93350-07-3; $Pd(PPh_3)_4$, 14221-01-3; $Pd(OAc)_2$, 3375-31-3; NaOMe, 124-41-4; (2-methoxyphenyl)magnesium bromide, 16750-63-3; thiophenol, 108-98-5; phenylboronic acid, 98-80-6; 6-hydroxynicotinic acid, 5006-66-6; methyl nicotinate, 93-60-7; 3,3′-dinitrobiphenyl, 958-96-3; nicotinic acid, 59-67-6; tri-*o*-tolylphosphine, 6163-58-2; toluene, 108-88-3; triisopropylborate, 5419-55-6; (3-methylphenyl)magnesium bromide, 28987-79-3; 2-furyllithium, 2786-02-9; 3-furyllithium, 53101-93-2.

A High-Yield Modification of the Pschorr Phenanthrene Synthesis

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A relationship between substituents on the aryl ring undergoing homolytic aromatic substitution and the yield of Pschorr reaction product has been demonstrated. The new variation in which a (phenylsulfonyl)oxy group is present on the acceptor ring has been used to synthesize several highly oxygenated 9-phenanthrenecarboxylic acids in significantly improved yields.

Since the initial report[1] of the use of an arenediazonium salt to effect intramolecular coupling and yield 9-phenanthrenecarboxylic acid, the Pschorr reaction has been very widely used and reviewed.[2] Stimulation for these studies has been, in part, provided by the fact that many naturally occurring compounds of biological and therapeutic interest contain a phenanthrene or reduced phenanthrene ring system.[2,3] A number of alternative methods have been developed to synthesize the phenanthrene ring system, but the Pschorr reaction remains the primary method.

A survey of the literature on the Pschorr reaction revealed the following salient points: (1) the reactive intermediate was an aryl radical resulting from the corresponding arenediazonium salt; (2) methodology has been reported for the preparation, handling, and decomposition of the arenediazonium salts to afford the intermediate aryl radical; (3) substituents on the aromatic ring being attacked always resulted in lower coupled yields than in the unsubstituted case. No clear relationship between the inductive effect, number, or position of substituents and the yields of coupled products has been demonstrated with the classical methods used for the decomposition of arenediazonium salts (copper, copper salts, thermolysis, zinc, and sodium hypophosphite).

Finally, the report[4] that iodide ion cleanly effected Pschorr coupling of the corresponding diazonium salts of (*E*)-2-amino-α-phenylcinnamic acid, and especially several of its derivatives, represents a synthetically useful, homogeneous, and convenient alternative to the previously reported methods for ring closure via arenediazonium salts. Of particular interest is the fact that consistently higher yields of substituted phenanthrenes were reported than by previous authors who decomposed the same diazonium salts with Gatterman copper according to the original procedure.[1]

The intermediacy of aryl radicals in the Pschorr reaction has been well documented.[2,5] Recent reports of newer methods[5d,e,6] of reacting arenediazonium salts in the Pschorr reaction merely represent new techniques for producing aryl radicals. Since it would be the same radical being formed, these changes in the immediate environment of the aryl radical have not resulted in any significant improvement of coupling yields as compared to the oxidation of iodide ion by arenediazonium salts. The mechanism of the oxidation of iodide ion and reduction of arenediazonium salts, which ultimately yields molecular nitrogen and the corresponding aryl radical, was understood[5a,d–f] long before the first applications to the intramolecular Pschorr synthesis of phenanthridones[7] and phenanthrenes.[4]

With the reported sodium iodide mediated Pschorr phenanthrene synthesis, consistent data became available demonstrating a relationship between the inductive effect of substituents on the aryl ring undergoing homolytic aromatic substitution and the yield of intramolecularly coupled product. However, the isolated yields of phenanthrenes were reported to drop by about 10% for every methyl or methoxy substituent. Since most natural products, and their derivatives and degradation products, which are of interest are highly methoxy substituted, this application of the Pschorr reaction to the synthesis of such phenanthrenes has resulted in comparatively low yields.

