m/z 250.157 (M^+, calcd for $C_{15}H_{22}O_3$ 250.157). **45**: 150 mg (30%); identical with material obtained from **44** with stannic chloride.

Irradiation of 47 in Methanol–Sodium Methoxide. To a solution of sodium methoxide, prepared from sodium hydride (50 mg of 50% mineral oil dispersion, 1 mmol) and dry methanol (180 mL) was added **47** (283 mg, 1.1 mmol) and the mixture was irradiated for 4 h with a Hanovia 450-W mercury lamp through a Pyrex filter. The mixture was worked up as for irradiation of **46** to give 263 mg of a semicrystalline material. This was a mixture of **45** and **65** as determined by TLC and NMR spectroscopy in a ratio of 1:1. During the same time period, a similar solution of **47** in methanolic sodium methoxide which was kept in the dark underwent no significant changes.

Acknowledgment. We are indebted to Todd C. Somers for experimental assistance. This work was supported by the National Science Foundation (CHE-8101223) and by the M.J. Murdock Charitable Trust, Vancouver, WA. R.W.S. is grateful to the Nicholas L. Tartar Fund for a summer fellowship.

Registry No. **8**, 53067-23-5; **9**, 110-93-0; **10**, 71135-95-0; **11**, 95998-91-7; **13**, 95998-92-8; **16**, 6138-90-5; **17**, 56523-17-2; **18**, 65794-68-5; **19**, 59633-88-4; **20**, 59633-89-5; **21**, 59633-91-9; **22**, 59633-92-0; **24**, 63598-65-2; **25** (isomer 1), 96148-62-8; **25** (isomer 2), 96092-87-4; **27**, 57345-08-1; **29**, 14506-63-9; **31**, 95998-93-9; **35**, 96020-99-4; **36**, 95998-94-0; **37**, 95998-95-1; **39**, 95998-96-2; **40**, 95998-98-4; **41**, 95998-99-5; **42**, 95998-97-3; **44**, 68380-12-1; **45**, 95999-05-6; **46**, 68380-14-3; **47**, 68380-16-5; **48**, 95999-00-1; **49**, 14901-07-6; **51**, 68380-13-2; **52** (isomer 1), 95999-01-2; **52** (isomer 2), 68380-17-6; **53**, 68380-20-1; **54**, 68380-21-2; **55** (isomer 1), 68380-19-8; **55** (isomer 2), 68380-18-7; **56**, 68380-15-4; **58**, 95999-02-3; **59**, 95999-04-5; **61**, 95999-03-4; **65**, 95999-06-7; $SnCl_4$, 7646-78-8; isoprene, 78-79-5; β-cyclocitral, 432-25-7; chlorotrimethylsilane, 75-77-4; dimethyl carbonate, 616-38-6; methyl acetylacetate, 105-45-3; trimethylsulfonium iodide, 2181-42-2; diethyl malonate, 105-53-3.

Supplementary Material Available: Elemental analyses data (1 page). Ordering information is given on any current masthead page.

Synthesis of Methylated Benzo[*b*]fluoranthenes and Benzo[*k*]fluoranthenes[1,2]

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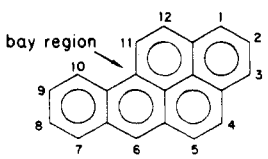
A series of monomethyl and dimethyl derivatives of benzo[*b*]fluoranthene (BbF) and benzo[*k*]fluoranthene (BkF) were synthesized in order to investigate the environmental occurrence and structural requirements for carcinogenicity of methylated nonalternant polycyclic aromatic hydrocarbons. 9-Methyl-BbF (**5**), 12-methyl-BbF (**6**), and 1-methyl-BbF (**7**) were prepared from the appropriate oxotetrahydro-BbF's (**17–19**). 8-Methyl-BbF (**8**) was synthesized from 1-methyl-3-oxo-1,2,3,10b-tetrahydrofluoranthene (**20**) in 11 steps. 3-Methyl-BbF (**9**) and 1,3-dimethyl-BbF (**10**) were prepared from 3-methyl-1-oxo-1,2,3,3a-tetrahydrobenzo[*b*]fluoranthene (**31**), which was synthesized from methyl 11*H*-benzo[*b*]fluorene-11-carboxylate (**28**). 7-Methyl-BbF (**11**) was obtained by condensation of 1-methylfluorene (**33**) with *o*-bromobenzaldehyde, followed by treatment with KOH and quinoline. 5,6-Dimethyl-BbF (**12**) was synthesized by reaction of 2,3-dimethylbutadiene with acephenanthrylene (**38**) followed by aromatization. 8-Methyl-BkF (**13**) was synthesized from 8-oxo-8,9,10,11-tetrahydro-BkF. 9-Methyl-BkF (**14**) was prepared by Friedel–Crafts reaction of 2-methylsuccinic anhydride with fluoranthene, followed by Wolff–Kishner reduction, cyclization, $LiAlH_4$ reduction, dehydration, and aromatization. 2-Methyl-BkF (**16**) was synthesized by an analogous sequence, beginning with 2-methylfluoranthene and succinic anhydride. 7,12-Dimethyl-BkF (**15**) was prepared by a two-step reduction of 7,12-dicyano-BkF (**51**).

Methyl substitution influences the carcinogenicity and tumor initiating activity of polycyclic aromatic hydrocarbons (PAH). For example, 6-, 7-, 8-, 9-, and 10-methylbenzo[*a*]pyrene, as well as 7,10-dimethylbenzo[*a*]pyrene, are less active as tumor initiators on mouse skin than is benzo[*a*]pyrene (**1**) whereas 11-methylbenzo[*a*]pyrene is a stronger tumor initiator than is **1**.[3,4] Chrysene (**2**) is a weak tumor initiator, but 5-methylchrysene is a powerful tumor initiator and carcinogen.[5,6] The other monomethylchrysenes are only weakly active or inactive.[5] Many other examples are available[7] and, among the alternant PAH, the structural requirements favoring tumorigenicity are the presence of a bay region methyl group and a free peri position, both adjacent to an unsubstituted angular ring.[8]



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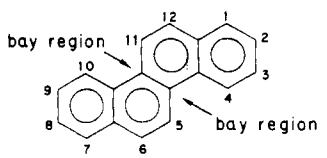

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It is not known, however, whether similar effects on carcinogenicity would occur upon methyl substitution of nonalternant PAH such as benzo[*b*]fluoranthene (BbF, **3**)

(1) Paper No. 75 in the series "A Study of Chemical Carcinogenesis".
(2) Supported by NCI Grant CA-32242 and Contract CP-15747.
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(4) Hecht, S. S.; Hirota, N.; Hoffmann, D. *Cancer Lett.* **1978**, *5*, 179.
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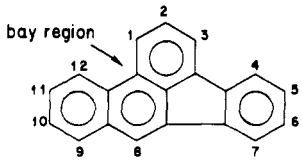
0022-3263/85/1950-1948$01.50/0

and benzo[k]fluoranthene (BkF, 4). Only one methylated compound in this series, 8-methyl-BkF, has been previously described.[9] The carcinogenic and mutagenic properties of the methylated benzofluoranthenes could provide important leads about the pathways of metabolic activation of the parent hydrocarbons. This is of considerable interest because 3 and 4 are among the most commonly detected PAH in the environment and their carcinogenic or tumor initiating activities are well established.[10-16] In addition, the availability of the methylated compounds would facilitate analytical studies on their possible presence in tobacco smoke or other pollutants. Therefore, we synthesized a series of monomethyl and dimethyl derivatives of 3 and 4, having substitution patterns which might



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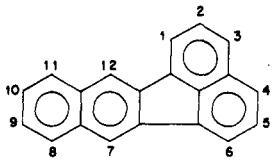

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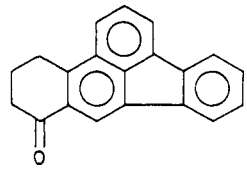
be expected to influence their tumorigenic activities. The compounds prepared were 9-methyl-BbF (5), 12-methyl-BbF (6), 1-methyl-BbF (7), 8-methyl-BbF (8), 3-methyl-BbF (9), 1,3-dimethyl-BbF (10), 7-methyl-BbF (11), 5,6-dimethyl-BbF (12), 8-methyl-BkF (13), 9-methyl-BkF (14), 7,12-dimethyl-BkF (15), and 2-methyl-BkF (16).

