Simple Synthesis of 1-, 2-, 3-, and 4-Hydroxydibenz[a,j]anthracenes and 2-, 3-, and 4-Hydroxydibenz[a,h]anthracenes

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Studies on the mechanism of chemical carcinogenesis require the use of potential metabolites of known carcinogens and noncarcinogens. The 1-, 2-, 3-, and 4-hydroxydibenz[a,j]anthracenes **7a–c** and 2-, 3-, and 4-hydroxydibenz[a,h]anthracenes **6b–d** have been synthesized. A Diels–Alder reaction between the appropriate methoxyphenanthracene-1,4-dione **1a–d** and styrene gave the respective methoxydibenz[a,h]anthracene-7,14-diones **2b–d** and methoxydibenz[a,j]anthracene-7,14-diones **3a–d**. These methoxy diones were reduced and demethylated to the hydroxydibenz[a,h]- and -[a,j]anthracenes in good yields.

The phenols of polycyclic aromatic hydrocarbons (PAHs) are important metabolites found in mammalian metabolism.[1] For example, 3- and 4-hydroxydibenz[a,h]anthracenes (DB[a,h]A) have been identified in metabolism studies.[2] In the case of the dibenz[a,j]anthracene (DB[a,j]A) analogues, the syntheses of the respective monophenols have not been reported, which has limited metabolic studies of the parent compound. We report here a simple procedure for the synthesis of 1-, 2-, 3-, and 4-hydroxy-substituted DB[a,j]A and an improvement in the synthesis of 2-, 3-, and 4-hydroxy-substituted DB[a,h]A.

Results

Our approach to the synthesis of the title compounds was to develop a shorter and more economical route to the methoxydibenz[a,h]anthracene-7,14-diones **2a–d** and methoxydibenz[a,j]anthracene-7,14-diones **3a–d** as shown in Scheme I. The quinones **2a–d** and **3a–d** are key intermediates because a variety of methods have been developed for the reduction of polycyclic aromatic hydrocarbon (PAH) quinones to the respective hydrocarbons and for demethylation to the phenols. The preparation of the 6-, 7-, and 8-methoxyphenanthrene-1,4-diones[4,5] **1b–d** and the 5-methoxyphenanthrene-1,4-dione (**1a**)[5] from [2 + 4] cycloaddition reactions of *p*-benzoquinone and *o*-, *m*-, and *p*-methoxystyrenes suggested a convenient pathway to compounds **1a–d**. The final step would consist of a [2 + 4] cycloaddition of styrene to compounds **1a–d** to yield compounds **2a–d** and **3a–d**. Reduction and demethylation by standard methods would give the required phenols.

Reacting a 2-fold excess of styrene with each of the methoxyphenanthrene-1,4-diones **1a–d** in toluene at 100 °C with chloranil and catalytic amounts of trichloroacetic acid for 1–4 weeks gave both the MeODB[a,h]A-7,14-diones **2b–d** and the MeODB[a,j]A-7,14-diones **3a–d**. The crude reaction mixtures were rapidly eluted through neutral alumina, sublimed and rechromatographed on silica gel (250:1) with 10% benzene/hexane as the eluting solvent for the separation of the isomeric products **2b–d** from **3b–d**. However, when the sterically crowded **1a** was reacted with excess styrene, only the more sterically crowded product, **3a**, was detected and isolated in 35% yield. The product ratios shown in Table I were determined from the weights of the individual isomers isolated by column chromatography and by GC[6] area integrations of the reaction mixture prior to column chromatography. The proton magnetic resonance spectra for protons H_1 and H_8 of **2b–d** and H_1 and H_{13} of **3b–d** were found to be consistent with the assigned position of substitution.[7] However, the assignment of *a,h* or *a,j* was based on the ^{13}C chemical shifts of C_7 and C_{14} for the methoxyquinones and on the H_7 and H_{14} chemical shifts for the methoxydibenz[a,h]- and -[a,j]anthracenes. The exact structure of the 1-MeODBAD was more difficult to establish spectroscopically. The proton NMR spectrum was sufficiently informative for the position of substitution (1-MeODBAD) to be established. The ^{13}C chemical shift difference of C_7 and C_{14} for the dibenz[a,h]anthracene-7,14-diones was less than 0.3 ppm, and for the dibenz[a,j]anthracene-7,14-diones it was 3–5 ppm. However, the 1-MeODBAD product had ^{13}C resonances 1.7 ppm apart and was not assignable as either the *a,h* or *a,j* isomer by ^{13}C NMR.

