46.52, 25.46; MS m/z (M^+ – $C_7H_7N_3O_2$) calcd 241.0851, obsd 241.0883.

Anal. Calcd for $C_{20}H_{18}N_6O_4 \cdot 0.3CH_2Cl_2$: C, 56.46; H, 4.21. Found: C, 56.53; H, 4.57.

Acknowledgment. We thank the National Science Foundation for financial support, Dr. Charles Cottrell for the variable-temperature and 2-D NMR studies, and C. R. Weisenberger for the high field mass spectral determinations.

Registry No. **5**, 108189-46-4; **6**, 93750-00-6; **7**, 93775-15-6; **8**, 88343-66-2; **9**, 102343-81-7; **10**, 124820-73-1; **11**, 102490-07-3; **12**, 124820-74-2; **13**, 124820-75-3; **14**, 124820-76-4; **15**, 124820-77-5; **16**, 124820-78-6; **17**, 124820-79-7; **18**, 102419-33-0; **19**, 124820-80-0; **22**, 108189-51-1; **23**, 124820-82-2; **24**, 4725-09-1; **25**, 124820-83-3; **26**, 85067-45-4; **27a**, 124820-70-8; **27b**, 124854-75-7; **27** (acid chloride), 124820-81-1; **28**, 124820-85-5; **28** (monoethylene glycol ester), 124820-99-1; **29**, 124820-86-6; **29** (monoethylene glycol ester), 124821-00-7; **30a**, 124820-71-9; **30b**, 124820-72-0; **31**, 124820-88-8; **32**, 124820-89-9; **33a**, 124820-84-4; **33b**, 124820-90-2; **34a**, 124820-87-7; **35**, 124820-92-4; **36a**, 124820-91-3; **36b**, 124820-95-7; **37**, 124820-94-6; **38a**, 124820-93-5; **38b**, 124820-98-0; **39**, 108189-49-7; **40**, 3469-26-9; **41**, 108189-50-0; **42**, 108167-63-1; **43**, 124854-76-8; **44**, 124820-96-8; **45**, 124986-03-4; **46**, 124854-77-9; **47**, 124986-04-5; **48**, 124854-78-0; **49**, 124820-97-9; **52**, 19539-78-7; MTAD, 13274-43-6; 2-methoxy-1,3-dioxolane, 497-26-7; trimethoxyphenanthrene, 124821-01-8; benzocyclooctatetraene, 265-49-6.

Supplementary Material Available: Tables of final fractional coordinates, thermal parameters, and least-squares planes (5 pages); observed/calculated structure factors for **5** (1 page). Ordering information is given on any current masthead page.

A Synthesis of Polycyclic Aromatic Compounds by the $Ca(OAc)_2$-Induced Aromatization of Polyoxoalkanedioates Generated from Diesters and Acetoacetate Dianion

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The dual-Claisen condensation of diesters with acetoacetate dianion generated tetraoxoalkanedioates, whose aromatization by $Ca(OAc)_2$-promoted intramolecular condensation constructed two carbocyclic rings containing phenol part. The reactions converted glutarates to bicyclic phenols and homophthalates to 1,9-dihydroxyanthracenes. The latters were air-oxidized to anthraquinones in the presence of K_2CO_3. The regiochemistry of the arene synthesis was studied. As the products of this synthesis also were glutarates, further extension of the aromatic ring system was carried out. Pentacenequinones were synthesized from anthracenes, while anthraquinones gave naphthacenequinones. The reactions are related to the biosynthesis of polycyclic aromatic compounds, and arenes obtained are useful intermediates in the natural products synthesis. A formal synthesis of aklavinone was achieved.

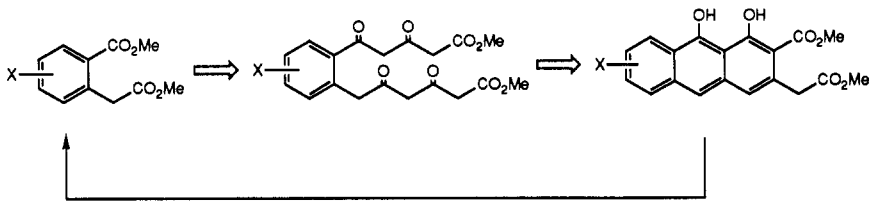
A variety of aromatic natural products are biosynthesized from simple acids such as acetic acid, propionic acid, and so on. It is considered that a series of Claisen condensations gives chain molecules with β-polyketone functionalities (polyketides), whose intramolecular condensation and enolization construct aromatic nuclei such as naphthalene, anthracene, naphthacene, and benz[a]anthracene.[1]

From the synthetic standpoint of view, the use of polyketides is quite attractive, since they give polyfunctionalized polycyclic aromatic compounds structurally related to the natural products. Generally, functionalization of polycyclic arenes at a particular position is not an easy

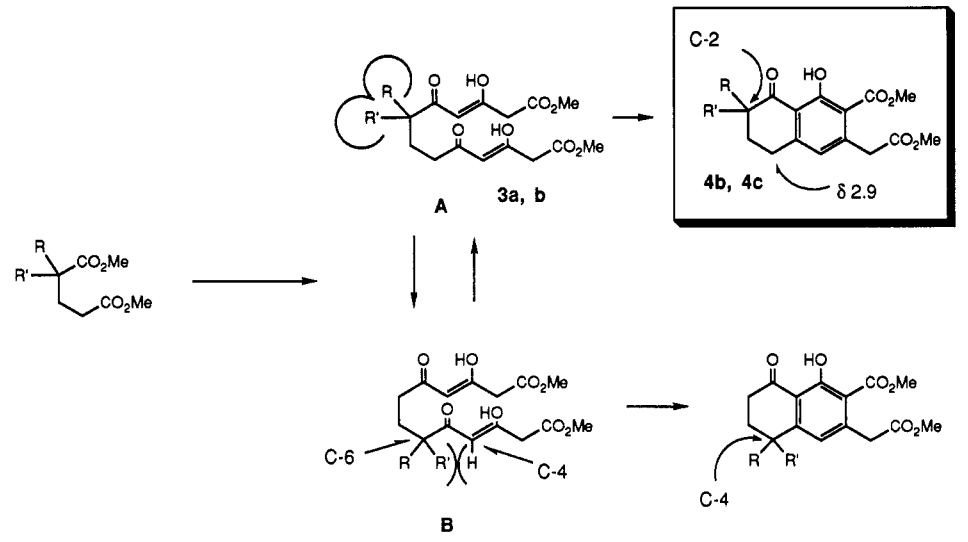
(1) Simpson, T. J. *Nat. Prod. Rep.* **1984**, *1*, 281; **1985**, *2*, 321; **1987**, *4*, 339.

0022-3263/90/1955-1611$02.50/0

Scheme I



Scheme II



task. Harris and co-workers have for years been studying on the synthesis employing polyketides.[2] The dual-Claisen condensation methodology, the formation of polyketides by the Claisen condensation of dicarboxylic acid derivatives with enolate anions, was developed by this group. Although acetylacetone dianion was first used as the nucleophile,[3] the use of acetoacetate dianion[4] seemed also interesting,[5] since the terminal ester groups could be used as handles for further functional manipulations. For examples, reduction, alkylation, decarboxylation, or extension of the aromatic ring system might be carried out. We started to examine the Claisen condensation of dicarboxylic acid derivatives with acetoacetate dianion and the aromatization of the resulted $\beta,\beta',\delta,\delta'$-tetraoxoalkanedioates and found $Ca(OAc)_2$ to be an effective catalyst for the intramolecular condensation.[6,7] Various polycyclic aromatic compounds were synthesized (Scheme I), and the details are presented in this paper.[8]

It should be noted that Harris recently reported the use of acetoacetate dianion in their dual-Claisen condensation methodology, and successfully applied it to the synthesis of pretetramide and related compounds.[9]

Results and Discussions

The reaction of dimethyl glutarate (**1a**) with sodium and lithium dianion **2**[4] of methyl acetoacetate in THF at room temperature gave a dual-Claisen condensation product—dimethyl 3,5,9,11-tetraoxodecanedioate (**3a**).[10] The polyketide intermediate **3a**, without isolation, was intramolecularly dehydrated in the presence of $Ca(OAc)_2$ in methanol, and methyl 8-hydroxy-7-(methoxycarbonyl)-1-oxo-1,2,3,4-tetrahydro-6-naphthylacetate (**4a**) was obtained (Table I, entry 1).

Several substituted glutarates were also subjected to the reactions. Dimethyl 6-substituted 3,5,9,11-tetraoxododecanedioate **3b** and **3c**, generated from α-alkyl-substituted glutarates **1b** and **1c**, were aromatized to 2-substituted 1,2,3,4-tetrahydronaphthylacetates **4b** and **4c**. No 4-isomer was detected (entries 2, 3). The structure was determined by ^1H NMR spectroscopy. 1,2,3,4-Tetrahydronaphthalen-1-one derivatives showed C-2 methylene at δ 2.6–2.7 and C-4 at around δ 2.9.[11] Both products **4b** and **4c** exhibited methylene peaks at about δ 2.9, indicating the absence of substituent at C-4 position. The regiose-

(2) Reviews: (a) Harris, T. M.; Harris, C. M. *Tetrahedron* **1977**, *33*, 2159. (b) Harris, T. M.; Harris, C. M. *Pure Appl. Chem.* **1986**, *58*, 283.

(3) (a) Harris, T M.; Webb, A. D.; Harris, C. M.; Wittek, P. J.; Murray, T. P. *J. Am. Chem. Soc.* **1976**, *98*, 6065. (b) Webb, A. D.; Harris, T. M. *Tetrahedron Lett.* **1977**, 2069.

(4) Huckin, S. N.; Weiler, L. *Tetrahedron Lett.* **1972**, 2405; *Can. J. Chem.* **1974**, *52*, 1343.

(5) The employment of acetone dianion as the nucleophile was reported by Bringmann: (a) Bringmann, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 200. (b) *Tetrahedron Lett.* **1982**, *23*, 2009. (c) *Justus Liebigs Ann. Chem.* **1985**, 2126.

(6) (a) Review: Yamaguchi, M. *J. Org. Synth. Jpn.* **1987**, *45*, 969. (b) Yamaguchi, M.; Shibato, K.; Hirao, I. *Chem. Lett.* **1985**, 1145. (c) Yamaguchi, M.; Shibato, K.; Nakashima, H.; Minami, T. *Tetrahedron* **1988**, *44*, 4767.

(7) Parker, K. A.; Breault, G. A. *Tetrahedron Lett.* **1986**, *27*, 3835. Interestingly, a phenol formed from "bent"-type polyketide was obtained as a byproduct from aromatization with sodium hydride and crown ether.

(8) Preliminary reports: (a) Yamaguchi, M.; Hasebe, K.; Minami, T., *Tetrahedron Lett.* **1986**, *27*, 2401. (b) Yamaguchi, M.; Hasebe, K.; Uchida, M.; Irie, A.; Minami, T. *Tetrahedron Lett.* **1987**, *28*, 2017.

(9) (a) Mahalingam, S.; Kuzuma, P. C.; Lee, J. Y.-C.; Harris, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 7760. (b) Gilbreath, S. G.; Harris, C. M.; Harris, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 6172. (c) Harris, T. M.; Harris, C. M.; Oster, T. A.; Brown, L. E., Jr.; Lee, J. Y.-C. *J. Am. Chem. Soc.* **1988**, *110*, 6180. (d) Harris, T. M.; Harris, C. M.; Kuzuma, P. C.; Lee, J. Y.-C.; Mahalingam, S.; Gilbreath, S. G. *J. Am. Chem. Soc.* **1988**, *110*, 6186.

(10) In the previous studies,[6] **3a** was generated by the BF_3-promoted Claisen condensation of *N,N,N',N'*-tetramethylglutaramide. Although the reaction proceeded under mild reaction conditions, it turned out to be less effective for sterically hindered or unreactive substrates.[6c] And the original Weiler's method[4] or its modification (use of THF–HMPA as the solvent) was employed throughout the present work.

(11) *The Aldrich Library of NMR Spectra*; Vol. VI, 11D, 12D, and 13C, 1974.

Scheme III

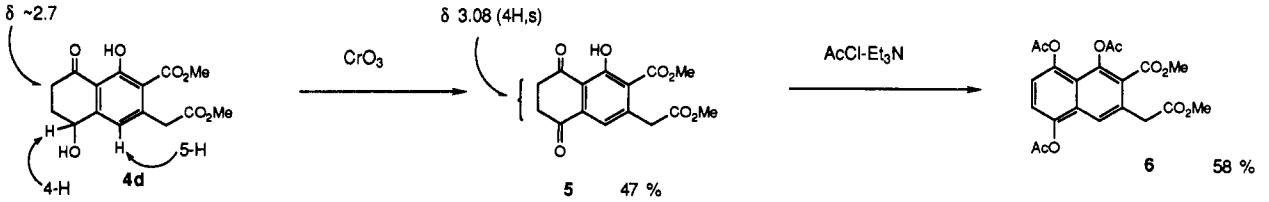
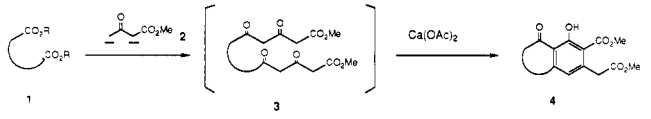


Table I. Synthesis of Aromatic Glutarates 4 from Simple Diesters 1



entries	diesters	aromatic glutarates	yield, %
1	1a	4a	77
2	1b	4b	30
3	1c	4c	44
4	1d	4d	16
5	1e	4e	50
6	1f	4f	37
7	1g	4g	24
8	1h	4h	58
9	1i	4i (syn)	13[a]
		4i (anti)	4[a]
10	1j	4j	56

[a] Isolated after methylation.

lectivities were explained as follows, taking account of the conformation of the polyketide intermediates **3b** and **3c** (Scheme II). The 2- and 4-substituted products would be formed via conformations A and B, respectively, in which 1,3-diketone moieties existed mainly as enol form.[6c] It was considered that the steric repulsion between vinylic hydrogen at 4-position and 6-substituents disfavored the conformation B, which resulted in the formation of 2-substituted products via conformation A.