Results and Discussion

The syntheses of 9-methyl-BbF (5), 12-methyl-BbF (6), and 1-methyl-BbF (7) were accomplished easily by treatment of the known ketones[17,18] 17–19 with methyllithium,



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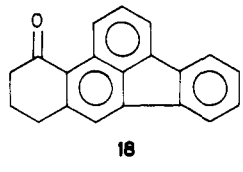

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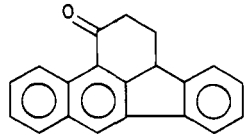

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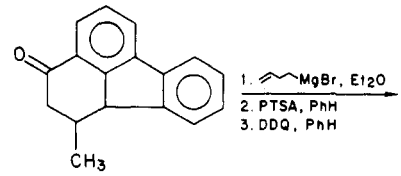
followed by dehydration and aromatization. The synthesis of 8-methyl-BbF (8) is illustrated in Scheme I. The

Scheme I. Synthesis of 8-Methylbenzo[b]fluoranthene (8)



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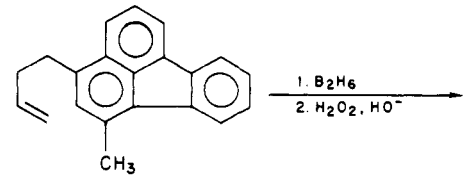

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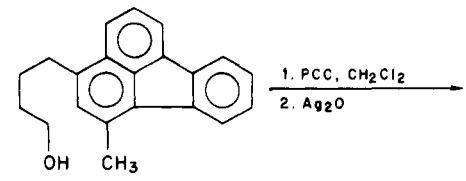

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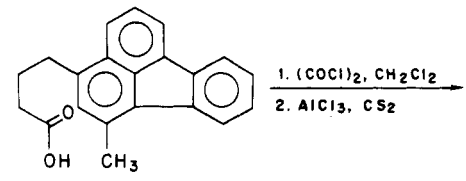

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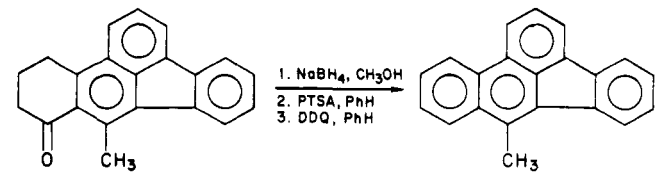

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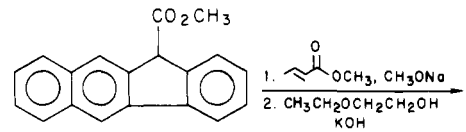
Scheme II. Synthesis of 3-Methylbenzo[b]fluoranthene



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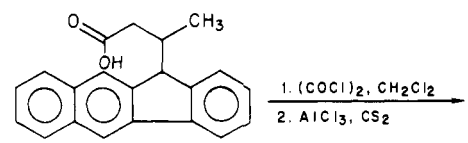

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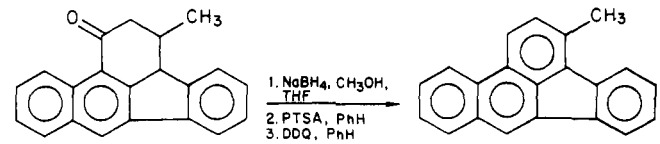

31 9

starting material, 20, was prepared from fluorene as previously reported.[19] The new ring was constructed by reaction of 1-buten-4-ylmagnesium bromide with 20, followed by dehydration of the resulting alcohol 21 and aromatization to give 22. Hydroboration gave 23, which

(9) Buu-Hoi, N. P.; Lavit, D. *J. Chem. Soc.* **1960**, 536.
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(17) Amin, S.; Bedenko, V.; LaVoie, E.; Hecht, S. S.; Hoffmann, D. *J. Org. Chem.* **1981**, *46*, 2573.
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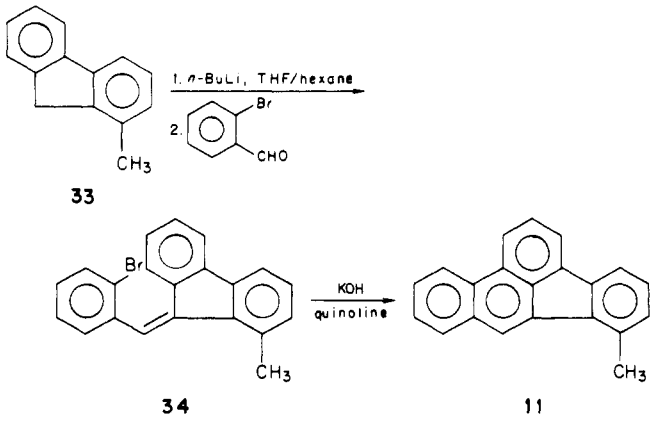
(19) Tucker, S. H. *J. Chem. Soc.* **1949**, 2182.

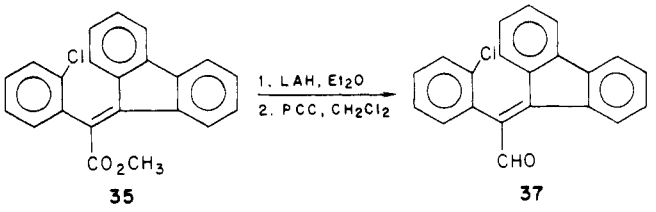
Scheme III. Synthesis of 7-Methylbenzo[b]fluoranthene



was oxidized via the aldehyde **24** to the acid **25**. Cyclization of the acid chloride of **25** yielded the ketone **26** which was readily converted to **8**.

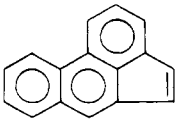
Scheme II illustrates the synthesis of 3-methyl-BbF (**9**). Methyl 11*H*-benzo[*b*]fluorene-11-carboxylate (**28**)[18] was converted to its anion and allowed to react with methyl crotonate. Hydrolysis and decarboxylation of the Michael addition product yielded the acid **30** which was converted to its acid chloride and allowed to cyclize under Friedel–Crafts conditions. The appropriate ketone **31** was formed exclusively. Cyclization to give the corresponding BkF derivative was not observed, as demonstrated by the NMR of **31** in which a downfield shift of proton 12 was seen and by the UV spectrum of **9** which was characteristic of a BbF but not a BkF. We had previously observed the analogous selective cyclization in our synthesis of **19**.[18] Conversion of **31** to **9** proceeded smoothly. The ketone **31** was also converted to 1,3-dimethyl-BbF (**10**) by treatment with methyllithium followed by dehydration and aromatization.

The synthesis of 7-methyl-BbF (**11**) is summarized in Scheme III. 1-Methylfluorene (**33**) was condensed with *o*-bromobenzaldehyde to give **34** in only 10% yield. Treatment of **34** with KOH and quinoline afforded **11**. This approach also appeared to have promise as a simple alternative synthesis of 8-methyl-BbF (**8**). Since condensation of fluorene with *o*-chloroacetophenone was unsuccessful, we prepared **35** by reaction of *o*-chlorophenylacetic acid with fluorenone, followed by esterification. Reduction



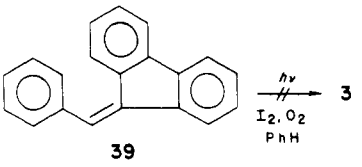
with LAH followed by oxidation with PCC gave **37**. Treatment of **37** with NH_2NH_2, KOH, and quinoline did not yield **8** as we had expected but instead gave a low yield of BbF.