Table I. Diels–Alder Product Ratios

compd	ratio (%) of isomer products
DB[a,j]A/DB[a,h]A	31/69
1-MeODB[a,j]A/1-MeODB[a,h]A	100/0
2-MeODB[a,j]A/2-MeODB[a,h]A	18/82
3-MeODB[a,j]A/3-MeODB[a,h]A	24/76
4-MeODB[a,j]A/4-MeODB[a,h]A	14/86

The diones **2b–d** and **3a–d** were reduced[8] to the methoxydibenz[a,h]anthracenes **4b–d** and methoxydibenz[a,j]anthracenes **5a–d** by using activated zinc, pyridine, and

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(6) High-temperature nematic liquid crystal GC phases have been shown to separate many positionally substituted isomers and structural isomers of polycyclic aromatic hydrocarbons. These separations tend to follow the length-to-breadth (L/B) ratios of the isomers. The larger the L/B ratio, the longer the retention times. The isomers **2a–d** and **3a–d** were easily resolved from each other by using these unique GC phases. See: Muschik, G. M.; Kelly, T.; Manning, W. B. *J. Chromatogr.* **1980**, *202*, 75–82 and references therein for the resolution of some of these and related isomers.

(7) **2b** had H_8 as a broad doublet at δ 9.2–9.3 and H_1 as a sharp doublet at δ 9.0–9.1. **2c** had H_8 and H_1 as a complex of doublets at δ 9.4–9.8. **2d** had H_8 as a broad dooublet at δ 9.5–9.6 and H_1 as a complex doublet at δ 9.1–9.2. **3a** had H_{13} as a broad doublet at δ 9.2–9.3. **3b** had H_{13} as a broad doublet at δ 9.3–9.4 and H_2 as a sharp doublet at δ 8.8–8.9. **3c** had H_{13} and H_1 as a complex multiplet at δ 9.1–9.5. **3d** had H_{13} as a complex doublet at δ 9.2–9.4 and H_1 as a broad doublet at 8.8–9.0. The other proton resonances were characteristically different for each isomer with the differences readily discernible. At present they are to complex to make unambiguous assignments for each specific proton.