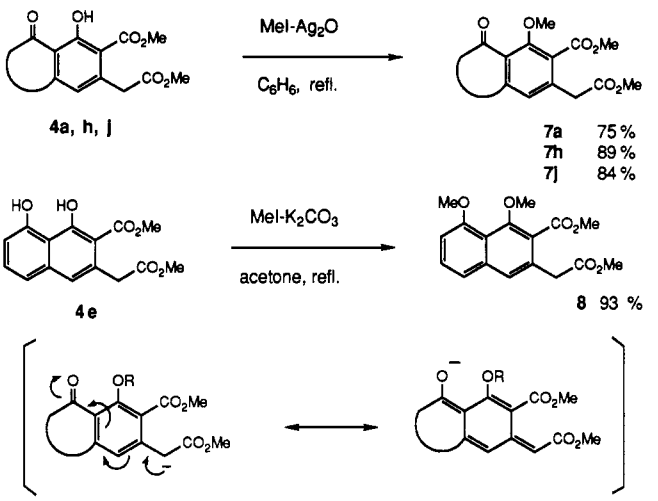
A reversal of the selectivity was observed with 6-hydroxy-3,5,9,11-tetraoxododecanedioate (**3d**) generated from α-hydroxyglutarate, **1d**. The tetraoxo ester **3d** gave 4-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene (**4d**) (entry 4), which showed methylene peaks centered at δ 2.7. The structure was further confirmed by the observation of NOE in diacetylated **4d** between the 4- and the 5-proton. It was presumed that a hydrogen bond between the 6-hydroxy group and the adjacent carbonyl in **3d** was playing an important role in the phenomenon. The product **4d** was oxidized with CrO_3 in aqueous acetic acid, giving 1,4-dioxo-1,2,3,4-tetrahydronaphthalene, **5**, which existed in keto form in $CDCl_3$, showing a singlet at δ 3.08. Acetylation with acetyl chloride and triethylamine converted **5** to triacetoxynaphthalene **6** (Scheme III).

When β-hydroxyglutarates **1e–g** were employed as the substrates, further dehydration reaction proceeded, and naphthalenediols **4e–g** were obtained (entries 5–7). The ethoxycarbonyl group attached to the tertiary carbon was not affected in the reaction of triethyl citrate **1g**. Harris obtained **4e** in poor yields from **1e** or diethyl 3-(1-pyrrolidinyl)glutarate with the dilithium salt of methyl acetoacetate. The aromatization step did not seem to have been examined in detail.[9b]

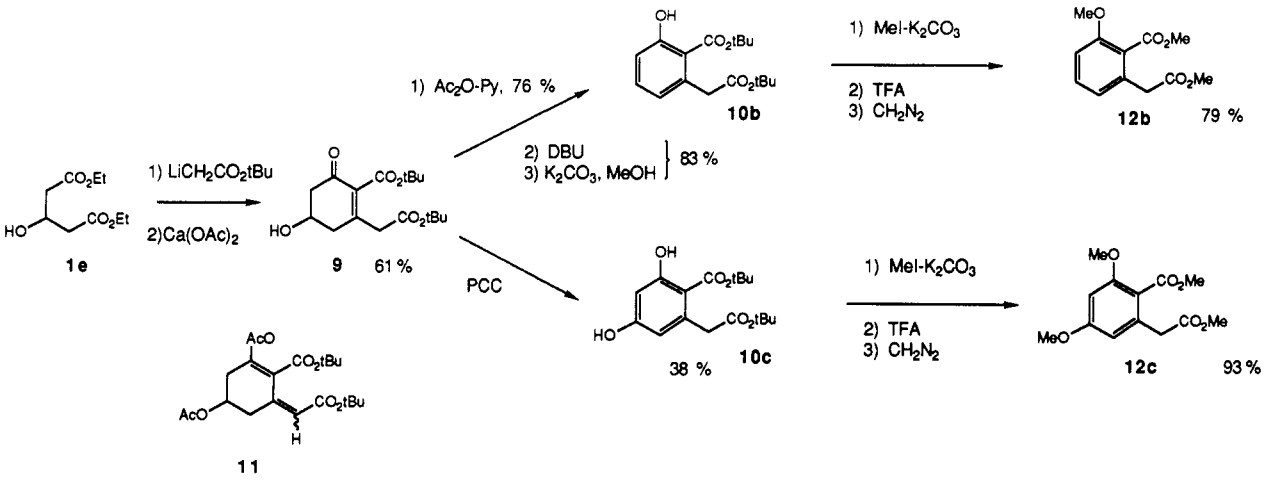
The reactions were applied not only to the glutarates but also to the succinates and adipiates. Diethyl phthalate **1h** gave 9-oxo-3-fluorenylacetate **4h** by five-membered ring formation (entry 8). With 1,2,4,5-benzenetetracarboxylate **1i**, aromatic rings were extended in two directions. As expected from the structure of the polyketide intermediate, two isomers, *syn*- and *anti*-indenofluorenone **4i**, were obtained with the former predominating (entry 9). The structure was determined by ^1H NMR spectroscopy: *syn*-**4i** showed three singlets in 2:1:1 ratio at aromatic region, while *anti*-**4i** exhibited two singlets in 1:1 ratio. Tribenzo[*a*,*c*,*e*]cycloheptatrien-5-one **4j** was synthesized from diethyl 2,2′-bibenzoate **1j** by seven-membered ring formation (entry 10).

Comments are required concerning methylation of these phenolic hydroxy groups (Scheme IV). The protection of phenols chelated to adjacent ketones—for example,

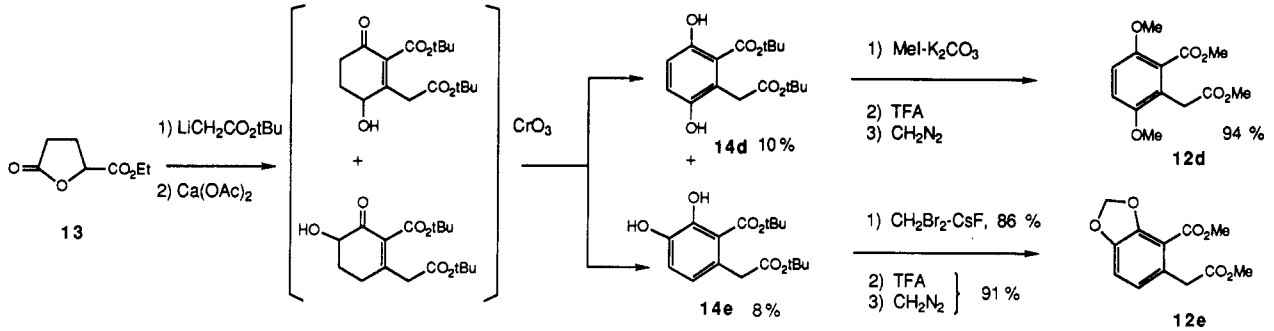
Scheme IV



Scheme V



Scheme VI



4a,h,j—had to be carried out with MeI–Ag_2O, since the use of MeI–K_2CO_3 resulted in methylation at benzylic position (cf. Scheme XIII). Naphthalenediol **4e**, however, was methylated with MeI–K_2CO_3. Presumably, the presence of electron-withdrawing carbonyl groups made the benzylic methylenes more acidic for the former compounds. As will be described later, methylation of phenolic compounds which were susceptible to oxidation, for example **15a,b,f**, was carried out with Me_2SO_4–K_2CO_3.

Our attention was next directed to the reaction of homophthalates—synthesis of anthracenes by constructing two aromatic rings. At first, several homophthalates were conveniently prepared from α- and β-hydroxyglutarates **1d** and **1e**, which also involved the Claisen condensation and intramolecular dehydration (Schemes V and VI). When β-hydroxyglutarate **1e** was treated with lithiated *tert*-butyl acetate followed by $Ca(OAc)_2$, 5-hydroxy-2-cyclohexenone **9** was obtained. Interestingly, a hydroxy group was not dehydrated,[12] which was contrasted to the synthesis of **4e–g**. Dehydration was carried out by two-step procedures. Acetic anhydride in pyridine acetylated both the hydroxy and the carbonyl group, giving diacetate **11**, which was aromatized with DBU. Methanol and K_2CO_3 were directly added to the reaction mixture to remove the remaining 3-acetyl group, affording **10b**. A simple PCC-oxidation of **9** gave 3,5-dihydroxyhomophthalate **10c** after spontaneous enolization. Methylation and transesterification converted **10b** and **10c** to homophthalates **12b**[13] and **12c**.[14]

Other dihydroxyhomophthalate **12d** and **12e** were synthesized from diethyl α-hydroxyglutarate (**4**). Lactone **13**, prepared from **4**, was reacted with lithiated *tert*-butyl acetate followed by $Ca(OAc)_2$, and the resulted crude mixture was oxidized with CrO_3 in acetic acid, giving 3,6-dihydroxyhomophthalate **14d** and 3,5-dihydroxy derivative **14e**, which were separable by silica gel chromatography. Attempts to improve the yields by using various oxidation reagents were unsuccessful. One of the two compounds was converted to an acetal **12e** with methylene bromide and CsF showing the presence of 1,2-diol moiety. The other isomer **14d** was transformed to dimethyl ether **12d**.

The syntheses of various 1,9-dihydroxyanthracene **15** and naphthacene **16** from **8** and **12** are summarized in Table II.[15] It is known that 9-hydroxyanthracenes are in tautomeric equilibrium between the enol (anthrol) and the keto form (anthrone). The predominant form in $CDCl_3$ was dependent on the substituents: 8-methoxy-, 5,8-dimethoxy, and 10-methylanthracene (**15b**, **15d**, and **15f**) existed in the enol form, and 7,8-methylenedioxyanthracene **15e** and naphthacene **16** in the keto form. Anthracene **15a** showed both peaks of anthrol and anthrone in 1:1 ratio. In contrast, all these compounds showed a peak at about 1620 cm^{-1} by IR assigned to a hydrogen-bonded diaryl ketone and seemed to exist in the keto form in the solid state.[16] A similar synthesis of **15a**

(12) A related compound was made use in the total synthesis of (+)-7-deoxynogarol: Kawasaki, M.; Matsuda, F.; Terashima, S., *Tetrahedron Lett.* **1988**, *29*, 791.

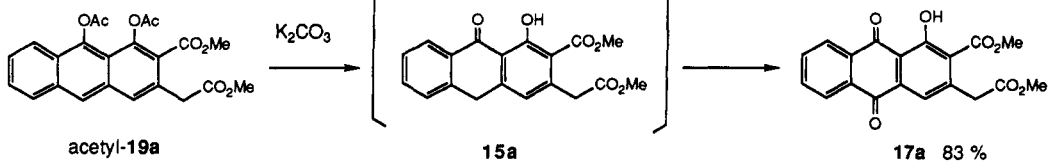
(13) (a) Arai, Y.; Kamikawa, T.; Kubota, T.; Masuda, Y.; Yamamoto, R. *Phytochemistry* **1973**, *12*, 2279. (b) Chan, T. H.; Brownbridge, P. *J. Chem. Soc., Chem. Commun.* **1981**, 20.

(14) (a) Hardegger, E.; Rieder, W.; Walser, A.; Kugler, F. *Helv. Chim. Acta* **1966**, *49*, 1283. (b) Also see: Kjaer, D.; Kjaer, A.; Risbjerg, E. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2815.

(15) An interesting effect of metal salts was observed. When $Pb(OAc)_2$ was used in place of $Ca(OAc)_2$ in the presence of oxygen, bianthrones were obtained through oxidative dimerization: Yamaguchi, M.; Hasebe, K.; Uchida, M.; Higashi, H.; Minami, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2745.

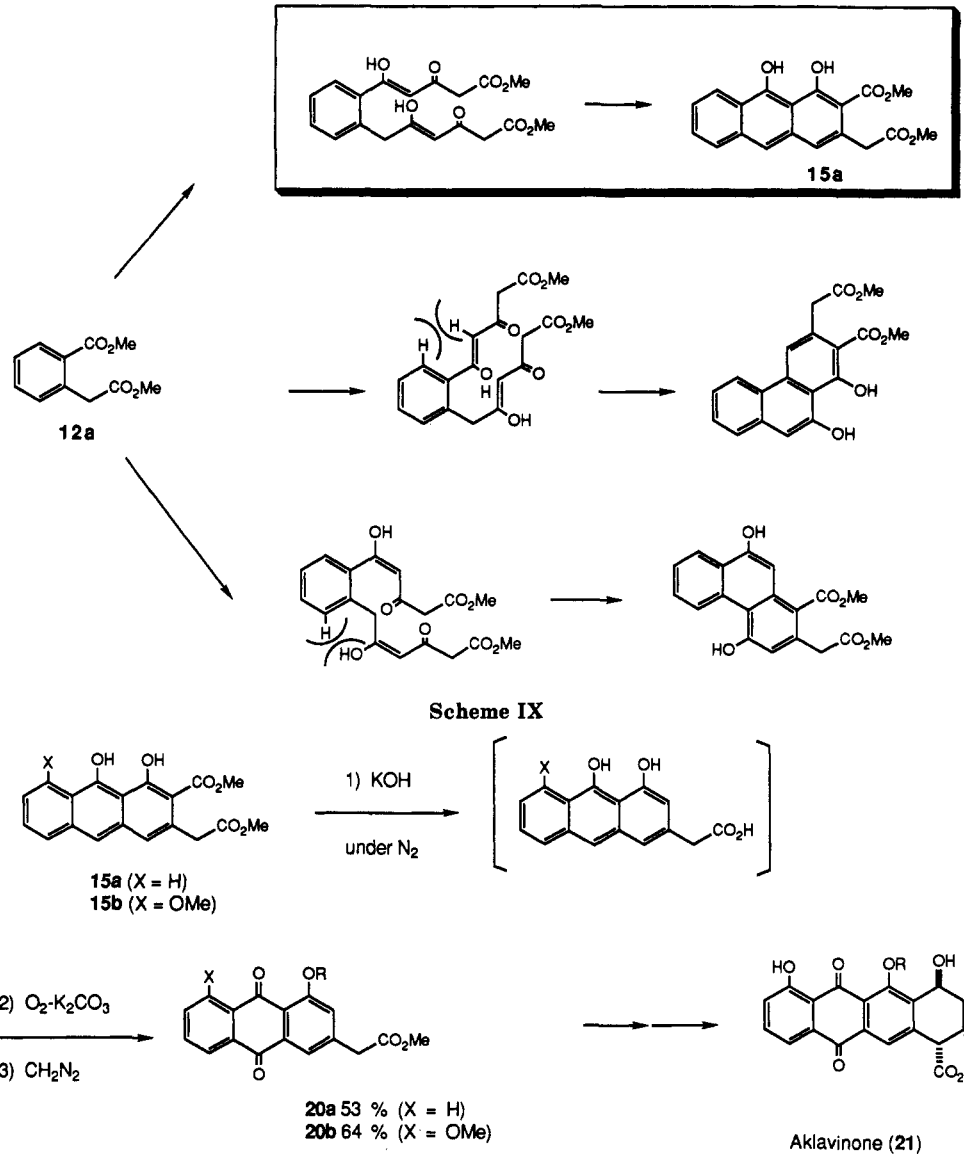
(16) Geiger, W. *Chem. Ber.* **1974**, *107*, 2976.