We now demonstrate improved coupling yields in the Pschorr phenanthrene synthesis by substituting the electron-withdrawing (phenylsulfonyl)oxy group for electron-donating alkoxy groups in two systems, a dioxygenated and a trioxygenated α-phenyl group of the corresponding di-

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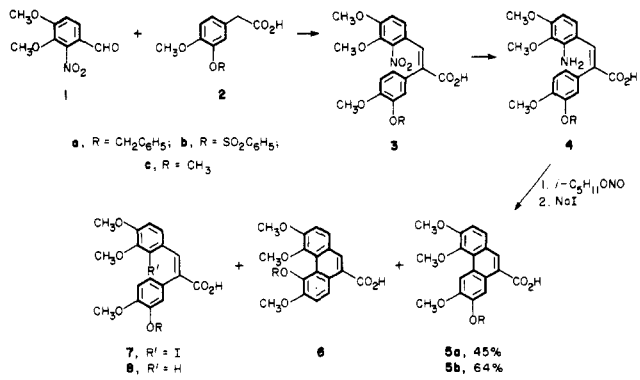
azonium salts of substituted (*E*)-2-amino-α-arylcinnamic acids. This procedure, in which an electron-donating substituent was masked as an electron-withdrawing group, represents a new modification of the Pschorr synthesis that is applicable for the synthesis of highly oxygenated phenanthrenes.

Results and Discussion

Preparation of the (*E*)-2-Diazonio-α-arylcinnamic Acid Bisulfate Derivatives as Educts for Phenanthrene Syntheses. Pure 2-nitroveratraldehyde (1),[8] 6-nitroveratraldehyde (**9**),[9] and the 5-nitroveratraldehyde isomer[10] were prepared, and each isomer was demonstrated to be free of the other two regioisomers by analytical HPLC.[11] Phenylacetic acids were prepared by homologation of the corresponding benzaldehyde derivatives. Then Perkin condensations of *o*-nitrobenzaldehydes with the phenylacetic acid derivatives were performed at 90 °C for 10 h; prolonged heating resulted in isomerization to the undesired (*Z*)-2-nitro-α-arylcinnamic acids. Ferrous sulfate reduction followed by diazotization of the (*E*)-2-amino-α-arylcinnamic acid derivatives with sulfuric acid and isoamyl nitrite gave the red (*E*)-2-diazonio-α-arylcinnamic acid bisulfate salts that were used without isolation in Pschorr reactions.

Phenanthrene Syntheses. The preparation of 3,4,6,7-tetramethoxy-9-phenanthrenecarboxylic acid (**5c**) and 2,3,5,6,7-pentamethoxy-9-phenanthrenecarboxylic acid (**13a**) was then investigated. Ring closures of the corresponding (*E*)-2-diazonio-α-arylcinnamic acid bisulfate derivatives were performed by two methods: (1) in aqueous dioxane with freshly prepared Gatterman copper and (2) in acetone with sodium iodide followed by sodium bisulfite.

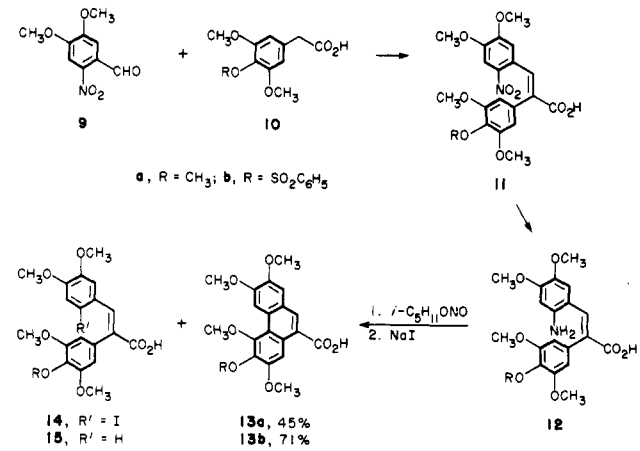
Decomposition of the arenediazonium salt from **4c** according to the original method of Pschorr[1] with Gatterman copper afforded a 20% yield of 3,4,6,7-tetramethoxy-9-phenanthrenecarboxylic acid (**5c**).[12] The regioisomer, 3,4,5,6-tetramethoxy-9-phenanthrenecarboxylic acid (**6c**) also was isolated, and the reduction product, stilbene **8c**, was detected. The benzyloxy derivative **4a** gave an



identical yield of **5a**, suggesting that the coupling yield was related to the inductive effects of the substituents, two alkoxy groups, in both of these cases. The other regioisomer **6a** was not isolated. Reaction of the arenediazonium salt from **11a** with Gatterman copper afforded a 36% yield of 2,3,5,6,7-pentamethoxy-9-phenanthrenecarboxylic acid (**13a**),[13] the only possible phenanthrene product.