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Scheme I

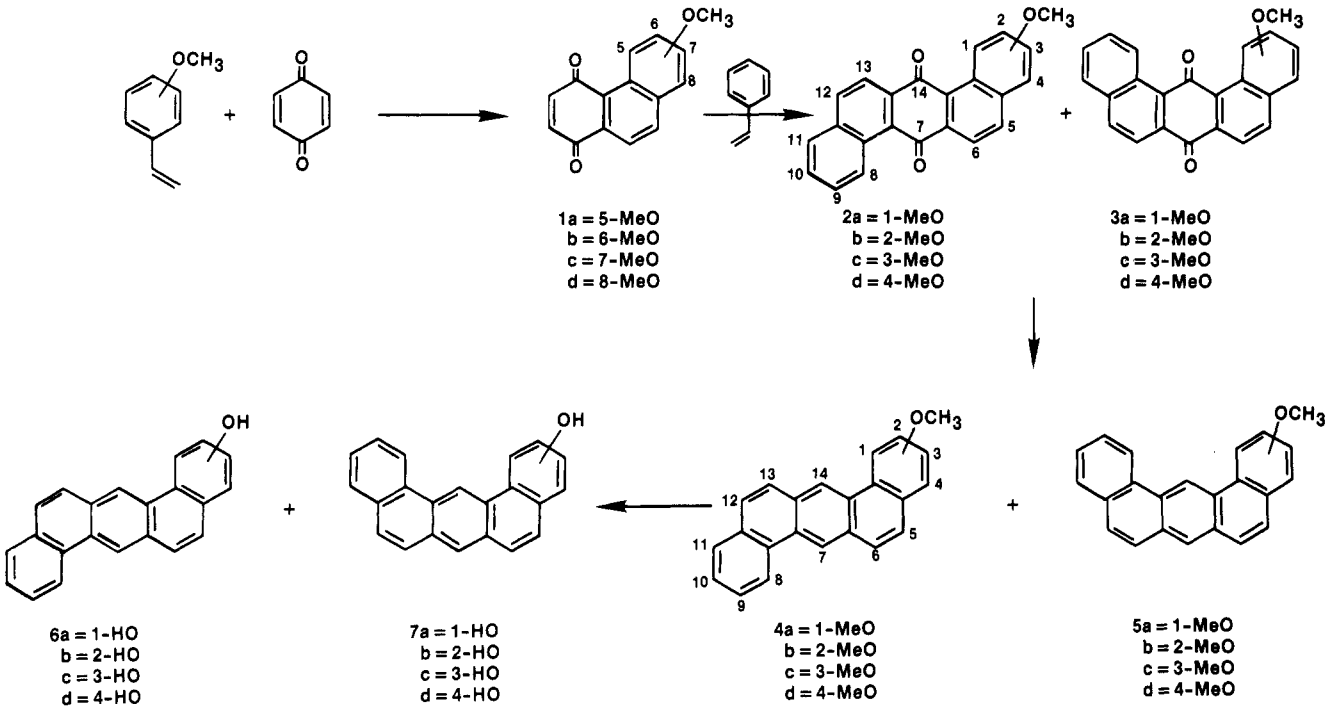

Table II. Selected ^{1}H NMR Chemical Shifts for Dibenzanthracenes

compd	shift, δ				
	H_7	H_{14}	H_1	H_8	H_{13}
unsubst [a,h]	9.2	9.2	8.8-9.0	8.8-9.0	
unsubst [a,j]	8.4	10.1	8.95-9.15		8.95-9.15
2-MeO[a,h]	9.0-9.2	9.0-9.2	8.75-8.95	8.75-8.95	
3-MeO[a,h]	9.05-9.2	9.05-9.2	8.75-8.95	8.75-8.95	
4-MeO[a,h]	9.25	9.25	9.25	8.85-9.0	
1-MeO[a,j]	9.15	10.25			8.8-8.95
2-MeO[a,j]	8.3	9.85	8.35-8.4		8.9-9.05
3-MeO[a,j]	8.35	9.95	8.85-9.0		8.85-9.05
4-MeO[a,j]	8.4	10.05	8.95-9.1		8.55-8.75

acetic acid in 38–65% yields. Interestingly, this method[8] and modifications[9] of it were quite successful in reducing other sterically crowded polycyclic aromatic hydrocarbon quinones. This was the best method for the reduction of **2b–d** and **3a–d**. The yield for the reduction of sterically crowded **3a** to **5a** was 60% by this method. Frequent TLC analyses with silica gel GF (Analtech) plates and benzene as the solvent were used to monitor the progress of these reductions. The ^{1}H NMR resonances for H_7, H_{14}, H_1, H_8, and H_{13} for the isomers of unsubstituted and methoxy-substituted dibenzanthracenes are given in Table II. These data lead to the structure assignment of 1-methoxydibenz[a,j]anthracene and therefore the structure of the 1-MeODBAD as **3a**. The melting point data for **5a** and **4a** were also different, 148–149 °C for 1-methoxydibenz[a,j]anthracene (**5a**) compared to 157–160 °C for 1-methoxydibenz[a,h]anthracene[3b] (**4a**). Compounds **4b–d** and **5a–d** were demethylated by using lithium methylmercaptide/dimethylformamide[10] at reflux followed by acidification. The yields obtained were greater than 70% for the formation of **6b–d** and **7a–d**. The proton NMR spectra of **2b–d** and **3a–d** were essential for establishing the position of substitution for the quinones; however, the spectrum of each phenolic isomer was characteristically different for each isomer but too complex to completely assign each aromatic proton.

Table III. Characteristic Infrared Bands from the Fingerprint Region of the Isomeric Phenol Spectra

compd	IR bands, cm^{-1} (1000-600 cm^{-1})
6b	875, 830
6c	888, 820, 810, 800, 740, 665
6d	888, 812, 800, 752
7a	900, 880, 815, 805, 745, 655
7b	907, 895, 883, 869, 845, 826, 805, 786, 743, 703
7c	957, 942, 884, 871, 855, 847, 812, 805, 788, 742, 705
7d	914, 888, 871, 850, 792, 738

The mass spectra of the phenols **6b–d** and **7a–d** showed characterisitic $M^{+\cdot}$, $M^{+\cdot} - 29$ (CHO) and $M^{+\cdot}/2$ for the double-charged ion. The double-charged ions for **6b–d** and **7a–d** were significantly larger than those observed for other PAHs having fewer rings.[8] The infrared bands in the fingerprint region (1000–600 cm^{-1}) of the isomeric hydroxyl derivatives (**6b–d** and **7a–d**) showed significant differences which were characteristic and readily discernible (Table III). Similarly, the ultraviolet absorption data for each of the phenols in 95% ethanol were characteristically different for each isomer (**6b–d** and **7a–b**) and were easily discernible (Table IV).