To provide an additional compound for structure activity studies in the monomethyl-BbF series, we had intended to prepare 4-methyl-BbF. We reasoned that reaction of 1,3-pentadiene with acephenanthrylene (**38**)

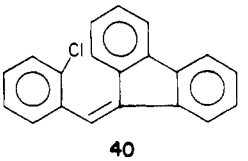


followed by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) would yield a mixture of 4-methyl-BbF and 7-methyl-BbF (**11**). Since a standard of **11** was available, the two products could be distinguished. The reaction did proceed to give what we presume to be a mixture of **11** and 4-methyl-BbF. However, we were not able to effect a separation by HPLC, TLC, column chromatography, or capillary GC. Therefore, we decided to synthesize 5,6-dimethyl-BbF (**12**) since the two methyl groups would be expected to inhibit enzymatic oxidation in the 4–7 ring. This compound was readily obtained by Diels–Alder reaction of **38** with 2,3-dimethylbutadiene followed by aromatization with DDQ.

In the course of our work on methylated BbFs we considered the application of photochemical methods which have been used successfully for preparation of substituted phenanthrenes and chrysenes.[20] However, photolysis of **39** under conditions which we have previously used in the



syntheses of chrysenes,[21] did not yield BbF (**3**), even after 80 h. Only starting material and small amounts of fluorenone were recovered. We thought that the chlorinated alkene **40** might be a better photolytic precursor to **3**, but



this was also unsuccessful, as was photolysis of **35**. Thus we conclude that the photochemical approach is not a useful method for preparation of BbFs.

8-Methyl-BkF (**13**) was prepared from 8-oxo-8,9,10,11-tetrahydro-BkF[22] by reaction with methyllithium, dehydration, and aromatization. The syntheses of 9-methyl-BkF (**14**) and 2-methyl-BkF (**16**) are shown in Scheme IV. Succinoylation of fluoranthene (**41**) is known to proceed at the 8-position.[22] The same selectivity was observed upon reaction of 2-methylsuccinic anhydride with fluoranthene to give **42**. The isomer of **42** resulting from attack at the other anhydride carbonyl was presumably also formed. Conversion of **42** to **14** proceeded smoothly by well-established methods. Succinoylation of 2-methylfluoranthene (**46**) proceeded in good yield to give a presumed mixture of isomers, resulting from reaction at the 8-position (**47**) or 9-position. This material was carried through the same series of steps employed for **14** to yield **16** in good overall yield. 7,12-Dimethyl-BkF (**15**) was prepared in two steps from 7,12-dicyano-BkF (**51**)[23] by reduction with *i*-Bu_2AlH to give the dialdehyde **52**, followed by Wolff–Kishner reduction to **15**.

The purities of all the methylated BbFs and BkFs were established by elemental analysis, and by HPLC, and capillary GC analysis. The capillary GC retention times, which should be useful for studies on their environmental occurrence, are summarized in Table I. The UV spectral data for the methylated BbFs and BkFs are summarized in Table II. In each case, the spectrum qualitatively

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(23) Vickery, E. H.; Eisenbraun, E. J. *Org. Prep. Proced. Int.* **1979**, *11*, 259.

Table I. Capillary GC Retention Times of Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), and Their Methylated Derivatives[a]

compound	t_R, min
BbF (3)	34.09
1-Me-BbF (7)	40.39
3-Me-BbF (9)	40.37
7-Me-BbF (11)	39.11
8-Me-BbF (8)	42.31
9-Me-BbF (5)	39.09
12-Me-BbF (6)	40.50
1,3-dimethyl-BbF (10)	48.29
5,6-dimethyl-B(b)F (12)	47.81
BkF (4)	34.39
2-Me-BkF (16)	39.19
8-Me-BkF (13)	39.14
9-Me-BkF (14)	39.51
7,12-dimethyl-BkF (15)	51.89

[a] A 25-m Carbowax 20M fused silica column was programmed from 180–250 °C at 2°/min.

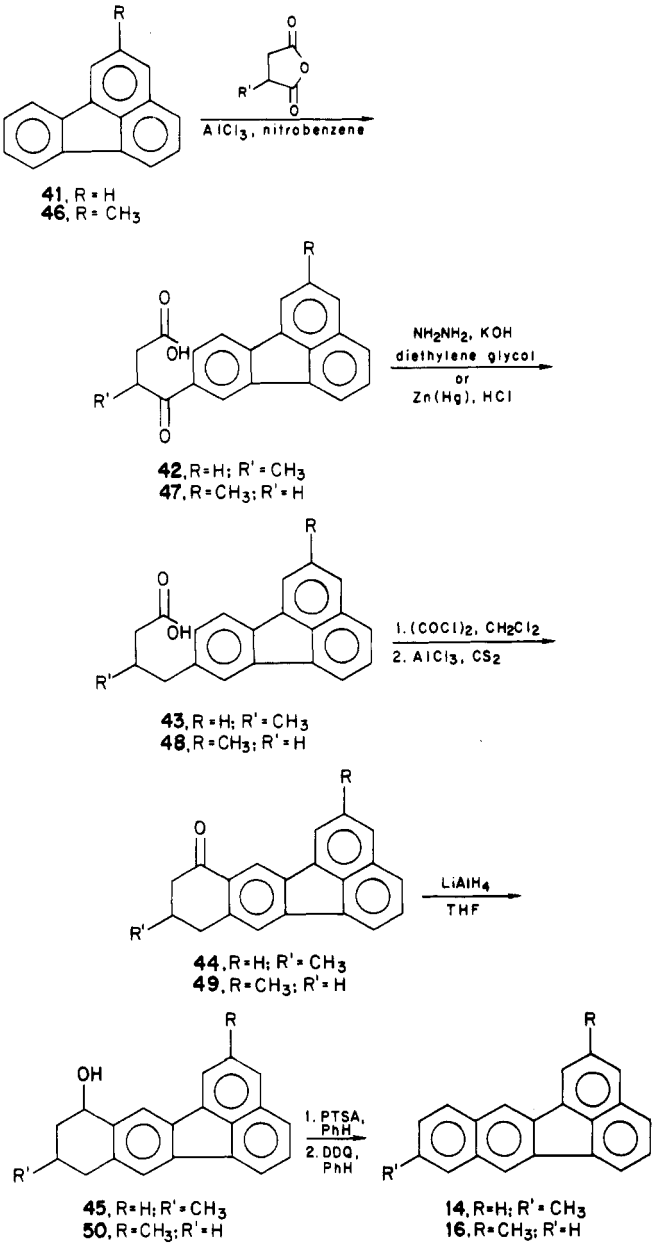
resembled that of the parent hydrocarbon, but marked differences in the intensities of the various bands were observed. The NMR and MS of the methylated benzofluoranthenes were typical of methylated PAH and showed no unusual features attributable to the five-membered ring.

The methylated benzofluoranthenes were evaluated for mutagenicity toward *S. typhimurium* TA 100 and tumor initiating activity on mouse skin. The details of these assays will be described separately. 3-Methyl-BbF and 1,3-dimethyl-BbF were strongly mutagenic and tumorigenic, with activities greater than those of BbF. The other methyl- and dimethyl-BbFs were less active than was BbF. 2-Methyl-BkF had mutagenic activity comparable to that of BkF, and 7,12-dimethyl-BkF was slightly less mutagenic than was BkF. Both 8-Me-BkF and 9-Me-BkF were inactive. However, on mouse skin 2-Me-BkF, 9-Me-BkF, 7,12-dimethyl-BkF, and BkF had comparable activity while 8-Me-BkF was slightly less active than was BkF.