When the procedure involving oxidation of iodide ion by the diazonium salt in the presence of sodium bisulfite[5d] was applied, a 45% yield of phenanthrene **5a** resulted. Under the same conditions, the diazonium salt prepared from **12a** afforded a 45% yield of phenanthrene **13a**. Thus, significantly improved yields were observed for both systems under the homogeneous reaction conditions. The corresponding aryl iodide byproduct **14a** was isolated in 20% yield.

Use of the (phenylsulfonyl)oxy derivatives in combination with the iodide procedure led to still greater increases in yield. Thus when the diazotized (phenylsulfonyl)oxy derivatives **4b** and **12b** were treated with iodide ion under the same conditions as above, the corresponding phenanthrenes **5b** and **13b** were isolated in yields of 64% and 71%, respectively, approximately a further 50% increase in yield. Since the hydrolysis of the arenesulfonate to the parent phenol is a quantitative reaction, this process becomes the method of choice for the synthesis of oxygenated phenanthrenes.



The 2-iodo-α-arylcinnamic acid derivatives **7** and **14** of the corresponding arenediazonium salts were often observed as byproducts of the iodide oxidation. Iodides **14a** and **14b** were isolated and efficiently converted to the corresponding phenanthrenes **13** by heteroatom-directed photoarylation.[4a] Subsequently, the mother liquors were routinely photolyzed in dioxane or methanol following isolation of the crystalline phenanthrenes, and improved yields of **13a** (67%) and **13b** (74%) were obtained.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded in $CHCl_3$, NMR spectra were recorded in $CDCl_3$ with Me_4Si as an internal standard unless otherwise indicated, and UV spectra were recorded in methanol. All reaction were stirred magnetically under a nitrogen atmosphere, and final organic solvent solutions were dried over $MgSO_4$ unless otherwise indicated. Gas chromatographic analysis of the 9-phenanthrenecarboxylic acid methyl esters, prepared by treatment of the acids with diazomethane in ether, was performed by using a 6-ft column of 10% SE-30 on Chromosorb W. HPLC analysis were done on a Lichrosorb Si-60 5-μm column (3.2 × 250 mm).

3,5-Dimethoxy-4-((phenylsulfonyl)oxy)benzaldehyde. To 3,5-dimethoxy-4-hydroxybenzaldehyde (22 g, 0.12 mol)[7] dissolved in CH_2Cl_2 (300 mL) was added pulverized sodium hydroxide (5.7 g, 0.14 mol), cetylethyldimethylammonium bromide (100 mg), and water (300 mL) followed by the dropwise addition of phenyl-

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(11) Analytical HPLC, 2/3 $CHCl_3$/isooctane, 0.75 mL min^{-1}, 280 nm: 6-nitroveraltraldehyde (**9**), t_R = 6 min; 5-nitroveratraldehyde, t_R = 6 min 25 s; 2-nitroveratraldehyde (1), t_R = 12 min 45 s.
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sulfonyl chloride (16.7 mL, 0.13 mol). After 20 min the organic layer was separated, washed with water (2 × 150 mL), dried, and evaporated. The residue was triturated with hexane to give 3,5-dimethoxy-4-((phenylsulfonyl)oxy)benzaldehyde: yield 35.3 g, 94%; mp 160–161 °C; ^{1}H NMR δ 9.65 (s, 1 H), 7.83–7.33 (m, 5 H), 6.83 (s, 2 H), 3.63 (s, 6 H); IR 2800, 1650 cm^{-1}.

3,5-Dimethoxy-4-((phenylsulfonyl)oxy)benzyl Alcohol. To a mixture of 3,5-dimethoxy-4-((phenylsulfonyl)oxy)benzaldehyde (35 g, 0.11 mol) in methanol (500 mL) was added sodium borohydride (4.7 g, 0.13 mol). After 2 h the methanol was evaporated and the residue, dissolved in chloroform (400 mL), was washed with H_2O (2 × 300 mL), dried, and evaporated to yield the benzyl alcohol (34.1 g, 97%) which was used without further purification: mp 85–87 °C; ^{1}H NMR (acetone-d_6/Me_4Si) δ 7.83–7.48 (m, 5 H), 6.55 (s, 2 H), 4.52 (d, 2 H), 3.55 (s, 6 H).