This work demonstrates the value of a single reaction that gave two products easily separable by column chro-

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Table IV. Ultraviolet Absorption Data of the Isomeric Phenol Spectra (95% Ethanol)

compd	λ_{max}, nm (log ϵ)
6b	275 (sh), 291 (4.83), 299 (4.85), 323 (4.19), 338 (4.06), 356 (4.03), 398 (3.06)
6c	216 (3.97), 222 (4.06), 232 (3.87), 278 (4.05), 290 (4.25), 302 (4.48), 322 (3.79), 338 (3.63), 351 (3.25), 376 (2.59), 397 (2.41)
6d	284 (4.66), 292 (4.89), 299 (sh), 329 (4.22), 337 (4.25), 352 (4.17), 381 (3.49), 401 (3.63)
7a	282 (4.86), 292 (5.13), 314 (4.42), 327 (4.56), 334 (4.45), 351 (4.36), 378 (3.71), 399 (4.63)
7b	229 (4.63), 249 (4.52), 254 (4.53), 260 (4.55), 280 (sh), 291 (4.72), 300 (4.74), 310 (4.78), 327 (sh), 343 (4.03), 358 (3.77)
7c	227 (4.35), 245 (4.16), 262 (4.18), 281 (4.30), 291 (4.55), 302 (4.80), 322 (4.10), 339 (3.98), 350 (3.52), 377 (2.87)
7d	236 (4.25), 253 (4.21), 285 (4.36), 295 (4.43), 305 (4.36), 324 (4.04), 339 (3.91), 354 (3.64)

matography. The reduction of the diones **2b–d** and **3a–d** to **4b–d** and **5a,b** followed by demethylation gave the required phenols **6b–d** and **7a–d**.

Experimental Section

All melting points were determined with a Fisher-Johns hot-stage apparatus and are uncorrected. Low-resolution mass spectra were taken on a Finnigan 3200 mass spectrometer equipped with a Finnigan 6000 data system. Exact mass measurements were obtained by using a VG Micromass ZAB 2F high-resolution mass spectrometer. The UV spectra were obtained by using a Cary 17 UV–vis spectrophotometer. Proton magnetic resonance spectra were taken by using a XL-100 or a NT-300 spectrometer with $DCCl_3$ (0.5% Me_4Si) as the solvent, while the IR spectra were obtained by using a Perkin-Elmer 467 or 180 spectrophotometer as KBr pellets. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. All new compounds gave elemental analyses within 0.4% of the theoretical value and/or exact masses within 5 ppm of the theoretical value.

General Procedure for Methoxydibenz[*a*,*h*]- and -[*a*,*j*]-anthracene-7,14-diones 2b–d and 3a–d. To 20 mL of toluene was added 4–10 mmol of methoxyphenanthrene-1,4-diones[4,5] **1a–d**, a 2 molar excess of styrene, chloranil, and aproximately 50 mg of trichloroacetic acid. The mixture was placed in an oil bath at 110 °C for 1–4 weeks. When little or no methoxyphenanthrene-1,4-dione remained, as observed by TLC on silica gel GF plates with benzene as the solvent, the reaction mixture was filtered rapidly through neutral alumina (Fisher) by using chloroform as the eluant. Removal of solvent gave a crude product to which was added 100 mL of hexane. The mixture was heated, cooled, and filtered to remove soluble polystyrene impurities. The insoluble material was sublimed to give a mixture of methoxydibenz[*a*,*h*]- and -[*a*,*j*]anthracene-7,14-diones (**2b–d** and **3c–d**). The isomeric methoxy diones were separated from each other by chromatography with Silicar CC-7 (250:1) and 10% hexane/benzene as the eluting solvent.