Experimental Section

Infrared spectra were run on a Perkin-Elmer Model 267 grating infrared spectrophotometer. NMR spectra were determined with a JEOL Model FX90Q spectrometer with $CDCl_3$ as solvent and are reported as parts per million downfield from Me_4Si as an internal reference. UV spectra were determined in CH_3OH with a Cary Model 118 instrument. HPLC was carried out with a Waters Associates Model ALC/GPC-204 high speed liquid chromatograph equipped with a Model 660 solvent programmer, a Model LC-25 UV/vis detector and a 4.6 mm (i.d.) × 250 mm Vydac 201 TP104 10 μm column with an elution program from 80% CH_3OH in H_2O to 100% CH_3OH in 1 h at 1 mL/min. Capillary GC was carried out with a Hewlett Packard Model 5710A gas chromatograph equipped with a Model 18740B capillary control unit, a Model 3380A calculating integrator, a 25-m Carbowax 20M fused silica column, and a flame ionization detector. The oven temperature was programmed from 180–250 °C at 2 °C/min. Helium was used as carrier gas with a flow rate of 1 mL/min. MS were run with a Hewlett-Packard Model 5982A dual source instrument using a membrane separator. Microanalyses were performed by Galbraith Laboratories.

Scheme IV. Syntheses of 9-Methylbenzo[k]fluoranthene and 2-Methylbenzo[k]fluoranthene



1-Methyl-BbF (7). To a stirred solution of 19[18] (0.57 g, 0.002 mol) in 50 mL of Et_2O at 0 °C under N_2 was added 3.6 mL (0.005 mol) of 1.4 M methyllithium in Et_2O. The reaction mixture was stirred for 2 h at room temperature, poured into H_2O, and extracted with ether. The combined ether extracts were dried ($MgSO_4$) and concentrated to afford 0.4 g of 1-hydroxy-1-methyl-1,2,3,3a-tetrahydro-BbF which was used without further

Table II. UV Spectra of Methylated Benzo[b]fluoranthenes (BbF) and Benzo[k]fluoranthenes (BkF) [λ_{max} (ϵ)]

1-Me-BbF (7)	222 (71 900), 261 (69 000), 276 (42 500), 293 (39 200), 304 (50 900), 337 (16 000), 350 (17 300), 364 (9510)
3-Me-BbF (9)	224 (48 100), 257 (51 300), 279 (33 400), 290 (32 600), 301 (33 800), 341 (14 700), 354 (14 700), 372 (7780)
7-Me-BbF (11)	225 (44 400), 258 (52 200), 278 (26 400), 292 (25 000), 300 (40 700), 335 (8960), 349 (12 500), 367 (10 100)
8-Me-BbF (8)	228 (52 800), 256 (65 900), 278 (36 200), 296 (37 900), 303 (40 000), 338 (13 300), 352 (14 400), 372 (9550)
9-Me-BbF (5)	228 (55 400), 259 (77 800), 277 (50 900), 296 (55 700), 305 (46 800), 343 (23 000), 356 (24 600), 376 (17 700)
12-Me-BbF (6)	229 (56 400), 263 (106 000), 274 (64 800), 295 (58 500), 302 (51 500), 342 (25 500), 354 (25 900), 374 (15 600)
1,3-dimethyl-BbF (10)	229 (39 400), 259 (29 200), 279 (20 000), 293 (27 800), 303 (35 900), 338 (8640), 355 (10 700), 374 (8670)
5,6-dimethyl-BbF (12)	224 (25 600), 261 (36 100), 279 (16 900), 295 (18 900), 306 (31 500), 334 (4470), 350 (6080), 368 (4700)
2-Me-BkF (16)	273 (57 700), 298 (111 000), 318 (129 000), 360 (16 900), 380 (29 200)
8-Me-BkF (13)	268 (14 100), 298 (30 000), 308 (42 700), 363 (4090), 382 (7730)
9-Me-BkF (14)	271 (20 000), 289 (21 200), 302 (40 800), 314 (61 200), 367 (5770), 386 (10 800)
7,12-dimethyl-BkF (15)	268 (54 400), 297 (66 700), 306 (71 100), 370 (11 100), 390 (18 900)

purification: mp 86–88 °C; NMR δ 1.7 (s, 3 H), 1.8–2.1 (m, 2 H), 2.35–2.5 (m, 2 H), 2.55 (s, 1 H), 4.0 (dd, 1 H), 7.2–8.1 (m, 8 H), 8.8–8.9 (m, 1 H); MS, *m/e* (relative intensity) 286 (M^+, 34.1), 268 (67.4).

A solution of the above alcohol (0.3 g, 0.001 mol) and PTSA (5 mg) in benzene was heated at reflux for 30 min using a Dean–Stark apparatus. The organic solution was washed with 10% aqueous $NaHCO_3$ and H_2O, dried, and concentrated to afford a dihydro compound which was sufficiently pure to be used in the subsequent step.

A solution of the above dihydro compound and DDQ (0.23 g, 0.001 mol) in benzene (50 mL) was heated at reflux for 1 h. Conventional workup followed by chromatography on silica gel eluted with hexane/CH_2Cl_2 (90/10) afforded **7** as a white solid: mp 145–146 °C (0.15 g, 58%); NMR δ 3.2 (s, 3 H), 7.2–8.3 (m, 10 H), 8.8–8.9 (m, 1 H); MS, *m/e* (relative intensity) 266 (M^+, 100). Anal. Calcd for $C_{21}H_{14}$: C, 94.73; H, 5.26. Found: C, 94.68; H, 5.33.

9-Methyl-BbF (5). The ketone **17**[17] (0.54 g, 0.002 mol) was converted to **5** as described above for **7**. The crude product was purified by chromatography on silica gel with elution by hexane/CH_2Cl_2 (90/10) to give **5** (0.35 g, 65%): mp 151–152 °C; NMR δ 2.9 (s, 3 H), 7.25–8.1 (m, 9 H), 8.4–8.65 (m, 2 H); MS, *m/e* (relative intensity) 266 (M^+, 100). Anal. Calcd for $C_{21}H_{14}$: C, 94.73; H, 5.26. Found: C, 94.55; H, 5.32.

12-Methyl-BbF (6) was prepared from **18**[18] (0.54 g, 0.002 mol) by the same method as described for **7**. Crude **6** was purified on silica gel by elution with hexane/CH_2Cl_2 (90/10) to give a solid, 0.3 g (56%): mp 134–136 °C; NMR δ 3.15 (s, 3 H), 7.3–8.26 (m, 10 H), 8.65–8.8 (d, 1 H); MS, *m/e* (relative intensity) 266 (M^+, 100). Anal. Calcd for $C_{21}H_{14}$: C, 94.73; H, 5.26. Found: C, 94.51; H, 5.33.

3-Hydroxy-3-(1-butenyl)-1-methyl-1,2,3,10b-tetrahydrofluoranthene (21). A Grignard reagent prepared from 4-bromo-1-butene (4.1 g, 0.03 mol), and Mg (1.2 g, 0.05 mol) in ether (50 mL) was added dropwise to a solution of **20**[19] (4.7 g, 0.02 mol) in 150 mL of THF. After 1 h of stirring at room temperature, the mixture was worked up as usual to yield 3.2 g of **21**, which was used directly in the next step: NMR δ 1.4–1.8 (m, 8 H), 1.9–2.6 (m, 3 H), 3.1–3.3 (m, 1 H), 5.0–5.4 (m, 2 H), 6.0–6.4 (m, 1 H), 7.1–7.8 (m, 7 H); MS, *m/e* (relative intensity) 290 (M^+, 10) 272 (100).

1-Methyl-3-(1-butenyl)fluoranthene (22). A solution of **21** (2.9 g, 0.01 mol) and PTSA (5 mg) in benzene was heated at reflux for 10 min using a Dean–Stark apparatus. Conventional workup followed by chromatography on silica gel eluted with hexane afforded a dihydro compound which was used directly in the next step: MS, *m/e* (relative intensity) 272 (M^+, 33.8), 257 (35), 231 (30), 229 (52.6), 215 (100).