Scheme VII



acetyl-**19a** **15a** **17a** 83 %

Scheme VIII



Scheme IX

and **15b** was recently reported by Harris using dilithium salt of methyl acetoacetate.[9c]

Some of the anthracene derivatives **15** were isolated as diacetates (Table II). In order to regenerate dihydroxyanthracene **15a**, diacetyl-**15a** was treated with K_2CO_3 in methanol. The product, however, was not **15a** but anthraquinone **17a** (Scheme VII). Since the same reaction under a nitrogen atmosphere gave **15a**, air-oxidation must have proceeded. Although it was known that anthrone was readily air-oxidized to anthraquinone under basic conditions,[17] the above procedures provided a useful method which gave the oxidation product in high yields under milder reaction conditions. As shown in Table II, crude arenediols **15** and **16** were air-oxidized, and various quinones **17** and **18** were synthesized.

Although anthracenes were shown as the products so far, two phenanthrene-type compounds could be formed from the same polyketone intermediates via "bent" conformers (Scheme VIII).[7] The phenanthrene formation seemed unlikely to occur because of the steric repulsion between the substituent on the aromatic ring and the polyketide side chain. In order to confirm the structure, one of the products was related to a known compound.

During the studies, decarboxylation of anthracene derivatives **15a** and **15b** was found to occur under basic conditions (Scheme IX). When **15a** or **15b** was refluxed in aqueous KOH under a nitrogen atmosphere, hydrolysis of two ester groups and decarboxylation of aromatic carboxylate proceeded. The products were isolated as an-

(17) Ogata, Y.; Kosugi, Y.; Nate, K. *Tetrahedron* **1971**, *27*, 1705.

Scheme X

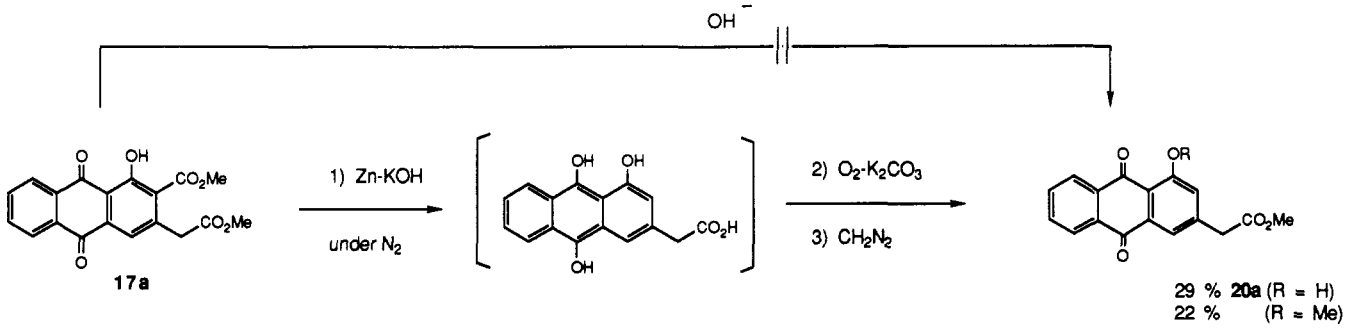
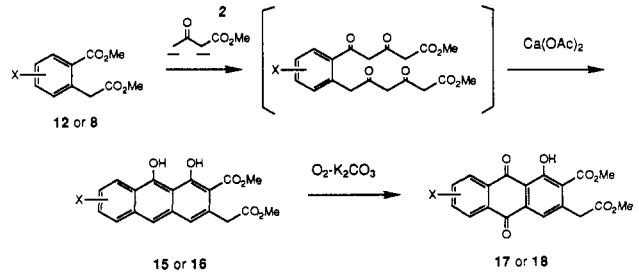


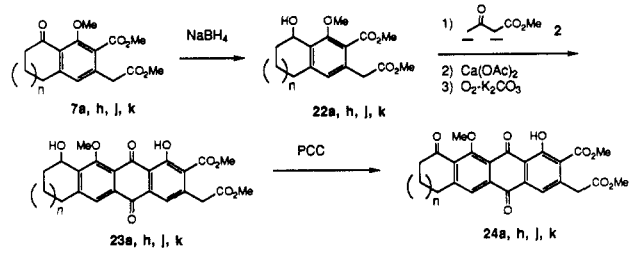
Table II. Synthesis of Anthracenes and Naphthacene from Homophthalates



aromatic glutarates	15 or 16	yields,[a] %	17 or 18	yields,[a] %
12a	15a	49 (36)[b]	17a	42
12b	15b	52 (25)[b]	17b	38
12c	15c	(48)[b]	17c	27
12d	15d	23	17d	26
12e	15e	36	17e	24
c) 12f	15f	31 (38)[b]		
8	16	37	18	27

[a] Overall yields from 12 or 8. [b] Isolated yields of diacetates. [c] Dimethyl α-methylhomophthalate (**12f**) was synthesized by treating homophthalate **12a** with MeI in the presence of NaH.

Table III. Synthesis of Polycyclic Quinones Involving Keto Function



aromatic glutarates	yields, % 22	24
7a	94	19
7h	95	14[b]
7l	a	22,[c] 47[d]
e) 7k	a	13

[a] Alcohol **22** was not isolated. [b] Air oxidation of intermediate gave **24h**, and PCC oxidation was not carried out. [c] Isolated yield of hydroxy quinone **23j**. [d] The yield of the conversion of **23j** to keto quinone **24j**. [e] Synthesized by methylation (MeI–Ag_2O) of 1-hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-9-benzocycloheptene.[6c]

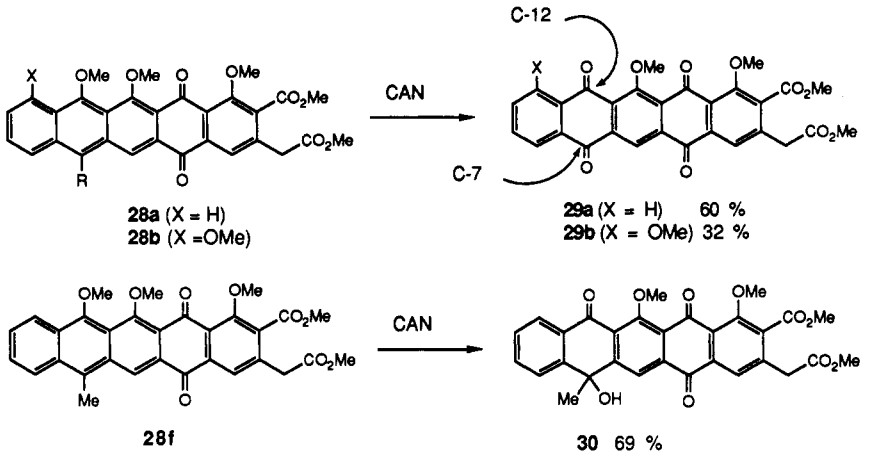
thraquinoneacetates **20a** and **20b** after K_2CO_3-induced air oxidation and esterification with diazomethane. To obtain reproducible results, it was important to carry out the decarboxylation under a nitrogen atmosphere using degassed aqueous solution. Otherwise, the oxidation of **15a** and **15b** to anthraquinones **17a** and **17b** competed, and **17a** and **17b** were not decarboxylated under these reaction conditions. Quinone **20b**, thus obtained, was identical with that utilized by Kishi in the total synthesis of aklavinone (**21**).[18] Above synthesis provided a facile approach to this intermediate by constructing the carbon framework from β-hydroxyglutarate, acetate, and acetoacetate.

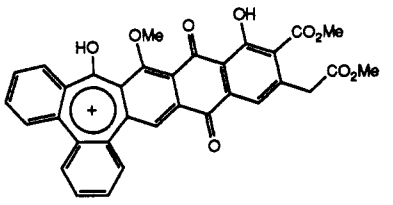
Although anthraquinone **17a** did not give the decarboxylation product **20a** by the base treatment, a reduced form of **17a** readily released carbon dioxide (Scheme X). When **17a** was reacted with zinc dust in refluxing aqueous KOH followed by air-oxidation and esterification, decarboxylated **20a** and its methyl ether were obtained. In this case, a potassium salt of anthrahydroquinone was presumed to be the species which lost carbon dioxide.

Prior protection of ketone moiety was required in the Claisen condensation of aromatic glutarates **7a,h,j,k** (Table III). Alcohols **22a,h,j,k**, synthesized by $NaBH_4$ reduction, were subjected to the Claisen condensation, aromatization, and air-oxidation, giving hydroxy quinones **23a,j,k** and oxoquinone **24h**, respectively. The benzylic hydroxy group

(18) McNamara, J. M.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 7371.

Scheme XI

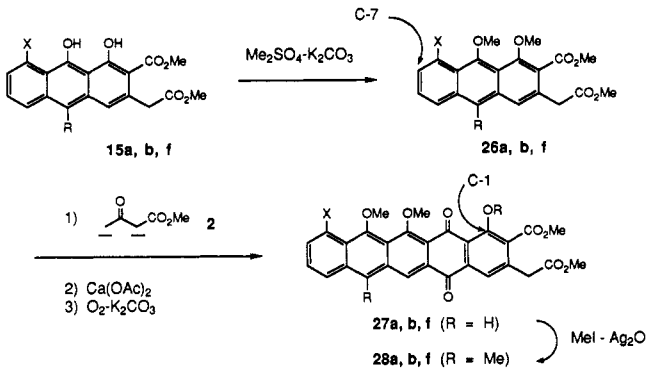




25

Figure 1.

Table IV. Synthesis of Pentacenequinone 27 and 28



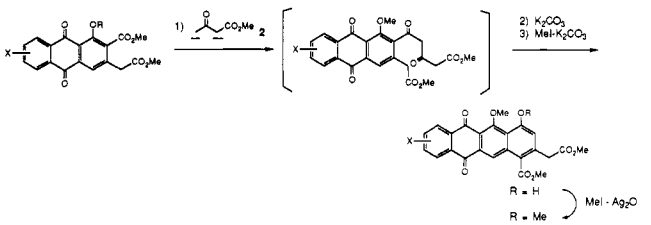
			yields, %		
15	X	R	26	27	28
15a	H	H	97	25	81
15b	MeO	H	quant	10	83
15f	H	Me	99	25	59

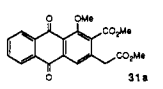
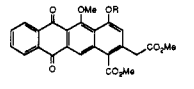
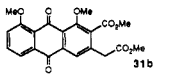
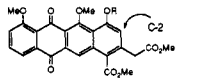
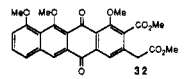
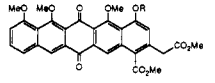
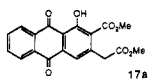
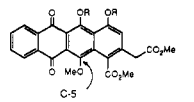
of **23h** was oxidized during the air-oxidation in the presence of K_2CO_3. The oxidation of **23a,j,k** was carried out with PCC. Tribenzotropone **24j** was capable of forming an aromatic tropylium cation **25** under acidic conditions (Figure 1). Although **24j** did not show any sign of aromatization in dilute acid solution, a change in UV spectra was observed in concentrated sulfuric acid. Compared with tropone, tribenzotropone was reported to be resistive to aromatization because of a severe steric repulsion between aromatic hydrogen atoms in the plane structure.[19]

The polycyclic aromatic compounds shown in Table II were expected to give compounds with the extended aromatic ring system. Two phenolic hydroxy groups of **15a**, **15b**, and **15f** were methylated with dimethyl sulfate in the presence of K_2CO_3 in quantitative yields. The use of methyl iodide gave unsatisfactory results. The Claisen condensation, aromatization, and oxidation converted anthracenes **26a,b,f** to pentacenequinones **27a,b,f** (Table IV). The 1-hydroxy group was methylated with MeI–Ag_2O, and the resulting pentacenequinones **28a,b,f** were oxidized with CAN, giving pentacenediquinone **29a,b** and pentacenetrione **30**, respectively (Scheme XI). The oxidation of the aromatic ring occurred at the 7,12-position, which was confirmed by an alternative synthesis of **29a** as described later (Scheme XIV).

The behavior of anthraquinone **31** was different from that of anthracene **26**. When **31b**, synthesized from **17b**, was treated with **2**, C–C bond formation occurred only at the aromatic carboxylate, and 6,11-naphthacenequinone **33b** was obtained after cyclization with K_2CO_3 (Table V).

Table V. Reaction of Quinones with Acetoacetate Dianion 2

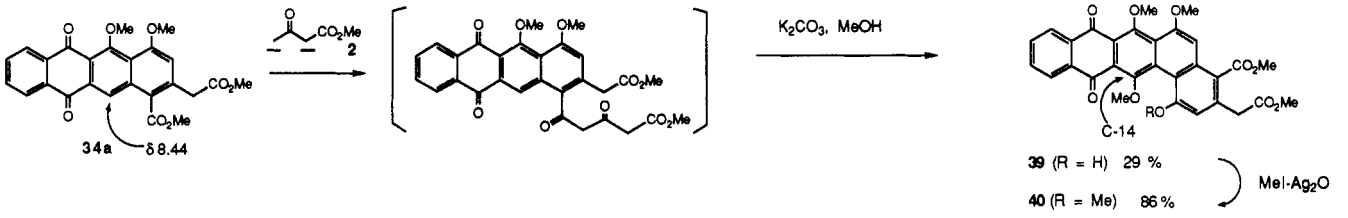


substrates[a]	products	yields, % 33, 35, 37	34, 36, 38
		20	87
		30	86
		46	93
		7	72

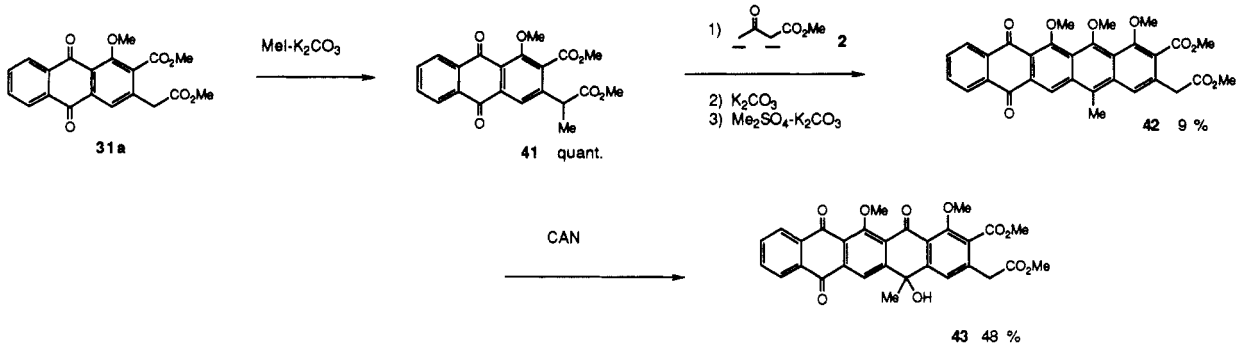
[a] Quinone **31a,b** and **32** were synthesized from **17a,b** and 18 by methylation with MeI–Ag_2O in 100, 88, and 85% yields, respectively.