1-MeODB[a,j]AD (3a) was obtained in a 35% yield after chromatography (mp 180–183 °C) as the only product from the reaction of **1a** and styrene: MS, *m/z* (relative intensity) 338 (100), 321 (61), 310 (18), 309 (15), 267 (14), 252 (13), 251 (16), 250 (11), 239 (17), 237 (14), 219 (28), 169 (15), 131 (12), 126 (18), 125 (15), 119 (17), 118 (12); $M^{+\cdot}$ calcd for $C_{23}H_{14}O_3$ *m/z* 338.0833, found *m/z* 338.0887; NMR δ 9.45–9.60 (H_{13}, complex doublet, 1 proton), 7.05–8.40 (aromatic protons, complex multiplets, 10 protons), 4.05 (methyl, s, 3 protons).

2-MeODB[*a*,*h*]AD (2b) was obtained in 41% yield after chromatography: mp 199–201 °C (lit.[3c] mp 210–212 °C); MS, *m/z* (relative intensity) 338 (100), 321 (1), 310 (10), 309 (10), 281 (4), 267 (22), 252 (5), 250 (5), 239 (23), 237 (18); NMR δ 9.50–9.65 (H_8, complex d, 1 proton), 9.05–9.15 (H_1, d, 1 proton), 7.15–8.40 (aromatic protons, complex multiplets, 9 protons), 4.05 (methyl, s, 3 protons). Anal. Calcd for $C_{23}H_{14}O_3$: C, 81.64; H, 4.17; O, 14.19. Found: C, 81.42; H, 4.37.

2-MeODB[*a*,*j*]AD (3b) was obtained in 14% yield after chromatography: mp 182–183 °C; MS, *m/z* (relative intensity) 338 (100), 321 (71), 310 (9), 309 (14), 307 (22), 295 (8), 281 (5), 267 (23), 252 (6), 250 (8), 239 (42), 237 (28); NMR δ 9.30–9.50 (H_{13}, complex d, 1 proton), 8.85–8.95 (H_1, d, 1 proton), 7.20–8.40 (aromatic protons, complex m, 9 protons), 4.10 (methyl, s, 3 protons). Anal. Calcd for $C_{23}H_{14}O_3$: C, 81.64;, H, 4.17; O, 14.19. Found: C, 81.45; H, 4.28.

3-MeODB[*a*,*h*]AD (2c) was obtained in 40% yield after chromatography: mp 236–237 °C (lit.[3c] mp 244–245 °C); MS, *m/z* (relative intensity) 338 (100), 321 (>1), 310 (10), 295 (8), 267 (27), 252 (3), 250 (4), 239 (25), 237 (15), 169 (10); NMR δ 9.55–9.75 (H_8 and H_1, multiplets, 2 protons), 7.20–8.50 (aromatic protons, complex multiplets, 9 protons), 4.00 (methyl, s, 3 protons). Anal. Calcd for $C_{23}H_{14}O_3$: C, 81.64; H, 4.17; O, 14.19. Found: C, 81.49; H, 4.01.

3-MeODB[*a*,*j*]AD (3c) was obtained in 20% yield after chromatography: mp 190–192 °C; MS, *m/z* (relative intensity) 338 (100), 321 (>1), 310 (12), 309 (7), 281 (2), 267 (38), 252 (4), 250 (6), 239 (51), 237 (33); NMR δ 9.20–9.45 (H_{13} and H_1, multiplets, 2 protons), 7.15–8.40 (aromatic protons, multiplets, 9 protons), 4.00 (methyl, s, 3 protons). Anal. Calcd for $C_{23}H_{14}O_3$: C, 81.64; H, 4.17; O, 14.19. Found: C, 81.42; H, 4.33.

4-MeODB[*a*,*h*]AD (2d) was obtained in 40% yield after chromatography: mp 253–255 °C; *MS*, *m/z* (relative intensity) 338 (100), 321 (>1), 310 (5), 309 (2), 307 (8), 295 (8), 281 (1), 26 (40), 252 (4), 239 (31), 237 (22); NMR δ 9.65–9.75 (H_8, complex d, 1 proton), 9.20–9.35 (H_1, complex m, 1 proton), 6.95–8.90 (aromatic protons, complex multiplets, 9 protons), 4.10 (methyl, s, 3 protons). Anal. Calcd for $C_{23}H_{14}O_3$: C, 81.64; H, 4.17; O, 14.19. Found: C, 81.42; H, 4.15.