A solution of the above dihydro compound and DDQ (2.3 g, 0.01 mol) in benzene was heated at reflux for 1 h. The reaction mixture was worked up in the usual manner. The crude product was chromatographed on 20 g of silica gel with elution by CH_2Cl_2/hexane (10/90) to afford **22** as a solid: mp 52–53 °C (1.8 g, 66%); NMR δ 2.2–2.6 (*m* + *s*, 5 H), 2.7–3.1 (m, 2 H), 4.6–5.2 (m, 2 H), 5.45–5.9 (m, 1 H), 6.8 (s, 1 H), 7.0–7.8 (m, 7 H); MS, *m/e* (relative intensity) 270 (M^+, 20), 229 (100), 216 (78.9), 215 (87.5).

1-Methyl-3-(4-hydroxybutyl)fluoranthene (23). To a solution of **22** (1.5 g, 0.0055 mol) in 250 mL of dry THF was added 15.0 mL of a 1 M solution of diborane in THF, over a 20-min period. The reaction mixture was stirred at room temperature for 12 h, cooled to 0 °C, and treated with 2 mL of H_2O dropwise. Aqueous NaOH (10 mL, 20%) was then added over 10 min followed by dropwise addition of 20 mL of 30% H_2O_2. The resulting solution was stirred for 2 h, refluxed for 3 h, and then worked up in the usual manner to give 1.4 g of crude product. Chromatography on silica gel with elution by CH_2Cl_2 yielded 1.1 g (70%) of **23** as an oil: NMR δ 1.3–1.8 (m, 4 H), 2.5 (s, 3 H), 2.6–2.9 (m, 2 H), 3.1–3.5 (m, 2 H), 6.85 (s, 1 H), 7.0–7.8 (m, 7 H); MS, *m/e* (relative intensity) 288 (M^+, 47.8), 229 (100).

1-Methyl-3-(4-oxobutyl)fluoranthene (24). Alcohol **23** (1.0 g, 0.0035 mol) was dissolved in 150 mL of dry CH_2Cl_2 and added dropwise to a suspension of pyridinium chlorochromate (PCC, 1.5 g, 0.007 mol) in dry CH_2Cl_2 (100 mL). The mixture was stirred for 3 h at room temperature and then filtered through Celite. The Celite was washed with CH_2Cl_2 (2 × 50 mL) and the combined filtrates were washed with 3 N HCl (2 × 100 mL), H_2O (2 × 100 mL), and dried ($MgSO_4$). The solvent was removed to give aldehyde **24** (0.7 g, 70%) as a solid, mp 98–101 °C, which was used without further purification: NMR δ 1.7–2.1 (m, 2 H), 2.1–2.4 (m, 2 H), 2.65 (s, 3 H), 2.75–3.1 (m, 2 H), 6.95 (s, 1 H), 7.0–7.8 (m, 7 H), 9.5 (bs, 1 H); MS, *m/e* (relative intensity), 286 (M^+, 38.1), 242 (66.9), 229 (100).

1-Methyl-3-(3-carboxypropyl)fluoranthene (25). To a solution of **24** (0.6 g, 0.002 mol) in 30 mL of THF/H_2O (3/1) was added 0.5 g of $AgNO_3$ in 10 mL of H_2O. The mixture was stirred at room temperature and 50 mL of 10% aqueous NaOH was added dropwise. The resulting mixture was stirred for 2 h, filtered, and washed several times with H_2O. The mixture was extracted with Et_2O and the aqueous phase was cooled and acidified with HCl. Extraction with CH_2Cl_2 followed by standard workup gave 0.4 g of **25** (66%) as a yellow solid: mp 166–167 °C; NMR δ 2.1–2.3 (m, 2 H), 2.5 (t, 2 H), 2.9 (s, 3 H), 3.2 (t, 2 H), 7.0–8.0 (m, 8 H); MS, *m/e* (relative intensity) 302 (M^+, 55.4), 229 (100). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.44; H, 5.96. Found: C, 83.32; H, 5.81.

8-Methyl-9-oxo-9,10,11,12-tetrahydro-BbF (26). The conversion of **25** (0.3 g, 0.001 mol) to **26** was accomplished in 70% yield according to the procedure described below for the preparation of **31**. The crude product was purified by chromatography on silica gel with elution by CH_2Cl_2, yielding 0.2 g of **26** as a light yellow compound: mp 136–137 °C; NMR δ 1.8–2.4 (m, 2 H), 2.45–2.7 (m, 2 H), 2.8 (s, 3 H), 2.9–3.2 (m, 2 H), 7.0–7.8 (m, 7 H); MS, *m/e* (relative intensity) 284 (M^+, 100), 256, (42.8), 228 (63.9). Anal. Calcd for $C_{21}H_{16}O$: C, 88.73; H, 5.63. Found: C, 88.55; H, 5.49.

8-Methyl-9-hydroxy-9,10,11,12-tetrahydro-BbF (27). The conversion of **26** (0.2 g, 0.0006 mol) into **27** was accomplished in 80% yield according to the procedure described below for **32**. This compound was used without further purification in the next step: MS, *m/e* (relative intensity) 286 (M^+, 51.1), 268 (100), 253 (83.3).

8-Methyl-BbF (8). The conversion of **27** (0.13 g, 0.00045 mol) to **8** was accomplished according to the procedure described below for preparation of **9**. The crude compound was purified by chromatography on 5 g of silica gel with elution by hexane to afford **8** as a yellow solid (60 mg, 50%): mp 134–135 °C; NMR δ 3.15 (s, 3 H), 7.25–8.5 (m, 9 H), 8.6–8.9 (m, 2 H); MS, *m/e* (relative intensity) 266 (M^+, 100). Anal. Calcd for $C_{21}H_{14}$: C, 94.73; H, 5.26. Found: C, 94.58; H, 5.50.

Methyl 3-[11-(Methoxycarbonyl)-11*H*-benzo[*b*]fluoren-11-yl]butyrate (29). A mixture containing 2.74 g (0.01 mol) of **28**,[18] 0.54 g (0.01 mol) of sodium methoxide, and 1.0 g of methyl crotonate in 250 mL of dry CH_3OH was stirred at 0 °C for 3 h. After the solvent was removed under reduced pressure, the residue was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel eluted with hexane/CH_2Cl_2 (3/1) to give **29** as a colorless oil (2.5 g, 66%): NMR δ 1.1–1.3 (m, 4 H), 2.0–2.2 (m, 2 H), 3.6 (s, 3 H), 3.7 (s, 3 H), 7.1–8.5 (m, 10 H); MS, *m/e* (relative intensity) 374 (M^+, 30), 315 (100).

3-(11*H*-Benzo[*b*]fluoren-11-yl)butyric Acid (30). Compound **29** (2.5 g, 0.007 mol), ethoxyethanol (100 mL), and 10 mL of 30% aqueous KOH were heated under reflux for 3 h. The mixture was cooled to room temperature and extracted with Et_2O (2 × 100 mL). The Et_2O layer was washed with H_2O, and the aqueous phase was cooled and acidified with concentrated HCl. Extraction with CH_2Cl_2 and standard workup gave 1.5 g (75%) of **30** as a white solid: mp 164–166 °C; NMR δ 0.9–1.1 (m, 4 H), 2.1–2.35 (m, 2 H), 4.2 (d, 1 H), 7.2–8.15 (m, 10 H); MS, *m/e* (relative intensity) 302 (M^+, 10.8), 258 (100). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.44; H, 5.96. Found: C, 83.21; H, 5.85.