(19) Stiles, M.; Libbey, A. J., Jr. *J. Org. Chem.* **1957**, *22*, 1243.

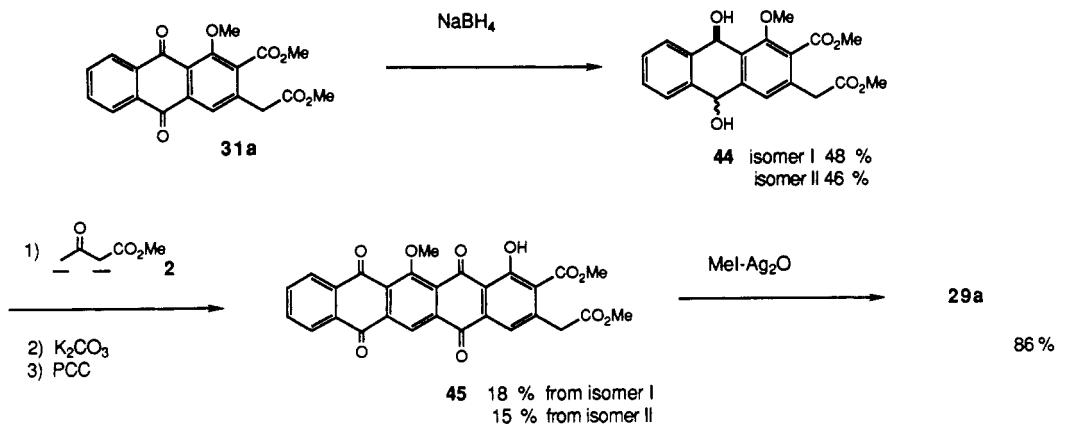
Scheme XII



Scheme XIII



Scheme XIV



In this case, $Ca(OAc)_2$ was not effective, presumably because of the less acidic nature of the benzylic methylenes compared with 1,3-diketone methylenes. The product contained two methoxycarbonyls (^1H NMR δ 3.70 and 3.83), 25 peaks by ^{13}C NMR, and the parent peak by MS corresponding to one additional methyl acetoacetate minus MeOH and H_2O from the starting material **31b**. The phenolic group was methylated with MeI–Ag_2O, and the product **34b** showed a characteristic peak at δ 105.5 by ^{13}C NMR, which was assigned to the 2-carbon. This high-field absorption of an aromatic carbon appeared when an ortho position of methoxy group was attached to a hydrogen and the aromatic ring was not condensed to a quinone ring, for example, the 7-carbon of **26b**. These observations were consistent with the structure assigned to **34b**. Similarly, anthraquinone **31a** and naphthacenequinone **32** gave naphthacenequinone **33a** and pentacenequinone **35**, respectively. It is interesting to note that quinone carbonyl survived the nucleophilic reaction conditions.

Unprotected quinone **17a** was also subjected to the reaction, and naphthacenequinone **37** was obtained in low yield. The presence of an additional methoxy peak was observed by ^1H NMR. The methoxylated carbon was determined to be C-5 by comparison of the ^1H NMR spectrum of methylated product **38** with that of **34a**. A singlet at δ 8.44 was missing in **38**. Presumably, the methoxylation occurred through the Michael addition of methanol to C-5 followed by the air-oxidation of the resulted hydroquinone. The phenomenon might be interesting in relation to the biosynthesis of daunomycinone from aklavinone, which involved hydroxylation of an aromatic ring condensed to quinone ring.[20]

When glutarate **34a** was reacted with **2**, the Claisen condensation again proceeded only at the aromatic carboxylate, and 8,13-benzo[*a*]naphthacenequinone **39** was obtained after K_2CO_3-induced intramolecular condensation (Scheme XII). Introduction of a methoxy group at 14-position was observed during the synthesis. The hydroxy group was methylated, and the site of newly introduced methoxy group was determined by the examination of ^1H NMR spectrum of methylated product **40**: a singlet at δ 8.44 of the starting material **34a** was missing in **40**.

It was considered that the deprotonation at benzylic methylenes, which were activated by electron-withdrawing quinone carbonyls (cf. Scheme IV), was disturbing the nucleophilic attack at the aliphatic carboxylate. Actually, introduction of a methyl group to the benzylic position allowed for the conduction the dual-Claisen condensation (Scheme XIII). Reaction of anthraquinone **31a** with

(20) Yoshimoto, A.; Oki, T. *J. Antibiot.* **1980**, *32*, 1199.

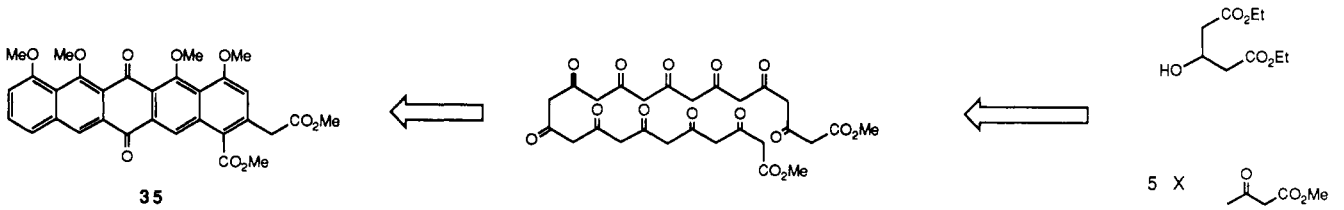


Figure 2.

MeI–K_2CO_3 gave α-methylanthraquinone **41** in quantitative yield. The Claisen condensation, aromatization, and O-methylation afforded 5-methyl-7,12-pentacenequinone, **42**. CAN-oxidation converted **42** to 5-hydroxypentacene-7,12,14-trione, **43**.

Another example of the synthesis of pentacenediquinone started from 9,10-dihydro-9,10-dihydroxyanthracene **44**, which lacked an electron-withdrawing quinone moiety (Scheme XIV). Anthraquinone **31a** was treated with $NaBH_4$ in THF–EtOH at room temperature, and **44** was obtained as a separable mixture of two diastereomers. Each of the isomers was reacted with acetoacetate dianion **2** and aromatized. Oxidation of the crude product with PCC gave 5,7,12,14-pentacenediquinone **45** from either isomers in 18 and 15% yields. Methylated compound **29a** was identical with that obtained from 5,14-pentacenequinone **28a** (Scheme XI), and locations of the quinone moiety in both molecules were determined unambiguously.

As a summary, the present synthesis produced various polycyclic aromatic compounds starting from simple acid derivatives via polyketide intermediates. The carbon framework of pentacenequinone **35**, for example, was constructed from one molecule of β-hydroxyglutarate and five molecules of acetoacetate, and was equivalent to 3,5,7,9,11,13,15,17,19,21,23-undecaoxopentacosanedioate (Figure 2). Since the process is related to the biosynthesis of aromatic compounds, the products will be useful intermediates for the synthesis of the natural products. For examples, naphthalene **6** and anthraquinone **17c** possess the partial structures of juglorin[21] and K-259-2.[22] Our studies are now directed to the synthesis of biologically active natural products and related compounds.

Experimental Section

Melting points were not corrected. Distilations were conducted by Kugelrohr method using a Shibata apparatus. NMR spectra were obtained on a JEOL JNM-FX-60 instrument. Chemical shift values were given in ppm relative to internal Me_4Si. IR spectra were recorded on a Shimadzu IR-408. High-resolution mass spectra were taken with a JEOL JMS-DX-300 instrument. UV spectra were obtained on a Hitachi Model 150-20 double beam spectrophotometer. Elemental analyses were performed with a YANACO MT-3 CHN Corder apparatus. THF was distilled from sodium and redistilled from $LiAlH_4$ prior to use. Methylene chloride and HMPA were distilled from CaH_2 and stored over molecular sieves (4A). Methanol was distilled from magnesium and stored over molecular sieves (3A).

Dual-Claisen Condensation and $Ca(OAc)_2$-Induced Aromatization. Methyl 1,9-Dihydroxy-2-(methoxycarbonyl)-3-anthrylacetate (15a). Under a nitrogen atmosphere, a THF (10 mL) solution of methyl acetoacetate (3.22 g, 27.9 mmol) was added to a THF (30 mL) suspension of sodium hydride (672 mg, 28 mmol) at 0 °C, and the mixture was stirred for 10 min. Butyllithium (28 mmol) in hexane (17.9 mL) was added at 0 °C, and, after 10 min, a THF (4 mL) solution of methyl 2-(methoxycarbonyl)phenylacetate (**12a**, 726 mg, 3.5 mmol) and HMPA (8 mL) was added at 0 °C (HMPA was not used in the synthesis of **4a–g**). The mixture was stirred at room temperature for 1 h and poured on 2 N HCl cooled to 0 °C. Organic materials were extracted twice and ethyl acetate, washed with water and brine, dried (Na_2SO_4), and concentrated. Methanol (10 mL) and $Ca(OAc)_2·H_2O$ (3.07 g, 17 mmol) were added to the residue, and the mixture was stirred for 2 h at room temperature (heated at reflux in the synthesis of **4a–g** and **4j**). Then, the mixture was acidified with 2 N HCl, and organic materials were extracted twice with ethyl acetate, washed with water and brine, dried (Na_2SO_4), and concentrated. After volatile materials were removed in vacuo for several hours, a small amount of a 1:1 mixture of ethyl acetate and hexane was added to the residue, and the precipitate was collected by filtration, washed with the same solvent, and dried in vacuo. Essentially pure **15a** (583 mg, 49%) was obtained. The purification could also be carried out by silica gel chromatography: mp 176–180 °C ($CHCl_3$–ether) (lit.[9c] mp 177.5–180 °C).

Methyl 8-Hydroxy-7-(methoxycarbonyl)-1-oxo-1,2,3,4-tetrahydro-6-naphthylacetate (4a). The structure was determined by the comparison with the literature data.[8c]

Methyl 8-hydroxy-7-(methoxycarbonyl)-2-methyl-1-oxo-1,2,3,4-tetrahydro-3-naphthylacetate (4b): mp 91–5 °C (benzene–hexane); ^1H NMR ($CDCl_3$–CCl_4) δ 1.28 (3 H, d, J = 7 Hz), 1.6–2.9 (3 H, m), 2.94 (2 H, t, J = 6 Hz), 3.69 (5 H, s), 3.89 (3 H, s), 6.60 (1 H, s), 13.06 (1 H, s); IR (KBr) 3400, 1735, 1715, 1625 cm^{-1}; HRMS calcd for $C_{16}H_{18}O_6$ 306.1103, found 306.1101.

Methyl 8-hydroxy-7-(methoxycarbonyl)-2,2-dimethyl-1-oxo-1,2,3,4-tetrahydro-3-naphthylacetate (4c): mp 98 °C (benzene–hexane); ^1H NMR ($CDCl_3$–CCl_4) δ 1.24 (6 H, s), 1.94 (2 H, t, J = 6 Hz), 2.94 (2 H, t, J = 6 Hz), 3.68 (5 H, s), 3.89 (3 H, s), 6.59 (1 H, s), 13.14 (1 H, s); IR (KBr) 3400, 1730, 1720, 1625 cm^{-1}; HRMS calcd for $C_{17}H_{20}O_6$ 320.1260, found 320.1237.

Methyl 4,8-dihydroxy-7-(methoxycarbonyl)-1-oxo-1,2,3,4-tetrahydro-3-naphthylacetate (4d): ^1H NMR ($CDCl_3$–CCl_4) δ 1.9–2.4 (2 H, m), 2.4–2.9 (2 H, m), 3.68 (5 H, s), 3.89 (3 H, s), 4.5–5.0 (1 H, m), 6.91 (1 H, s), 12.9 (1 H, s); IR (neat) 3400, 1740–1710, 1620 cm^{-1}; HRMS calcd for $C_{15}H_{16}O_7$ 308.0896, found 308.0939. Diacetylated **4d** was synthesized with Ac_2O–pyridine at room temperature for 3 h: ^1H NMR ($CDCl_3$, 400 MHz) δ 2.13 (3 H, s), 2.2–2.4 (2 H, m), 2.34 (3 H, s), 2.62 (ddd, J = 5, 6, 17 Hz), 2.88 (ddd, J = 5, 10, 17 Hz), 3.70 (3 H, s), 3.80 (2 H, s), 3.89 (3 H, s), 6.80 (1 H, dd, J = 4, 6 Hz), 7.34 (1 H, s). An NOE was observed between a double doublet at δ 6.80 and a singlet at δ 7.34: IR (neat) 1780–1680, 1600 cm^{-1}; HRMS calcd for $C_{17}H_{18}O_8$ 350.1001, found 350.9431 (M – CH_3CO).

Methyl 1,8-dihydroxy-2-(methoxycarbonyl)-3-naphthylacetate (4e): mp 157–8 °C ($CHCl_3$–hexane); ^1H NMR ($CDCl_3$–CCl_4) δ 3.67 (3 H, s), 3.91 (5 H, s), 6.84 (1 H, dd, J = 1.5, 7 Hz), 7.02 (1 H, s), 7.22 (1 H, dd, J = 1.5, 7 Hz), 7.45 (1 H, t, J = 7 Hz), 9.53 (1 H, br s), 14.2 (1 H, br s); IR (KBr) 3350, 1745, 1640 cm^{-1}; HRMS calcd for $C_{15}H_{14}O_6$ 290.0794, found 290.0794. Anal. Calcd for $C_{15}H_{14}O_6$: C, 62.06; H, 4.86. Found: C, 61.88; H, 4.95.