3,5-Dimethoxy-4-((phenylsulfonyl)oxy)benzyl Bromide. 3,5-Dimethoxy-4-((phenylsulfonyl)oxy)benzyl alcohol (34 g, 106 mmol) was dissolved in chloroform (100 mL) and cooled to 0 °C. Then PBr_3 (10.8 mL, 0.12 mol) was added dropwise so that the internal temperature remained below 10 °C. The solution was stirred for 2 h after which 100 mL of ice water was added followed by 100 mL of saturated sodium bicarbonate solution. The organic layer was separated, washed with water (3 × 70 mL), dried, and evaporated to give the benzyl bromide (35 g, 86%) which was used without further purification: mp 158–159 °C; ^{1}H NMR δ 7.91–7.38 (m, 5 H), 6.47 (s, 2 H), 4.3 (s, 2 H), 3.63 (s, 6 H).

3,5-Dimethoxy-4-((phenylsulfonyl)oxy)phenylacetonitrile. 3,5-Dimethoxy-4-((phenylsulfonyl)oxy)benzyl bromide (34.8 g, 91 mmol) was dissolved in DMF (300 mL) and pulverized sodium cyanide (22 g, 0.45 mol) was added in one portion to the mechanically stirred solution. After 30 min the mixture was poured into water (300 mL) and then extracted with chloroform (3 × 300 mL). The organic layers were combined and backwashed with water (3 × 200 mL), dried, and evaporated to afford nitrile (24.8 g, 83%): mp 120 °C; ^{1}H NMR δ 7.82–7.33 (m, 5 H), 6.33 (s, 2 H), 3.60 (s, 2 H), 3.57 (s, 6 H); IR 3500, 2850 cm^{-1}.

3,5-Dimethoxy-4-((phenylsulfonyl)oxy)phenylacetic Acid (10b). 3,5-Dimethoxy-4-((phenylsulfonyl)oxy)phenylacetonitrile (24.8 g, 74 mmol) was refluxed in 12 M HCl (300 mL) and acetic acid (20 mL) for 2.5 h at which time water (200 mL) was added and the reaction cooled to room temperature. The aqueous phase was extracted with $CHCl_3$ (3 × 200 mL), and the organic layers were combined and extracted with saturated $NaHCO_3$ (3 × 300 mL). The bicarbonate extracts were combined, acidified to pH 2 with concentrated HCl, and then extracted with $CHCl_3$ (3 × 200 mL) which was dried and evaporated. Crystallization of the residue from EtOAc/hexane gave pure acid **10b**: 23.6 g, 90% yield; mp 153.5 °C; ^{1}H NMR δ 8.48 (br s, 1 H), 8.02–7.50 (m, 5 H), 6.48 (s, 2 H), 3.63 (s, 6 H), 3.55 (s, 2 H); IR 2950, 1700 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_7S$: C, 54.5; H, 4.6. Found: C, 54.7; H, 4.6.

3-(Benzyloxy)-4-methoxybenzaldehyde. To slurry of K_2CO_3 (118 g, 0.86 mol) in ethanol (1.52 L, absolute) was added freshly recrystallized 3-hydroxy-4-methoxybenzaldehyde (118 g, 0.78 mol), and benzyl chloride (132 g, 1.0 mol) was added over 5 min. The reaction was stirred and refluxed for 5 h, the ethanol was evaporated, and the residue was partitioned between $CHCl_3$ (1 L) and water (1 L). The aqueous phase was extracted with $CHCl_3$ (2 × 500 mL), and the combined organic phases were washed with 0.5 N NaOH solution (2 × 500 mL), and brine (1 × 500 mL). Drying and evaporating the organic phase gave a residue which was recrystallized from ether: 148 g, 78% yield; mp 60–61 °C; ^{1}H NMR δ 9.17 (s, 1 H), 7.1–7.5 (m, 7 H), 6.70 (d, 2 H, J = 9 Hz), 5.11 (s, 2 H), 3.88 (s, 3 H); IR (KBr) 2900, 2775, 2700, 1665 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.7; H, 6.5. Found: C, 74.0; H, 6.8.

