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Regioselectively Nucleus and/or Side-Chain Fluorinated 2-(Phenanthryl)propionic Acids by an Effective Combination of Radical and Organometallic Chemistry

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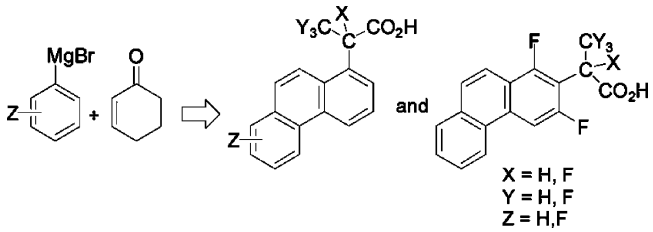

Regioselectively nucleus and/or side-chain fluorinated 2-(phenanthr-1-yl)- and 2-(phenanthr-2-yl)-propionic acids **1**−**5** were prepared using phenanthren-1(2*H*)-ones **6a**−**c** as key intermediates. Thus, ethyl 2-(fluorophenanthryl)propionates **11** were obtained in good yields by Reformatsky reaction of **6a**−**c** with ethyl 2-bromopropionate followed by dehydratation and DDQ-promoted aromatization of the resulting *β*-hydroxyesters. Side-chain alkyl 2-hydroxy-2-(phenanthr-1-yl)propionates **14** were obtained by bromine/lithium permutation of dihydrophenanthryl bromides **12a**−**c** with butyllithium followed by quenching of the lithiated intermediates with methyl pyruvate or ethyl 3,3,3-trifluoropyruvate and subsequent DDQ-promoted aromatization. The alkyl 2-hydroxy-2-(phenanthr-1-yl)propionates **25** were prepared by reacting 8-bromo-1,3-difluorophenanthrene **24** with butyllithium for 10 seconds at −110 °C and subsequent addition of the suitable pyruvate to the lithiated intermediates. Alkyl 2-hydroxy-2-(phenanthr-2-yl)propionates **26** and **29** were suitably obtained by site-selective metalation of 1,3-difluorophenanthrene **28** and the bromophenanthrene **24**, respectively, with LDA followed by quenching of the metalated intermediates with the suitable alkyl pyruvate. Fluorination of the above α-hydroxypropionates with DAST, followed by the alkaline hydrolysis, allowed the expected 2-(phenanthryl)propionic acids **1**−**5** to be obtained in satisfactory overall yields.

Introduction

Owing to its surprising peculiarities,[1] fluorine, a fascinating element, is a cornerstone in the synthesis of modern drugs. Fluorinated drugs include a vast range of pharmaceutical applications from anesthetics to chemotherapeutic drugs, from corticoids to neuroleptics, and more recently, even cardiovascular drugs.[2] Fluorinated nonsteroidal antiinflammatory drugs (NSAIDs), especially those belonging to the "Profen" family, have received particular attention. For example, 2-(fluoroaryl)-propionic acids such as flurbiprofen and flunoxaprofen belong to the most successful NSAIDs. Of course, the use of fluorinated aromatics in the synthesis of different biologically active compounds has stimulated the research toward new fluorination techniques and new regioselectively fluorinated aromatics to be used as valuable building blocks. In this respect, the organometallic approach developed by M. Schlosser[3] looks quite

(1) Schlosser, M. The Chemical and Physiological Size of Fluorine. In *Enantiocontrolled Synthesis of Fluoro-Organic Compounds: Stereochemical Challenges and Biomedical Targets*; Soloshonok, V. A., Ed.; Wiley: Chichester, 1999. Schlosser, M. *Angew. Chem.* **1998**, *110*, 1538−1556; *Angew. Chem., Int. Ed.* **1998**, *37*, 1496−1513. Schlosser, M.; Michel, D. *Tetrahedron* **1996**, *52*, 99−108. Schlosser, M. *Tetrahedron* **1978**, *34*, 3−17. Welch, T.; Eswarakrishnan, S. *Fluorine in Bioorganic Chemistry*; Wiley: New York, 1991. *Biomedical Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Kodansha, Ltd.: Tokyo and Elsevier Biomedical: Amsterdam, 1982.

(2) *Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications*; Filler, R., Kobayashi, Y., Yagupolskii, L. M., Eds.; Elsevier: Amsterdam, 1993.

(3) Schlosser, M.; Rausis, T. *Eur. J. Org. Chem.* **2004**, 1018−1024. Schlosser, M.; Mangano, G.; Leroux, F. *Eur. J. Org. Chem.* **2004**, 1014−1017. Marull, M.; Schlosser, M. *Eur. J. Org. Chem.* **2003**, 1576−1588. Schlosser, M.; Gorecka, J.; Castagnetti, E. *Eur. J. Org. Chem.* **2003**, 452−462. Heiss, C.; Schlosser, M. *Eur. J. Org. Chem.* **2003**, 447−451.

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promising. Given that C−F bonds are stronger than C−H bonds, replacing the α-hydrogen of a 2-arylpropionic acid with the quasi-isosteric fluorine[1] conveys a higher configurational stability to the chiral carbon,[4] thus allowing the drug pharmacodynamics, as well as the stereochemical matching with the receptor, to be investigated.

Up to now, only a limited number of methods have been disclosed for the synthesis of side-chain fluorinated 2-arylpropionic acids. One of them, developed by G. Haufe et al.,[5] was a novel access to ibuprofen and naproxen. It consists of oxidizing 2-aryl-2-fluoropropanols obtained either by bromofluorination of 2-arylpropenes followed by hydroxylation or, more conveniently, by BF_3-catalyzed hydrolytic ring opening of 2-arylpropene oxides. In the same time period, M. Schlosser et al.[6] prepared the α-fluorinated analogue of ibuprofen by treating ethyl 2-hydroxy-2-(4-isobutylphenyl)propionate with diethylaminosulfur trifluoride (DAST) followed by the hydrolysis of the resulting ester or nitrile. More recently, S. Rozen reported a quite general entry to α-fluoroalcanoic acids, including 2-aryl-2-fluoropropionic acids, based on the acyl hypofluorite-promoted electrophilic fluorination of ketene-acetals.[7]

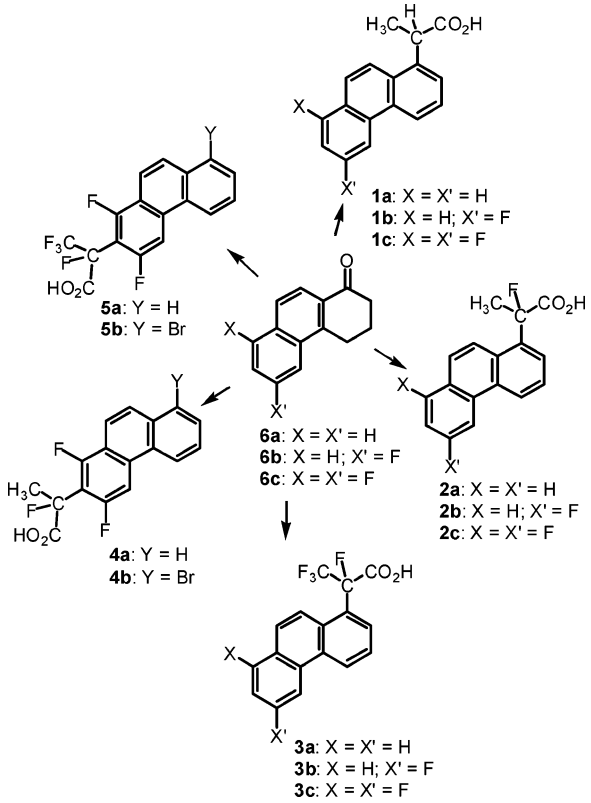
To date, only a few α-fluorinated profens are known, and 2-arylperfluoropropionic acids are even less common. To our knowledge, these kinds of compounds have been isolated in only three instances and each time by mere accident.[8]

The increasing attention to the pharmacological properties of fluorinated profens and the lack of a method to prepare them spurred us to search for a general approach to new fluorinated 2-arylpropionic acids, particularly 2-(phenanthryl)propionic acids. Apart from the intrinsic importance of the selective functionalization of polycyclic arenes, our interest in this class of aromatics arose from the observation that phenanthrene nucleus is at the base of several enzyme inhibitors and other pharmacologically important drugs.[9] In this connection, it was reported that 2-(phenanthr-1-yl)propionic acid (**1a**) exhibits a biological activity as NSAID comparable to that of common registered profens such as fenbufen.[10] In this article, we suggest a general approach to nucleus and/or side-chain regioselectively fluorinated 2-(phenanthryl)propionic acids on the basis of an original combination of radical and organometallic chemistry.

Results and Discussion

Nucleus and side-chain regioselectively polyfluorinated 2-phenanthrylpropionic acids **1**−**5** were prepared using

CHART 1



3,4-dihydrophenanthren-1(2*H*)-one (**6a**) and its 6-fluoro- (**6b**) and 6,8-difluoro- (**6c**) analogues as the starting materials (Chart 1).

Ketones **6a**−**c** were prepared by an oxidative annulation method developed in our laboratory.[11] This method is based on the ceric ammonium nitrate (CAN)-mediated addition of the easily accessible 3-(fluoroaryl)-1-trimethylsilyloxycyclohexenes (**7**)[12] to ethyl vinyl ether, which affords a mixture of cyclic (**8**) and acyclic (**9**) acetals (Scheme 1).

Cyclization of the latter in concentrated sulfuric acid and in the presence of a stoichiometric amount of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) provides the targeted phenanthrenones **6a**−**c** in satisfactory (41−53%) yield.[13]

The Reformatsky reaction of phenanthrenones **6b**,**c** with ethyl α-bromopropionate,[10] followed by the dehydratation of the resulting *β*-hydroxyester in refluxing formic acid (Scheme 2), proved to be the most convenient route leading to ethyl 2-(3,4-dihydrophenanthren-1-yl)-propionates **10a**−**c**. DDQ-promoted aromatization of the latter in benzene at 55 °C, followed by the hydrolysis of the resulting 2-phenanthrylpropionates **11a**−**c** in methanolic KOH, afforded the corresponding 2-(phenanthren-1-yl)propionic acids **1a**−**c** in approximately 70% overall yields.

(4) Hamman, S. *J. Fluorine Chem.* **1993**, *60*, 225−232.
(5) Goj, O.; Kotila, S.; Haufe, G. *Tetrahedron* **1996**, *52*, 12761−12774. Goj, O.; Haufe, G. *Liebigs Ann.* **1996**, 1289−1294.
(6) Schlosser, M.; Michel, D.; Guo, Z.-W.; Sih, C. J. *Tetrahedron* **1996**, *52*, 8257−8262.
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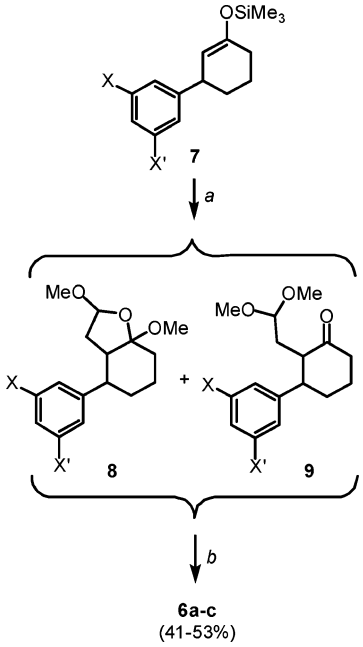
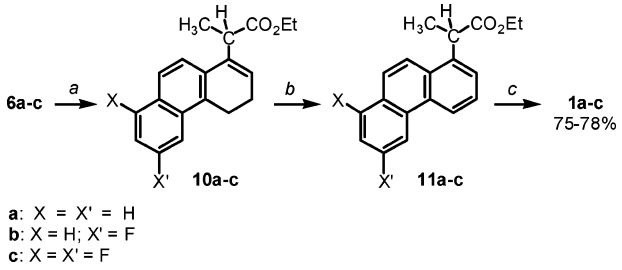
(8) Barna, P. M. *Chem. Ind. (London)* **1966**, 2054.
(9) Toegersen, H. S.; Peschke, B.; Hansen, T. K.; Andersen, K. E. PCT Int. Appl. WO 96 05195, 1996; *Chem. Abstr.* **1996**, *125*, 58521m. Adams, J. L.; Garigipati, R. S. U.S. Patent 5,140,047, 1992; *Chem. Abstr.* **1993**, *118*, 80647j. Berlin, K. D.; Durham, N. N.; Desjardins, C. U.S. Patent 3,987,055, 1976; *Chem. Abstr.* **1977**, *86*, 106893j. Brown, G. R.; Bamford, A. M.; Bowyer, J.; James, D. S.; Rankine, N.; Tang, E.; Torr, V.; Culbert, E. J. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 575−579.
(10) Eirín, A.; Fernández, F.; Gómez, G.; López, C.; Santos, A. *Arch. Pharm. (Weinheim, Ger.)* **1987**, *320*, 1110−1118.
(11) Gourvès, J.-P.; Ruzziconi, R.; Vilarroig, L. *J. Org. Chem.* **2001**, *66*, 617−619. Lupattelli, P.; Ruzziconi, R.; Scafato, P.; Alunni, S.; Belli Paolobelli, A. *J. Org. Chem.* **1998**, *63*, 4506−4509.
(12) Reetz, M. T.; Kindler, A. *J. Organomet. Chem.* **1995**, *502*, C5−C7.
(13) To avoid using the expensive DDQ, in one experiment cyclization of **8** and **9** was carried out in 85% aq phosphoric acid at 60 °C by employing $Fe_2(SO_4)_3$ as the oxidant. However, although the reaction mixture worked up better, much lower yields (∼15%) of pure ketone **6a**−**c** were obtained.

SCHEME 1[a]



[a] (*a*) CH_2=CHOEt, CAN, MeOH, rt; (*b*) 80% aq H_2SO_4, DDQ, 0 °C.

SCHEME 2[a]



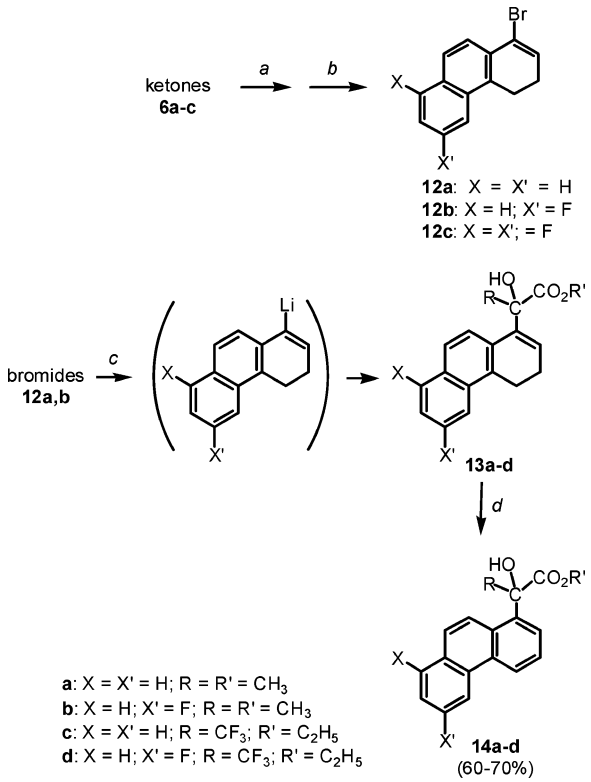
[a] (*a*) 1. $CH_3CHBrCO_2Et$, Zn/Hg, C_6H_5-DEE, refl; 2. HCO_2H, refl; (*b*) DDQ, C_6H_6, 55 °C; (*c*) KOH, MeOH, rt.

The key products for the synthesis of side-chain fluorinated 2-(phenanthryl)propionic acids **2a**−**c** and **3a**−**c** were 1-bromo-3,4-dihydrophenanthrene (**12a**) and its 6-fluoro- (**12b**) and 6,8-difluoro- (**12c**) analogues. They were prepared from ketones **6a**−**c** by lithium *tert*-butoxide/$CuBr_2$-promoted bromination of the corresponding hydrazones in anhydrous THF.[14]

Butyllithium-promoted bromine/lithium permutation in **12a**,**b** in THF at −75 °C, followed by the addition of either methyl pyruvate or ethyl 3,3,3-trifluoropyruvate, gave the corresponding 2-(3,4-dihydrophenanthren-1-yl)-2-hydroxypropionates **13a**−**b** or the 3,3,3-trifluoropropionate analogues **13c**−**d** thereof (Scheme 3). Once again, DDQ-promoted aromatization enabled the conversion of hydroxyesters **13a**−**d** into the corresponding 2-(phenanthren-1-yl)-2-hydroxypropionates **14a**−**d** in 60−70% overall yield.[15]

In an extension of previous work by Olah,[17] C. J. Li [16] recently elaborated the synthesis of several methyl 2-aryl-2-hydroxy-3,3,3-trifluoropropionates by Lewis acid-

SCHEME 3[a]



[a] (*a*) $NH_2NH_2{\cdot}H_2O$, C_6H_6/EtOH, 80 °C; (*b*) $CuBr_2$-^{t}BuOLi, THF, 20 °C; (*c*) 1. BuLi, THF, 2. $RCOCO_2R'$, THF, −75 °C; 3. aq NH_4Cl; (*d*) DDQ; toluene, 90 °C.

catalyzed Friedel−Crafts alkylation of substituted benzenes with methyl trifluoropyruvate. A copper(II)-catalyzed enantioselective method for the formation of optically active alkyl 2-aryl-2-hydroxy-3,3,3-trifluoropropionates making use of chiral bisoxazoline ligands was published by Jørgensen.[18] However, in both cases, acceptable yields were only achieved when the reaction was assisted by powerful electron-releasing groups present in the aromatic substrate. In contrast, our method does not suffer from such restrictions.