1-Oxo-3-methyl-1,2,3,3a-tetrahydro-BbF (31). Oxalyl chloride (1.3 g, 0.01 mol) was added dropwise to a suspension of the acid **30** (1.5 g, 0.005 mol) in dry CH_2Cl_2 (150 mL). The mixture was stirred for 1 h at room temperature and then the solvent was removed. The crude product was dissolved in 150 mL of CS_2 and the solution was cooled to 0 °C in an N_2 atmosphere. $AlCl_3$ (1.5 g, 0.011 mol) was added in portions and the mixture was stirred at room temperature for 2 h and then heated under reflux for 30 min. The solution was then poured into ice water containing 10 mL of 4 N HCl. The resulting mixture was extracted with $CHCl_3$. The organic layer was washed with H_2O, dried ($MgSO_4$), and

concentrated to give 0.8 g (57%) of **31**: mp 136–137 °C; NMR δ 1.3 (d, 3 H), 2.4–3.0 (m, 3 H), 4.05 (d, 1 H), 7.1–7.8 (m, 7 H), 7.98 (s, 1 H), 9.35 (d, 1 H). Anal. Calcd for $C_{21}H_{16}O$: C, 88.73; H, 5.63. Found: C, 88.45; H, 5.42.

1-Hydroxy-3-methyl-1,2,3,3a-tetrahydro-BbF (32). A solution of the ketone **31** (0.5 g, 0.0018 mol) in THF and CH_3OH (50 mL) was stirred with $NaBH_4$ (0.6 g, 0.018 mol) at ambient temperature for 30 min. The reaction mixture was then poured into ice. The mixture was extracted with CH_2Cl_2 (3 × 150 mL), washed with H_2O, and dried ($MgSO_4$). The usual workup gave **32** as a white solid (0.4 g) which was employed directly for the synthesis of **9**: MS, *m/e* (relative intensity) 286 (M^+, 42.7), 242 (100).

3-Methyl-BbF (9). A solution of **32** (0.28 g, 0.001 mol) and *p*-toluenesulfonic acid (PTSA, 5 mg) in benzene was heated at reflux for 30 min using a Dean–Stark apparatus. Conventional workup followed by chromatography on silica gel, eluted with hexane/CH_2Cl_2 (4/1), afforded 3-methyldihydro-BbF: MS, *m/e* (relative intensity) 268 (M^+, 100), 240 (100).

A solution of the above dihydro compound and DDQ (0.23 g, 0.001 mol) in dry benzene was heated at reflux for 10 min. The reaction mixture was worked up in the usual manner. The crude product was chromatographed on 20 g of silica gel with elution by hexane to afford **9** (0.15 g, 66%) as a white solid: mp 166–167 °C; NMR δ 2.85 (s, 3 H), 7.3–8.4 (m, 10 H), 8.45–8.6 (m, 1 H); MS, *m/e* (relative intensity) 266 (M^+, 100). Anal. Calcd for $C_{21}H_{14}$: C, 94.70; H, 5.29. Found: C, 94.90; H, 5.44.

1,3-Dimethyl-BbF (10). The conversion of **31** (0.27 g, 0.001 mol) to **10** was carried out as described for the preparation of **7**. The crude **10** was purified on silica gel by elution with hexane to give a solid: 0.1 g (35%); mp 201–202 °C; NMR δ 2.8 (s, 3 H, 3-CH_3), 3.15 (s, 3 H, 1-CH_3), 7.25–8.1 (m, 8 H), 8.25 (s, 1 H, H_8), 8.8–9.0 (dd, 1 H, H_{12}); MS, *m/e* (relative intensity) 280 (M^+, 100). Anal. Calcd for $C_{22}H_{16}$: C, 94.28; H, 5.70. Found: C, 94.61; H, 5.82.

9-(*o*-Bromobenzylidene)-1-methylfluorene (34). To a cold (−20 °C) solution of 1.8 g (0.01 mol) of 1-methylfluorene (**33**) in 30 mL of THF was added in one portion 6.2 mL of *n*-BuLi (0.01 mol, 1.6 M in hexane). After 30 min of stirring at 0 °C, *o*-bromobenzaldehyde (1.9 g, 0.01 mol) was added dropwise. The reaction mixture was stirred for 8 h at room temperature and then worked up as usual. The crude product was purified by chromatography on silica gel with hexane as the eluent, yielding **34** (0.36 g, 10%) as an oil: NMR δ 3.7 (s, 3 H), 7.0–7.7 (m, 12 H); MS, *m/e* (relative intensity) 348 (M^+, 6), 346 (6), 179 (100).

7-Methyl-BbF (11). A mixture of **34** (0.2 g, 0.0057 mol) and KOH (0.56 g, 0.01 mol) in 20 mL of quinoline was heated under reflux for 4 h. The reaction mixture was cooled to 10 °C and then 30 mL of 6.6 N H_2SO_4 was added slowly. After being stirred and cooled, the reaction mixture was extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O, dried, and concentrated to give crude **11** which was purified by chromatography on silica gel with elution by hexane/CH_2Cl_2 (80/20). Pure **11** (30 mg) was obtained as a light yellow solid: mp 134–135 °C; NMR δ 2.9 (s, 3 H), 7.15–8.1 (m, 8 H), 8.25 (s, 1 H), 8.47 (d, 1 H), 8.6–8.7 (m, 1 H); HPLC retention time, 41 min. Anal. Calcd for $C_{21}H_{14}$: C, 94.73; H, 5.26. Found: C, 95.00; H, 5.29.

Methyl 2-Chloro-α-9*H*-fluoren-9-ylidenebenzeneacetate (35). A solution of fluorenone (5.4 g, 0.03 mol), *o*-chlorophenylacetic acid (5.1 g, 0.03 mol), 5 mL of triethylamine, and 5 mL of acetic anhydride was heated with stirring at 150 °C for 6 h. After cooling, the dark solution was diluted with H_2O (150 mL) and acidified with 50 mL of HCl. The resulting suspension was extracted with $CHCl_3$ (2 × 150 mL). The $CHCl_3$ layer was washed with H_2O (2 × 100 mL) and extracted with 10% aqueous NaOH (3 × 50 mL). The basic extract was acidified with concentrated HCl and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried ($MgSO_4$), and concentrated to afford 1.5 g of crude product. A mixture of this material, K_2CO_3 (3.0 g, 0.022 mol), and dimethyl sulfate (1.1 g, 0.0088 mol) in 100 mL of acetone was heated under reflux for 4 h. The reaction mixture was then filtered and the K_2CO_3 was washed several times with CH_2Cl_2. The organic layer was washed with H_2O, dried ($MgSO_4$), and evaporated to give the crude ester. This was purified by chromatography on silica gel with elution by hexane/CH_2Cl_2 (80/20) to give 0.5 g (4.8%) of pure ester **35**: mp 134–135 °C; NMR δ 3.85 (s, 3 H), 6.2 (d, 1 H), 6.65–7.8 (m, 11 H); MS, *m/e* (relative intensity) 348 (M^+, 17.4), 346 (46.6), 311 (90.1), 252 (100).

7(4)-Methyl-BbF. A mixture of acephenanthrylene (**38**)[24] (0.2 g, 0.001 mol), pentadiene (10 mL), and hydroquinone (5 mg) was heated at 180 °C for 16 h in a sealed tube. The mixture was cooled and extracted with CH_2Cl_2. The organic layer was washed with 10% aqueous NaOH and H_2O, dried ($MgSO_4$), and concentrated to afford the crude tetrahydro compound (100 mg).

A solution of this material and DDQ (0.11 g, 0.0005 mol) in benzene (50 mL) was heated at reflux for 1 h. Conventional workup followed by chromatography on silica gel with elution by hexane afforded a hydrocarbon which was further purified by preparative TLC on silica gel, with elution by CH_2Cl_2–hexane (30/70). HPLC showed a single major peak with a retention volume of 41 mL, identical with that of **11**. Capillary GC showed a single peak with a retention time of 39.11 min, the same as that of **11**. Its UV spectrum was identical with that of **11**. This material was presumed to be a mixture of **11** and 4-methyl-BbF.