3-(Benzyloxy)-4-methoxyphenylacetic Acid (2a). Conversion of 3-(benzyloxy)-4-methoxybenzaldehyde to the phenylacetic acid was performed as described for the preparation of 3,5-dimethoxy-4-((phenylsulfonyl)oxy)phenylacetic acid (**10b**): mp 124–125 °C (lit.[14] mp 115–120 °C); ^{1}H NMR δ 7.1–7.5 (m, 5 H), 6.77 (s, 3 H), 5.02 (s, 2 H), 3.76 (s, 3 H), 3.43 (s, 2 H); IR (KBr) 2950, 1695 cm^{-1}; UV λ_{max} 227 nm (sh), 279 (ε 2890). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.6; H, 5.9. Found: C, 70.7; H, 6.0.

4-Methoxy-3-((phenylsulfonyl)oxy)phenylacetic Acid (2b). To 3-hydroxy-4-methoxyphenylacetic acid[14] (8.1 g, 25 mmol) dissolved in aqueous NaOH (2.3 g, 50 mmol in 90 mL) was added phenylsulfonyl chloride (8.8 g, 50 mmol) dropwise with stirring. Sodium hydroxide was added to raise the pH from 5 to 9, and additional benzenesulfonyl chloride (2.2 g, 13 mmol) was added. After 1 h, water (100 mL) was added, the pH was adjusted to 3 with 12 M HCl, and the mixture was extracted with CH_2Cl_2 (5 × 30 mL). The organic phases were extracted with saturated $NaHCO_3$ solution (3 × 50 mL), the bicarbonate extracts were acidified to pH 4 with 12 M HCl and then extracted with ether (3 × 50 mL), and the ether was dried and evaporated to give **2b** which was crystallized from EtOAc/hexane: 5.5 g, 67% yield; mp 103–105 °C; ^{1}H NMR (acetone-d_6) δ 6.85–8.07 (m, 9 H), 3.57 (s, 2 H), 3.52 (s, 3 H). Anal. Calcd for $C_{15}H_{14}O_6S$: C, 55.9; H, 4.4. Found: C, 56.0; H, 4.4.

General Procedure for Preparation of Nitrocinnamic Acids. Nitroaldehyde [2-nitroveratraldehyde (**1**)[8] or 6-nitroveratraldehyde (**9**),[9] 20 mmol] and the phenylacetic acid (20 mmol) were dissolved in acetic anhydride (60 mmol), triethylamine (20 mmol) was added dropwise, and the solution was stirred at 90 °C for 10 h. At this point, H_2O (90 mmol) was added and the reaction was allowed to continue for 15 min. After K_2CO_3 (160 mmol) in water (200 mL) was added dropwise and the reaction warmed to 60 °C, the reaction was stirred for an additional hour, then cooled to 10 °C, and acidified to pH 3 with 12 M HCl. The aqueous solution was extracted with CH_2Cl_2 (3 × 50 mL), and the organic phases were combined, washed with brine (3 × 50 mL), dried, and evaporated. Crystallization from EtOAc/hexane yielded the nitro acid.

(*E*)-α-(3-(Benzyloxy)-4-methoxyphenyl)-3,4-dimethoxy-2-nitrocinnamic acid (3a) was obtained in 72% yield: mp 182–184 °C; ^{1}H NMR δ 7.51 (s, 1 H), 7.1–7.4 (m, 5 H), 6.8–6.95 (m, 3 H), 6.54 (d, 1 H, J = 9.0 Hz), 6.40 (d, 1 H, J = 9.0 Hz), 4.95 (s, 2 H), 3.84 (s, 3 H), 3.81 (s, 3 H), 3.75 (s, 3 H); IR (KBr) 2940 (br), 1680 cm^{-1}; UV λ_{max} 229 nm (sh), 284 (ε 11 900). Anal. Calcd for $C_{25}H_{23}NO_8$: C, 64.5; H, 5.0; N, 3.0. Found: C, 64.3; H, 5.1; N, 2.9.