The reaction of 1-bromo-6,8-difluoro-3,4-dihydrophenanthrene (**12c**) with butyllithium turned out to be a more complex process than expected. Of course, the acidity of the C_7−H bond flanked by two fluorine atoms should increase the deprotonation rate to such an extent that it could effectively compete with the bromine/metal exchange. As a matter of the fact, the reaction of bromodihydrophenanthrene **12c** with butyllithium in THF at

(14) Takeda, T.; Sasaki, R.; Yamauchi, S.; Fujiwara, T. *Tetrahedron* **1997**, *53*, 557−566.

(15) Similar results were obtained by changing the metalation/alkylation/aromatization sequences. Namely, aromatization of **10a**,**b** with DDQ followed butyllithium-promoted halogen−lithium exchange and successive alkylation of the resulting 1-lithiophenanthrene intermediate with alkyl pyruvates. However, because of the low stability of the vinylic bromide in the presence of DDQ, lower yields of the corresponding aromatic 1-bromophenanthrenes were obtained, and they were contaminated by substantial amounts of unidentified dibromoderivatives.

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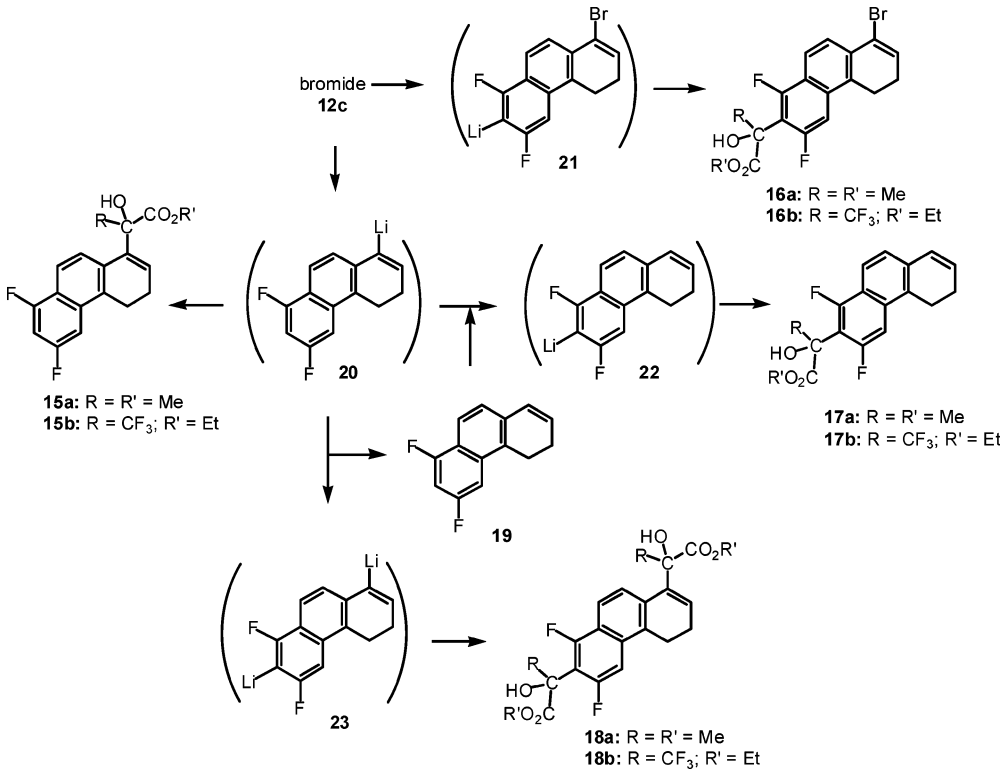
(17) Prakash, G. K. S.; Yan, P.; Török, B.; Olah, G. A. *Synlett*. **2003**, 527−531.

(18) Zhuang, W.; Gathergood, N.; Hazell, R. G.; Jørgensen, K. A. *J. Org. Chem.* **2001**, *66*, 1009−1013. See also Corma, A.; García, H.; Moussaif, A.; Sabater, M. J.; Zniber, R.; Redouane, A. *Chem. Commun.* **2002**, 1058−1059.

SCHEME 4



−100 °C for 90 min, before quenching with methyl pyruvate, afforded a mixture of five products that were easily separated by chromatography on silica gel and identified as methyl 2-(6,8-difluoro-3,4-dihydrophenanthren-1-yl)-2-hydroxypropionate (**15a**, 7%), methyl 2-(8-bromo-1,3-difluoro-5,6-dihydrophenanthren-2-yl)-2-hydroxypropionate (**16a**, 16%), methyl 2-(1,3-difluoro-5,6-dihydrophenanthren-2-yl)-2-hydroxypropionate (**17a**, 54%), the 2,8-dialkylated derivative (**18a**, <1%), and 6,8-difluoro-3,4-dihydrophenanthrene (**19**, 14%) (Scheme 4).

In fact, the product composition varied substantially as a function of the reaction time. The yield of trapping product **15a** diminished from 38% to 22% and to 7% after 5, 20, 35, and 90 min, respectively, whereas that of **17a** increased in the same intervals from 17% to 32%, 34%, and 50%, respectively. The relative amounts of **16a**, **18a**, and **19** remained practically unchanged.

From a mechanistic point of view, it is quite likely that the initial attack of butyllithium at **12c** turns into both halogen/metal exchange at C-1 and deprotonation at C-7 to give the 1-lithio derivative **20**, and the C-7-lithiated bromophenanthrene **21**, respectively, with bromine/lithium permutation being 3 times faster. Then, slow transmetalation occurs, converting the more basic species **20** into the less basic species **22** and **23**. After quenching with methyl pyruvate, the α-hydroxyesters **15a**, **16a**, **17a**, and **18a** were obtained from **20**, **21**, **22**, and **23**, respectively (Scheme 4). In the same way, the replacement of methyl pyruvate by ethyl trifluoropyruvate led to a mixture of the corresponding ethyl 2-(phenanthryl)-3,3,3-trifluoropropionates **15b**, **16b**, **17b**, and **18b** of practically identical composition.

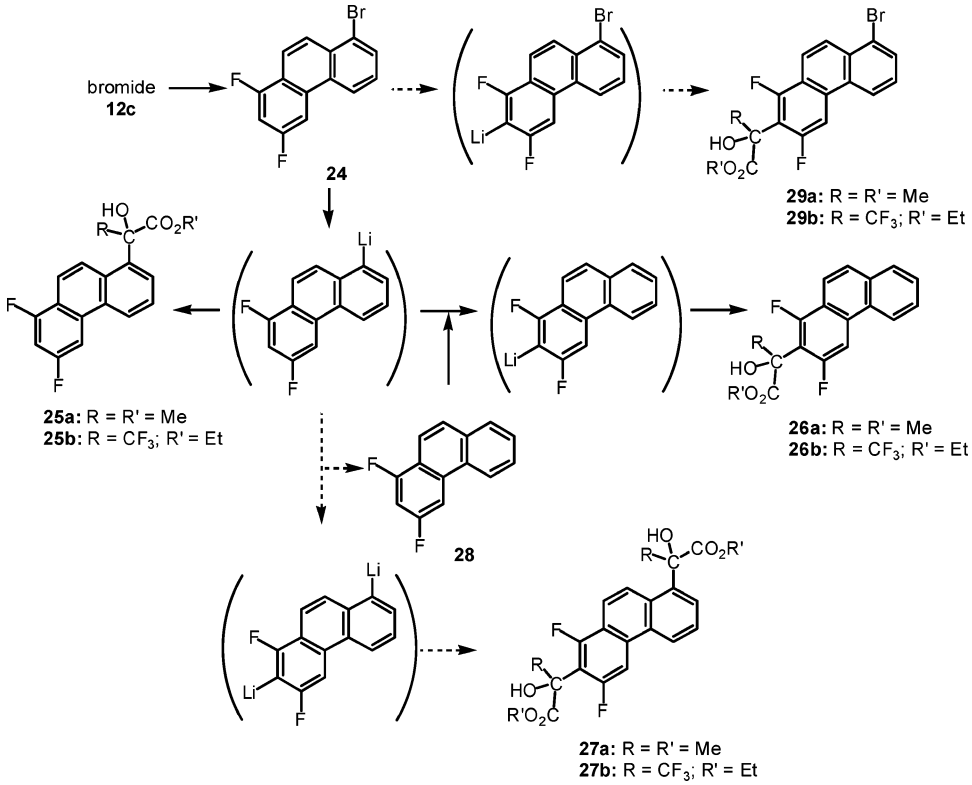
To find a more selective process leading to regioisomerically pure hydroxyester **25**, the dihydrobromophenanthrene **12c** was replaced by the corresponding 8-bromo-1,3-difluorophenanthrene (**24**), obtained in 65% yield by DDQ-promoted aromatization of **12c**.[19] This was done because we believed that two interdependent favorable conditions would have been accomplished: a faster bromine/lithium exchange that could compete efficaciously with the deprotonation at C-7 and a slower equilibration as a consequence of a lower basicity of the aryllithium with respect to a vinyllithium species.

Similar to dihydrophenanthrene **12c**, the reaction of **24** with butyllithium at −100 °C for 90 min, followed by the addition of methyl pyruvate, afforded a mixture of four products that were identified as methyl 2-(6,8-difluorophenanthren-1-yl)-2-hydroxypropionate (**25a**, 46%), 2-(1,3-difluorophenanthren-2-yl)-2-hydroxypropionate (**26a**, 31%), the 1,7-dialkylated 6,8-difluorophenanthrene (**27a**, <1%), and 1,3-difluorophenanthrene (**28**, 7%) (Scheme 5). Traces of methyl 2-(8-bromo-1,3-difluorophenanthryl)-2-hydroxypropionate (**29**) were also detected.

As above, a quantitative GLC analysis of the mixture was carried out at various reaction times. The pattern looked quite different from that observed in the reaction of the corresponding dihydroderivative **12c**. Here, a nearly quantitative bromine/lithium permutation was observed, and the equilibration toward the most thermodynamically stable intermediate 1,3-difluoro-2-lithiophenenthrene was significantly slower. Like dihydrophenanthrene **19** in the reaction of **12c**, 1,3-difluorophenanthrene **28** most probably works as the catalyst of the whole process, as the amount remains low and practically unchanged. At lower temperatures, equilibration could be controlled to the point that the expected

(19) A one-step procedure to prepare **21** by reacting the ketone **3c** with PBr_3 at 90 °C was unsuccessful. The product was obtained in very low yield and was contaminated by unidentified dibromo derivatives.

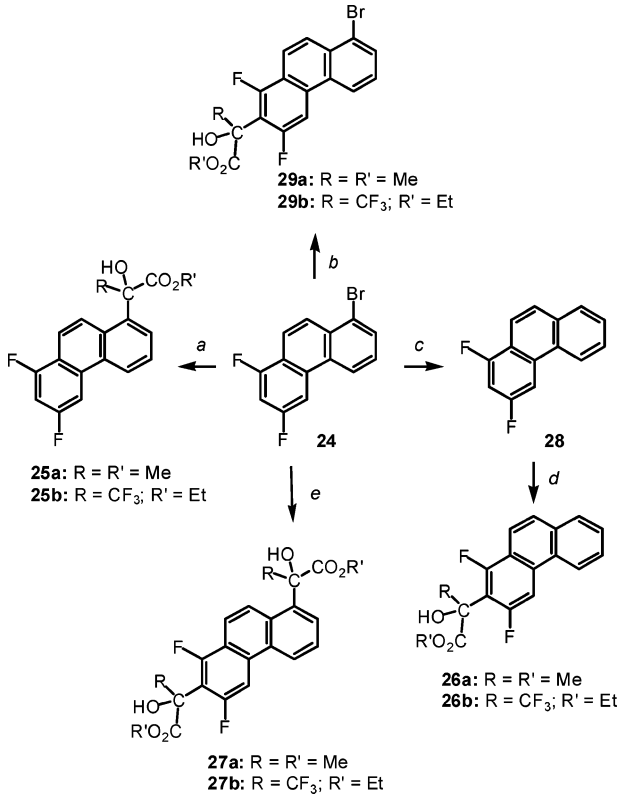
SCHEME 5



1-alkylated difluorophenanthrenes **25a** and **25b** were obtained as the only products in 61 and 65% of yield, respectively, when **24** was made to react with butyllithium at −110° for only 10 seconds before the mixture was quenched with methyl pyruvate or ethyl trifluoropyruvate. The product, contaminated by only a small amount (6%) of the starting bromoarene, was easily purified by chromatography on silica gel. This proved to be the only way to prepare **25a**,**b** cleanly.[20]

The regioselective lithiation of fluoroaromatics by lithium dialkylamide bases, without problems of competing halogen/metal exchange, was thoroughly examined by M. Schlosser.[21] It can also be successfully exploited in our case. As evidence, both regioisomerically pure bromoarylpropionate **29a** and the corresponding trifluoro analogue **29b** were easily obtained in 83 and 88% yield, respectively, by metalation of **24** with lithium diisopropylamide (LDA) in THF at −50 °C and subsequent quenching of the reaction mixture with methyl pyruvate or ethyl trifluoropyruvate. Of course, both propionate **26a** and its trifluoro analogue **26b** can be prepared in fairly good yield (67 and 73%, respectively) by metalation of 1,3-difluorophenanthrene (**28**) with either butyllithium or LDA in THF at −50 °C and subsequent quenching with the suitable pyruvate (Scheme 6).

SCHEME 6[a]

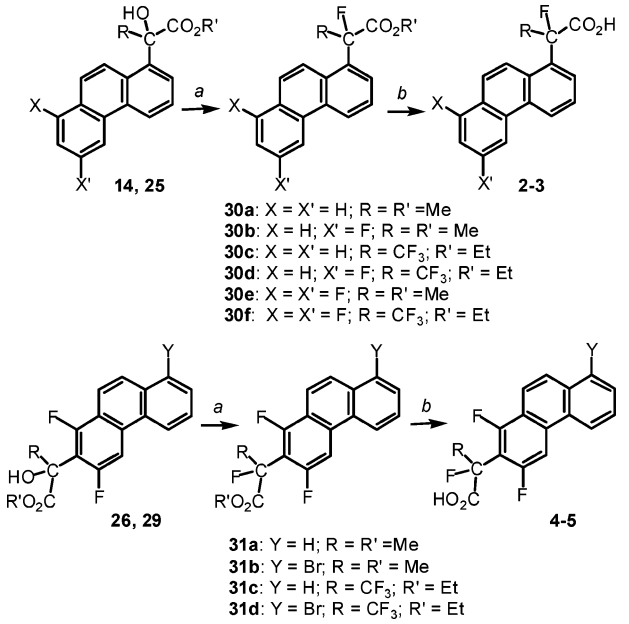


[a] (*a*) 1. BuLi, THF, −110 °C, 10 s; 2. RCOCOOR′; 3. H_3O^+; (*b*) 1. LDA, THF, −50 °C, RCOCOOR′; 3. H_3O^+; (*c*) 1. BuLi, 1.5 equiv, THF, −50 °C, H_2O; (*d*) LDA (or BuLi), THF, −50 °C, RCOCOOR′; 3. H_3O^+; (*e*) 1. BuLi, 2.5 equiv, THF, −75 °C, 2. RCOCOOR′ 2 equiv; 3. H_3O^+.

(20) Indeed, a three-step alternative approach to **12h** could be envisaged consisting of protecting C-7 by the $SiMe_3$ group by reacting **21** with LDA and by quenching the reaction mixture with trimethylchlorosilane, butyllithium-promoted bromine/metal exchange and successive alkylation with methyl pyruvate, and last, removal of TMS group.[21] Unfortunately, this strategy did not fit our case. Deprotection of the silylated intermediate by tetrabutylammonium fluoride in THF resulted in an extended degradation of the hydroxy ester.