5,6-Dimethyl-BbF (12). A mixture of acephenanthrylene (**38**) (0.1 g, 0.0005 mol), 2,3-dimethyl-1,3-butadiene (4 mL), and hydroquinone was heated at 160 °C for 16 h in a sealed tube. The mixture was cooled and extracted with CH_2Cl_2 (2 × 100 mL). The CH_2Cl_2 layer was washed with 10% aqueous NaOH (2 × 25 mL) and H_2O, dried ($MgSO_4$), and concentrated to afford 100 mg of the crude tetrahydro compound.

A solution of the above crude compound and DDQ (0.1 g, 0.0005 mol) in dry benzene was heated at reflux for 10 min. The reaction mixture was worked up in the usual manner. The crude product was chromatographed on 20 g of silica gel by elution with hexane to give a solid, 27 mg (20%): mp 145–146 °C; NMR δ 2.3 (s, 6 H), 7.15 (s, 2 H), 7.5–8.0 (m, 5 H), 8.07 (s, 1 H), 8.25–8.7 (m, 2 H); MS, *m/e* (relative intensity) 280 (M^+, 100), 265 (56.8). Anal. Calcd for $C_{22}H_{16}$: C, 94.28; H, 5.70. Found: C, 94.60; H, 5.47.

4-(8-Fluoranthenyl)-4-oxo-3(2)-methylbutyric Acid (42). To a solution of fluoranthene (**41**) (6.0 g, 0.03 mol) and methyl succinic anhydride (3.42 g, 0.03 mol) in dry nitrobenzene (60 mL) was added 4.0 g (0.03 mol) of $AlCl_3$ in small portions with stirring. The mixture was stirred for 6 h at room temperature and poured into 150 mL of 1.3 N HCl. The product was extracted with 3 × 50 mL of ether, and the ether extracts were washed with 3 × 50 mL of 4 N NaOH. The aqueous solution was washed with ether, after which the pH was brought to 2. Extraction with ether, drying ($MgSO_4$), and evaporation to dryness yielded the crude product which was recrystallized from CH_3OH–ether to give yellow crystals: mp 205–206 °C (5.6 g, 60%); IR (Nujol) 1685, 1700 cm^{-1}; NMR δ 1.3 (d, 3 H, J = 9 Hz), 2.85–3.2 (m, 2 H), 3.3–3.6 (m, 1 H), 7.5–8.1 (m, 8 H), 8.4 (s, 1 H); MS, *m/e* (relative intensity) 316 (M^+, 51), 229 (100), 200 (29.4). Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.74; H, 5.06. Found: C, 79.52; H, 5.22.

4-(8-Fluoranthenyl)-3(2)-methylbutyric Acid (43). A solution of the acids **42** (1.6 g, 0.005 mol), KOH (0.5 g, 0.01 mol), and anhydrous hydrazine (1.45 g) in diethylene glycol (25 mL) was heated at reflux for 4 h. The reaction mixture was diluted with H_2O and acidified with concentrated HCl, and the resulting solid was collected and washed with H_2O giving 1.1 g (72%) of **43**: mp 135–136 °C; NMR δ 1.35 (d, 3 H, J = 9 Hz), 1.7–2.2 (m, 2 H), 2.5–2.9 (m, 3 H), 7.2 (dd, 1 H), 7.5–7.8 (m, 8 H); MS *m/e* (relative intensity) 302 (M^+, 43.9), 228 (52.9), 215 (83), 84 (100). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.44; H, 5.96. Found: C, 83.48; H, 5.98.

8-Oxo-10(9)-methyl-8,9,10,11-tetrahydro-BkF (44). Cyclization of **43** (6.0 g, 0.03 mol) to the ketones **44** was accomplished according to the procedure described for the preparation of **31**. Chromatography of the crude product on silica gel with elution by CH_2Cl_2/hexane (50/50) afforded 2.1 g (74%) of **44**: mp 147–148 °C; IR (Nujol) 1680 cm^{-1}; NMR δ 1.35 (d, 3 H, J = 9 Hz), 2.0–2.35 (m, 2 H), 2.5–2.8 (m, 1 H), 3.0–3.2 (m, 2 H), 7.5–8.0 (m, 7 H), 8.5 (s, 1 H); MS, *m/e* (relative intensity) 284 (M^+, 100), 242 (39.4). Anal. Calcd for $C_{21}H_{16}O$: C, 88.73; H, 5.63. Found: C, 88.67; H, 5.77.

8-Hydroxy-(10)9-methyl-8,9,10,11-tetrahydro-BkF (45). Ketone **44** (0.57 g, 0.002 mol) was dissolved in dry THF (10 mL)

(24) Acephenanthrylene was prepared from 9-phenanthrylacetic acid by cyclization, reduction, and dehydration. This method, which will be described separately, was more efficient than those previously published.

and added dropwise to a suspension of $LiAlH_4$ (0.072 g, 0.002 mol) in dry THF (20 mL). The mixture was stirred for 1 h at room temperature, diluted with H_2O, and extracted with ethyl acetate. The ethyl acetate was dried ($MgSO_4$) and concentrated, leaving **45** as a solid (0.5 g, 74%), mp 83–84 °C, which was used without further purification: MS, *m/e* (relative intensity) 286 (M^+, 89), 243 (69.1), 215 (100).

9-Methyl-BkF (14). The alcohol **45** (0.5 g, 0.0018 mol) was converted to 9-methyl-BkF (**14**) as described for the preparation of **9**. The crude product was purified by chromatography on silica gel with elution by hexane/CH_2Cl_2 (90/10) to afford **14** (0.32 g, 70%) as a yellow solid: mp 156–157 °C; NMR δ 2.85 (s, 3 H), 7.3–7.55 (m, 3 H), 7.6–8.1 (m, 5 H), 8.35–8.75 (m, 3 H); MS, *m/e* (relative intensity) 266 (M^+, 100), 239 (12). Anal. Calcd for $C_{21}H_{14}$: C, 94.73; H, 5.26. Found: C, 94.59; H, 5.55.

4-(2-Methylfluoranthen-8(9)-yl)-4-oxobutyric Acid (47). The reaction of 2-methylfluoranthene (**46**) (2.16 g, 0.01 mol), succinic anhydride (1.0 g, 0.01 mol), and $AlCl_3$ (1.33 g, 0.01 mol) in nitrobenzene (10 mL) was effected as described for preparation of **42**. Crystallization of the crude product from CH_3OH/ether gave **47** as a light yellow solid: mp 194–196 °C (2.0 g, 66%); IR (Nujol) 1680, 1700 cm^{-1}; NMR δ 2.6 (s, 3 H), 2.85 (t, 2 H), 3.5 (t, 2 H), 7.35–8.2 (m, 7 H), 8.5 (s, 1 H); MS, *m/e* (relative intensity) 316 (M^+, 29.1), 243 (100), 215 (57.1). Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.74; H, 5.06. Found: C, 79.92; H, 5.21.

4-(2-Methylfluoranthen-8(9)-yl)butyric Acid (48). A mixture of Zn(Hg) (1.3 g, 0.02 mol), 1.65 mL of concentrated HCl, 10.0 mL of acetic acid, 10 mL of toluene, and 0.43 g (0.002 mol) of **47** was heated under reflux for 3 h. After dilution with H_2O (50 mL), the mixture was worked up as usual to yield 0.3 g of the crude acid. The purified acid(s) **48** was obtained by recrystallization from CH_3OH/ether: mp 138–139 °C; IR (Nujol) 1700 cm^{-1}; NMR δ 2.5 (s, 3 H), 2.0–2.5 (m, 4 H), 2.7–3.1 (m, 2 H), 7.0–7.9 (m, 8 H); MS, *m/e* (relative intensity) 302 (M^+, 42), 242 (30), 228 (100). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.44, H, 5.96. Found: C, 83.69; H, 6.09.