4-MeODB[*a*,*h*]AD (4d) was obtained in 13% yield after chromatography: mp 242–243 °C; MS, *m/z* (relative intensity) 338 (100), 323 (24), 295 (8), 267 (24), 252 (2), 250 (4), 239 (38), 238 (22); NMR δ 9.30–9.45 (H_8, m, 1 proton), 8.85–9.00 (H_1, complex d, 1 proton), 6.90–8.85 (aromatic protons, complex multiplets, 9 protons), 4.05 (methyl, s, 3 protons). Anal. Calcd for $C_{23}H_{16}O$: C, 81.64; H, 4.17; O, 14.19. Found: C, 81.44; H, 4.03.

General Procedure for the Reduction of 2b–d and 3a–d to Methoxydibenz[*a*,*h*]- and -[*a*,*j*]anthracenes 4b–d and 5a–d. To a refluxing solution of 0.1–0.3 mmol of methoxyquinone (**4b–d** or **5a–d**) in 3–8 mL of pyridine were added 2–4 g of activated zinc and 1 mL of glacial acetic acid. An additional 10–20 mL of 80% acetic acid was added to the refluxing mixture over a period of 5–8 h. The progress of the reaction was monitored by the disappearance of the quinone by using silica gel GF TLC plates, benzene as the eluting solvent, and long-wavelength UV light for visualization. The zinc was removed by filtration and the organic material acidified by the addition of 25–30 mL of 6 N HCl. The crude product was isolated by extraction with chloroform, back-extracted with water, and dried with anhydrous $MgSO_4$, and the solvent was removed under vacuum. Further purification was accomplished by column chromatography with Silicar CC-7 (Mallinckrodt, 80–200 mesh) eluted with a gradient of hexane to 50% hexane–benzene.

1-MeODB[*a*,*j*]A (5a) was obtained in 60% yield after chromatography: mp 148–149 °C; MS, *m/z* (relative intensity) 308 (100), 293 (13), 265 (35), 263 (11), 154 (7), 139 (8), 132 (12); $M^{+\cdot}$ calcd for $C_{23}H_{16}O_1$ *m/z* 308.1176, found *m/z* 308.1188; NMR δ 10.2 (H_{14}, br s, 1 proton), 9.1 (H_7 br s, 1 proton), 8.8–8.95 (H_8, complex d, 1 proton), 7.05–8.05 (aromatic protons, complex multiplets, 10 protons), 4.20 (methyl, s, 3 protons).

2-MeODB[*a*,*h*]A (4b) was obtained in 54% yield after chromatography: mp 215–216 °C (lit.[3c] mp 205–207 °C); MS, *m/z* (relative intensity) 308 (100), 293 (24), 365 (81), 363 (24), 154 (14); NMR δ 7.2–9.2 (aromatic protons, complet multiplets, 13 protons), 4.07 (methyl, s, 3 protons).

2-MeODB[*a*,*j*]A (5b) was obtained in 42% yield after chromatography: mp 169–171 °C; MS, *m/z* (relative intensity) 308 (70), 293 (13), 265 (100), 263 (36), 154 (34), 133 (42); NMR δ 9.85 (H_{14}, br s, 1 proton), 8.90–9.05 (H_7, complex d, 1 proton), 7.20–8.0

(aromatic protons, complex multiplets, 9 protons), 4.10 (methyl, s, 3 protons). Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23; O, 5.19. Found: C, 89.33; H, 5.31.

3-MeODB[*a*,*h*]A (4c) was obtained in 65% yield after chromatography: mp 240–241 °C; MS, *m/z* (relative intensity) 308 (72), 293 (4), 265 (100), 263 (29), 154 (50), 133 (79), 132 (77), 131 (53), 120 (22), 119 (29), 118 (22); NMR δ 9.05–9.1 (H_7 and H_{14}, 2 s, 2 protons), 8.75–9.95 (H_{13} and H_1, multiplets, 2 protons), 7.20–8.1 (aromatic protons, complex multiplets, 9 protons), 4.0 (methyl, s, 3 protons). Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23; O, 5.19. Found: C, 89.70; H, 5.20.