Methyl 1,8-dihydroxy-6-methyl-2-(methoxycarbonyl)-3-naphthylacetate (4f): mp 170–3 °C (benzene–hexane); ^1H NMR ($CDCl_3$–CCl_4) δ 2.42 (3 H, s), 3.67 (3 H, s), 3.89 (2 H, s), 3.93 (3 H, s), 6.72 (1 H, s), 6.93 (2 H, s), 9.58 (1 H, s), 14.16 (1 H, s); IR (KBr) 3370, 1740, 1640 cm^{-1}; HRMS calcd for $C_{16}H_{16}O_6$ 304.0946, found 304.0939.

Methyl 1,8-Dihydroxy-6-(ethoxycarbonyl)-2-(methoxycarbonyl)-3-naphthylacetate (4g): mp 124–5 °C (benzene–hexane); ^1H NMR ($CDCl_3$–CCl_4) δ 1.43 (3 H, t, J = 7 Hz), 3.69 (3 H, s), 3.93 (2 H, s), 3.96 (3 H, s), 4.41 (2 H, q, J = 7 Hz), 7.15 (1 H, s), 7.42 (1 H, d, J = 1.5 Hz), 7.84 (1 H, d, J = 1.5 Hz), 9.69 (1 H, s), 14.14 (1 H, s); IR (KBr) 3400, 1735, 1720, 1650 cm^{-1};

(21) Hamaguchi, K.; Iwakiri, T.; Imamura, K.; Furihara, K.; Seto, H.; Otake, N. *J. Antibiot.* **1987**, *40*, 717.
(22) Yasuzawa, T.; Yoshida, M.; Shirahama, K.; Sano, H. *J. Antibiot.* **1987**, *40*, 1101.

HRMS calcd for $C_{18}H_{18}O_8$ 362.1002, found 362.1041.

Methyl 1-hydroxy-2-(methoxycarbonyl)-9-oxo-3-fluorenylacetate (4h): mp 168–73 °C (AcOEt); ^{1}H NMR ($CDCl_3$–CCl_4) δ 3.72 (3 H, s), 3.92 (5 H, s), 6.92 (1 H, s), 7.1–7.7 (4 H, m), 11.37 (1 H, s); ^{13}C NMR ($CDCl_3$–CCl_4) δ 42.5, 52.2, 52.5, 116.4, 118.1, 121.1, 124.0, 130.4, 134.1, 134.9, 141.7, 144.9, 149.3, 159.3, 169.2, 170.7, 191.4; IR (KBr) 3400–2500, 1730, 1705, 1660, 1620 cm^{-1}; UV ($CHCl_3$) λ_{max} 377, 265 nm; HRMS calcd for $C_{18}H_{14}O_6$ 326.0790, found 326.0794.

1,9-Dimethoxy-2,8-bis(methoxycarbonyl)-3,7-bis((methoxycarbonyl)methyl)indeno[2,3-*b*]fluorene-10,12-dione (*syn*-4i) and 1,7-Dimethoxy-2,8-bis(methoxycarbonyl)-3,9-bis((methoxycarbonyl)methyl)indeno[3,2-*b*]fluorene-6,12-dione (*anti*-4i). These compounds were isolated after methylation with methyl iodide–Ag_2O according to the procedures shown in the synthesis of **7k**. *syn*-**4i**: mp 231–4 °C (AcOEt); ^{1}H NMR ($CDCl_3$) δ 3.75 (10 H, s), 3.93 (6 H, s), 4.15 (6 H, s), 7.32 (2 H, s), 7.67 (1 H, s), 7.86 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 32.9, 52.5, 63.3, 112.7, 118.5, 119.7, 122.9, 130.8, 135.6, 140.9, 145.5, 148.9, 156.5, 166.8, 170.2, 187.7, 224.4; IR (KBr) 1750–1710, 1610 cm^{-1}; UV ($CHCl_3$) λ_{max} 297, 286 nm; HRMS calcd for $C_{32}H_{26}O_{12}$ 602.1424, found 602.1466. *anti*-**4i**: mp 259–62 °C (AcOEt); ^{1}H NMR ($CDCl_3$) δ 3.74 (10 H, s), 3.93 (6 H, s), 4.16 (6 H, s), 7.26 (2 H, s), 7.79 (2 H, s); IR (KBr) 1740, 1700, 1600 cm^{-1}; UV ($CHCl_3$) λ_{max} 323, 296, 285 nm; HRMS calcd for $C_{32}H_{26}O_{12}$ 602.1424, found 602.1464.

4-Hydroxy-3-(methoxycarbonyl)-2-((methoxycarbonyl)methyl)-5*H*-tribenzo[*a*,*c*,*e*]cycloheptatrien-5-one (4j): mp 174–6 °C; ^{1}H NMR ($CDCl_3$–CCl_4) δ 3.66 (3 H, s), 3.85 (2 H, s), 3.90 (3 H, s), 7.02 (1 H, s), 7.0–8.0 (8 H, m), 11.53 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 41.7, 52.1, 52.4, 114.7, 124.1, 125.9, 128.3, 128.6, 128.7, 129.2, 130.8, 131.4, 135.4, 136.1, 136.9, 138.0, 141.7, 143.6, 157.1, 169.3, 170.9, 196.6; IR (KBr) 3400–2500, 1740, 1690, 1665, 1600 cm^{-1}; HRMS calcd for $C_{24}H_{18}O_6$ 402.1104, found 402.1115.

Methyl 1,9-dihydroxy-8-methoxy-2-(methoxycarbonyl)-3-anthrylacetate (15b): mp 169–70 °C ($CHCl_3$–ether) (lit.[9c] mp 168 °C).

Methyl 1,9-dihydroxy-5,8-dimethoxy-2-(methoxycarbonyl)-3-anthrylacetate (15d): mp 158–9 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.71 (3 H, s), 3.91 (2 H, s), 3.93 (3 H, s), 3.98 (3 H, s), 4.05 (3 H, s), 6.61 (2 H, s), 7.16 (1 H, s), 8.02 (1 H, s), 11.37 (1 H, s), 13.06 (1 H, s); IR (KBr) 3400, 1730, 1625 cm^{-1}; HRMS calcd for $C_{21}H_{20}O_8$ 400.1157, found 400.1154.

Methyl 1,9-dihydroxy-7,8-(methylenedioxy)-2-(methoxycarbonyl)-3-anthrylacetate (15e): mp 206–8 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.70 (3 H, s), 3.76 (2 H, s), 3.94 (3 H, s), 4.30 (2 H, s), 6.21 (2 H, s), 6.82 (1 H, s), 6.88 (1 H, d, J = 8 Hz), 7.09 (1 H, d, J = 8 Hz), 13.48 (1 H, s); IR (KBr) 3400, 1750, 1710, 1610, 1585 cm^{-1}; HRMS calcd for $C_{20}H_{16}O_8$ 384.0844, found 384.0822.

Methyl 1,9-dihydroxy-10-methyl-2-(methoxycarbonyl)-3-anthrylacetate (15f): mp 167–8 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 2.79 (3 H, s), 3.71 (3 H, s), 3.93 (5 H, s), 7.3–7.8 (2 H, m), 7.34 (1 H, s), 8.0–8.2 (1 H, m), 8.3–8.5 (1 H, m), 10.86 (1 H, d, J = 1 Hz), 14.95 (1 H, d, J = 1 Hz); IR (KBr) 3300, 1735, 1620, 1570 cm^{-1}; UV ($CHCl_3$) λ_{max} 478, 451, 430, 386, 366, 350, 278 nm; HRMS calcd for $C_{20}H_{18}O_6$ 354.1104, found 354.1112.

Methyl 1,12-dihydroxy-10,11-dimethoxy-2-(methoxycarbonyl)-3-naphthacenylacetate (16): mp 207–9 °C (AcOEt); ^{1}H NMR ($CDCl_3$) δ 3.71 (3 H, s), 3.76 (2 H, s), 3.95 (3 H, s), 3.99 (3 H, s), 4.02 (3 H, s), 4.38 (2 H, s), 6.76 (1 H, s), 6.6–6.9 (1 H, m), 7.4–7.7 (1 H, m), 7.50 (1 H, t, J = 8 Hz), 7.50 (1 H, s), 13.97 (1 H, s); IR (KBr) 3350, 1745, 1715, 1620, 1600 cm^{-1}; HRMS calcd for $C_{25}H_{22}O_8$ 450.1315, found 450.1341.

Methylation of Phenols with Ag_2O–MeI. 1-Methoxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-9-benzocycloheptenone (7k). Under a nitrogen atmosphere, a mixture of 1-hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-9-benzocycloheptenone[6d] (269 mg, 0.88 mmol), methyl iodide (1 mL), and Ag_2O (927 mg, 4.0 mmol) in benzene (5 mL) was refluxed for 2 h. The mixture was filtered, concentrated, and chromatographed on silica gel to give **7k** (272 mg, 97%): ^{1}H NMR ($CDCl_3$–CCl_4) δ 1.6–2.0 (4 H, m), 2.4–2.9 (4 H, m), 3.64 (2 H, s), 3.67 (3 H, s), 3.79 (3 H, s), 3.88 (2 H, s), 6.83 (1 H, s); IR (neat) 1740–1720, 1690, 1600, 1580 cm^{-1}; HRMS calcd for $C_{17}H_{20}O_6$ 320.1260, found 320.1294.

8-Methoxy-7-(methoxycarbonyl)-6-((methoxycarbonyl)methyl)-1,2,3,4-tetrahydronaphthalen-1-one (7a): mp 65.5–66.5 °C (hexane); ^{1}H NMR ($CDCl_3$–CCl_4) δ 1.8–2.3 (2 H, m), 2.62 (2 H, t, J = 6 Hz), 2.95 (2 H, t, J = 6 Hz), 3.61 (2 H, s), 3.68 (3 H, s), 3.82 (3 H, s), 3.88 (3 H, s), 6.94 (1 H, s); IR (KBr) 1730, 1670, 1600 cm^{-1}; HRMS calcd for $C_{16}H_{18}O_6$ 306.1104, found 306.1131.

Methyl 1-methoxy-2-(methoxycarbonyl)-9-oxo-3-fluorenylacetate (7h): ^{1}H NMR ($CDCl_3$–CCl_4) δ 3.68 (2 H, s), 3.72 (3 H, s), 3.91 (3 H, s), 4.14 (3 H, s), 7.0–7.7 (5 H, m); IR (neat) 1750–1700, 1605 cm^{-1}; HRMS calcd for $C_{19}H_{16}O_6$ 340.0947, found 340.0950.

4-Methoxy-3-(methoxycarbonyl)-2-((methoxycarbonyl)methyl)-5*H*-tribenzo[*a*,*c*,*e*]cycloheptatrien-5-one (7j): ^{1}H NMR ($CDCl_3$–CCl_4) δ 3.66 (3 H, s), 3.73 (2 H, s), 3.90 (3 H, s), 4.00 (3 H, s), 7.0–7.8 (5 H, m); IR (KBr) 1750–1680 cm^{-1}; HRMS calcd for $C_{25}H_{20}O_6$ 416.1260, found 416.1281.

2-(Methoxycarbonyl)-3-((methoxycarbonyl)methyl)-1,12,13-trimethoxy-5,14-pentacenequinone (28a): mp 183–4 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.72 (3 H, s), 3.79 (2 H, s), 3.98 (3 H, s), 4.07 (3 H, s), 4.12 (3 H, s), 4.18 (3 H, s), 7.4–7.7 (2 H, m), 7.8–8.1 (1 H, m), 8.01 (1 H, s), 8.36 (1 H, s), 8.2–8.5 (1 H, m), 8.66 (1 H, s); IR (KBr) 1735, 1670, 1655, 1585, 1565 cm^{-1}; UV ($CHCl_3$) λ_{max} 465, 348, 333, 277 nm; HRMS calcd for $C_{30}H_{24}O_9$ 528.1420, found 528.1397.

2-(Methoxycarbonyl)-3-((methoxycarbonyl)methyl)-1,11,12,13-tetramethoxy-5,14-pentacenequinone (28b): mp 209–10 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.72 (3 H, s), 3.79 (2 H, s), 3.98 (3 H, s), 4.04 (3 H, s), 4.07 (6 H, s), 4.16 (3 H, s), 6.85 (1 H, dd, J = 2, 6 Hz), 7.2–7.6 (2 H, m), 8.05 (1 H, s), 8.27 (1 H, s), 8.59 (1 H, s); IR (KBr) 1730, 1720, 1660, 1615 cm^{-1}; UV ($CHCl_3$) λ_{max} 478, 350, 335, 284 nm; HRMS calcd for $C_{31}H_{26}O_{10}$ 558.1526, found 558.1526.

7-Methyl-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-1,12,13-trimethoxy-5,14-pentacenequinone (28f): mp 233–4 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.17 (3 H, s), 3.73 (3 H, s), 3.81 (2 H, s), 3.98 (3 H, s), 4.09 (6 H, s), 4.15 (3 H, s), 7.5–7.9 (2 H, m), 8.05 (1 H, s), 8.1–8.6 (2 H, m), 9.12 (1 H, s); IR (KBr) 1740, 1675, 1590 cm^{-1}; UV ($CHCl_3$) λ_{max} 479, 352, 338, 281 nm; HRMS calcd for $C_{31}H_{26}O_9$ 528.1421, found 528.1433.

1-Methoxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)anthraquinone (31a): mp 160–1 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.72 (3 H, s), 3.80 (2 H, s), 3.97 (3 H, s), 4.00 (3 H, s), 7.6–7.9 (2 H, m), 8.07 (1 H, s), 8.1–8.4 (2 H, m); IR (KBr) 1740, 1720, 1680, 1590 cm^{-1}; HRMS calcd for $C_{20}H_{16}O_7$ 368.0896, found 368.0914.

1,8-Dimethoxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)anthraquinone (31b): mp 171–3 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.71 (3 H, s), 3.78 (2 H, s), 3.96 (3 H, s), 4.01 (3 H, s), 4.02 (3 H, s), 7.30 (1 H, dd, J = 2, 8 Hz), 7.67 (1 H, t, J = 8 Hz), 7.86 (1 H, dd, J = 2, 8 Hz), 7.96 (1 H, s); IR (KBr) 1745, 1725, 1670, 1590 cm^{-1}; UV ($CHCl_3$) λ_{max} 381, 259 nm; HRMS calcd for $C_{21}H_{18}O_8$ 398.1001, found 398.1013.

1,10,11-Trimethoxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-5,12-naphthacenequinone (32): mp 189.5–190 °C ($CHCl_3$–hexane); ^{1}H NMR ($CDCl_3$) δ 3.71 (3 H, s), 3.79 (2 H, s), 3.96 (3 H, s), 4.00 (3 H, s), 4.05 (3 H, s), 4.08 (3 H, s), 7.03 (1 H, t, J = 4 Hz), 7.5–7.7 (2 H, m), 7.99 (1 H, s), 8.46 (1 H, s); IR (KBr) 1740, 1710, 1670, 1600 cm^{-1}; UV ($CHCl_3$) λ_{max} 406, 337, 256 nm; HRMS calcd for $C_{26}H_{22}O_9$ 478.1263, found 478.1263.