8(11)-Oxo-8,9,10,11-tetrahydro-2-methyl-BkF (49). The acid(s) **48** (3.0 g, 0.01 mol) was converted to the ketone **49** as described for **31**. Crystallization of the crude product from CH_2Cl_2–hexane gave **49** as a yellow solid: mp 123–125 °C (1.8 g, 63%); NMR δ 2.1 (s, 3 H), 2.3–3.0 (m, 6 H), 7.0–7.5 (m, 6 H), 8.2 (s, 1 H); MS, *m/e* (relative intensity) 284 (M^+, 100), 270 (23.6) 256 (40.1). Anal. Calcd for $C_{21}H_{16}O$: C, 88.73; H, 5.63. Found: C, 88.47; H, 5.68.

8(11)-Hydroxy-8,9,10,11-tetrahydro-2-methyl-BkF (50). The conversion of **49** (0.57 g, 0.002 mol) to **50** (0.45 g) was accomplished in 80% yield, according to the procedure described above for **45**. The alcohol **50** was obtained as a white solid, mp 73–76 °C, which was used without further purification: MS, *m/e* (relative intensity) 286 (M^+, 72), 243 (60), 215 (100).

2-Methyl-BkF (16). The alcohol **50** (0.14 g, 0.0005 mol) was converted to **16** as described above for **9**. The crude product was chromatographed on silica gel using hexane/CH_2Cl_2 (90/10) as the eluting solvent to give **16** (65 mg, 50%): mp 139–140 °C; NMR δ 2.7 (s, 3 H), 7.5–8.1 (m, 9 H), 8.3 (s, 2 H); MS, *m/e* (relative intensity) 266 (M^+, 100). Anal. Calcd for $C_{21}H_{14}$: C, 94.73; H, 5.26. Found: C, 94.91; H, 5.20.

BkF-7,12-dicarboxaldehyde (52). A solution of *i*-Bu_2AlH (1.4 g, 0.01 mol) in 10 mL of hexane was added at 0 °C, with stirring under N_2, to 7,12-dicyano-BkF (**51**)[23] (0.99 g, 0.0033 mol) in 50 mL of benzene. After 12 h of stirring at room temperature, the reaction mixture was poured into ice–water and extracted with ethyl acetate. The organic layer was collected and washed with H_2O, dried ($MgSO_4$), and evaporated. The residue was recrystallized from CH_2Cl_2–hexane to give **52** as a yellow solid: 0.8 g (87%); mp 278–280 °C; IR (Nujol) 1780 cm^{-1}; NMR δ 7.2–8.2 (m, 10 H), 11.3 (s, 2 H); MS, *m/e* (relative intensity) 308 (M^+, 11.6).

7,12-Dimethyl-BkF (15). A mixture of the dialdehyde **52** (1.0 g, 0.0033 mol), KOH (1 g, 0.028 mol), and NH_2NH_2 (1.4 g, 0.023 mol) in diethylene glycol was heated under reflux for 3 h. Conventional workup followed by silica gel chromatography with elution by hexane/CH_2Cl_2 (90/10) gave 0.5 g (57%) of a yellow solid, which was recrystallized from EtOH: mp 194–195 °C; NMR δ 3.0 (s, 6 H), 7.25–8.4 (m, 10 H). Anal. Calcd for $C_{22}H_{16}$: C, 94.28; H, 5.70. Found: C, 94.53; H, 5.62.

8-Methyl-BkF (13). 8-Methyl-BkF was prepared from 8-oxo-8,9,10,11-tetrahydro-BkF (0.81 g, 0.003 mol) by the same method as described above for **7**. The crude compound was purified on silica gel by elution with hexane/CH_2Cl_2 (90/10) to give a solid: 0.56 g (70%); mp 204–205 °C (lit.[9] mp 207 °C); NMR δ 2.55 (s, 3 H), 7.26–8.4 (m, 11 H); MS, *m/e* (relative intensity) 266 (100).

Registry No. **3**, 205-99-2; **5**, 95741-46-1; **6**, 95741-47-2; **7**, 95741-49-4; **9**, 95741-50-7; **10**, 95741-51-8; **11**, 95741-52-9; **12**, 95741-53-0; **13**, 95741-54-1; **14**, 95741-55-2; **15**, 95741-56-3; **16**, 95741-57-4; **17**, 77061-01-9; **18**, 88746-63-8; **19**, 88746-52-5; **20**, 39627-37-7; **21**, 95741-58-5; **22**, 95741-59-6; **23**, 95741-60-9; **24**, 95741-61-0; **25**, 95741-62-1; **25** (acid chloride), 95741-98-3; **26**, 95741-63-2; **27**, 95741-64-3; **28**, 88746-49-0; **29**, 95741-65-4; **30**, 95741-66-5; **30** (acid chloride), 95741-99-4; **31**, 95741-67-6; **32**, 95741-68-7; **33**, 1730-37-6; **34**, 95741-69-8; **35**, 95741-70-1; **35** (acid chloride), 95763-34-1; **36**, 95741-71-2; **37**, 95741-72-3; **38**, 201-06-9; **39**, 1836-87-9; **40**, 1643-49-8; **41**, 206-44-0; **42**, 95741-73-4; **43**, 95741-74-5; **43** (acid chloride), 95742-01-1; **44**, 95741-75-6; **45**, 95741-76-7; **47**, 95741-77-8; **48**, 95741-78-9; **48** (acid chloride), 95742-02-2; **49**, 95741-79-0; **50**, 95741-80-3; **51**, 72851-41-3; **52**, 95741-81-4; 8-methyl-10,11-dihydroBkF, 95741-94-9; 9-hydroxy-9-methyl-9,10,11,12-tetrahydroBbF, 95741-82-5; 9-methyl-11,12-dihydroBbF, 95741-83-6; 12-hydroxy-12-methyl-9,10,11,12-tetrahydroBbF, 95741-84-7; 12-methyl-9,10-dihydroBbF, 95741-85-8; 1-hydroxy-1-methyl-1,2,3,3a-tetrahydroBbF, 95741-86-9; 1-methyl-3,3a-dihydroBbF, 95741-87-0; 8-methyl-11,12-dihydroBbF, 95741-88-1; 3-methyldihydroBbF, 95741-89-2; 1,3-dimethyl-3,3a-dihydroBbF, 95741-90-5; 4-methylBbF, 63040-52-8; 4-methyl-6,7-dihydroBbF, 95741-91-6; 4-methyl-4,5,6,7-tetrahydroBbF, 95741-92-7; 5,6-dimethyl-4,5,6,7-tetrahydroBbF, 95741-93-8; 9-methyl-10,11-dihydroBkF, 95741-95-0; 2-methyl-8,9-dihydroBkF, 95741-96-1; 4-bromo-1-butene, 5162-44-7; 1-methyl-3-(3-butenyl)-1,10a-dihydrofluoranthene, 95741-97-2; methyl 8-benzo[*b*]fluoranthenoate, 95742-00-0; methyl succinic anhydride, 1944-45-2; 8-oxo-8,9,10,11-tetrahydroBkF, 33942-82-4; 8-methyl-8-hydroxy-8,9,10,11-tetrahydroBkF, 95742-03-3; 1,3-dimethyl-1-hydroxy-1,2,3,3a-tetrahydroBbF, 95742-04-4; *o*-chlorophenylacetic acid, 2444-36-2; methyl crotonate, 18707-60-3; 2-bromobenzaldehyde, 6630-33-7; 1,3-pentadiene, 504-60-9; 2,3-dimethyl-1,3-butadiene, 513-81-5; succinic anhydride, 108-30-5; 9-fluorenone, 486-25-9.