(21) Mongin, F.; Schlosser, M. *Tetrahedron Lett.* **1996**, *37*, 6551−6554. Schlosser, M.; Heiss, C. *Eur. J. Org. Chem.* **2003**, 4618−4624.

SCHEME 7[a]



[a] (*a*) DAST, CH_2Cl_2, 0 °C; (*b*) 1. KOH, MeOH, 25 °C; 2. H_3O^+.

Side-chain fluorination of all the above alkyl 2-phenanthryl-2-hydroxypropionates **14**, **25**, **26**, and **29** did not present any surprises. Their reaction with DAST proceeded smoothly in CH_2Cl_2 at 0 °C, as described in the literature, to give the corresponding alkyl 2-fluoro-2-phenanthrylpropionates **30** and **31** in excellent yields (65−93%) (Scheme 7). Finally, the alkaline hydrolysis of the alkyl α-fluoropropionates **30** and **31** under mild conditions allowed the targeted fluoropropionic acids **2**−**5** to be obtained in satisfactory overall yields (76−94%).

With reference to the biological activity of fluorinated analogues of known profens, it has been reported that replacement of an α-hydrogen of the arylpropionic acid by fluorine usually brings about a substantial decrease in antiinflammatory activity; therefore, a drop in biological activity of our side-chain fluorinated 2-phenanthrylpropionic acids is quite probable. On the contrary, numerous examples of increased activity of fluoroaryl-containing drugs compared with the hydrogenated parent, cause us to expect an analogous positive effect from 2-(fluorophenanthryl)propionic acids.[22−24] Biological tests are under way.

Of course, the synthesis of the above fluorinated products is only one applicative example of our strategy. In general, this method provides a valuable access to regioselectively functionalized and fluorinated polycyclic aromatic compounds.

Experimental Section

If not specified otherwise, ^{1}H NMR and ^{1}H-decoupled ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, in $CDCl_3$ solution using tetramethylsilane as an internal standard. ^{19}F NMR spectra were recorded at 376 MHz in $CDCl_3$ solution using $CFCl_3$ as a reference standard. IR spectra were registered in $CHCl_3$ solution in the 4000−625 cm^{-1} range. Gas-chromatographic analyses were performed using 30 m × 0.32 mm capillary columns loaded with two different stationary phases: DB-5 MS (5% phenyl-methylpolysiloxane) and DB-35 MS (5% phenylmethylpolysiloxane) at 70−310 °C. Mass spectra were obtained at 70 eV. Melting points were corrected after calibration performed with authentic standards.

Reagents and Solvents. 3,4-dihydrophenanthren-(2*H*)-1-one (**6a**), 6-fluoro-3,4-dihydrophen-anthren-(2*H*)-1-one (**6b**), and 6,8-difluoro-3,4-dihydrophenanthren-(2*H*)-1-one (**6c**) were available from a previous study.[11] All organic and inorganic reagents of the highest purity were used as purchased. Tetrahydrofuran and diethyl ether were distilled from potassium hydroxide in the presence of cuprous chloride and redistilled from sodium wire in the presence of benzophenone.

Standard Procedure for the Synthesis of Nucleus-Fluorinated Ethyl 2-(Phenanthren-1-yl)propionates (11b,c). The fluorinated phenanthrenones **6b,c** (10.0 mmol) and a solution of ethyl 2-bromopropionate (3.9 g, 21 mmol) in benzene (25 mL) were added to a freshly prepared zinc amalgam (5.0 g) in a 1:1 (v/v) benzene/DEE mixture (50 mL). After addition of iodine (0.050 g, 0.2 mmol), the mixture was refluxed for 90 min. During this time, further zinc amalgam (0.5 g) and an iodine crystal were added every 20 min. The reaction mixture was treated with 5% aq HCl (50 mL), the organic phase was separated, washed with 5% aq NH_3 (50 mL) and then with water (50 mL) and dried with Na_2SO_4. After solvent evaporation, formic acid (30 mL) was added, and the mixture was ref1uxed for 30 min. Water (30 mL) was added, and the mixture was extracted with hexanes (2 × 30 mL). The organic phase was washed with saturated aq Na_2CO_3 (30 mL) and dried with Na_2SO_4. After solvent evaporation, the crude product was dissolved in benzene (10 mL) together with 2,3-dichloro-5,6-dihydrobenzoquinone (DDQ) (2.19 g, 9.7 mmol), and the mixture was made to react for 40 min at 55 °C. Most of the solvent was evaporated, and the remaining brown slurry was passed through a silica gel column (100 mL) by eluting with 9:1 (v/v) hexane/ethyl acetate mixture. They were identified as **ethyl 2-(6-fluorophenanthren-1-yl)propionate** (**11b**) (65% from **6b**) and **ethyl 2-(6,8-difluorophenanthren-1-yl)-propionate** (**11c**) (78% from **6c**) on the basis of their analytical and spectroscopic properties.

11b: (75% from **6b**); viscous oil; ^{1}H NMR (200 MHz) δ 8.58−8.48 (six peaks, X portion of an ABX system, 1 H), 8.32 (dd, J = 11.4 and 2.5 Hz, 1 H), 8.01 (d, J = 9.3 Hz, 1 H), 7.89 (dd, J = 8.8 and 6.0 Hz, 1 H), 7.79 (d, J = 9.3 Hz, 1 H), 7.71−7.54 (7 peaks, AB portion of an ABX system, 2 H), 7.37 (td, J = 8.4 and 2.5 Hz, 1 H), 4.57 (q, J = 7.1 Hz, 1 H), 4.17 (q, J = 7.1 Hz, 2 H), 1.70 (d, J = 7.1 Hz, 3 H), 1.19 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (50 MHz) δ 169.7, 156.5 (d, J = 243 Hz), 132.6, 127.0 (d, J = 8.4 Hz), 125.3 (d, J = 8.8 Hz), 124.9 (d, J = 11.9 Hz), 124.8, 121.5, 121.2, 120.7, 117.0, 115.8, 110.6 (d, J = 23.8 Hz), 102.9 (d, J = 22.3 Hz), 55.8, 36.6, 13.2, 8.9; ^{19}F NMR δ −113.60 (ddd, J = 11.3, 8.0, and 6.0 Hz); IR (CCl_4) ν_{max} 3062 (w), 2983−2868, 1736 (s), 1631 (m), 1602 (m), 1461 (s), 1205 (s), 1192 (s) cm^{-1}; MS *m/z* (%) 299 (M^+, 31), 223 (100), 202 (11), 183 (3). Elem anal. calcd for $C_{19}H_{17}FO_2$: C, 77.01; H, 5.78. Found: C, 76.77; H, 5.83.

(22) The structure was tentatively assigned, with high confidence level, on the basis of the GLC retention time and mass-spectrum analogy of the corresponding hydrogeno-derivative **27a**.

(23) According to the well-established structure of cyclooxygenase (COX),[24] the sickle-shaped phenanthryl moiety could allow the above nucleus-fluorinated phenanthrylpropionic acids to be docked, to some extent, into the COX-2 active pocket with the carboxylic group anchored to Arg 120 and the fluorinated ring placed within the van der Waals contact of Thyr 385. This could bring about a selective inhibition of COX-2 that would avoid ulcerogenic side effects associated with most of the currently NSAIDs.

(24) Picot, D.; Loll, P. J.; Garavito, M. *Nature* **1994**, *367*, 243. See also Soliva, R.; Almansa, C.; Kalko, S. G.; Luque, F. J.; Orozco, M. *J. Med. Chem.* **2003**, *46*, 1372−1382. Palomer, A.; Cabré, F.; Pascual, J.; Campos, J.; Trujillo, M. A.; Entrena, A.; Gallo, M. A.; García, L.; Mauleón, D.; Espinosa, A. *J. Med. Chem.* **2002**, *45*, 1402−1411. Makara, G. M. *J. Med. Chem.* **2001**, *44*, 3563−3571. Palomer, A.; Pérez, J. J.; Navea, S.; Lorenz, O.; Pascual, J.; García, L.; Mauleón, D. *J. Med. Chem.* **2000**, *43*, 2280−2284.

11c: (78% from **6c**); mp 102−103 °C (from ethanol); ^{1}H NMR (200 MHz) δ 8.53−8.45 (six peaks, X portion of an ABX system, 1 H), 8.12 (br d, J = 11.4 Hz, 1 H), 8.05 (A portion of an AB system, J = 9.6 Hz, 1 H), 8.04 (B portion of an AB system, J = 9.6 Hz, 1 H), 7.72−7.63 (7 peaks, AB portion of an ABX system, 2 H), 7.12 (ddd, J = 9.9, 8.6, and 2.3 Hz, 1 H), 4.56 (q, J = 7.1 Hz, 1 H), 4.17 (q, J = 7.1 Hz, 2 H), 1.70 (d, J = 7.1 Hz, 3 H), 1.19 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 174.6, 160.8 (dd, J = 244.6 and 13.0 Hz), 159.5 (dd, J = 251.5 and 13.2 Hz), 138.0, 132.9, 130.3, 129.6, 126.8, 126.4, 122.4, 121.5, 18.6 (d, J = 5.5 Hz), 117.9 (d, J = 15.5 Hz), 104.0 (dd, J = 22.2 and 4.0 Hz), 101.7 (dd, J = 27.6 and 24.4 Hz), 61.0, 41.7, 18.3, 14.1; ^{19}F NMR δ −111.09 (dt, J = 10.7 and 8.0 Hz), −118.48 (t, J = 8.6 Hz); IR (CCl_4) ν_{max} 3078 (w), 2965−2869, 1735 (s), 1637 (s), 1257 (m), 1189 (s), 1113 (s) cm^{-1}; MS *m/z* (%) 314 (M^+, 44), 241 (100), 220 (15), 201 (8). Elem anal. calcd for $C_{19}H_{16}F_2O_2$: C, 72.60; H, 5.13. Found: C, 72.42; H, 5.17.

Synthesis of 1-Bromo-3,4-dihydrophenanthrenes (12a−c). Hydrazine monohydrate (4.1 g, 82 mmol) was added to a solution of the suitable phenanthrenone (20 mmol) in a 1:1 benzene/dry ethanol mixture (60 mL), and the solvent was slowly distilled until the disappearance of the ketone monitored by TLC (after about 40 mL of distilled benzene/ethanol/water mixture). The solvent was further evaporated at reduced pressure (15 mmHg), and the remaining solid was dried at 50 °C/1 mmHg until constant weight. Butyllithium (37.5 mL, 1.6 M in hexanes, 60 mmol) was added dropwise to a solution of *tert*-butyl alcohol (5.0 g, 60 mmol) in anhyd THF (80 mL) at 0 °C under nitrogen atmosphere. After 5 min, $CuBr_2$ (26.8 g, 0.12 mol) was added, and the resulting brown mixture was further stirred for 20 min before a THF (40 mL) solution of the above hydrazone was added dropwise. After 3 h of stirring at 20 °C, water (150 mL) was added, the fine precipitate was filtered on Celite, and the solid was washed with THF (3 × 50 mL). The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 × 100 mL). The collected organic phases were dried with Na_2SO_4, and the solvent was evaporated at reduced pressure. The remaining crude was passed through a SiO_2 column (80 g) by eluting with petroleum ether to get the pure bromodihydrophenanthrene.

1-Bromo-3,4-dihydrophenanthrene (12a): (77%); mp 59−61 °C; ^{1}H NMR (200 MHz) δ 8.06−7.99 (m, 1 H), 7.82 (dd, J = 7.6 and 2.0 Hz, 1 H), 7.82 (d, J = 8.7 Hz, 1 H), 7.74 (d, J = 8.7 Hz, 1 H), 7.57−7.42 (m, 2 H), 6.55 (t, J = 4.9 Hz, 1 H), 3.26 (t, J = 8.2 Hz, 2 H), 2.48 (td, J = 8.9 and 4.9 Hz, 2 H); ^{13}C NMR δ 133.4, 132.2, 132.1, 130.7, 130.0, 128.6, 126.5, 126.3, 125.8, 124.7, 123.6, 121.8, 25.1, 22.7; IR ($CHCl_3$) ν_{max} 3063, 3019, 2945, 2887, 2835, 1612, 1036 cm^{-1}; MS *m/z* (%) 260 (M^+ + 1, 31), 258 (M^+ − 1, 32), 179 (100), 151 (10), 152 (12), 76 (12). Elem anal. calcd for $C_{14}H_{11}Br$: C, 64.89; H, 4.28. Found: C, 64.98; H, 4.19.

1-Bromo-6-fluoro-3,4-dihydrophenanthrene (12b): (68%); mp 80−81°C; ^{1}H NMR δ 7.83 (dd, J = 8.9 and 6.0 Hz, 1H), 7.80−7.74 (four peaks, AB system, J_{AB} = 8.7 Hz, 2H), 7.65 (dd, J = 11.5 and 2.2 Hz, 1H), 7.27 (td, J = 8.7 and 2.4 Hz, 1H), 6.60 (t, J = 4.9 Hz, 1H), 3.20 (t, J = 8.4 Hz, 2H), 2.52 (td, J = 8.7 and 4.9 Hz, 2H); ^{13}C NMR δ 161.1 (d, J = 244.2 Hz), 131.6 (d, J = 8.6 Hz), 131.4 (d, J = 5.9 Hz), 130.9 (d, J = 9.1 Hz), 130.8, 130.6, 130.4 126.4, 124.0 (d, J = 1.8 Hz), 121.5, 116.1 (d, J = 25.4 Hz), 107.2 (d, J = 21.6 Hz), 25.0, 22.7; ^{19}F NMR δ −113.6 (ddd, J = 11.6, 7.6, and 6.3 Hz); IR ($CHCl_3$) ν_{max} 3062, 2946−2835, 1617, 1516, 1200, 1172, 840 cm^{-1}; MS *m/z* (%) 278 (M^+ + 1, 37), 276 (M^+ − 1, 40), 197 (100), 177 (20), 98 (17). Elem anal. calcd for $C_{14}H_{10}BrF$: C, 60.68; H, 3.64. Found: C, 60.81; H, 3.56.

1-Bromo-6,8-difluoro-3,4-dihydrophenanthrene (12c): (72%); mp 91−93 °C; ^{1}H NMR δ 7.94 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.41 (dt, J = 11.0 and 1.1 Hz, 1H), 6.95 (ddd, J = 10.1, 8.7, and 2.3 Hz, 1H), 6.59 (t, J = 4.9, 1H), 3.12 (t, J = 8.4 Hz, 2H), 2.51−2.45 (m, 2H); ^{13}C NMR (50 MHz) δ 160.2 (dd, J = 244.5 and 12.8 Hz), 159.6 (dd, J = 253.4 and 13.4 Hz), 132.0 (d, J = 5.1 Hz), 131.9, 131.3, 124.4, 121.2, 120.9, 120.6, 119.2 (d, J = 4.7 Hz), 103.4 (dd, J = 21.7 and 4.4 Hz), 101.3 (dd, J = 29.4 and 23.9 Hz), 24.9, 21.4; ^{19}F NMR δ −111.3 (dt, J = 11.0 and 8.5 Hz, 1 F), −118.0 (t, J = 8.5 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3091, 2947−2835, 1643, 1222, 1116, 1067 cm^{-1}; MS *m/z* (%) 296 (M^+ + 1, 45), 294 (M^+ − 1, 45), 215 (100), 195 (24), 107 (18). Elem anal. calcd for $C_{14}H_9BrF_2$: C, 56.98; H, 3.07. Found: C, 57.08; H, 3.13.

General Procedure for the Preparation of Alkyl 2-Hydroxy-2-(phenanthren-1-yl)propionates (14a−d). Butyllithium (1.60 M in hexane, 1.25 mL, 2.0 mmol) was added to a solution of bromo derivative **12a** (or **12b**) (2.0 mmo1) in THF (10 mL) at −75 °C under nitrogen atmosphere. After 30 min, methyl pyruvate or ethyl 3,3,3-trifluoropyruvate (2.2 mmol) was added, the co1d bath was removed, and the temperature was allowed to rise at 25 °C. Saturated aq NH_4Cl (30 mL) was added, the mixture was extracted with diethyl ether (3 × 25 mL), and the collected organic phase was dried with Na_2SO_4. After solvent was evaporated, the crude product was dissolved in toluene (50 mL) together with DDQ (3.0 mmol), and the mixture was allowed to react 2 h at 80 °C. The solvent was evaporated at reduced pressure, and the crude solid was passed through a short column of silica gel (eluent, 7:3 petroleum ether/diethyl ether) to collect pure α-hydroxyester.