1,12-Dimethoxy-4-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-6,11-naphthacenequinone (34a): mp 200–2 °C ($CHCl_3$–ether–hexane); ^{1}H NMR ($CDCl_3$) δ 3.70 (3 H, s), 3.96 (2 H, s), 3.99 (3 H, s), 4.02 (3 H, s), 4.05 (3 H, s), 7.4–7.9 (2 H, m), 7.46 (1 H, s), 7.9–8.1 (1 H, m), 8.3–8.5 (1 H, m), 8.44 (1 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.0, 52.4, 52.7, 53.2, 56.3, 105.4, 123.3, 125.7, 126.0, 126.1, 128.6, 129.3, 129.7, 129.9, 131.7, 131.7, 132.5, 133.6, 134.8, 134.9, 160.0, 168.3, 169.2, 170.5, 183.0; IR (KBr) 1720, 1660, 1610, 1595 cm^{-1}; HRMS calcd for $C_{25}H_{19}O_8$ 447.1078, found 447.1050 (M – H).

4-(Methoxycarbonyl)-3-((methoxycarbonyl)methyl)-1,10,12-trimethoxy-6,11-naphthacenequinone (34b): mp 180–1 °C ($CHCl_3$–ether–hexane); ^{1}H NMR ($CDCl_3$) δ 3.70 (3 H, s), 3.77 (3 H, s), 3.83 (3 H, s), 3.96 (2 H, s), 4.00 (3 H, s), 4.06 (3 H, s), 7.19 (1 H, dd, J = 2, 8 Hz), 7.48 (1 H, s), 7.53 (1 H, t, J = 8 Hz),

8.05 (1 H, dd, J = 2, 8 Hz), 8.31 (1 H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.1, 52.1, 52.4, 52.7, 55.2, 56.5, 105.5, 115.7, 116.6, 120.3, 123.5, 125.7, 126.1, 128.9, 129.6, 130.2, 131.7, 132.5, 133.7, 134.1, 156.6, 156.7, 165.9, 168.4, 170.6, 183.6; IR (KBr) 1740, 1710, 1675, 1605, 1590 cm^{-1}; HRMS calcd for $C_{26}H_{22}O_9$ 478.1263, found 478.1258.

4-(Methoxycarbonyl)-3-((methoxycarbonyl)methyl)-1,11,12,14-tetramethoxy-6,13-pentacenequinone (36): mp 219–20 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.46 (3 H, s), 3.73 (3 H, s), 3.80 (5 H, s), 3.96 (3 H, s), 4.09 (3 H, s), 4.18 (3 H, s), 7.1–7.4 (1 H, m), 7.5–7.9 (2 H, m), 8.17 (1 H, s), 8.78 (1 H, s), 9.39 (1 H, s); IR (KBr) 1740, 1650, 1590 cm^{-1}; HRMS calcd for $C_{31}H_{26}O_{10}$ 558.1524, found 558.1519.

4-(Methoxycarbonyl)-3-((methoxycarbonyl)methyl)-1,5,12-trimethoxy-6,11-naphthacenequinone (38): mp 168–9 °C (AcOEt–hexane); ^{1}H NMR ($CDCl_3$) δ 3.69 (3 H, s), 4.03 (12 H, s), 4.12 (2 H, s), 7.4–7.7 (2 H, m), 7.53 (1 H, s), 7.8–8.1 (1 H, m), 8.2–8.5 (1 H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.8, 52.6, 52.8, 53.2, 56.3, 63.1, 104.9, 118.7, 125.1, 125.7, 125.7, 126.8, 127.8, 129.1, 129.5, 132.7, 133.2, 133.2, 134.0, 134.5, 154.7, 158.4, 167.4, 169.2, 169.9, 182.6; IR (KBr) 1740, 1720, 1650, 1610, 1600 cm^{-1}; UV ($CHCl_3$) λ_{max} 442, 386, 349, 301, 265 nm; HRMS calcd for $C_{26}H_{22}O_9$ 478.1262, found 478.1252.

4-(Methoxycarbonyl)-3-((methoxycarbonyl)methyl)-1,6,7,14-tetramethoxy-8,13-benzo[*a*]naphthacenequinone (40): mp 204.5–5.0 °C (AcOEt–hexane); ^{1}H NMR ($CDCl_3$) δ 3.68 (3 H, s), 4.03 (6 H, s), 4.06 (3 H, s), 4.10 (3 H, s), 4.14 (3 H, s), 4.26 (2 H, s), 7.5–7.7 (2 H, m), 7.57 (1 H, s), 7.85 (1 H, s), 8.3–8.6 (2 H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.3, 52.5, 52.8, 53.0, 53.0, 56.5, 56.6, 105.8, 106.3, 119.5, 120.2, 120.4, 120.5, 126.9, 127.0, 128.0, 128.0, 128.1, 128.3, 128.4, 130.2, 130.3, 130.6, 132.3, 154.9, 155.0, 169.5, 170.2, 170.2, 170.7; IR (KBr) 1725, 1600 cm^{-1}; HRMS calcd for $C_{31}H_{26}O_{10}$ 558.1526, found 558.1533.

8-Hydroxy-7-(methoxycarbonyl)-6-((methoxycarbonyl)methyl)-1,2,3,4-tetrahydronaphthalene-1,4-dione (5). To a solution of **4d** (103 mg, 0.33 mmol) in 80% acetic acid was added CrO_3 (200 mg, 2.0 mmol), and the mixture was stirred at room temperature for 30 min. The mixture was diluted with water and extracted twice with ethyl acetate. The combined extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), concentrated, and chromatographed on silica gel to give **5** (46 mg, 47%). A rapid chromatography using methylene chloride as the eluent was required to avoid the decomposition of **5**: mp 94–7 °C (AcOEt–hexane); ^{1}H NMR ($CDCl_3$–CCl_4) δ 3.08 (4 H, s), 3.69 (3 H, s), 3.77 (2 H, s), 3.93 (3 H, s), 7.40 (1 H, s), 12.51 (1 H, s); IR (KBr) 3400–2300, 1740, 1695, 1640, 1605 cm^{-1}; HRMS calcd for $C_{15}H_{14}O_7$ 306.0739, found 306.0713.

Methyl 2-(Methoxycarbonyl)-1,5,8-triacetoxy-3-naphthylacetate (6). Under a nitrogen atmosphere, acetyl chloride (0.2 mL) was added to a methylene chloride solution of **5** (39 mg, 0.13 mmol) and triethylamine (0.5 mL) at 0 °C, and the resulted mixture was stirred for 30 min at that temperature. Then, water was added, and the organic materials were extracted twice with ethyl acetate. The combined extracts were washed with water and brine, dried (Na_2SO_4), concentrated, and chromatographed on silica gel to give **6** (33 mg, 58%): mp 144–6 °C (benzene–hexane); ^{1}H NMR ($CDCl_3$–CCl_4) δ 2.33 (3 H, s), 2.36 (3 H, s), 2.45 (3 H, s), 3.66 (3 H, s), 3.88 (5 H, s), 7.09 (1 H, d, J = 8 Hz), 7.37 (1 H, d, J = 8 Hz), 7.71 (1 H, s); IR (KBr) 1770, 1730 cm^{-1}; HRMS calcd for $C_{21}H_{20}O_{10}$ 432.1056, found 432.1057.

Synthesis of Quinones via Air-Oxidation. 1-Hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)anthraquinone (17a). Crude **15a** (obtained by the Claisen condensation–aromatization procedures from 408 mg (1.96 mmol) of **12a**) was dissolved in methylene chloride (6 mL), and K_2CO_3 (2 g, 14.6 mmol) was added. The mixture was stirred for 5 h under an oxygen atmosphere, and acidified with 2 N HCl. Organic materials were extracted twice with ethyl acetate, washed with water and brine, dried (Na_2SO_4), and concentrated. Silica gel chromatography gave **17a** (292 mg, 42% yield from **12a**): mp 166–9 °C (benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 3.72 (3 H, s), 3.85 (2 H, s), 3.98 (3 H, s), 7.75 (1 H, s), 7.7–8.0 (2 H, m), 8.1–8.5 (2 H, m), 13.06 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 39.8, 52.5, 52.8, 115.4, 121.3, 127.0, 127.5, 128.4, 132.9, 133.3, 133.7, 134.5, 135.0, 141.7, 160.4, 165.9, 169.8, 181.5, 188.0; IR (KBr) 3400, 1740, 1720, 1670, 1630, 1590 cm^{-1}; UV ($CHCl_3$) λ_{max} 418, 396, 257 nm; HRMS calcd for $C_{19}H_{14}O_7$ 354.0738, found 354.0695. The reaction of diacetyl-**19a** (29 mg, 0.069 mmol) with K_2CO_3 (50 mg, 0.36 mmol) in methanol (1 mL) at room temperature for 2 h gave **17a** (18 mg, 73%). Under a nitrogen atmosphere, **19a** was detected by TLC.

8-Methoxy-1-hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)anthraquinone (17b): mp 188–9 °C ($CHCl_3$–ether–hexane); ^{1}H NMR ($CDCl_3$) δ 3.71 (3 H, s), 3.80 (2 H, s), 3.97 (3 H, s), 4.07 (3 H, s), 7.36 (1 H, dd, J = 2, 8 Hz), 7.67 (1 H, s), 7.74 (1 H, t, J = 8 Hz), 7.96 (1 H, dd, J = 2, 7 Hz), 13.38 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 39.6, 52.4, 52.7, 56.6, 116.2, 118.5, 120.1, 120.4, 128.7, 132.9, 135.2, 136.1, 140.4, 160.3, 160.9, 166.1, 169.8, 181.7, 187.9; IR (KBr) 3400, 1740, 1730, 1670, 1630, 1585 cm^{-1}; UV ($CHCl_3$) λ_{max} 417, 285, 260 nm; HRMS calcd for $C_{20}H_{16}O_8$ 385.0924, found 385.0924 (M + H).

6,8-Dimethoxy-1-hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)anthraquinone (17c): mp 176–9 °C ($CHCl_3$–ether–hexane); ^{1}H NMR ($CDCl_3$) δ 3.72 (6 H, s), 3.80 (2 H, s), 3.97 (6 H, s), 4.01 (3 H, s), 6.76 (1 H, d, J = 2.5 Hz), 7.41 (1 H, d, J = 2.5 Hz), 7.63 (1 H, s), 13.59 (1 H, s); IR (KBr) 3400, 1740, 1670, 1625, 1595 cm^{-1}; UV ($CHCl_3$) λ_{max} 425, 285 nm; HRMS calcd for $C_{21}H_{18}O_9$ 414.0951, found 414.0980.

5,8-Dimethoxy-1-hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)anthraquinone (17d): mp 207–9 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.70 (3 H, s), 3.81 (2 H, s), 3.96 (3 H, s), 4.00 (6 H, s), 7.38 (2 H, s), 7.59 (1 H, s), 13.18 (1 H, s); IR (KBr) 3400, 1730, 1670, 1630 cm^{-1}; HRMS calcd for $C_{21}H_{18}O_9$ 414.0950, found 414.0949.

7,8-(Methylenedioxy)-1-hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)anthraquinone (17e): mp 250 °C dec ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.72 (3 H, s), 3.84 (2 H, s), 3.98 (3 H, s), 6.35 (2 H, s), 7.16 (1 H, d, J = 8 Hz), 7.74 (1 H, s), 7.97 (1 H, d, J = 8 Hz), 13.04 (1 H, s); IR (KBr) 3400, 1740, 1720, 1665, 1625 cm^{-1}; HRMS calcd for $C_{20}H_{14}O_9$ 398.0637, found 398.0637.

10,11-Dimethoxy-1-hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-5,12-naphthacenequinone (18): mp 209–10 °C ($CHCl_3$–hexane); ^{1}H NMR ($CDCl_3$) δ 3.72 (3 H, s), 3.83 (2 H, s), 3.98 (3 H, s), 4.03 (3 H, s), 4.06 (3 H, s), 7.59 (1 H, s), 6.9–7.8 (3 H, m), 8.56 (1 H, s), 13.88 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 39.7, 52.4, 52.6, 56.5, 62.9, 110.1, 117.5, 120.2, 123.0, 123.5, 126.3, 128.5, 130.0, 131.2, 133.9, 138.6, 140.4, 158.6, 160.8, 162.9, 166.3, 169.9, 181.5, 187.4; IR (KBr) 3350, 1730, 1710, 1670, 1640, 1600, 1590 cm^{-1}; UV ($CHCl_3$) λ_{max} 458, 262 nm; HRMS calcd for $C_{25}H_{20}O_9$ 464.1107, found 464.1110.

12,13-Dimethoxy-1-hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-5,14-pentacenequinone (27a): mp 229–30 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.73 (3 H, s), 3.83 (2 H, s), 3.99 (3 H, s), 4.16 (3 H, s), 7.5–7.8 (2 H, m), 7.72 (1 H, s), 7.8–8.2 (1 H, m), 8.2–8.5 (1 H, m), 8.36 (1 H, s), 8.73 (1 H, s), 13.95 (1 H, s); IR (KBr) 3400, 1740, 1720, 1670, 1620, 1590 cm^{-1}; UV ($CHCl_3$) λ_{max} 493, 349, 334, 280 nm; HRMS calcd for $C_{29}H_{22}O_9$ 514.1263, found 514.1259.

1-Hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-11,12,13-trimethoxy-5,14-pentacenequinone (27b): mp 238–9 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.73 (3 H, s), 3.84 (2 H, s), 4.00 (3 H, s), 4.06 (3 H, s), 4.11 (3 H, s), 4.14 (3 H, s), 6.92 (1 H, dd, J = 3, 6 Hz), 7.2–7.6 (2 H, m), 7.75 (1 H, s), 8.32 (1 H, s), 8.71 (1 H, s), 14.04 (1 H, s); IR (KBr) 3400, 1735, 1660, 1620 cm^{-1}; UV ($CHCl_3$) λ_{max} 514, 352, 336, 287 nm; HRMS calcd for $C_{30}H_{24}O_{10}$ 544.1369, found 544.1387.