3-MeODB[*a*,*j*]A (5c) was obtained in 60% yield after chromatography: mp 169–170 °C; MS, *m/z* (relative intensity) 308 (72), 293 (4), 265 (100), 263 (29), 154 (50), 133 (79), 132 (77), 131 (53), 120 (22), 119 (29), 118 (22); NMR δ 9.95 (H_{14}, s, 1 proton), 8.85–9.05 (H_{13}, complex d, 1 proton), 8.85–8.95 (H_1, broadened d, 1 proton), 8.35 (H_7, s, 1 proton), 7.25–8.0 (aromatic protons, complex multiplets, 9 protons), 4.0 (methyl, s, 3 protons). Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23; O, 5.19. Found: C, 89.54; H, 5.20.

4-MeODB[*a*,*h*]A (4d) was obtained in 38% yield after chromatography: mp 218–219 °C (lit.[3c] mp 220–222 °C); MS, *m/z* (relative intensity) 308 (89), 293 (19), 265 (94), 263 (28), 154 (71), 139 (37), 133 (100), 132 (96), 131 (59), 119 (31); NMR δ 7.1–9.25 (aromatic protons, complex multiplets, 13 protons), 4.1 (methyl, s, 3 protons).

4-MeODB[*a*,*j*]A (5d) was obtained in 38% yield after chromatography: mp 183–185 °C; MS, *m/z* (relative intensity) 308 (82), 292 (14), 265 (100), 154 (43), 133 (19), 132 (32), 121 (20); NMR δ 10.00–10.05 (H_{14}, s, 1 proton), 8.95–9.10 (H_7, complex d, 1 proton), 9.55–8.75 (H_1, complex d, 1 proton), 8.55 (H_7, s, 1 proton), 7.0–8.4 (aromatic protons, complex multiplets, 9 protons), 4.10 (methyl, s, 3 protons). Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23; O, 5.19. Found: C, 89.40; H, 5.41.

General Procedure for the Demethylation[10] of 4b–d and 5a–d to 6b–d and 7a–d. To 6–10 mL of dried DMF (passed through basic alumina, activity 1) were added 1–5 mmol of methoxydibenz[*a*,*h*]- or [*a*,*j*]anthracene and a 2–5-fold excess of lithium methylmercaptide. This mixture was refluxed under nitrogen for 2–3 h. The progress of the reaction was followed by TLC on silica gel GF plates with benzene as the eluting solvent. When the reaction was complete (the starting material had disappeared), the mixture was cooled and 10 mL of 3 N HCl added over 15 min, while maintaining a nitrogen atmosphere. The crude reaction mixture was extracted with benzene–ether (1:1). The organic extracts were combined, extracted with water, and dried with anhydrous $MgSO_4$. Removal of solvent and purification by chromatography (Silicar CC-7, benzene solvent) gave the respective phenols.

1-HODB[*a*,*j*]A (7a) was obtained in 50% yield after chromatography: mp 233–236 °C dec; MS, *m/z* (relative intensity) 294 (100), 266 (8), 265 (28), 263 (10), 147 (17), 132 (11), 131 (8); M^+· calcd for $C_{22}H_{14}O$ *m/z* 294.1043, found *m/z* 294.1035. NMR δ 9.90 (H_{14}, s, 1 proton), 8.98 (d, 1 proton), 8.90 (d, 1 proton), 8.38 (H_7, s, 1 proton), 7.60–8.0 (aromatic protons, complex multiplets), 7.25–7.40 (aromatic protons, complex multiplets).

2-HODB[*a*,*j*]A (7b) was obtained in 87% yield after chromatography: mp 215–235 °C dec; MS, *m/z* (relative intensity) 294 (100), 265 (417), 263 (9), 147 (46), 133 (18), 132 (21), 120 (7), 119 (4); M^+· calcd for $C_{22}H_{14}O$ *m/z* 294.1043, found *m/z* 294.1039; NMR δ 9.90 (H_{14}, 1 proton), 9.0 (d, 1 proton), 8.38 (d, 1 proton), 8.34 (H_7, s, 1 proton), 7.60–7.95 (aromatic protons, complex multiplets), 7.15–7.23 (aromatic protons, multiplets). The acetate derivative gave a melting point of 184–186 °C.

2-HODB[*a*,*h*]A (6b) was obtained in 85% yield after chromatography: mp 239–245 °C dec; MS, *m/z* (relative intensity) 294 (100), 265 (41), 263 (21), 147 (42), 133 (28), 132 (32), 131 (16), 120 (13), 119 (14); M^+· calcd for $C_{22}H_{14}O$ *m/z* 294.1043, found *m/z* 294.1039; NMR δ 9.13 and 9.02 (H_7 and H_{14}, 2 s, 2 protons), 8.86 (d, 1 proton), 8.24 (aromatic protons, m), 7.60–8.0 (aromatic protons, complex multiplets), 7.35–7.20 (aromatic protons, multiplets). The acetatee derivative gave a melting point of 221–223 °C.