Methyl 2-hydroxy-2-(phenanthr-1-yl)propionate (14a): (60%); mp 154−155 °C; ^{1}H NMR δ 8.75 (d, J = 8.4 Hz, 1 H), 8.69 (dd, J = 8.1 and 0.5 Hz, 1 H), 8.12 (d, J = 9.3 Hz, 1 H), 7.87 (dd, J = 7.7 and 1.4 Hz, 1 H), 7.78 (dd, J = 7.5 and 1.0 Hz, 1 H), 7.75 (d, J = 9.4 Hz, 1 H), 7.66−7.57 (m, 3 H), 3.67 (s, 3 H), 3.65 (br s, 1 H), 2.05 (s, 3 H); ^{13}C NMR δ 178.0, 137.3, 131.3, 131.3, 130,6, 130.0, 128.3, 127.4, 126.7, 126.6, 125.5, 124.7, 123.7, 123.0, 122.9, 76.2, 53.2, 27.6; IR ($CHCl_3$) ν_{max} 3535, 3020, 2953, 2855, 1729, 1602, 1263, 1222, 1131 cm^{-1}; MS *m/z* (%) 280 (M^+, 37), 221 (92), 205 (12), 176 (25), 43 (100). Elem anal. calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.89; H, 5.81.

Methyl 2-hydroxy-2-(6-fluorophenanthren-1-yl)propionate (14b): (70%); mp 131−132 °C; ^{1}H NMR δ 8.63 (d, J = 8.4 Hz, 1 H), 8.33 (dd, J = 11.3 and 2.3 Hz, 1 H), 8.12 (d, J = 9.3 Hz, 1 H), 7.88 (dd, J = 8.7 and 6.0 Hz, 1 H), 7.83 (d, J = 7.4 Hz, 1 H), 7.76 (d, J = 9.3 Hz, 1 H), 7.67 (t, J = 7.8 Hz, 1 H), 7.38 (td, J = 8.5 and 2.3 Hz, 1 H), 3.71 (s, 3 H), 3.67 (s, 1 H), 2.08 (s, 3 H); ^{13}C NMR δ 177.9, 161.6 (d, J = 243.8 Hz), 137.4, 132.1 (d, J = 8.3 Hz), 130.7 (d, J = 4.2 Hz), 130.5 (d, J = 8.8 Hz), 130.2, 128.0, 127.2, 125.6, 125.3, 123.8, 122.3, 115.9 (d, J = 23.9 Hz), 108.0 (d, J = 22.3 Hz), 76.2, 53.3, 27.6; ^{19}F NMR −113.6 (ddd, J = 11.4, 7.7, and 6.4 Hz); IR ($CHCl_3$) ν_{max} 3537, 3023, 2956, 2848, 1730, 1605, 1458, 1260, 1133, 838 cm^{-1}; MS *m/z* (%) 298 (M^+, 34), 239 (100), 223 (14), 195 (18), 175 (10), 43 (87). Elem anal. calcd for $C_{18}H_{15}FO_3$: C, 72.47; H, 5.07. Found: C, 72.60; H, 5.11.

Ethyl 2-hydroxy-2-(phenanthren-1-yl)-3,3,3-trifluoropropionate (14c): (63%); mp 114−115 °C; ^{1}H NMR δ 8.79 (d, J = 8.5 Hz, 1 H), 8.67 (d, J = 8.2 Hz, 1 H), 8.06 (d, J = 9.4 Hz, 1 H), 7.89−7.85 (m, 2 H), 7.75 (d, J = 9.4 Hz, 1 H), 7.67−7.58 (m, 3 H), 4.53 (br s, 1 H), 4.37−4.15 (sym m, ABX_3 system, 2 H), 1.08 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (50 MHz) δ 170.6, 131.6, 131.2, 130.4, 130.1, 129.3, 128.4, 127.9, 127.0, 126.9, 126.4 (q, J = 2.9 Hz), 125.3, 124.7, 123.7 (q, J = 286.5 Hz), 122.9, 122.3, 80.2 (q, J = 28.6 Hz), 64.3, 13.6; ^{19}F NMR δ −73.0 (s); MS (70 eV) *m/z* (%) 348 (M^+, 45), 275 (80), 205 (37), 178 (100), 88 (13). Elem anal. calcd For $C_{19}H_{15}F_3O_3$: C, 65.52; H, 4.34. Found: C, 65.31; H,4.27.

Ethyl 2-hydroxy-2-(6-fluorophenanthren-1-yl)-3,3,3-trifluoropropionate (14d): (65%); mp 132−134 °C; ^{1}H NMR δ 8.63 (d, J = 8.4 Hz, 1 H), 8.27 (dd, J = 11.3 and 2.3 Hz, 1 H), 8.04 (d, J = 9.4 Hz, 1 H), 7.93 (br d, J = 7.6 Hz, 1 H), 7.84 (dd, J = 8.7 and 6.0 Hz, 1 H), 7.72 (d, J = 9.4 Hz, 1 H), 7.64 (t, J = 8.1 Hz, 1 H), 7.36 (td, J = 8.5 and 2.4 Hz, 1 H), 4.58 (s, 1H), 4.36 (dq, J = 10.7 and 7.1 Hz, 1 H), 4.22 (dq, J = 10.7 and 7.1 Hz, 1 H), 1.11 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 170.4, 161.7 (d, J = 244.3 Hz), 131.9 (d, J = 8.4 Hz), 130.9 (d, J = 4.2 Hz), 130.5 (d, J = 8.8 Hz), 130.4, 129.4, 127.9, 127.2, 127.0

(d, J = 2.8 Hz), 125.4, 124.8, 123.6 (q, J = 286.5 Hz), 121.6, 116.1 (d, J = 23.8 Hz), 108.0 (d, J = 22.5 Hz), 80.1 (q, J = 28.6 Hz), 64.3, 13.6; ^{19}F NMR δ −73.1 (s, 3 F), −113.6 (ddd, J = 12.1, 8.2, and 6.8 Hz, 3 F); IR ($CHCl_3$) ν_{max} 3574, 3501, 3032, 2988, 2940, 1739, 1602, 1464, 1251, 1171, 994, 838 cm^{-1}; MS m/z (%) 366 (M^+, 50), 293 (77), 223 (30), 196 (100). Elem anal. calcd for $C_{19}H_{14}F_4O_3$: C, 62.30; H, 3.85. Found: C, 62.21; H, 3.78.

Products from the Reaction of 1-Bromo-6,8-difluoro-2,3-dihydrophenanthrene with Butyllithium and Successive Alkylation with Either Methyl Pyruvate or Ethyl Trifluoropyruvate. Butyllithium (1.60 M in hexane, 1.3 mL, 2.0 mmol) was added to a solution of **12c** (2.0 mmo1) in THF (10 mL) at −98 °C under nitrogen atmosphere. After 90 min, methyl pyruvate (1.5 equiv) was added, and the temperature was allowed to rise at 25 °C. Water (20 mL) was added, the mixture was extracted with diethyl ether (3 × 10 mL), and the collected organic phases were dried with Na_2SO_4. After the solvent was evaporated, chromatography of the crude product on silica gel (eluent, 7:3 petroleum ether/diethyl ether) allowed five products to be separated that were identified as follows on the basis of the following spectroscopic and analytical characteristics.

Methyl 2-(6,8-difluoro-3,4-dihydrophenanthren-1-yl)-2-hydroxypropionate (15a): (7%); mp 116−118 °C; ^{1}H NMR δ 7.87−7.66 (AB system, J = 9.0 Hz, 2 H), 7.45 (d, J = 11.3 Hz, 1 H), 6.91 (ddd, J = 10.4, 8.8, and 2.2 Hz, 1 H), 6.45 (t, J = 4.8 Hz, 1 H), 3.69 (s, 3 H), 3.51(s, 1 H), 3.04 (t, J = 8.2 Hz, 2 H), 2.44 (dd, J = 8.2 and 4.9 Hz, 2 H), 1.76 (s, 3 H); ^{13}C NMR δ 177.6, 160.0 (dd, J = 244.0 and 12.9 Hz), 159.6 (dd, J = 253.0 and 13.5 Hz), 137.2, 132.7 (dd, J = 9.7 and 6.0 Hz), 131.9 (dd, J = 5.8 and 2.6 Hz), 128.6, 122.4, 119.9 (d, J = 16.1 Hz), 118.5 (d, J = 4.7 Hz), 103.5 (dd, J = 21.4 and 4.1 Hz), 100.6 (dd, J = 29.3 and 24.0 Hz), 75.8, 53.2, 26.7, 23.2, 22.7; ^{19}F NMR δ −118.8 (t, J = 8.7 Hz, 1 F), −112.3 (q, J = 9.2 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3693, 3027, 2954−2837, 1729, 1640, 1404, 1241, 1116, 991, 848 cm^{-1}; MS m/z (%) 318 (M^+, 53), 301 (7), 259 (100), 241 (12), 215 (30), 201 (20); Elem anal. calcd for $C_{18}H_{16}F_2O_3$: C, 67.92; H, 5.07. Found: C, 67.73; H, 5.14.

Methyl 2-(8-bromo-1,3-difluoro-5,6-dihydrophenanthren-2-yl)-2-hydroxypropionate (16a): (16%); mp 121−122 °C; ^{1}H NMR δ 7.96−7.78 (AB system, J_{AB} = 8.9 Hz, 2 H), 7.43 (d, J = 14.0 Hz, 1 H), 6.59 (t, J = 4.9 Hz, 1 H), 4.00 (s, 1 H), 3.83 (s, 3 H), 3.10 (t, J = 8.18, 2 H), 2.47 (td, J = 8.5, 4.9 Hz, 2 H), 2.04 (dd, 4.2 and 1.5 Hz, 3 H); ^{13}C NMR δ 175.9, 159.0 (dd, J = 246.6 and 9.2 Hz), 157.2 (dd, J = 255.9 and 9.2 Hz), 132.3, 131.6, 130.9 (dd, J = 5.9 and 3.0 Hz), 130.8 (dd, J = 11.4 and 6.5 Hz), 124.8, 121.2 (d, J = 18.5 Hz), 121.0, 119.7 (d, J = 8.1 Hz), 115.1 (dd, J = 18.5 and 13.6 Hz), 104.4 (dd, J = 24.5 and 3.7 Hz), 73.4, 53.5, 26.4 (dd, J = 8.1 and 3.3 Hz), 24.9, 22.7; ^{19}F NMR δ −118.2 (t, J = 8.7 Hz, 1 F), −113.1 (dd, J = 13.5 and 4.0 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3525, 3023, 2955−2836, 1742, 1644, 1498, 1259, 1230, 1138 cm^{-1}; MS m/z (%) 398 (M^+ + 1, 10), 396 (M^+ − 1, 10), 339 (93), 337 (100), 257 (9), 207 (14). Elem anal. calcd for $C_{18}H_{15}BrF_2O_3$: C, 54.43; H, 3.81. Found: C, 54.32; H, 3.73.

Methyl 2-(1,3-difluoro-5,6-dihydrophenanthren-2-yl)-2-hydroxypropionate (17a): (54%); mp 101−103 °C; ^{1}H NMR δ 7.87 (d, J = 8.6 Hz, 1 H), 7.41 (d, J = 14.2 Hz, 1 H), 7.20 (d, J = 8.6 Hz, 1 H), 6.54 (dt, J = 9.5 and 1.7 Hz, 1 H), 6.17 (dt, J = 9.5 and 4.3 Hz, 1 H), 3.99 (s, 1 H), 3.82 (s, 3 H), 3.05 (t, J = 8.8 Hz, 2 H), 2.45 (tdd, J = 8.8, 4.4, and 1.8 Hz, 2 H), 2.03 (dd, J = 4.1 and 1.6 Hz, 3 H); ^{13}C NMR δ 176.0, 158.8 (dd, J = 245.7 and 9.4 Hz), 157.3 (dd, J = 255.0 and 9.3 Hz), 133.3, 131.5 (dd, J = 11.0 and 6.8 Hz), 129.9, 129.0 (dd, J = 5.6 and 2.8 Hz), 127.8, 125.3, 120.7 (d, J = 18 Hz), 119.4 (d, J = 8.2 Hz), 114.2 (dd, J = 18.4 and 13.9 Hz), 103.9 (dd, J = 24.2 and 3.7 Hz), 73.4, 53.4, 26.4 (dd, J = 4.6 and 2.9 Hz), 22.8, 22.5; ^{19}F NMR δ −114.1 (d, J = 13.9 Hz, 1 F), −118.7 (s, 1 F); IR ($CHCl_3$) ν_{max} 3524, 3024, 2953−2834, 1742, 1642, 1256, 1232, 1138, 1017, 848 cm^{-1}; MS m/z (%) 318 (M^+, 12), 259 (100), 43 (21). Elem anal. calcd for $C_{18}H_{16}F_2O_3$: C, 67.92; H, 5.07. Found: C, 68.09; H, 4.98.

Methyl 2-[1,3-difluoro-5,6-dihydro-8-(1-hydroxy-1-methoxycarbonylethyl)phenanthren-2-yl]-2-hydroxypropionate (18a): (<1%); mp 143−145 °C; ^{1}H NMR δ 7.86−7.67 (AB system, J_{AB} = 8.9 Hz, 2 H), 7.45 (d, J = 14.3 Hz, 1 H), 6.44 (t, J = 7.7 Hz, 1 H), 4.01 (s, 1 H), 3.80 (s, 3 H), 3.66 (s, 3 H), 3.52 (s, 1 H), 3.00 (t, J = 7.7 Hz, 2 H), 2.42 (m, 2 H), 2.01 (d, J = 2.5 Hz, 3 H), 1.74 (s, 3 H); ^{13}C NMR δ 177.5, 176.0, 158.6 (dd, J = 245.5 and 9.3 Hz), 157.1 (dd, J = 255.6 and 9.6 Hz), 137.05, 132.8, 132.7, 131.3 (dd, J = 11.8 and 6.0 Hz), 128.7, 122.8, 120.3 (d, J = 18.0 Hz), 119.0 (d, J = 8.4 Hz), 114.4 (dd, J = 19.0 and 13.6 Hz), 104.4 (d, J = 23.7 Hz), 75.7, 73.4, 53.4, 26.6, 26.3 (dd, J = 7.2 and 2.4 Hz), 22.9, 22.6; ^{19}F NMR δ −118.8 (d, J = 13.0 Hz, 1 F), −114.2 (s, 1 F); IR ($CHCl_3$) ν_{max} 3529, 3023, 2955−2839, 1737, 1643, 1261, 1136 cm^{-1}; MS m/z (%) 420 (M^+, 10), 361 (100), 207 (23). Elem anal. calcd for $C_{22}H_{22}F_2O_6$: C, 62.85; H, 5.27. Found: C, 62.98; H, 5.31.

6,8-Difluoro-3,4-dihydrophenanthrene (19): (14%); mp 49−50 °C; ^{1}H NMR δ 7.89 (d, J = 8.5 Hz, 1 H), 7.41 (br d, J = 11.1 Hz, 1 H), 7.20 (d, J = 8.5 Hz, 1 H), 6.91 (ddd, J = 10.3, 8.7, and 2.3 Hz, 1 H), 6.56 (dt, J = 9.5 and 1.8 Hz, 1 H), 6.18 (dt, J = 9.5 and 4.4 Hz, 1 H), 3.09 (t, J = 8.8 Hz, 2 H), 2.48 (tdd, J = 8.9, 4.4, and 1.8 Hz, 2 H); ^{13}C NMR δ 160.0 (dd, J = 244 and 12.9 Hz), 159.6 (dd, J = 253 and 13.6 Hz), 133.0, 132.8 (dd, J = 9.9 and 5.9 Hz), 129.6, 129.4 (dd, J = 6.2 and 3.1 Hz), 127.9, 124.8, 120.3 (d, J = 15.6 Hz), 118.9 (d, J = 5.7 Hz), 103.0 (dd, J = 21.3 and 4.3 Hz), 100.3 (dd, J = 29.3 and 24.1 Hz), 22.9, 22.7; ^{19}F NMR δ −112.25 (dt, J = 11.0 and 8.3 Hz, 1 F), −118.59 (dd, J = 10.0 and 8.0 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3083, 3042, 2935−2834, 1645, 1634, 1517, 1401, 1245, 1115 cm^{-1}; MS m/z (%) 216 (M^+, 100), 201 (52), 188 (15), 107 (8). Elem anal. calcd for $C_{14}H_{10}F_2$: C, 77,77; H, 4.66. Found: C, 77.57; H, 4.59.

In a second experiment, using a precooled syringe, samples of the reaction mixture (200 μL) were taken at different reaction times (5, 20, 35, and 90 min) and poured into a solution of methyl pyruvate (1.5 equiv) in THF (5 mL). Water (20 mL) was added, the mixture was extracted with diethyl ether (3 × 10 mL), and the collected organic phases were analyzed by GLC after calibration with known amounts of pure products.

In the same way, the corresponding hydroxytrifluoropyruvates were obtained by just replacing methyl pyruvate by ethyl 3,3,3-trifluoropyruvate as alkylating reagent. They were characterized as follows.