1-Hydroxy-12,13-dimethoxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-7-methyl-5,14-pentacenequinone (27f): mp 225–6 °C ($CHCl_3$–ether); ^{1}H NMR ($CDCl_3$) δ 3.16 (3 H, s), 3.73 (3 H, s), 3.84 (2 H, s), 4.00 (3 H, s), 4.12 (3 H, s), 4.14 (3 H, s), 7.4–7.8 (2 H, m), 7.75 (1 H, s), 8.1–8.5 (2 H, m), 9.16 (1 H, s), 13.99 (1 H, s); IR (KBr) 3400, 1740, 1715, 1665, 1615, 1590 cm^{-1}; HRMS calcd for $C_{30}H_{24}O_9$ 528.1421, found 528.1433.

Decarboxylation. 1-Hydroxy-8-methoxy-3-((methoxycarbonyl)methyl)anthraquinone (20b). Under a nitrogen atmosphere, a mixture of **15b** (70 mg, 0.19 mmol) and NaOH (127 mg, 3 mmol) in water (10 mL, degassed by bubbling nitrogen for 30 min) was heated at reflux for 4 h and acidified with 2 N HCl. Organic materials were extracted twice with chloroform, washed with brine, dried (Na_2SO_4), and concentrated. Methanol (3 mL) and K_2CO_3 (142 mg, 1.0 mmol) were added to the residue, and the mixture was stirred vigorously under an oxygen atmosphere

for 3 h. The reaction mixture was acidified with 2 N HCl, extracted with chloroform, washed with brine, dried (Na_2SO_4), and concentrated. The crude products were suspended in ether, and excess diazomethane in ether was added at 0 °C. After 30 min, a small amount of 2 N HCl was added, and the solvent was evaporated. Silica gel chromatography gave **20b** (42 mg, 64%): mp 205–6 °C ($CHCl_3$–ethanol); ^1H NMR ($CDCl_3$) δ 3.73 (5 H, s), 4.08 (3 H, s), 7.22 (1 H, d, J = 2 Hz), 7.35 (1 H, dd, J = 2, 8 Hz), 7.68 (1 H, d, J = 2 Hz), 7.74 (1 H, t, J = 8 Hz), 7.98 (1 H, dd, J = 2, 8 Hz), 12.91 (1 H, s); IR (KBr) 3400, 1735, 1670, 1630 cm^{-1}; HRMS calcd for $C_{18}H_{14}O_6$ 326.0791, found 326.0815. The physical data agreed well with those provided by Professor Kishi.[18]

1-Hydroxy-3-((methoxycarbonyl)methyl)anthraquinone (20a): mp 140–3 °C (benzene–hexane); ^1H NMR ($CDCl_3$) δ 3.74 (5 H, s), 7.23 (1 H, d, J = 2 Hz), 7.5–8.0 (3 H, m), 8.0–8.4 (2 H, m), 12.53 (1 H, s); IR (KBr) 1730, 1670, 1640, 1590 cm^{-1}; HRMS calcd for $C_{17}H_{12}O_5$ 296.0685, found 296.0710. The same compound was obtained from anthraquinone **17a**: a mixture of **17a** (81 mg, 0.23 mmol), NaOH (203 mg, 5.1 mmol), and zinc powder (285 mg, 4.4 mmol) in water (10 mL) was heated at reflux for 5 h. A similar workup as mentioned above followed by air-oxidation and esterification gave **20a** (19 mg, 29%) and 1-methoxy-3-((methoxycarbonyl)methyl)anthraquinone (14 mg, 22%): mp 173–4 °C ($CHCl_3$–ether–hexane); ^1H NMR ($CDCl_3$) δ 3.74 (3 H, s), 3.78 (2 H, s), 4.06 (3 H, s), 7.2–7.3 (1 H, m), 7.6–7.9 (3 H, m), 8.1–8.3 (2 H, m); IR (KBr) 1730, 1670, 1600, 1590 cm^{-1}; HRMS calcd for $C_{18}H_{14}O_5$ 310.0841, found 310.0818.

Dual-Claisen Condensation and $Ca(OAc)_2$-Induced Aromatization with Prior Protection of Ketone Functionalities by Reduction. 10-Hydroxy-12-methoxy-8-(methoxycarbonyl)-9-((methoxycarbonyl)methyl)-1-oxo-1,2,3,4-tetrahydro-6,11-naphthacenequinone (24a). To an ethanol (2 mL) solution of **7a** (171 mg, 0.56 mmol) was added $NaBH_4$ (38 mg, 1.0 mmol) at 0 °C, and the mixture was stirred for 30 min at the temperature. Then, 2 N HCl was added, and the organic materials were extracted twice with ethyl acetate. The combined extracts were washed with brine, dried (Na_2SO_4), concentrated, and chromatographed on silica gel, giving alcohol **22a** (160 mg, 94%): ^1H NMR ($CDCl_3$–CCl_4) δ 1.5–2.0 (4 H, m), 2.4–2.8 (2 H, m), 3.27 (1 H, br s), 3.61 (5 H, s), 3.83 (6 H, s), 4.8–5.1 (1 H, m), 6.76 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 17.1, 29.1, 30.6, 38.5, 51.3, 51.6, 61.8, 62.3, 124.4, 126.7, 131.3, 132.1, 140.8, 157.0, 167.1, 170.4; IR (neat) 3450, 1730, 1600, 1565 cm^{-1}; HRMS calcd for $C_{16}H_{18}O_5$ 290.1154, found 290.1156 (M – H_2O).

A similar treatment of **22a** (513 mg, 1.66 mmol) as mentioned in the synthesis of **15a** gave crude 1,10-dihydroxy-11-methoxy-2-((methoxycarbonyl)methyl)-7,8,9,10-tetrahydro-5,12-naphthacenequinone (**23a**), which was dissolved in methylene chloride (5 mL). Under a nitrogen atmosphere, PCC (860 mg, 4.0 mmol) was added, and the mixture was stirred overnight. Water was added, and the organic materials were extracted twice with ethyl acetate. The combined extracts were washed with brine, dried (Na_2SO_4), concentrated, and chromatographed on silica gel, giving **24a** (86 mg, 19%): mp 172–4 °C; ^1H NMR ($CDCl_3$) δ 1.9–2.3 (2 H, m), 2.75 (2 H, t, J = 6 Hz), 3.10 (2 H, t, J = 6 Hz), 3.72 (3 H, s), 3.82 (2 H, s), 3.98 (3 H, s), 4.01 (3 H, s), 7.68 (1 H, s), 7.99 (1 H, s), 13.36 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 22.1, 31.0, 39.4, 40.5, 52.3, 52.6, 63.2, 116.2, 120.5, 123.5, 124.3, 129.0, 132.6, 136.4, 140.8, 153.5, 160.3, 162.8, 165.8, 169.6, 181.1, 186.9, 195.6; IR (KBr) 3400, 1740, 1730, 1700, 1670, 1630, 1580 cm^{-1}; UV ($CHCl_3$) λ_{max} 413, 267 nm; HRMS calcd for $C_{24}H_{20}O_9$ 452.1106, found 452.1102.

10-Hydroxy-12-methoxy-9-(methoxycarbonyl)-8-((methoxycarbonyl)methyl)-11*H*-indeno[2,3-*b*]anthracene-6,11,13-trione (24h). The following spectral data were obtained for the reduced intermediate, 1-methoxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-9-fluorenol (**22h**): viscous oil; ^1H NMR ($CDCl_3$–CCl_4) δ 2.39 (1 H, d, J = 7 Hz), 3.68 (5 H, s), 3.89 (3 H, s), 4.08 (3 H, s), 5.76 (1 H, d, J = 7 Hz), 7.2–7.7 (5 H, m); ^{13}C NMR ($CDCl_3$–CCl_4) δ 39.2, 52.0, 52.1, 60.8, 73.7, 117.2, 120.3, 125.1, 126.3, 128.5, 128.9, 133.6, 134.9, 138.5, 144.0, 146.1, 155.5, 167.7, 170.8; IR (CCl_4 solution) 3400, 1740–1720, 1605 cm^{-1}; HRMS calcd for $C_{19}H_{18}O_6$ 342.1103, found 342.1120. Synthesis of **24h** was carried out as described in the synthesis of **15a**. The oxidation of 13-hydroxy moiety proceeded during K_2CO_3 treatment, and PCC-oxidation was not performed: mp 262–4 °C (AcOEt); ^1H NMR ($CDCl_3$) δ 3.72 (3 H, s), 3.83 (2 H, s), 3.98 (3 H, s), 4.21 (3 H, s), 7.3–7.8 (4 H, m), 7.70 (1 H, s), 8.23 (1 H, s), 13.22 (1 H, s); IR (KBr) 3400, 1740–1720, 1625, 1600 cm^{-1}; UV ($CHCl_3$) λ_{max} 440, 274 nm; HRMS calcd for $C_{27}H_{18}O_9$ 486.0950, found 486.0926.

1-Hydroxy-16-methoxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-15*H*-dibenzo[*c*,*e*]cycloheptatrieno-[1,2-*b*]anthracene-5,15,17-trione (24j). The intermediate, 1,15-dihydroxy-16-methoxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-15*H*-dibenzo[*c*,*e*]cycloheptatrieno[1,2-*b*]-anthracene-5,17-dione (**23j**), was isolated: mp 95–100 °C; ^1H NMR ($CDCl_3$–CCl_4) δ 3.70 (3 H, s), 3.79 (2 H, s), 3.96 (3 H, s), 4.04 (3 H, s), 6.49 (1 H, s), 7.1–8.0 (9 H, m), 8.32 (1 H, s), 13.34 (1 H, s); IR (KBr) 3400, 1730, 1660, 1630, 1570 cm^{-1}. PCC-oxidation of **23j** gave **24j**: mp 263–5 °C; ^1H NMR ($CDCl_3$) δ 3.71 (3 H, s), 3.83 (2 H, s), 3.98 (3 H, s), 4.12 (3 H, s), 7.3–8.0 (9 H, m), 8.43 (1 H, s), 13.34 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 39.7, 52.5, 52.9, 65.2, 116.3, 121.1, 124.3, 124.9, 128.7, 130.2, 130.8, 131.3, 133.0, 134.3, 135.4, 137.5, 141.3, 143.8, 157.1, 160.6, 166.0, 169.7, 181.1, 187.1, 196.0; IR (KBr) 3400, 1740, 1710, 1680, 1625, 1570 cm^{-1}; UV ($CHCl_3$) λ_{max} 419, 267 nm; UV (H_2SO_4) λ_{max} 530, 282 nm; HRMS calcd for $C_{33}H_{22}O_9$ 562.1262, found 562.1212.

1-Hydroxy-12-methoxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)cyclohepteno[*b*]anthracene-5,11,13-trione (24k). The synthesis was conducted without isolating intermediates: mp 145–6 °C; ^1H NMR ($CDCl_3$) δ 1.6–2.0 (4 H, m), 2.4–3.0 (4 H, m), 3.72 (3 H, s), 3.83 (2 H, s), 3.95 (3 H, s), 3.98 (3 H, s), 7.70 (1 H, s), 7.93 (1 H, s), 13.32 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 24.3, 25.5, 33.5, 39.4, 42.6, 52.3, 52.6, 64.2, 116.0, 120.7, 124.1, 126.6, 128.8, 132.7, 135.5, 141.0, 143.5, 146.7, 157.8, 160.3, 165.8, 169.6, 181.1, 187.1, 205.5; IR (KBr) 3400, 1740, 1730, 1700, 1670, 1630, 1570 cm^{-1}; UV ($CHCl_3$) λ_{max} 412, 262 nm; HRMS calcd for $C_{25}H_{22}O_9$ 466.1263, found 466.1280.

1-Hydroxy-13-methoxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-5,7,12,14-pentacenediquinone (45). Methyl 9,10-dihydro-9,10-dihydroxy-1-methoxy-2-(methoxycarbonyl)-3-anthrylacetate (**44**) was synthesized by the reduction of anthraquinone **31a** with $NaBH_4$ according to the procedures shown in the synthesis of **24a** except that the reaction mixture was stirred at room temperature for 3 h and extracted with chloroform after dilution with water. Quenching with 2 N HCl gave unsatisfactory results. Two stereoisomers were obtained in 48 and 46% yields by a silica gel chromatography. Isomer I (with higher R_f): mp 123–4 °C (ether); ^1H NMR ($CDCl_3$) δ 3.65 (5 H, s), 3.89 (3 H, s), 3.95 (3 H, s), 3.8–4.3 (2 H, m), 5.32 (1 H, br s), 5.76 (1 H, br s), 7.0–7.6 (5 H, m); IR (KBr) 3410, 3360, 1730, 1710 cm^{-1}; HRMS calcd for $C_{20}H_{20}O_7$ 372.1209, found 372.1176. Isomer II (with lower R_f): ^1H NMR ($CDCl_3$) δ 2.68 (2 H, br s), 3.66 (3 H, s), 3.70 (2 H, s), 3.91 (3 H, s), 3.94 (3 H, s), 5.74 (1 H, s), 5.98 (1 H, s), 7.34 (1 H, s), 7.1–7.5 (4 H, m); IR (neat) 3350, 1740–1700 cm^{-1}; HRMS calcd for $C_{20}H_{20}O_7$ 372.1209, found 372.1281. Dihydrodihydroxyanthracene **44** (Isomer I) was subjected to the Claisen condensation and K_2CO_3-induced aromatization. In this case, K_2CO_3 gave better results than $Ca(OAc)_2$. PCC-oxidation of the crude products in methylene chloride gave **45** in 18% yield. Isomer II gave the same product in 15% yield: mp 235–6 °C ($CHCl_3$–ether); ^1H NMR ($CDCl_3$) δ 3.73 (3 H, s), 3.85 (2 H, s), 3.99 (3 H, s), 4.16 (3 H, s), 7.77 (1 H, s), 7.7–8.0 (2 H, m), 8.1–8.4 (2 H, m), 9.05 (1 H, s), 13.15 (1 H, s); IR (KBr) 3400, 1735, 1715, 1675, 1630, 1590, 1570 cm^{-1}; UV ($CHCl_3$) λ_{max} 416, 265 nm; HRMS calcd for $C_{28}H_{18}O_{10}$ 514.0889, found 514.0895. Methylation of **45** with Ag_2O–MeI gave **29a**, which was identical with that obtained from **28a**.