(*E*)-α-(3-((Phenylsulfonyl)oxy)-4-methoxyphenyl)-3,4-dimethoxy-2-nitrocinnamic acid (3b): 65% yield; mp 218–219.5 °C; ^{1}H NMR (acetone-d_6) δ 6.59–7.83 (m, 1 H), 3.94 (s, 6 H), 3.54 (s, 3 H); IR (KBr) 2930, 1660 cm^{-1}. Anal. Calcd for $C_{24}H_{21}NO_{10}S$: C, 55.0; H, 4.1;, N, 2.7. Found: C, 55.6; H, 4.1; N, 2.7.

(*E*)-α-(3,4,5-Trimethoxyphenyl)-4,5-dimethoxy-2-nitrocinnamic acid (11a): 75% yield; mp 195.5–196 °C; ^{1}H NMR δ 8.23 (s, 1 H), 7.60 (s, 1 H), 6.40 (s, 2 H), 3.93 (s, 3 H), 3.81 (s, 3 H), 3.71 (s, 6 H), 3.48 (s, 3 H); IR 2950, 1675 cm^{-1}. Anal. Calcd for $C_{20}H_{21}NO_9$: C, 57.3; H, 5.1; N, 3.3. Found: C, 57.3; H, 5.1; N, 3.3.

(*E*)-α-(3,5-Dimethoxy-4-((phenylsulfonyl)oxy)phenyl)-4,5-dimethoxy-2-nitrocinnamic acid (11b): 60% yield; mp 236.5–237 °C; ^{1}H NMR (acetone-d_6) δ 8.16 (s, 1 H), 7.7–7.89 (m, 6 H), 6.55 (s, 1 H), 6.50 (s, 2 H), 3.92 (s, 3 H), 3.61 (s, 3 H), 3.44 (s, 6 H); IR 2900, 1700 cm^{-1}. Anal. Calcd for $C_{25}H_{23}NO_{11}S$: C, 55.0; H, 4.3; N, 2.6. Found: C, 54.9; H, 4.3; N, 2.7.

General Method for Reducing 2-Nitrocinnamic Acids to 2-Aminocinnamic Acids. To 40 mL of 7.5 M NH_4OH degassed with N_2 and heated to 100 °C was added $FeSO_4 \cdot 7H_2O$ (58 mmol) with stirring. The 2-nitrocinnamic acid (5.8 mmol), dissolved in the minimum amount of NH_4OH/H_2O, was added dropwise, and the reaction was maintained under N_2 at 100 °C for 2 h at which time it was allowed to cool to room temperature, decolorizing carbon was added, and the mixture was filtered. The filtrate was cooled to 5 °C, acidified to pH 3 with 15 M H_3PO_4, and extracted with 3/1 $CHCl_3$/2-propanol (4 × 175 mL). The combined organic phase was washed with water (2 × 150 mL), dried, and evaporated to give the 2-aminocinnamic acid which was used immediately without further purification.

(*E*)-α-(3-(Benzyloxy)-4-methoxyphenyl)-2-amino-3,4-dimethoxycinnamic acid (4a): 87% yield, ^{1}H NMR ($CDCl_3$/Me_2SO-d_6, 5/95) δ 7.62 (s, 1 H), 7.19 (br s, 5 H), 6.74 (s, 3 H), 6.27 (d, 1 H, J = 9.3 Hz), 5.90 (d, 1 H, J = 9.3 Hz), 4.82 (s, 2 H), 3.73 (s, 3 H), 3.65 (s, 6 H); UV λ_{max} 224 nm (sh), 254 (sh), 296 (ε 9950), 330 (10 300).

(*E*)-α-(4-Methoxy-3-((phenylsulfonyl)oxy)phenyl)-2-amino-3,4-dimethoxycinnamic acid (4b): 95% yield; ^{1}H NMR (acetone-d_6) δ 6.06–7.83 (11 H, m), 3.76 (6 H, s), 3.53 (3 H, s).

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(*E*)-α-(3,4,5-Trimethoxyphenyl)-2-amino-4,5-dimethoxycinnamic acid (12a): 99% yield; ^{1}H NMR (acetone-d_6) δ 7.87 (s, 1 H), 6.52 (s, 2 H), 6.38 (s, 1 H), 6.25 (s, 1 H), 3.73 (s, 9 H), 3.70 (s, 3 H), 3.25 (s, 3 H).