Ethyl 2-(6,8-difluoro-3,4-dihydrophenanthren-1-yl)-2-hydroxy-3,3,3-trifluoropropionate (15b): (6%); mp 77−79 °C; ^{1}H NMR δ 7.87−7.61 (AB system, J_{AB} = 9.0 Hz, 2 H), 7.46 (d, J = 11.3 Hz, 1 H), 6.94 (ddd, J = 10.3, 8.3, 2.0 Hz, 1 H), 6.73 (br s, 1 H), 4.30 (s, 1 H), 4.20 (sym m, 2 H), 3.14 (dt, J = 15.8 and 6.8 Hz, 1 H), 2.95 (ddd, J = 15.8, 12.6, and 6.8 Hz, 1 H), 2.54−2.38 (m, 2 H), 1.01 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 169.8, 160.1 (dd, J = 244.0 and 12.7 Hz), 159.5 (dd, J = 253.3 and 13.5 Hz), 132.4, 131.3, 129.9, 127.5, 124.7, 123.2 (q, J = 286.4 Hz), 121.8, 120.1 (d, J = 16.0 Hz), 118.7, 103.5 (dd, J = 21.6 and 4.3 Hz), 101.0 (dd, J = 29.3 and 23.9 Hz), 79.4 (q, J = 28.6 Hz), 64.1, 22.8 (2 C), 13.5; ^{19}F NMR δ −118.5 (t, J = 8.7 Hz, 1 F), 111.8 (q, J = 8.7 Hz, 1 F), −73.2 (s, 3 F); IR ($CHCl_3$) ν_{max} 3692, 3496, 3090, 3027, 2985−2834, 1741, 1641, 1599, 1249, 1177, 1116, 897, 849 cm^{-1}; MS m/z (%) 386 (M^+, 100), 313 (47), 243 (37), 215 (67). Elem anal. calcd for $C_{19}H_{15}F_5O_3$: C, 59.07; H, 3.91. Found: C, 58.96; H, 4.03.

Ethyl 2-(8-bromo-1,3-difluoro-5,6-dihydrophenanthren-2-yl)-2-hydroxy-3,3,3-trifluoropropionate (16b): (15%); viscous oil; ^{1}H NMR δ 7.98−7.80 (AB system, J_{AB} = 8.9 Hz, 2 H), 7.48 (d, J = 14.5 Hz, 1 H), 6.61 (t, J = 4.8 Hz, 1 H), 4.64 (br s, 1 H), 4.49−4.31 (m, 2 H), 3.10 (t, J = 8.6 Hz, 2 H), 2.48 (td, J = 8.6 and 4.8 Hz, 2 H), 1.30 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 168.0, 157.9 (dd, J = 247.5 and 8.0 Hz), 157.1 (dd, J = 259.0 and 8.0 Hz), 133.0, 132.2, 131.6 (dd, J = 11.2 and 6.8 Hz), 130.9 (dd, J = 6.0 and 2.8 Hz), 125.2, 123.9, 122.8 (q, J =

284.0 Hz), 120.8 (t, J = 9.8 Hz), 120.0 (d, J = 7.1 Hz), 108.7 (dd, J = 18.6 and 14.9 Hz), 104.7 (dd, J = 24.6 and 4.2 Hz), 76.2 (q, J = 32.5 Hz), 63.7, 24.8, 22.6, 13.7; ^{19}F NMR δ −114.5 (q, J = 24.2 Hz, 1 F), −112.5 (quint, J = 11.8 Hz, 1 F), −75.6 (dd, J = 24.2 and 10.8 Hz, 3 F); IR ($CHCl_3$) ν_{max} 3588, 3481, 3024, 2987−2837, 1755, 1644, 1296, 1174, 1120, 1024 cm^{-1}; MS *m/z* (%) 466 (M^+ + 1, 53), 464 (M^+ − 1, 53), 393 (93), 391 (93), 323 (100), 321 (99), 293 (10), 241 (19), 214 (84). Elem anal. calcd for $C_{19}H_{14}BrF_5O_3$: C, 49.05; H, 3.03. Found: C, 49.11; H, 3.12.

Ethyl 2-(1,3-difluoro-5,6-dihydrophenanthren-2-yl)-2-hydroxy-3,3,3-trifluoropropionate (17b): (48%); viscous oil; ^{1}H NMR δ 7.91 (d, J = 8.6 Hz, 1 H), 7.47 (d, J = 14.3 Hz, 1 H), 7.24 (d, J = 8.6 Hz, 1 H), 6.55 (dt, J = 9.6 and 1.8 Hz, 1 H), 6.21 (dt, J = 9.5 and 4.4 Hz, 1 H), 4.59 (t, J = 2.0 Hz, 1 H), 4.48−4.35 (sym m, 2 H), 3.07 (t, J = 8.8 Hz, 2 H), 2.48 (tdd, J = 8.9, 4.4, and 1.8 Hz, 2 H), 1.31 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 168.0, 157.7 (dd, J = 246.6 and 8.2 Hz), 157.2 (dd, J = 258.0 and 8.2 Hz), 134.2, 132.3, (dd, J = 10.9 and 7.0 Hz), 130.5, 129.1 (dd, J = 5.4 and 3.0 Hz), 127.6, 122.9 (q, J = 284.0 Hz), 120.3 (d, J = 17.7 Hz), 119.6 (t, J = 8.3 Hz), 107.6 (dd, J = 18.2 and 15.2 Hz), 104.2 (dd, J = 24.1 and 3.6 Hz), 74.6 (q, J = 32.5 Hz), 64.1, 22.8, 22.4 13.6; ^{19}F NMR δ −115.2 (q, J = 23.0 Hz, 1 F), −113.6 (q, J = 11.2 Hz, 1 F), −75.7 (dd, J = 23.0 and 11.2 Hz, 3 F); IR ν_{max} 3593, 3481, 3032, 2942−2835, 1755, 1643, 1295, 1229, 1171 cm^{-1}; MS *m/z* (%) 386 (M^+, 56), 313 (96), 243 (100), 214 (21). Elem anal. calcd for $C_{19}H_{15}F_5O_3$: C, 59.07; H, 3.91. Found: C, 59.18; H, 4.02.

8-Bromo-1,3-difluorophenanthrene (24). To a solution of **12c** (2.9 g, 10 mmol) in toluene (60 mL) was added DDQ (3.6 g, 16 mmol), and the mixture was stirred for 5 h at 90 °C. The solvent was evaporated at reduced pressure (15 mmHg), and the remaining crude was passed through a short SiO_2 column by eluting with petroleum ether to collect pure **24** as white flat crystals (1.9 g, 65%): mp 141−143 °C; ^{1}H NMR δ 8.34 (d, J = 8.3 Hz, 1 H), 8.09 (d, J = 9.3 Hz, 1 H), 7.93 (d, J = 9.0 Hz, 2 H), 7.87 (d, J = 7.6 Hz, 1 H), 7.42 (t, J = 7.9 Hz, 1 H), 7.08 (td, J = 9.5 and 1.7 Hz, 1 H); ^{13}C NMR δ 161.0 (dd, J = 245.7 and 12.9 Hz), 159.6 (dd, J = 252.4 and 13.2 Hz), 132.1 (dd, J = 9.7 and 5.7 Hz), 131.8, 131.1, 130.6 (dd, J = 4.4 and 3.0 Hz), 127.3, 125.0, 123.9, 122.7, 119.7 (dd, J = 6.4 and 1.3 Hz), 118.4 (dd, J = 15.6 and 1.9 Hz), 104.0 (dd, J = 22.4 and 4.2 Hz), 102.3 (dd, J = 27.7 and 24.2 Hz); ^{19}F NMR δ −110.3 (q, J = 8.7 Hz, 1 F), −117.7 (t, J = 8.7 Hz, 1 F); IR ν_{max} 3082, 1637, 1521, 1437, 1126, 998, 850 cm^{-1}; MS *m/z* (%) 294 (M^+ + 1, 100), 292 (M^+ − 1, 93), 213 (35), 212 (47), 193 (39), 106 (17). Elem anal. calcd for $C_{14}H_7BrF_2$: C, 57.37; H, 2.41. Found: C, 57.29; H, 2.48.

Products from the Reaction of 8-Bromo-1,3-difluorophenanthrene with Butyllithium and Subsequent Alkylation with Methyl Pyruvate and Ethyl Trifluoropyruvate. The procedure was identical to that used in the reaction of butyllithium with **12c**. After 90 min, usual workup and chromatography of the crude product on silica gel (eluent 7:3 petroleum ether/diethyl ether mixture) allowed five products to be separated that were identified by their analytical and spectroscopic characteristics as follows.

Methyl 2-(6,8-difluorophenanthren-1-yl)-2-hydroxypropionate (25a): (46%); mp 149−151 °C; ^{1}H NMR δ 8.56 (d, J = 8.5 Hz, 1 H), 8.13 (d, J = 9.6 Hz, 1 H), 8.10 (br d, J = 11.1 Hz, 1 H), 7.96 (d, J = 9.6 Hz, 1 H), 7.83 (dd, J = 7.5 and 0.9 Hz, 1 H), 7.66 (dd, J = 8.3 and 7.6 Hz, 1 H), 7.09 (ddd, J = 9.9 Hz, 8.7 and 2.3 Hz, 1 H), 3.69 (s, 3 H), 3.66 (s, 1 H), 2.05 (s, 3 H); ^{13}C NMR δ 117.8, 160.7 (dd, J = 224.6 and 12.9 Hz), 159.5 (dd, J = 251.8 and 13.3 Hz), 137.6, 132.8 (dd, J = 9.7 and 5.8 Hz), 130.6, 130.0 (t, J = 3.4 Hz), 126.0, 125.9, 124.1, 122.8, 118.7 (d, J = 5.4 Hz), 117.8 (d, J = 15.7 Hz), 104.0 (dd, J = 22.3 and 4.0 Hz), 101.9 (dd, J = 27.7 and 24.3 Hz), 76.1, 53.4, 27.6; ^{19}F NMR δ −111.1 (dd, J = 10.9 and 8.0 Hz), −118.5 (t, J = 8.6 Hz); IR ($CHCl_3$) ν_{max} 3538, 3025, 2956, 2849, 1730, 1261, 1128, 810 cm^{-1}; MS *m/z* (%) 316 (M^+, 37), 257 (100), 241 (12), 193 (11), 43 (66). Elem anal. calcd for $C_{18}H_{14}F_2O_3$: C, 68.35; H, 4.46. Found: C, 68.52; H, 4.39.

Methyl 2-(8-bromo-1,3-difluorophenanthren-2-yl)-2-hydroxypropionate (29a): (1%); mp 160−162 °C; ^{1}H NMR δ 8.26 (d, J = 8.4 Hz, 1 H), 8.04 (d, J = 9.5 Hz, 1 H), 7.90 (d, J = 13.9 Hz, 1 H), 7.87 (d, J = 9.5 Hz, 1 H), 7.84 (d, J = 8.1 Hz, 1 H), 7.39 (t, J = 8.0 Hz, 1 H), 4.13 (s, 1 H), 3.85 (s, 3 H), 2.07 (dd, J = 3.6 and 2.1 Hz, 3 H); ^{13}C NMR δ 175.8, 154.9 (dd, J = 247.4 and 9.3 Hz), 157.2 (dd, J = 254.6 and 9.1 Hz), 131.9, 130.9 (d, J = 11.2 and 6.5 Hz), 130.9, 129.9 (dd, J = 4.4 and 2.8 Hz), 127.3, 125.3 (t, J = 2.4 Hz), 123.7, 122.5, 119.7 (dd, J = 9.1 and 1.9 Hz), 118.7 (dd, J = 17.6 and 1.8 Hz), 116.3 (dd, J = 17.6 and 14.2 Hz), 104.7 (dd, J = 25.4 and 4.0 Hz), 73.3, 53.6, 26.4 (dd, J = 7.1 and 4.0 Hz); ^{19}F NMR δ −111.5 (dd, J = 13.4 and 3.2 Hz, 1 F), −117.8 (s, 1 F); IR ($CHCl_3$) ν_{max} 3524, 3023, 2956−2848, 1743, 1641, 1255, 1137 cm^{-1}; MS *m/z* (%) 396 (M^+ + 1, 8),394 (M^+ − 1, 10), 337 (100), 335 (100), 257 (13), 212 (22), 43 (46). Elem anal. calcd for $C_{18}H_{13}BrF_2O_3$: C, 54.71; H, 3.32. Found: C, 54.55; H, 3.42.

Methyl 2-(1,3-difluorophenanthren-2-yl)-2-hydroxypropionate (26a): (31%); mp 122−124 °C; ^{1}H NMR δ 8.48−8.45 (m, 1 H), 8.08 (d, J = 13.3 Hz, 1 H), 7.93 (d, J = 9.1 Hz, 1 H), 7.91−7.87 (m, 1 H), 7.76 (d, J = 9.1 Hz, 1 H), 7.69−7.63 (m, 2 H), 4.03 (s, 1 H), 3.84 (s, 3 H), 2.07 (dd, J = 3.6 and 2.2 Hz, 3 H); ^{13}C NMR δ 176.0, 159.2 (dd, J = 246.6 and 9.2 Hz), 157.3 (dd, J = 253.6 and 9.0 Hz), 132.5, 131.5 (dd, J = 11.0 and 6.7 Hz), 128.8, 128.5, 127.9, 127.1, 127.0, 123.0, 118.8 (d, J = 17.3 Hz), 118.3 (d, J = 8.9 Hz), 115.7 (dd, J = 17.1 and 14.6 Hz), 104.6 (dd, J = 24.9 and 3.3 Hz), 73.4, 53.5, 26.4 (d, J = 4.0 Hz); ^{19}F NMR δ −112.6 (br d, J = 13.8 Hz), −118.3 (br s); IR ($CHCl_3$) ν_{max} 3524, 3023, 2956, 2850, 1742, 1640, 1260, 1140, 814 cm^{-1}; MS *m/z* (%) 316 (M^+, 14), 257 (100), 241 (7), 209 (11). Elem anal. calcd for $C_{18}H_{14}F_2O_3$: C, 68.35; H, 4.46. Found: C, 68.62; H, 4.54.

Methyl 2-[6,8-Difluoro-7-(1-hydroxy-1-methoxycarbonylethyl)phenanthren-1-yl]-2-hydroxypropionate (27a): (<1%); mp 181 °C dec; ^{1}H NMR (acetone-d_6) δ 8.76 (d, J = 8.4 Hz, 1 H), 8.37 (d, J = 14.1 Hz, 1 H), 8.30 (d, J = 9.6 Hz, 1 H), 7.96 (d, J = 7.5 Hz, 1 H), 7.93 (d, J = 9.6 Hz, 1 H), 7.72 (t, J = 8.3 Hz, 1 H), 3.76 (s, 3 H), 3.59 (s, 3 H), 3.2 (very br, 2 H), 1.99 (s, 3 H), 1.97 (dd, J = 2.8 and 1.9 Hz, 3 H); ^{13}C NMR (acetone-d_6) δ 176.1, 174.6 (d, J = 3.1 Hz), 159.3 (dd, J = 250 and 9.5 Hz), 156.8 (dd, J = 257 and 9.5 Hz), 139.8, 131.6 (dd, J = 11.2 and 6.5 Hz), 130.4, 129.4 (dd, J = 6.2 and 3.1 Hz), 126.5, 125.7, 124.3 (t, J = 2.5 Hz), 123.6, 117.9 (d, J = 17.8 Hz), 117.6 (d, J = 8.0 Hz), 112.6, 105.0 (dd, J = 25.6 and 3.5 Hz), 75.7, 73.3, 52.2, 51.9, 26.9, 26.1 (dd, J = 6.1 and 3.6 Hz); ^{19}F NMR (acetone-d_6) δ −112.8 (m), −120.15 (br d, J = 16.6 Hz); IR ($CHCl_3$) ν_{max} 3690, 3525, 3040, 2956, 2852, 1740, 1602, 1262, 1134 cm^{-1}; MS *m/z* (%) 418 (M^+, 9), 359 (100), 299 (7), 239 (11), 43 (17). Elem anal. calcd for $C_{22}H_{20}F_2O_6$: C, 63.16; H, 4.82. Found: C, 63.38; H, 4.95.