CAN-Oxidation. 2-(Methoxycarbonyl)-3-((methoxycarbonyl)methyl)-1,13-dimethoxy-5,7,12,14-pentacenediquinone (29a). To a THF–water (2 and 6 mL) solution of **28a** (26 mg, 0.05 mmol) was added CAN (144 mg, 0.26 mmol), and the mixture was stirred for 10 min before being diluted with water. The organic materials were extracted twice with chloroform, dried (Na_2SO_4), concentrated, and chromatographed on silica gel to give **29a** (16 mg, 60%): mp 254 °C ($CHCl_3$–AcOEt); ^1H NMR ($CDCl_3$) δ 3.72 (3 H, s), 3.80 (2 H, s), 3.98 (3 H, s), 4.02 (3 H, s), 4.18 (3 H, s), 7.7–8.0 (2 H, m), 8.00 (1 H, s), 8.1–8.5 (2 H, m), 8.96 (1 H, s); IR (KBr) 1740, 1710, 1675, 1590 cm^{-1}; UV ($CHCl_3$) λ_{max} 381, 265 nm; HRMS calcd for $C_{29}H_{20}O_{10}$ 528.1056, found 528.1068.

2-(Methoxycarbonyl)-3-((methoxycarbonyl)methyl)-1,11,13-trimethoxy-5,7,12,14-pentacenediquinone (29b): mp 249–50 °C ($CHCl_3$–AcOEt); ^1H NMR ($CDCl_3$) δ 3.72 (3 H, s), 3.80

(2 H, s), 3.97 (3 H, s), 4.01 (3 H, s), 4.05 (3 H, s), 4.18 (3 H, s), 7.2–8.0 (3 H, m), 8.00 (1 H, s), 8.83 (1 H, s); IR (KBr) 1730, 1675, 1585 cm^{-1}; UV ($CHCl_3$) λ_{max} 389, 264 nm; HRMS calcd for $C_{30}H_{22}O_{11}$ 558.1161, found 558.1139.

7-Hydroxy-7-methyl-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-12-oxo-1,13-dimethoxy-5,14-pentacenequinone (30): mp 97–99 °C ($CHCl_3$–ether–hexane); ^1H NMR ($CDCl_3$) δ 1.68 (3 H, s), 3.03 (1 H, br s), 3.72 (3 H, s), 3.77 (2 H, s), 3.96 (3 H, s), 4.00 (3 H, s), 4.05 (3 H, s), 7.3–8.2 (4 H, m), 7.88 (1 H, s), 8.56 (1 H, s); IR (KBr) 3400, 1735, 1675, 1590 cm^{-1}; UV ($CHCl_3$) λ_{max} 416, 368, 292 nm; HRMS calcd for $C_{30}H_{24}O_{10}$ 544.1370, found 544.1406.

1,14-Dimethoxy-5-hydroxy-5-methyl-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-13-oxo-7,12-pentacenequinone (43): mp 240–2 °C ($CHCl_3$–ether–hexane); ^1H NMR ($CDCl_3$) δ 1.68 (3 H, s), 3.58 (1 H, s), 3.70 (3 H, s), 3.80 (2 H, s), 3.95 (9 H, s), 7.6–8.3 (4 H, m), 7.73 (1 H, s), 8.52 (1 H, s); IR (KBr) 3400, 1740, 1730, 1670, 1590, 1580 cm^{-1}; UV ($CHCl_3$) λ_{max} 330, 266 nm; HRMS calcd for $C_{30}H_{24}O_{10}$ 544.1369, found 544.1353.

Claisen Condensation and K_2CO_3-Induced Aromatization of Quinoid Glutarates. 1-Hydroxy-12-methoxy-4-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-6,11-naphthacenequinone (33a). Under a nitrogen atmosphere, a THF–HMPA (12 and 3 mL) solution of methyl acetoacetate (0.67 mL, 6.2 mmol) was added to a THF–HMPA (8 and 2 mL) suspension of sodium hydride (156 mg, 6.8 mmol) at 0 °C. After 10 min, butyllithium (16 mmol) in hexane (10.2 mL) was added at 0 °C, and stirring was continued for 10 min. Then, **31a** (281 mg, 0.76 mmol) in THF–HMPA (12 and 3 mL) was added at 0 °C, and the mixture was warmed to room temperature. Stirring was continued for 2 h before 2 N HCl was added. Organic materials were extracted twice with ethyl acetate, washed with water and brine, dried (Na_2SO_4), and concentrated. Methanol (5 mL) and K_2CO_3 (4.2 g, 30 mmol) was added to the residue, and the mixture was stirred for 2 h. The reaction was quenched by adding 2 N HCl, and the mixture was extracted with chloroform, dried (Na_2SO_4), concentrated, and chromatographed on silica gel to give **33a** (63 mg, 20%): mp 223–4 °C ($CHCl_3$–ether–hexane); ^1H NMR ($CDCl_3$) δ 3.74 (3 H, s), 3.85 (3 H, s), 3.96 (2 H, s), 4.06 (3 H, s), 7.3–7.6 (4 H, m), 8.1–8.5 (3 H, m); IR (KBr) 3300, 1740, 1710, 1655, 1610 cm^{-1}; HRMS calcd for $C_{24}H_{18}O_8$ 434.1001, found 434.1006.

1-Hydroxy-10,12-dimethoxy-4-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-6,11-naphthacenequinone (33b): mp 207–8 °C ($CHCl_3$–ether–hexane); ^1H NMR ($CDCl_3$) δ 3.70 (6 H, s), 3.83 (3 H, s), 3.93 (2 H, s), 4.05 (3 H, s), 7.18 (1 H, dd, J = 1.5, 8 Hz), 7.50 (1 H, s), 7.52 (1 H, t, J = 8 Hz), 8.02 (1 H, dd, J = 1.5, 8 Hz), 8.27 (1 H, s), 9.76 (1 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.7, 52.3, 52.4, 52.8, 56.0, 110.4, 116.0, 118.5, 120.5, 122.9, 126.2, 127.4, 128.9, 129.2, 130.3, 132.4, 132.5, 133.4, 134.6, 155.4, 156.5, 168.2, 170.1, 170.5, 183.9; IR (KBr) 3300, 1725, 1700, 1660, 1610, 1585 cm^{-1}; HRMS calcd for $C_{25}H_{20}O_9$ 464.1105, found 464.1080.

1-Hydroxy-4-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-11,12,14-trimethoxy-6,13-pentacenequinone (35): mp 228–9 °C ($CHCl_3$–ether); ^1H NMR ($CDCl_3$) δ 3.40 (3 H, s), 3.74 (3 H, s), 3.78 (3 H, s), 3.82 (2 H, s), 3.96 (3 H, s), 4.18 (3 H, s), 7.2–7.4 (1 H, m), 7.5–7.9 (2 H, m), 8.14 (1 H, s), 8.74 (1 H, s), 9.39 (1 H, s), 10.07 (1 H, s); IR (KBr) 3200, 1740, 1680, 1650, 1580 cm^{-1}; HRMS calcd for $C_{30}H_{24}O_{10}$ 544.1368, found 544.1279.

1,12-Dihydroxy-5-methoxy-4-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-6,11-naphthacenequinone (37): mp 246.5–7.5 °C ($CHCl_3$–ether); ^1H NMR ($CDCl_3$) δ 3.70 (3 H, s), 3.88 (3 H, s), 4.04 (3 H, s), 4.14 (2 H, s), 7.5–8.0 (4 H, m), 8.3–8.6 (1 H, m), 15.04 (1 H, br s); ^1H NMR ($CDCl_3$-d_6–DMSO) δ 3.70 (3 H, s), 4.04 (3 H, s), 4.06 (3 H, s), 4.16 (2 H, s), 7.6–8.0 (2 H, m), 7.82 (1 H, s), 8.0–8.3 (1 H, m), 8.5–8.7 (1 H, m), 10.1 (1 H, br s), 15.38 (1 H, br s); IR (KBr) 3250, 1730, 1720, 1620, 1595, 1570 cm^{-1}; HRMS calcd for $C_{24}H_{18}O_9$ 450.0951, found 450.0960.

1-Hydroxy-4-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-6,7,14-trimethoxy-8,13-benzo[*a*]naphthacenequinone (39): mp 209–12 °C (AcOEt–hexane); ^1H NMR ($CDCl_3$) δ 3.70 (3 H, s), 3.81 (3 H, s), 4.07 (6 H, s), 4.12 (3 H, s), 4.16 (2 H, s), 7.3–7.5 (2 H, m), 7.56 (1 H, s), 7.6–7.9 (1 H, m), 7.76 (1 H, s), 8.1–8.4 (1 H, m), 9.61 (1 H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.5, 52.4, 52.7, 56.6, 107.0, 110.8, 111.3, 118.9, 119.8, 120.2, 126.3, 126.5, 127.8, 128.3, 129.8, 130.2, 130.4, 131.2, 132.7, 133.1, 154.9, 156.2, 169.1, 170.0, 170.3, 172.1; IR (KBr) 3400, 1720, 1670, 1600 cm^{-1}; HRMS calcd for $C_{30}H_{24}O_{10}$ 544.1369, found 544.1356.

5-Methyl-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-1,13,14-trimethoxy-7,12-pentacenequinone (42). Anthraquinone **41** was treated as depicted in the synthesis of **33a**, and the crude product obtained was methylated with K_2CO_3–Me_2SO_4 in refluxing acetone: mp 255 °C ($CHCl_3$–ether); ^1H NMR ($CDCl_3$) δ 3.15 (3 H, s), 3.75 (3 H, s), 3.89 (2 H, s), 3.96 (3 H, s), 4.01 (6 H, s), 4.18 (3 H, s), 7.6–7.9 (2 H, m), 8.00 (1 H, s), 8.1–8.5 (2 H, m), 9.16 (1 H, s); IR (KBr) 1730, 1710, 1670, 1650, 1615, 1570 cm^{-1}; UV ($CHCl_3$) λ_{max} 472, 352, 338, 280 nm; HRMS calcd for $C_{31}H_{26}O_9$ 542.1578, found 542.1586.

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Registry No. **1a**, 111-40-0; **1b**, 14035-94-0; **1c**, 13051-32-6; **1d**, 69134-53-8; **1e**, 32328-03-3; **1f**, 107182-05-8; **1g**, 77-93-0; **1h**, 84-66-2; **1i**, 6634-01-1; **1j**, 5807-65-8; **4a**, 100420-09-5; **4b**, 107182-00-3; **4c**, 107182-01-4; **4d**, 107182-02-5; **4e**, 107182-04-7; **4f**, 107182-06-9; **4g**, 107182-07-0; **4h**, 111171-70-1; *syn*-**4i**, 114629-22-0; *anti*-**4i**, 114629-23-1; **4j**, 109873-11-2; **5**, 107182-03-6; **6**, 107205-96-9; **7a**, 111171-68-7; **7h**, 111171-53-0; **7j**, 111171-56-3; **7k**, 111171-69-8; **8**, 107182-10-5; **9**, 109873-38-3; **10b**, 109873-39-4; **10c**, 109873-40-7; **11**, 124563-37-7; **12a**, 716-43-8; **12b**, 1214-87-5; **12c**, 6512-26-1; **12d**, 16101-72-7; **12e**, 66271-21-4; **12f**, 104292-98-0; **13**, 1126-51-8; **14d**, 111171-67-6; **14e**, 111171-66-5; **15a**, 114629-24-2; **15b**, 114629-25-3; **15c**, 124581-17-5; **15d**, 114629-26-4; **15e**, 114629-27-5; **15f**, 114629-29-7; **16**, 114629-28-6; **17a**, 109873-46-3; **17b**, 109873-47-4; **17c**, 109873-48-5; **17d**, 111171-65-4; **17e**, 111171-64-3; **18**, 109873-56-5; **20a**, 96303-61-6; **20b**, 105245-46-3; **21**, 16234-96-1; **22a**, 111171-48-3; **22h**, 111171-54-1; **23j**, 111171-57-4; **24a**, 111171-51-8; **24h**, 111171-55-2; **24j**, 111171-50-7; **24k**, 111171-52-9; **26a**, 114629-30-0; **26b**, 114629-31-1; **26f**, 114629-32-2; **27a**, 114629-34-4; **27b**, 114629-35-5; **27f**, 114629-36-6; **28a**, 114629-37-7; **28b**, 114629-38-8; **28f**, 114629-39-9; **29a**, 114629-15-1; **29b**, 114629-40-2; **30**, 114672-13-8; **31a**, 109873-49-6; **31b**, 109873-50-9; **32**, 109873-57-6; **33a**, 109873-53-2; **33b**, 109873-54-3; **34a**, 111171-59-6; **34b**, 111171-71-2; **35**, 109873-58-7; **36**, 111171-62-1; **37**, 111171-60-9; **38**, 111171-61-0; **39**, 111193-35-2; **40**, 111171-72-3; **41**, 124581-18-6; **42**, 124563-33-3; **43**, 124563-34-4; *cis*-**44**, 124563-35-5; *trans*-**44**, 124581-19-7; **45**, 124563-36-6; $H_3CCOCH_2CO_2CH_3$, 105-45-3; H_3CCO_2Bu-t, 540-88-5; 1-hydroxy-2-(methoxycarbonyl)-3-((methoxycarbonyl)methyl)-9-benzocycloheptenone, 100420-20-0; 2-(*tert*-butoxycarbonyl)-3-((*tert*-butoxycarbonyl)methyl)-4-hydroxy-2-cyclohexenone, 124563-38-8; 2-(*tert*-butoxycarbonyl)-3-((-*tert*-butoxycarbonyl)methyl)-6-hydroxy-2-cyclohexenone, 124563-39-9; *tert*-butyl 2-(*tert*-butoxycarbonyl)-3,4-(methylenedioxy)phenylacetate, 124563-40-2; methyl 1,9-diacetoxy-2-(methoxycarbonyl)-3-anthrylacetate, 107182-08-1; methyl 1,9-diacetoxy-8-methoxy-2-(methoxycarbonyl)-3-anthrylacetate, 107182-09-2; methyl 1,9-diacetoxy-6,8-dimethoxy-2-(methoxycarbonyl)-3-anthrylacetate, 109873-45-2; methyl 1,9-diacetoxy-10-methyl-2(methoxycarbonyl)-3-anthrylacetate, 124563-41-3.

Supplementary Material Available: Preparative procedures, spectra, and/or analytical data for compounds **8**, **9**, **10b,c**, **11**, **12b–f**, **14d,e**, *tert*-butyl 2-(*tert*-butoxycarbonyl)-3,4-(methylenedioxy)phenylacetate, **26a,b,f**, **41**, methyl 1,9-diacetoxy-2-(methoxycarbonyl)-3-anthrylacetate, methyl 1,9-diacetoxy-8-methoxy-2-(methoxycarbonyl)-3-anthrylacetate, methyl 1,9-diacetoxy-6,8-dimethoxy-2-(methoxycarbonyl)-3-anthrylacetate, and methyl 1,9-diacetoxy-10-methyl-2-(methoxycarbonyl)-3-anthrylacetate and spectral data of compounds **15a** and **15b** (9 pages). Ordering information is given on any current masthead page.