3-HODB[*a*,*j*]A (7c) was obtained in 92% yield after chromatography: mp 221–232 °C dec; MS, *m/z* (relative intensity) 294 (100), 265 (15), 267 (8), 147 (27), 133 (17), 132 (14), 120 (7), 119 (6); M^+· calcd for $C_{22}H_{14}O$ *m/z* 294.1043, found, *m/z* 294.1034; NMR δ 9.90 (H_{14}, s, 1 proton), 8.98 (d, 1 proton), 8.33 (H_7, s, 1 proton), 7.80–7.95 (aromatic protons, multiplets), 7.6–7.78 (aromatic protons, complex multiplets), 7.28–7.35 (aromatic protons, multiplets). The acetate derivative gave a melting point of 213–215 °C.

3-HODB[*a*,*h*]A (6c) was obtained in 94% yield after chromatography: mp 272–275 °C dec; MS, *m/z* (relative intensity) 294 (100), 265 (38), 263 (22), 147 (18), 133 (9), 132 (9), 131 (9), 120 (4), 119 (5); M^+· calcd for $C_{22}H_{14}O$ *m/z* 294.1043, found, *m/z* 294.1034; NMR δ 9.15 and 9.05 (H_7 and H_{14}, 2 s, 2 protons), 8.95–8.75 (aromatic protons, complex multiplets), 8.05–7.50 (aromatic protons, complex multiplets), 7.35–7.20 (aromatic protons, multiplets). The acetate derivative gave melting point of 245–247 °C.

4-HODB[*a*,*j*]A (7d) was obtained in 74% yield after chromatography: mp 220–232 °C dec; MS, *m/z* (relative intensity) 294 (100), 265 (31), 263 (11), 147 (26), 133 (16), 132 (15), 120 (5), 119 (4); M^+· calcd for $C_{22}H_{14}O$ *m/z* 294.1043, found *m/z* 294.1049; NMR δ 10.0 (H_{14}, s, 1 proton), 8.97 (d, 1 proton), 8.58 (d, 1 proton), 8.35 (H_7, s, 1 proton), 8.13 (d, 1 proton), 7.53–7.99 (aromatic protons, complex multiplets), 7.00 (d, 1 proton). The acetate derivative gave a melting point of 190–192 °C.

4-HODB[*a*,*h*]A (6d) was obtained in 80% yield after chromatography: mp 245–252 °C dec; MS, *m/z* (relative intensity) 294 (100), 265 (74), 273 (25), 147 (36), 133 (24), 132 (33), 131 (20), 120 (9), 119 (11), 118 (9); M^+· calcd for $C_{22}H_{14}O$ *m/z* 294.1043, found *m/z* 294.1049; NMR δ 9.07 and 9.12 (H_7 and H_{14}, 2 s, 2 protons), 8.78 (d, 1 proton), 8.42 (d, 1 proton), 8.11 (d, 1 proton), 7.85–8.00 (aromatic protons, multiplets), 7.40–7.75 (aromatic protons, complex multiplets), 6.84–6.98 (aromatic protons, multiplets). The acetate derivative gave a melting point of 279–281 °C.

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Registry No. 1a, 73453-72-2; **1b**, 63216-06-8; **1c**, 63216-07-9; **1d**, 63216-08-0; **2b**, 76214-32-9; **2c**, 76214-33-0; **2d**, 76214-34-1; **3a**, 76214-35-2; **3b**, 76214-36-3; **3c**, 76214-37-4; **3d**, 76214-38-5; **4b**, 83136-23-6; **4c**, 83136-24-7; **4d**, 83136-25-8; **5a**, 83136-26-9; **5b**, 83136-27-0; **5c**, 83136-28-1; **5d**, 83136-29-2; **6b**, 72007-85-3; **6c**, 1421-80-3; **6d**, 1421-81-4; **7a**, 83136-30-5; **7b**, 83136-31-6; **7c**, 83136-32-7; **7d**, 83136-33-8; styrene, 100-42-5.