1,3-Difluorophenanthrene (28): (6%); mp 90−92 °C; ^{1}H NMR δ 8.51−8.46 (m, 1 H), 8.07 (br d, J = 10.7 Hz, 1 H), 7.95 (d, J = 9.1 Hz, 1 H), 7.92−7.87 (m, 1 H), 7.73 (d, J = 9.1 Hz, 1 H), 7.69−7.62 (m, 2 H), 7.09 (ddd, J = 10.1, 8.7, and 2.3 Hz, 1 H); ^{13}C NMR δ 160.8 (dd, J = 245 and 12.9 Hz), 159.6 (dd, J = 251 and 13.0 Hz), 132.6 (dd, J = 9.7 and 5.8 Hz), 132.5, 129.0 (dd, J = 4.8 and 2.9 Hz), 128.8, 127.7, 127.0, 126.5, 123.0, 118.4 (dd, J = 5.5 and 2.3 Hz), 118.2 (dd, J = 6.5 and 1.6 Hz), 103.7 (dd, J = 22.3 and 4.2 Hz), 101.7 (dd, J = 28.0 and 24.3 Hz); ^{19}F NMR δ −111.51 (q, J = 9.0 Hz, 1 F), −118.24 (t, J = 9.0 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3059, 1638, 1604, 1529, 1118, 996, 852, 820 cm^{-1}; MS *m/z* (%) 214 (M^+, 100), 193 (7), 107 (8), 94 (7). Elem anal. calcd for $C_{14}H_8F_2$: C, 78,50; H, 3.76. Found: C, 78.48; H, 3.69.

GLC analysis of the reaction products at variable reaction times was performed in the same way as described above for the reaction of the bromodihydrophenanthrene **12c**.

In the same way, the following 2-hydroxy-2-(phenanthryl)-3,3,3-trifluoropropionates were obtained by just replacing

methyl pyruvate by ethyl 3,3,3-trifluoropyruvate as alkylating reagent. They were identified as follows.

Ethyl 2-(6,8-difluorophenanthren-1-yl)-2-hydroxy-3,3,3-trifluoropropionate (25b): (39%); mp 124−126 °C; ^{1}H NMR δ 8.55 (d, J = 8.5 Hz, 1 H), 8.09 (d, J = 9.6 Hz, 1 H), 8.03 (d, J = 10.8 Hz, 1 H), 7.94 (d, J = 9.5 Hz, 2 H), 7.63 (t, J = 8.0 Hz, 1 H), 7.08 (ddd, J = 9.8, 8.7, and 2.2 Hz, 1 H), 4.63 (s, 1 H), 4.41−4.19 (sym m, 2 H), 1.12 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 170.3, 160.9 (dd, J = 245.3 and 12.9 Hz), 159.4 (dd, J = 252.2 and 13.3 Hz), 132.6 (dd, J = 9.8 and 5.6 Hz), 130.7, 130.2 (dd, J = 4.4 and 3.0 Hz), 129.7, 127.5 (q, J = 3.1 Hz), 125.8, 125.0, 123.6 (q, J = 286.4 Hz), 122.0, 119.2 (d, J = 5.0 Hz), 117.7 (dd, J = 15.6 and 1.6 Hz), 104.0 (dd, J = 22.5 and 4.2 Hz), 102.1 (dd, J = 27.7 and 24.0 Hz), 80.1 (q, J = 28.7 Hz), 64.4, 13.4; ^{19}F NMR δ −73.1 (s, 3 F), −110.5 (q, J = 8.5 Hz, 1 F), −118.3 (t, J = 8.5 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3500, 3227, 3025, 2986−2872, 1740, 1639, 1258, 1207, 1177, 1118, 1006, 809 cm^{-1}; MS *m/z* (%) 384 (M^+, 41), 311 (67), 241 (31), 214 (100), 193 (11), 106 (4). Elem anal. calcd for $C_{19}H_{13}F_5O_3$: C, 59.38; H, 3.41. Found: C, 59.21; H, 3.48.

Ethyl 2-(1,3-difluorophenanthren-2-yl)-2-hydroxy-3,3,3-trifluoropropionate (26b): (32%, from the reaction of **24** with butyllithium at −98 °C in THF followed by quenching the reaction mixture with ethyl trifluoropyruvate 90 min after; 63%, as the only reaction product from the reaction of **21** with LDA or butyllithium at −50 °C followed by quenching with methyl pyruvate 1 h after): mp 99−101 °C; ^{1}H NMR δ 8.38 (m, 1 H), 8.04 (d, J = 13.8 Hz, 1 H), 7.88−7.84 (m, 2 H), 7.71−7.62 (m, 3 H), 4.69 (t, J = 1.9 Hz, 1 H), 4.52−4.38 (sym m, 2 H), 1.32 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 168.1, 158.3 (dd, J = 247.8 and 8.1 Hz), 157.1 (dd, J = 256.2 and 7.8 Hz), 132.7, 132.6 (dd, J = 11.2 and 7.0 Hz), 128.8, 128.4, 128.2 (dd, J = 3.9 and 2.9 Hz), 127.5, 127.3, 123.0, 122.9 (q, J = 284.2 Hz), 118.4, 118.1 (d, J = 7.9 Hz), 109.2 (dd, J = 17.0 and 15.3 Hz), 104.8 (dd, J = 25.0 and 3.9 Hz), 76.3 (q, J = 32.5 Hz), 64.5, 14.1; ^{19}F NMR δ −75.5 (dd, J = 21.9 and 13.0 Hz, 3 F), −111.9 (quint, J = 13.0 Hz, 1 F), −115.2 (q, J = 21.9 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3479, 3231, 3023, 2988−2870, 1755, 1641, 1290, 1245, 1174, 1121, 1023, 815 cm^{-1}; MS *m/z* (%) 384 (M^+, 37), 311 (62), 292 (4), 241 (100), 213 (22), 193 (11), 106 (6). Elem anal. calcd for $C_{19}H_{13}F_5O_3$: C, 59.38; H, 3.41. Found: C, 59.48; H, 3.32.

Ethyl 2-(8-bromo-1,3-difluorophenanthren-2-yl)-2-hydroxy-3,3,3-trifluoropropanoate (29b): (∼1%); mp 98−100 °C; ^{1}H NMR δ 8.41 (d, J = 8.3 Hz, 1 H), 8.20 (d, J = 9.4 Hz, 1 H), 8.08 (d, J = 13.7 Hz, 1 H), 8.00 (d, J = 9.4 Hz, 1 H), 7.96 (d, J = 7.4 Hz, 1 H), 7.52 (t, J = 8.0 Hz, 1 H), 4.66 (br s, 1 H), 4.54−4.40 (sym m, 2 H), 1.34 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 168.0, 158.6 (dd, J = 249 and 8.0 Hz), 157.1 (dd, J = 257 and 7.8 Hz), 132.5, 132.3 (dd, J = 11.2 and 6.7 Hz), 131.4, 129.8 (dd, J = 4.0 and 2.9 Hz), 127.7, 126.1, 122.8 (q, J = 284 Hz), 122.7, 119.8 (d, J = 7.8 Hz), 118.7 (d, J = 17.6 Hz), 110.1 (dd, J = 17.2 and 15.2 Hz), 105.2 (dd, J = 25.3 and 3.9 Hz), 76.3 (q, J = 32.6 Hz), 64.6, 13.7; ^{19}F NMR δ −75.47 (dd, J = 22.6 and 12.9, 3 F), −110.61 (quint J = 12.9 Hz, 1 F), −114.50 (q, J = 22.6 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3479, 3215, 3038−3022, 2987−2874, 1755, 1642, 1304, 1243, 1174, 1126, 1021 cm^{-1}; MS *m/z* (%) 464 (M^+ + 1, 26), 462 (M^+ − 1, 25), 391 (46), 389 (46), 321 (90), 319 (89), 212 (100), 106 (16). Elem anal. calcd for $C_{19}H_{12}BrF_5O_3$: C, 49.27; H, 2,61. Found: C, 49.11; H, 2.52.

1,3-Difluorophenanthrene (**28**) (6%) and traces of ethyl 2-[6,8-difluoro-7-(1-hydroxy-1-ethoxycarbonylethyl)phenanthr-1-yl]-2-hydroxypropionate (**27b**) were also detected. The latter was identified on the basis of the analogy of its mass spectrum with that of **27a**.

The relative amounts of the above product at different reaction times were determined by GLC after calibration with known amounts of pure products.

Regioselective Alkylation of 8-Bromo-1,3-difluorophenanthrene and 1,3-Difluorophenanthrene. Pure hydroxyester **25a** was prepared by performing the reaction of **24** with butyllithium in THF at −108 °C followed by quenching of the mixture with methyl pyruvate only 10 s after the addition of butyllithium. Usual workup and chromatography of the crude product on silica gel (eluent, petroleum ether, and then 1:3 petroleum ether/diethyl ether mixture) allowed pure product (58%) to be separated from the unreacted bromo derivative (∼5%). In the same way, the corresponding ethyl 3,3,3-trifluorpropionate derivative **25b** was prepared in 61% of yield by using ethyl 3,3,3-trifluoropyruvate as the alkylating reagent.

The following procedure was used to prepare hydroxyester **29a** as the sole reaction product in 88% yield. Butyllithium (1.59 M in hexane, 1.25 mL 2.0 mmol) was added to a solution of diisopropylamine (300 μL, 220 mg, 2.1 mmol) in anhyd THF (10 mL) at −30 °C under nitrogen. After cooling to −50 °C, solid 8-bromo-1,3-difluorophenanthrene (**24**) was added under stirring, and the mixture was allowed to react for 1 h before methyl pyruvate (200 mg, 2.0 mmol) was added. The temperature was increased to 25 °C, saturated aq NH_4Cl (30 mL) was added, the phases were separated, and the aqueous phase was again extracted with diethyl ether (3 × 25 mL). The collected organic phases were dried with Na_2SO_4, and the solvent was evaporated at reduced pressure. The remaining crude product was passed through a short SiO_2 column by eluting with a 7:3 v/v petroleum ether/diethyl ether mixture to get the pure product. In the same way, the corresponding trifluoropionate **25b** was obtained in 83% yield just by replacing methyl pyruvate with ethyl trifluoropyruvate as the alkylating reagent.

1,3-Difluorophenanthrene (**28**) was obtained in 73% of yield from the reaction of the bromide **24** with butyllithium (1.5 equiv) at −75 °C in THF followed by quenching of the reaction mixture with H_2O).

Hydroxyester **26a** was obtained as the sole reaction product as follows. Butyllithium (1.61 M in hexanes, 0.6 mL, 1.0 mmol) was added to a solution of 1,3-difluorophenanthrene (**28**), (0.21 g, 1.0 mmol) in anhyd THF (5 mL) at −50 °C. After 10 min, methyl pyruvate was added, the cold bath was removed, and the temperature was increased to 25 °C. After usual work up, chromatography of the crude product on silica gel (eluent, 7:3 petroleum ether/diethyl ether) allowed the pure **26a** (57%) to be obtained. In the same way, using ethyl trifluoropyruvate as the alkylating reagent, the corresponding trifluoropropionate **26b** was obtained in 63% yield.

General Procedure for the Side-Chain Fluorination of the 2-Hydroxy-2-(phenanthryl)propionic esters 14, 25, 26, and 29. Diethylaminosulfur trifluoride (DAST) (0.17 mL, 0.21 g, 1.28 mmol) was added to a solution of the hydroxyester (1.0 mmol) in dry dichloromethane (2 mL) at 0°C under nitrogen atmosphere. The mixture was made to react for 30 min before water (10 mL) was carefully added. The organic phase was separated, washed with water (20 mL), and dried with sodium su1fate. After solvent evaporation, chromatography of the crude product on silica gel (100 mL, eluent 4:1 (v/v) petroleum ether/diethyl ether) allowed the alkyl 2-fluoro-2-phenanthrenylpropionates **30** and **31** to be obtained with the following spectroscopic and analytical characteristics.

Methyl 2-fluoro-2-(phenanthren-1-yl)propionate (30a): (93%); mp 121−122 °C; ^{1}H NMR δ 8.78 (d, J = 7.5 Hz, 1 H), 8.68 (dd, J = 7.1 and 1.8 Hz, 1 H), 8.12 (ddd, J = 9.4, 2.2, and 0.6 Hz, 1 H), 7.88 (dd, J = 7.7 and 1.6 Hz, 1 H), 7.79 (d, J = 9.3 Hz, 1 H), 7.78 (dt, J = 7.5 and 1.4 Hz, 1 H), 7.68−7.58 (m, 3 H), 3.70 (s, 3 H), 2.20 (d, J = 22.6 Hz, 3 H); ^{13}C NMR δ 172.5 (d, J = 26.4 Hz), 134.7 (d, J = 20.0 Hz), 131.4, 131.2, 130.3, 129.5, 128.4, 127.9, 126.9, 126.8, 125.5, 124.7 (d, J = 7.6 Hz), 124.4, 122.9, 122.7, (d, J = 6.6 Hz), 95.0 (d, J = 182.0 Hz), 53.0, 24.4 (d, J = 24.8); ^{19}F NMR δ −139.5 (q, J = 22.5 Hz); MS (70 eV) *m/z* (%) 282 (M^+, 45), 223 (100), 202 (40), 101 (10). Elem anal. calcd $C_{18}H_{15}FO_2$: C, 76.58; H, 5.36. Found: C, 76.39; H, 5.43.

Methyl 2-fluoro-2-(6-fluorophenanthren-1-yl)propionate (30b): (87%); mp 157−159 °C; ^{1}H NMR δ 8.62 (d, J = 8.3 Hz, 1 H), 8.28 (d, J = 112 Hz, 1 H), 8.10 (d, J = 9.2 Hz, 1

H), 7.85 (dd, J = 8.7 and 6.3 Hz, 1 H), 7.80 (d, J = 7.4 Hz, 1 H), 7.76 (d, J = 9.2 Hz, 1 H), 7.65 (t, J = 8.0 Hz, 1 H), 7.35 (td, J = 8.5 and 1.9 Hz, 1 H), 3.72 (s, 3 H), 2.21 (d, J = 22.6 Hz, 3 H); ^{13}C NMR δ 172.4 (d, J = 26.4 Hz), 161.6 (d, J = 244.5 Hz), 134.8 (d, J = 20.1 Hz), 131.8 (d, J = 8.4 Hz), 130.5 (d, J = 8.9 Hz), 129.8, 128.1, 127.2, 125.6, 125.3 (d, J = 7.5 Hz), 124.6, 122.0 (d, J = 4.8 Hz), 116.0 (d, J = 23.9 Hz), 108.0 (d, J = 22.4 Hz), 95.8, 94.0, 53.0, 24.4 (d, J = 24.8 Hz); ^{19}F NMR δ −113.2 (dt, J = 11.7 and 6.6 Hz), −139.6 (q, J = 22.6 Hz); IR (CHCl3) ν_{max} 3026, 2956, 2852, 1749, 1608, 1263, 1127, 840 cm^{-1}; MS *m/z* (%) 300 (M$^+$, 39), 241 (100), 220 (36). Elem anal. calcd for $C_{18}H_{14}F_2O_2$: C, 71.99; H, 4.70. Found: C, 71.88; H, 4.61.

Ethyl 2-(phenanthren-1-yl)-2,3,3,3-tetrafluoropropionate (30c): (92%); mp 81−83 °C; ^{1}H NMR δ 8.85 (d, J = 8.4 Hz, 1 H), 8.67 (d, J = 8.2 Hz, 1 H), 8.11 (d, J = 9.4 Hz, 1 H), 7.92−7.87 (m, 2 H), 7.81 (d, J = 9.4 Hz, 1 H), 7.70−7.60 (m, 3 H), 4.40−4.23 (sym m, ABX$_3$ system, 2 H), 1.19 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 164.8 (d, J = 25.0 Hz), 131.4, 131.2, 130.2, 129.6, 128.5, 128.4, 127.2, 127.1, 126.6 (d, J = 19.4 Hz), 126.2 (d, J = 6.5 Hz), 125.7, 125.4, 122.8, 122.1, (qd, J = 285.1 and 29.3 Hz), 121.9 (d, J = 7.7 Hz), 94,4 (dq, J = 190.0 and 31.1 Hz), 63.6, 13.7; ^{19}F NMR δ −157.8 (q, J = 9.0 Hz), −73.8 (d, J = 9.0 Hz); MS (70 eV) *m/z* (%) 350 (M$^+$, 56), 277 (100), 257 (18), 227 (34), 207 (20). Elem anal. calcd for $C_{19}H_{14}F_4O_2$: C, 65.14; H, 4.03. Found: C, 65.35; H, 4.11.