(*E*)-α-(3,5-Dimethoxy-4-((phenylsulfonyl)oxy)phenyl)-2-amino-4,5-dimethoxycinnamic acid (12b): 97% yield; ^{1}H NMR (acetone-d_6) δ 7.60–7.98 (m, 6 H), 6.51 (s, 2 H), 6.38 (s, 2 H), 6.33 (s, 1 H), 6.20 (s, 1 H), 3.73 (s, 3 H), 3.53 (s, 6 H), 3.33 (s, 3 H).

Synthesis of Phenanthrenes. General Procedure. A. Classical Method. The 2-aminocinnamic acid (3.4 mmol) was dissolved in dioxane (32 mL), the solution was degassed with N_2 for 15 min, and then 18 M sulfuric acid (6.8 mmol) was added dropwise followed by the addition of isoamyl nitrite (6.8 mmol). The reaction was stirred for 1 h after which the diazonium salt solution was added dropwise to a stirred mixture of sodium hypophosphite (48 mmol) and freshly prepared Gatterman copper (12 mmol) in water (7 mL) and maintained at 90 °C for 3 h. A solution of 15 M ammonia (3.1 mL) in water (54 mL) was added, and the mixture was filtered. The filtrate was cooled to 5 °C, acidified to pH 3 with 12 M HCl, and extracted with CH_2Cl_2 (3 × 80 mL). The organic phases were combined, washed with water (3 × 100 mL), dried, and evaporated to give the crude product.

7-(Benzyloxy)-3,4,6-trimethoxy-9-phenanthrenecarboxylic Acid (5a). The crude product was dissolved in boiling acetone, filtered hot, and recrystallized (2 times) from acetone to give pure phenanthrene **5a** in 20% yield: mp 185 °C; ^{1}H NMR (acetone-d_6) δ 9.22 (s, 1 H), 8.71 (s, 1 H), 8.33 (s, 1 H), 7.70 (d, 1 H, J = 8.7 Hz), 7.15–7.55 (m, 6 H), 5.14 (s, 2 H), 3.94 (s, 3 H), 3.91 (s, 3 H), 3.86 (s, 3 H); IR (KBr) 2930, 1655 cm^{-1}; UV λ_{max} 265 nm (ε 6740), 281 (sh), 317 (10 600), 345 (2800), 364 (1800). Anal. Calcd for $C_{25}H_{26}O_6$: C, 71.8; H, 5.3. Found: C, 71.8; H, 5.4.

2,3,5,6,7-Pentamethoxy-9-phenanthrenecarboxylic Acid (13a). The crude reaction mixture was methylated, and the methyl esters of **13a**, **14a**, and **15a** were separated by chromatography (SiO_2, EtOAc). Subsequent hydrolysis with KOH in CH_3OH/H_2O gave phenanthrene **13a** in 36% yield: ^{1}H NMR δ 9.11 (s, 1 H), 8.27 (s, 1 H), 8.23 (s, 1 H), 7.25 (s, 1 H), 4.07 (s, 3 H), 4.14 (s, 6 H), 4.00 (s, 3 H), 3.97 (s, 3 H); IR 2900, 1675 cm^{-1}. Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.5; H, 5.4. Found: C, 64.4; H, 5.3.

B. Modified Method. 2-Aminocinnamic acid (1.9 mmol) was dissolved in acetone (150 mL), and H_2SO_4 (3.8 mmol) was added dropwise at 0 °C followed by isoamyl nitrite (3.8 mmol). In those cases where a precipitate was still present after 30 min of stirring, water was added until the solution became homogeneous. After 1 h, sodium iodide (7.8 mol) was added in four portions over a 5-h period, the solution was stirred for an additional hour, and enough sodium bisulfite was added to turn the reaction mixture yellow, whereupon it was poured into water (400 mL) and extracted with chloroform (4 × 50 mL). The organic phases were combined, washed with water (3 × 100 mL), dried, and evaporated to give the crude phenanthrene.

7-(Benzyloxy)-3,4,6-trimethoxy-9-phenanthrenecarboxylic acid (5a) was obtained after crystallization from EtOAc/hexane in 36% yield, mp 185 °C.