Ethyl 2-(6-fluorophenanthren-1-yl)-2,3,3,3-tetrafluoropropionate (30d): (83%); mp 77−79 °C; ^{1}H NMR δ 8.67 (d, J = 8.4 Hz, 1 H), 8.25 (d, J = 11.2 Hz, 1 H), 8.07 (d, J = 9.3 Hz, 1 H), 7.94 (d, J = 7.6 Hz, 1 H), 7.84 (dd, J = 8.5 and 6.2 Hz, 1 H), 7.77 (d, J = 9.3 Hz, 1 H), 7.67 (t, J = 8.0 Hz, 1 H), 7.36 (td, J = 8.4 and 1.3 Hz, 1 H), 4.39 (dq, J = 10.7 and 7.1 Hz, 1 H), 4.31 (dq, J = 10.7 and 7.1 Hz, 1 H), 1.22 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 164.7 (d, J = 25 Hz), 161.8 (d, J = 244.9 Hz), 131.7 (d, J = 8.4 Hz), 130.8 (d, J = 4.0 Hz), 130.6 (d, J = 8.9 Hz), 129.9, 128.0, 127.9, 126.8 (d, J = 6.5 Hz), 126.7, 125.8, 125.4, 121.8 (qd, J = 285.0 and 29.3 Hz), 121.2 (d, J = 7.6 Hz), 116.4 (d, J = 23.9), 108.0 (d, J = 22.5), 94.3 (dq, J = 199.4 and 31.4 Hz), 63.6, 13.7; ^{19}F NMR δ −73.8 (d, J = 8.5 Hz, 3 F), −112.6 (m, 1 F), −158.0 (q, J = 8.5, 1 F); IR ($CHCl_3$) ν_{max} 3032, 2988−2863, 1759, 1608, 1514, 1296, 1254, 1183, 1030, 840 cm^{-1}; MS *m/z* (%) 368 (M$^+$, 63), 295 (100), 275 (17), 245 (32), 225 (15). Elem anal. calcd for $C_{19}H_{13}F_5O_2$: C, 61.96; H, 3.56. Found: C, 62.00; H, 3.49.

Methyl 2-(6,8-difluorophenanthren-1-yl)-2-fluoropropionate (30e): (85%); mp 138−140 °C; ^{1}H NMR δ 8.59 (d, J = 8.2 Hz, 1 H), 8.17 (dd, J = 9.6 and 1.7 Hz, 1 H), 8.10 (d, J = 11.0 Hz, 1 H), 8.02 (d, J = 9.6 Hz, 1 H), 7.85 (d, J = 7.5 Hz, 1 H), 7.69 (t, J = 7.9 Hz, 1 H), 7.11 (ddd, J = 9.9, 8.6, and 2.2 Hz, 1 H), 3.75 (s, 3 H), 2.23 (d, J = 22.6 Hz, 3 H); ^{13}C NMR δ 172.2 (d, J = 26.4 Hz), 160.8 (dd, J = 245 and 12.9 Hz), 159.5 (dd, J = 252 and 13.2 Hz), 135.1 (d, J = 20.1 Hz), 132.6 (dd, J = 9.8 and 5.7 Hz), 130.2, 129.9 (t, J = 3.2 Hz), 126.1, 125.9 (d, J = 7.5 Hz), 124.8, 122.5 (d, J = 7.0 Hz), 119.3 (d, J = 6.1 Hz), 117.9 (d, J = 15.6 Hz), 104.0 (dd, J = 22.3 and 4.2 Hz), 102.1 (dd, J = 27.8 and 24.2 Hz), 94.9 (d, J = 183 Hz), 53.1, 24.4 (d, J = 24.8 Hz); ^{19}F NMR δ −110.71 (dt, J = 10.7 and 8.2 Hz, 1 F), −118.19 (t, J = 8.5 Hz, 1 F), −139.6 (q, J = 22.6 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3085, 3034, 2958, 2848, 1749, 1640, 1274, 1258, 1210, 1126, 998, 852 cm^{-1}; MS *m/z* (%) 318 (M$^+$, 33), 259 (100), 239 (53), 219 (8), 119 (12). Elem anal. calcd for $C_{18}H_{13}F_3O_2$: C, 67.92; H, 4.12. Found: C, 67.79; H, 3.98.

Ethyl 2-(6,8-difluorophenanthren-1-yl)-2,3,3,3-tetrafluoropropionate (30f): (82%); mp 100−102 °C dec; ^{1}H NMR δ 8.65 (d, J = 8.4 Hz, 1 H), 8.11 (d, J = 9.5 Hz, 1 H), 8.07 (d, J = 10.8 Hz, 1 H), 8.03 (d, J = 9.5 Hz, 1 H), 7.96 (dd, J = 7.7 and 1.1 Hz, 1 H), 7.70 (t, J = 8.0 Hz, 1 H), 7.12 (ddd, J = 9.8, 8.6, and 2.3 Hz, 1 H), 4.43−4.28 (sym m, 2 H), 1.23 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 164.6 (d, J = 24.9 Hz), 161.0 (dd, J = 246 and 12.9 Hz), 159.5 (dd, J = 253 and 13.2 Hz), 132.5 (dd, J = 9.9 and 5.6 Hz), 130.3, 130.2 (ddd, J = 4.6, 2.9, and 1.1 Hz), 127.4 (d, J = 6.7 Hz), 127.1 (d, J = 19.5 Hz), 126.1, 125.9, 121.8 (qd, J = 285 and 29.2 Hz), 121.7 (d, J = 8.0 Hz), 119.9 (d, J = 5.9 Hz), 117. 9 (d, J = 15.2 Hz), 104.0 (dd, J = 22.6 and 4.1 Hz), 102.4 (dd, J = 27.6 and 24.1 Hz), 94.2 (dq, J = 199 and 31.3 Hz), 63.7, 13.7; ^{19}F NMR δ −73.88 (d, J = 8.7 Hz, 3 F), −110.00 (q, J = 9.0 Hz, 1 F), −117.94 t, J = 9.0 Hz, 1 F), −158.09 (q, J = 8.7 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3089, 3036, 2987−2841, 1758, 1640, 1298, 1186, 1119, 1084, 852, 815 cm^{-1}; MS *m/z* (%) 386 (M$^+$, 45), 313 (100), 293 (18), 263 (44), 243 (23), 131 (11). Elem anal. calcd for $C_{19}H_{12}F_6O_2$: C, 59.08; H, 3.13. Found: C, 58.89; H, 2.99.

Methyl 2-(1,3-difluorophenanthren-2-yl)-2-fluoropropionate (31a): (90%); mp 127−129 °C; ^{1}H NMR δ 8.39−8.36 (m, 1 H), 8.01 (d, J = 13.4 Hz, 1 H), 7.86 (d, J = 9.0 Hz, 1 H), 7.86−7.83 (m, 1 H), 7.70 (d, J = 9.0 Hz, 1 H), 7.64−7.61 (m, 2 H), 3.88 (s, 3 H), 2.21 (ddd, J = 22.7, 3.0, and 2.0 Hz, 3 H); ^{13}C NMR δ 170.9 (d, J = 26.0 Hz), 158.6 (ddd, J = 248.5, 8.4, and 2.5 Hz), 157.3 (ddd, J = 256.0, 8.3, and 3.9 Hz), 132.6, 132.4 (dd, J = 10.6 and 6.9 Hz), 128.8, 128.3 (t, J = 3.4 Hz), 128.2, 127.2, 123.0, 118.5 (d, J = 16.7 Hz), 118.1 (d, J = 8.6 Hz), 112.2 (q, J = 13.8 Hz), 104.6 (dd, J = 24.3 and 3.5 Hz), 91.7 (d, J = 184.7 Hz), 53.2, 24.2 (ddd, J = 24.6, 5.9, and 4.0 Hz); ^{19}F NMR δ −112.5 (t, J = 14.0 Hz, 1 F), −117.3 (d, J = 14.9 Hz, 1 F), −137.6 to −137.9 (sym m, 1 F); IR ($CHCl_3$) ν_{max} 3024, 2957−2850, 1760, 1642, 1301, 1131, 1035, 814 cm^{-1}; MS *m/z* (%) 318 (M$^+$, 25), 298 (11), 259 (100), 238 (32), 207 (11). Elem anal. calcd for $C_{18}H_{13}F_3O_2$: C, 67.92; H, 4.12. Found: C, 67.79; H, 3.98.

Methyl 2-(8-bromo-1,3-difluorophenanthren-2-yl)-2-fluoropropionate (31b): (70%); mp 121−123 °C; ^{1}H NMR δ 8.39 (d, J = 8.4 Hz, 1 H), 8.17 (d, J = 9.4 Hz, 1 H), 8.05 (d, J = 13.3 Hz, 1 H), 7.98 (d, J = 9.4 Hz, 1 H), 7.94 (d, J = 7.6 Hz, 1 H), 7.49 (t, J = 7.9 Hz, 1 H), 3.91 (s, 3 H), 2.23 (ddd, J = 22.7, 3.0, and 1.9 Hz, 3 H); ^{13}C NMR δ 170.7 (d, J = 26.0 Hz), 158.9 (ddd, J = 252, 8.3, and 2.6 Hz), 157.3 (ddd, J = 257, 8.5, and 4.0 Hz), 132.3, 132.0 (ddd, J = 11.0, 6.5, and 1.5 Hz), 131.3, 130 (t, J = 3.5 Hz), 127.6, 127.1, 125.7, 123.9, 122.7, 119.8 (d, J = 8.2 Hz), 118.7 (d, J = 17.4 Hz), 113.1 (ddd, J = 22.5, 17.8, and 14.0 Hz), 105.0 (dd, J = 24.7 and 3.7 Hz), 53.3, 24.2 (ddd, J = 24.6, 6.1, and 3.8 Hz); ^{19}F NMR δ −111.34 (t, J = 15.1 Hz, 1 F), −116.86 (d, J = 15.4 Hz, 1 F), −138.28 (qt, J = 22.7 and 15.4 Hz, 1 F); IR ($CHCl_3$) ν_{max} 3038, 2956−2851, 1762, 1643, 1300, 1147, 1131, 916 cm^{-1}; MS *m/z* (%) 398 (M$^+$ + 1, 23), 396 (M$^+$ − 1, 24), 378 (11), 376 (9), 339 (99), 337 (100), 320 (36), 318 (38), 258 (57), 238 (70), 218 (31), 109 (24). Elem anal. calcd for $C_{18}H_{12}BrF_3O_2$: C, 54.43; H, 3,05. Found: C, 54.29; H, 2.96.

Ethyl 2-(1,3-difluorophenanthren-2-yl)-2,3,3,3-tetrafluoropropionate (31c): (75%); mp 76−78 °C; ^{1}H NMR δ 8.44 (m, 1 H), 8.10 (d, J = 13.3 Hz, 1 H), 7.92−7.88 (m, 2 H), 7.74 (d, J = 9.1 Hz, 1 H), 7.70−7.66 (m, 2 H), 4.47 (sym m, 2 H), 1.37 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 162.8 (d, J = 22.6 Hz), 157.8 (ddd, J = 250, 7.1, and 3.3 Hz), 157.6 (ddd, J = 259, 7.1, and 3.7 Hz), 133.6 (dd, J = 10.5 and 6.7 Hz), 132.9, 132.9, 128.9, 128.7, 128.2 (dd, J = 4.4 and 3.0 Hz), 127.7 (t, J = 2.5 Hz), 127.5, 123.1, 121.3 (qd, J = 283 and 29.1 Hz), 118.5 (dd, J = 16.2 and 2.0 Hz), 117.9 (8.7 and 1.6 Hz), 105.0 (dd, J = 23.9 and 4.2 Hz), 90.5 (dq, J = 201 and 34.1 Hz), 63.7, 13.7; ^{19}F NMR δ −77.53 (q, J = 10.2 Hz, 3 F), −111.97 (sept J = 11.3 Hz, 1 F), −114.67 (sext, J = 13.0 Hz, 1 F), −168.40 (m, 1 F); IR ($CHCl_3$) ν_{max} 3038, 3026, 2929, 2857, 1769, 1641, 1310, 1270, 1199, 1035, 820 cm^{-1}; MS *m/z* (%) 386 (M$^+$, 41), 313 (100), 293 (17), 263 (42), 243 (22), 131 (14). Elem anal. calcd for $C_{19}H_{12}F_6O_2$: C, 59.08; H, 3,13. Found: C, 59.21; H, 3.20.

Ethyl 2-(8-bromo-1,3-difluorophenanthren-2-yl)-2,3,3,3-tetrafluoropropionate (31d): (65%); mp 98−100 °C; ^{1}H NMR δ 8.34 (d, J = 8.3 Hz, 1 H), 8.13 (d, J = 9.6 Hz, 1 H), 8.04 (d, J = 13.2 Hz, 1 H), 7.93 (d, J = 7.3 Hz, 1 H), 7.92 (d, J = 9.6 Hz, 1 H), 7.47 t, J = 8.1 Hz, 1 H), 4.54−4.42 (sym m, 2 H), 1.38 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ 162.7 (d, J = 22.6 Hz), 158.1 (ddd, J = 251, 7.1, and 3.3 Hz), 157.6 (ddd, J = 260, 7.1, and 3.6 Hz), 133.1 (dd, J = 10.7 and 6.6 Hz), 132.7, 131.4, 129.7 (dd, J = 4.1 and 2.7 Hz), 127.7, 126.2 (t, J = 2.3

Hz), 123.9, 122.7, 121.3 (qd, J = 284 and 29.0 Hz), 119.4 (dd, J = 8.5 and 1.3 Hz), 118.5 (dd, J = 16.5 and 2.0 Hz), 106.0 (ddd, J = 21.8, 17.2, and 13.7 Hz), 105.3 (dd, J = 24.3 and 4.2 Hz), 90.4 (dq, J = 201 and 34.2 Hz), 63.8, 13.7; ^{19}F NMR δ −77.48 (q, J = 10.2 Hz, 3 F), −110.79 (quint, J = 11.2 Hz, 1 F), −114.04 (sext, J = 11.1 Hz, 1 F), −168.58 (m, 1 F); IR ($CHCl_3$) ν_{max} 3058, 2954−2858, 1769, 1644, 1303, 1270 cm^{-1}; MS *m/z* (%) 466 (M^+ + 1, 63), 464 (M^+ − 1, 70), 393 (100), 391 (94), 374 (12), 372 (12), 343 (78), 341 (86), 313 (23), 261 (50), 243 (59), 207 (58), 106 (14). Elem anal. calcd for $C_{19}H_{11}BrF_6O_2$: C, 49.06; H, 2.38. Found: C, 48.89; H, 2.25.

General Procedure for the Preparation of 2-(Phenanthryl)-2-fluoropropionic acids 2−5. Each alkyl 2-fluoro-2-(phenanthryl)propionate **30**−**31** (1.0 mmol) was made to react for 2 h in 5% methanolic KOH (25 mL) at 20 °C. The solvent was evaporated, the resu1ting so1id was dissolved in water (30 mL), and the mixture was extracted with diethyl ether (2 × 20 mL). The clear solution was acidified with 5% aq HCl until pH 1, the resu1ting white suspension was extracted with ethyl acetate (3 × 20 mL), and the collected organic phases were dried with Na_2SO_4. After solvent evaporation, the remaining white solid was crystallized from ethanol to obtain the pure acid. The acids **2**−**5** were identified on the basis of their spectroscopic and analytical characteristics.

2-(6-Fluorophenanthren-1-yl)propionic acid (1b): (88%); mp 213−215 °C; ^{1}H NMR (DMSO-d_6) δ 12.45 (s, 1 H), 8.73 (d, J = 8.1 Hz, 1 H), 8.61 (dd, J = 11.7 and 1.6 Hz, 1 H), 8.04 (m, 2 H), 7.89 (d, J = 9.3, 1 H), 7.66−7.48 (m, 3 H), 4.54 (q, J = 6.9 Hz, 1 H), 1.52 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (DMSO-d_6) δ 176.1, 161.6 (d, J = 242 Hz), 138.8, 132.2 (d, J = 8.6 Hz), 131.3 (d, J = 8.9 Hz), 130.1 (d, J = 3.9 Hz), 130.0, 128.4, 126.9, 126.9, 126.4, 122.9, 121.8, 116.2 (d, J = 23.8 Hz), 108.7 (d, J = 22.3 Hz), 41.6, 18.7; ^{19}F NMR (DMSO-d_6) δ −113.1 (ddd, J = 11.7, 8.3, and 6.3 Hz); IR (KBr) ν_{max} 3447−2370 (br), 3076, 2986−2931, 1691, 1603, 1461, 1206, 838 cm^{-1}; MS (70 eV) *m/z* (%) 268 (M^+, 47), 223 (100), 209 (16), 196 (20). Elem anal. calcd for $C_{17}H_{13}FO_2$: C, 76.11; H, 4.88. Found: C, 76.05; H, 4.79.