7-((Phenylsulfonyl)oxy)-3,4,6-trimethoxy-9-phenanthrenecarboxylic acid (5b) was obtained in 64% yield after crystallization from acetone/hexane: mp 243–244 °C; ^{1}H NMR (acetone-d_6) δ 9.37 (s, 1 H), 9.03 (s, 1 H), 8.50 (s, 1 H), 7.12–7.45 (m, 11 H), 4.04 (s, 3 H), 3.95 (s, 3 H), 3.78 (s, 3 H); IR (KBr) 2900, 1653 cm^{-1}. Anal. Calcd for $C_{24}H_{20}O_{16}S$: C, 61.5; H, 4.4. Found: C, 61.6; H, 4.4.

2,3,5,6,7-Pentamethoxy-9-phenanthrenecarboxylic acid (13a) was obtained in 45% yield by crystallization of the crude mixture from EtOAc/hexane: mp 137–138 °C; ^{1}H NMR δ 9.11 (s, 1 H), 8.27 (s, 1 H), 8.23 (s, 1 H), 7.25 (s, 1 H), 4.07 (s, 3 H), 4.04 (s, 6 H), 4.00 (s, 3 H), 3.97 (s, 3 H); IR 2900, 1675 cm^{-1}. Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.5; H, 5.4. Found: C, 64.4; H, 5.3. From the mother liquor residue, crystallization from EtOAc/hexane yielded 2-iodo-4,5-dimethoxy-3′,4′,5′-trimethoxycinnamic acid (**14a**, 20%): mp 184–184.5 °C; ^{1}H NMR δ 7.99 (s, 1 H), 7.22 (s, 1 H), 6.43 (s, 2 H), 6.40 (s, 1 H), 3.81 (s, 6 H), 3.74 (s, 6 H), 3.29 (s, 3 H); IR 2950, 1675 cm^{-1}. Anal. Calcd for $C_{20}H_{21}O_7I$: C, 48.0; H, 4.2. Found: C, 48.3; H, 4.3.

6-((Phenylsulfonyl)oxy)-2,3,5,7-tetramethoxy-9-phenanthrenecarboxylic acid (13b) was obtained in 71% yield by crystallization from EtOAc/hexane: mp 155.5–158.5 °C; ^{1}H NMR δ 8.97 (s, 1 H), 8.65 (s, 1 H), 8.60 (s, 1 H), 7.58–8.10 (m, 5 H), 7.30 (s, 1 H), 4.09 (s, 3 H), 4.06 (s, 3 H), 3.86 (s, 3 H), 3.78 (s, 3 H). Anal. Calcd for $C_{25}H_{22}O_7S$: C, 60.2; H, 4.5. Found: C, 60.1; H, 4.5.

Photolysis of Iodocinnamic Acids to Phenanthrenes. The iodocinnamic acid was dissolved in methanol (0.01 M), the solution was degassed with N_2, and photolysis for 4 h using a medium-pressure Hanovia UV light with a Pyrex filter yielded phenanthrene after evaporation and crystallization.

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Registry No. 1, 55149-84-3; **2a**, 5487-33-2; **2b**, 93279-67-5; **3a**, 93279-68-6; **3b**, 93279-69-7; **4a**, 93279-70-0; **4b**, 93279-71-1; **5a**, 93279-72-2; **5b**, 93279-73-3; **9**, 20357-25-9; **10a**, 951-82-6; **10b**, 93279-74-4; **11a**, 93279-75-5; **11b**, 93279-76-6; **12a**, 93279-77-7; **12b**, 93279-78-8; **13a**, 35323-66-1; **13a** methyl ester, 93279-79-9; **13b**, 93279-80-2; **14a**, 93279-81-3; **14a** methyl ester, 93279-82-4; **14b**, 93279-83-5; NaI, 7681-82-5; 3,5-dimethoxy-4-hydroxybenzaldehyde, 134-96-3; 3,5-dimethoxy-4-[(phenylsulfonyl)oxy]benzaldehyde, 93279-84-6; 3,5-dimethoxy-4-[(phenylsulfonyl)oxy]benzyl alcohol, 93279-85-7; 3,5-dimethoxy-4-[(phenylsulfonyl)oxy]benzyl bromide, 93279-86-8; 3,5-dimethoxy-4-[(phenylsulfonyl)oxy]benzeneacetonitrile, 93279-87-9; 3-(benzyloxy)-4-methoxybenzaldehyde, 6346-05-0; 3-hydroxy-4-methoxybenzaldehyde, 621-59-0; 3-hydroxy-4-methoxybenzeneacetic acid, 1131-94-8.