2-(6,8-Difluorophenanthr-1-yl)propionic acid (1c): (93%); mp 205−207 °C; ^{1}H NMR (DMSO-d_6) δ 8.82 (d, J = 8.2 Hz, 1 H), 8.60 (br d, J = 11.4 Hz, 1 H), 8.22−8.02 (AB system, J_{AB} = 9.5 Hz, 2 H), 7.76 (t, J = 7.8 Hz, 1 H), 7.70 (d, J = 7.3 Hz, 1 H), 7.63 (ddd, J = 11.0, 9.2, and 223 Hz, 1 H), 4.61 (q, J = 7.1 Hz, 1 H), 3.37 (br s, 1 H), 1.58 (d, J = 7.1 Hz, 3 H); ^{13}C NMR (DMSO-d_6) δ 175.6, 160.4 (dd, J = 242.7 and 13.3), 158.8 (dd, J = 249.7 and 13.6 Hz), 138.7, 132.6 (dd, J = 9.9 and 5.4 Hz), 129.9, 129.2, 127.1, 126.7, 122.9, 122.4, 117.8, 117.3 (d, J = 15.3 Hz), 104.9 (d, J = 22.2 Hz), 102.1 (t, J = 26.4 Hz), 41.1, 18.2; ^{19}F NMR (DMSO-d_6) δ −110.6 (ddd, J = 11.3, 8.9, and 7.5 Hz), −118.6 (dd, J = 10.1 and 7.5 Hz); IR ($CHCl_3$) ν_{max} 3430, 3025, 1638, 1596 cm^{-1}; MS *m/z* (%) 240 (M^+ − HCOOH, 100), 239 (96), 219 (12), 119 (13). Elem anal. calcd for $C_{17}H_{12}F_2O_2$: C, 71.32; H, 4.23. Found: C, 71.38; H, 4.25.

2-Fluoro-2-(phenanthr-1-yl)propionic acid (2a): (87%); mp 155−157 °C; ^{1}H NMR (DMSO-d_6) δ 9.00 (d, J = 8.2 Hz, 1 H), 8.91 (d, J = 8.1 Hz, 1 H), 8.21 (dd, J = 9.4 and 2.5 Hz, 1 H), 8.03 (dd, J = 7.7 and 1.4 Hz, 1 H), 7.96 (d, J = 9.4 Hz, 1 H), 7.92 (d, J = 7.7 Hz, 1 H), 7−80−7.70 (m, 3 H), 2.18 (d, J = 22.8 Hz, 3 H), 3,5 (br s, 1 H); ^{13}C NMR (DMSO-d_6, 50 MHz) δ 173.1 (d, J = 25.9 Hz), 135.0 (d, J = 20.0 Hz), 130.8, 130.6, 129.9, 129.2, 128.3, 127.4, 127.2, 127.2, 126.0, 125.6 (d, J = 5.6 Hz), 124.6, 123.3, 122.8 (d, J = 6.7 Hz), 94.5, (d, J = 180.2 Hz), 24.0 (d, J = 24.1 Hz); ^{19}F NMR (DMSO-d_6, 376 MHz) δ −139.11 (q, J = 22.5 Hz). Elem anal. calcd for $C_{17}H_{13}FO_2$: C, 76.11; H, 4.88. Found: C, 75.99; H, 4.93.

2-Fluoro-2-(6-fluorophenanthr-1-yl)propionic acid (2b): (93%); mp 180−182 °C; ^{1}H NMR (acetone-d_6) δ 8.87 (d, J = 8.5 Hz, 1 H), 8.53 (dd, J = 11.6 and 2.4 Hz, 1 H), 8.27 (dd, J = 9.4 and 2.4 Hz, 1 H), 8.03 (dd, J = 8.8 and 8.6 Hz, 1 H), 7.95 (ddd, J = 7.5, 1.7, and 1.1 Hz, 1 H), 7.88 (d, J = 9.4 Hz, 1 H), 7.73 (ddd, J = 8.5, 7.5, and 1.2 Hz, 1 H), 7.46 (td, J = 8.6 and 2.5 Hz, 1 H), 2.21 (d, J = 22.6 Hz, 3 H); ^{13}C NMR (acetone-d_6, 50 MHz) δ 173.2 (d, J = 26 Hz), 162.6 (d, J = 242 Hz), 136.2 (d, J = 20 Hz), 132.8 (d, J = 8.5 Hz), 131.7 (d, J = 8.9 Hz), 131.4 (d, J = 4.2 Hz), 130.9, 129.1, 127.7, 126.9, 126.8, 125.7, 123.5 (dd, J = 7.6 and 2.4 Hz), 116.8 (d, J = 24 Hz), 108.9 (d, J = 23 Hz), 95.4 (d, J = 181 Hz), 24.6 (d, J = 25 Hz); ^{19}F NMR (acetone-d_6) δ −139.3 (q, J = 22.5 Hz, 1 F), −114.5 (ddd, J = 12.8, 7.3, 5.5 Hz, 1 F); IR (KBr) ν_{max} 3200−1944 (br), 1712, 1509, 1300, 1100, 948, 837 cm^{-1}; Elem anal. calcd for $C_{17}H_{12}F_2O_2$: C, 71,32; H, 4,23. Found: C, 71.24; H, 4.15.

2-(6,8-Difluorophenanthr-1-yl)-2-fluoropropionic acid (2c): (76%); mp 181 °C dec; ^{1}H NMR (acetone-d_6) δ 8.84 (d, J = 8.5 Hz, 1 H), 8.38 (dd, J = 11.2 and 0.9 Hz, 1 H), 8.34 (dd, J = 9.8 and 2.2 Hz, 1 H), 8.01−7.98 (m, 2 H), 7.60 (td, J = 8.5 and 1.1 Hz, 1 H), 7.34 (ddd, J = 10.3, 8.9, and 2.3 Hz, 1 H), 2.22 (d, J = 22.6 Hz, 3 H); ^{13}C NMR (acetone-d_6) δ 172.2 (d, J = 26.3 Hz), 160.9 (dd, J = 244 and 13.2 Hz), 159.4 (dd, J = 250 and 13.5 Hz), 135.6 (d, J = 20.1 Hz), 132.8 (dd, J = 10.1 and 5.6 Hz), 130.3, 129.9 (t, J = 3.1 Hz), 126.6 (d, J = 6.3 Hz), 126.5, 125.1, 123.3 (d, J = 7.7 Hz), 118.2 (d, J = 6.3 Hz), 117.7 (dd, J = 17.5 and 2.0 Hz), 104.5 (dd, J = 22.7 and 4.3 Hz), 101.9 (dd, J = 28.4 and 24.4 Hz), 94.5 (d, J = 181 Hz), 23.7 (d, J = 24.6 Hz); ^{19}F NMR (acetone-d_6) δ −111.89 (q, J = 9.1 Hz, 1 F), −119.83 (t, J = 8.5 Hz, 1 F), −139.22 (q, J = 22.4 Hz, 1 F); IR (KBr) ν_{max} 3436, 3300−2000 (br), 3083, 2922, 1733, 1638, 1302, 1114, 996, 811 cm^{-1}. Elem anal. calcd for $C_{17}H_{11}F_3O_2$: C, 67.11; H, 3.64. Found: C, 66.98; H, 3.49.

2-(Phenanthr-1-yl)-2,3,3,3-tetrafluoropropionic acid (3a): (93%); mp 50−52 °C; ^{1}H NMR δ 8.80 (d, J = 8.4 Hz, 1 H), 8.62 (d, J = 8.1 Hz, 1 H), 8.11 (d, J = 9.3 Hz, 1 H), 7.89 (d, J = 7.5 Hz, 1 H), 7.80 (d, J = 7.7 Hz, 1 H), 7.73 (d, J = 9.4 Hz, 1 H), 7.65−7.54 (m, 3 H), 7.26 (br s, 1 H); ^{13}C NMR δ 168.1 (d, J = 25.6 Hz), 131.5, 131.2, 130.1, 129.7, 128.7, 128.4, 127.3, 127.2, 126.2 (d, J = 9.6 Hz), 126.0 (d, J = 22.2 Hz), 125.9, 125.3, 122.8, 121.7 (qd, J = 285.1 and 29.1 Hz), 121.8 (d, J = 8.8 Hz), 94.4 (dq, J = 199.6 and 31.0 Hz); ^{19}F NMR δ −157.9 (q, J = 7.9 Hz, 1 F), −73.6 (d, J = 7.9 Hz, 3 F). Elem anal. calcd For $C_{17}H_{10}F_4O_2$: C, 63.36; H, 3.13. Found: C, 63.45; H, 3.02.

2-(6-Fluorophenanthr-1-yl)-2,3,3,3-tetrafluoropropionic acid (3b): (81%); mp 179 °C dec; ^{1}H NMR (acetone-d_6) δ 9.03 (d, J = 8.0 Hz, 1 H), 8.7 (very br s, 1 H), 8.57 (dd, J = 11.5 and 2.4 Hz, 1 H), (8.19 (dd, J = 9.5 and 1.5 Hz, 1 H), 8.06 (dd, J = 8.9 and 6.0 Hz, 1 H), 8.04 (dd, J = 7.7 and 1.2 Hz, 1 H), 7.97 (d, J = 9.4 Hz, 1 H), 7.84 (td, J = 8.0 and 1.0 Hz, 1 H), 7.51 (td, J = 8.5 and 2.5 Hz, 1 H); ^{13}C NMR (acetone-d_6) δ 164.9 (d, J = 24.8 Hz), 161.9 (d, J = 243 Hz), 131.8 (d, J = 8.7 Hz), 131.0 (d, J = 9.0 Hz), 130.9 (d, J = 3.7 Hz), 129.8, 128.2, 127.9, 126.9 (dd, J = 8.5 and 2.3 Hz), 126.6, 126.5, 125.8, 122.2 (qd, J = 284 and 29.4 Hz), 121.2 (d, J = 7.6 Hz), 116.4 (d, J = 24.1 Hz), 108.2 (d, J = 22.9 Hz), 94.3 (dq, J = 197 and 30.8 Hz); ^{19}F NMR (acetone-d_6) δ −74.56 (d, J = 8.8 Hz, 3 F), −113.78 (q, J = 8.3 Hz, 1 F), −158.25 (q, J = 8.8 Hz, 1 F); IR (KBr) ν_{max} 3250−2000 (br), 3034, 2897, 1736, 1633, 1436, 1267, 1175, 998, 906, 833 cm^{-1}. Elem anal. calcd for $C_{17}H_9F_5O_2$: C, 60.01; H, 2.67. Found: C, 60.15; H, 2.56.

2-(6,8-Difluorophenanthr-1-yl)-2,3,3,3-tetrafluoropropionic acid (3c): (88%); mp 204 °C dec; ^{1}H NMR (acetone-d_6) δ 9.02 (d, J = 8.3 Hz, 1 H), 8.45 (dd, J = 11.3 and 1.1 Hz, 1 H), 8.27 (d, J = 9.8 Hz, 1 H), 8.09−8.07 (m, 2 H), 7.87 (td, J = 8.0 and 1.0 Hz, 1 H), 7.41 (ddd, J = 10.2, 8.9, and 2.3 Hz, 1 H); ^{13}C NMR (acetone-d_6) δ 164.8 (d, J = 24.8 Hz), 161.2 (dd, J = 244 and 13.2 Hz), 159.4 (dd, J = 251 and 13.6 Hz), 132.7 (dd, J = 10.1 and 5.4 Hz), 130.3 (t, J = 3.4 Hz), 130.1, 127.6 (dd, J = 8.5 and 2.3 Hz), 127.1(d, J = 19.4 Hz), 126.8, 126.4, 122.1 (qd, J = 284 and 29.3 Hz), 122.0 (d, J = 8.3 Hz), 119.4 (d, J = 6.3 Hz), 117.7 (d, J = 15.6 Hz), 104.6 (dd, J = 23.0 and 4.3 Hz), 102.5 (dd, J = 28.4 and 24.3 Hz), 94.2 (dq, J = 197 and 30.8 Hz); ^{19}F NMR (acetone-d_6) δ −74.62 (d, J = 9.2 Hz, 3 F), −111.12 (q, J = 9.2 Hz, 1 F), 119.56 (t, J = 9.2 Hz, 1 F), −158.29 (br, 1 F); IR (KBr) ν_{max} 3588, 3300−2000 (br), 1750, 1640, 1294, 1270, 1185, 1119, 1000, 852 cm^{-1}. Elem anal. calcd for $C_{17}H_8F_6O_2$: C, 57.00; H, 2.25. Found: C, 57.19; H, 2.26.

2-(1,3-Difluorophenanthr-2-yl)-2-fluoropropionic acid (4a): (87%); mp 219 °C dec; ^{1}H NMR (acetone-d_6) δ 8.69−8.67 (m, 1 H), 8.58 (d, J = 13.4 Hz, 1 H), 7.98−7.96 (m, 1 H), 7.92−7.84 (four peaks, AB system, J_{AB} = 9.0 Hz, 2 H), 7.72−7.69 (m, 2 H), 2.20 (ddd, J = 22.8, 3.2, and 2.1 Hz, 3 H); ^{13}C NMR (acetone-d_6) δ 170.5 (d, J = 26.1 Hz), 158.8 (dd, J = 247 and 7.2 Hz), 157.1 (ddd, J = 255, 8.1, and 3.2 Hz), 132.7, 132.7, 132.4 (dd, J = 11.1 and 7.2 Hz), 128.8, 128.4, 127.6, 127.5, 123.5, 118.4 (d, J = 16.7 Hz), 117.7 (d, J = 8.6 Hz), 112.9 (ddd, J = 22.5, 17.9, and 15.0 Hz), 104.9 (dd, J = 24.5 and 2.6 Hz), 91.5 (d, J = 183 Hz), 23.7 (dt, J = 24.4 and 4.0 Hz); ^{19}F NMR (acetone-d_6) δ −112.77 (t, J = 13.7 Hz, 1 F), −118.40 (d, J = 14.8 Hz, 1 F), −137.70 (m, 1 F); IR (KBr) ν_{max} 3300−2000 (br), 3005, 2922, 1740, 1642, 1397, 1217, 1145, 1028, 919, 818, 754 cm^{-1}. Elem anal. calcd for $C_{17}H_{11}F_3O_2$: C, 67.11; H, 3.64. Found: C, 67.31; H, 3.59.

2-(8-Bromo-1,3-difluorophenanthr-2-yl)-2-fluoropropionic acid (4b): (94%); mp 164 °C dec; ^{1}H NMR (acetone-d_6) δ 8.58 (d, J = 8.6 Hz, 1 H), 8.26 (d, J = 13.5 Hz, 1 H), 8.01 (d, J = 9.4 Hz, 1 H), 7.93 (dd, J = 7.6 and 0.9 Hz, 1 H), 7.90 (d, J = 9.4 Hz, 1 H), 7.52 (dd, J = 8.3 and 7.7 Hz, 1 H), 2.20 (ddd, J = 22.9, 3.6, and 2.0 Hz, 3 H); ^{13}C NMR (acetone-d_6) δ 170.5 (d, J = 26.0 Hz), 159.1 (ddd, J = 248, 8.6, and 2.6 Hz), 157.1 (ddd, J = 256, 8.8, and 4.0 Hz), 132.4, 131.8 (ddd, J = 11.2, 6.3, and 1.3 Hz), 130.7, 129.9 (t, J = 3.0 Hz), 127.9, 125.3 (t, J = 2.3 Hz), 123.4, 123.0, 119.5 (dd, J = 9.2 and 1.5 Hz), 118.3 (d, J = 17.3 Hz), 113.5 (ddd, J = 22.7, 18.4, and 14.0 Hz), 105.3 (dd, J = 25.0 and 3.7 Hz), 91.4 (d, J = 184 Hz), 23.7 (ddd, J = 24.5, 6.7, and 3.7 Hz); ^{19}F NMR (acetone-d_6) δ −111.54 (t, J = 14.6 Hz, 1 F), −117.97 (d, J = 15.7 Hz, 1 F), 137.97 (m, 1 F); IR (KBr) ν_{max} 3421, 3300−2000 (br), 3068, 2924, 2842, 1749, 1643, 1235, 1143, 1029, 802, 757 cm^{-1}; Elem anal. calcd for $C_{17}H_{10}BrF_3O_2$: C, 53.29; H, 2.63. Found: C, 53.11; H, 2.55.

2-(1,3-Difluorophenanthr-2-yl)-2,3,3,3-tetrafluoropropionic acid (5a): (86%); mp 178 °C dec; ^{1}H NMR (acetone-d_6) δ 8.73 (m, 1 H), 8.47 (d, J = 13.7 Hz, 1 H), 8.04−7.99 (m, 1 H), 7.98−7.89 (m, 2 H), 7.77−7.72 (m, 2 H); ^{13}C NMR (acetone-d_6, 50 MHz) δ 163.3 (d, J = 22.0 Hz), 157.9 (ddd, J = 249, 7.4, and 3.2 Hz), 157.3 (ddd, J = 258, 7.3, and 3.8 Hz), 133.6 (dd, J = 10.6 and 6.7 Hz), 132.9, 128.9, 128.9, 128.7 (d, J = 20.7 Hz), 128.3 (dd, J = 7.2 and 4.3 Hz), 128.2, 127.7, 123.7, 121.8 (qd, J = 283 and 29 Hz), 118.3, (dd, J = 16.2 and 1.8 Hz), 117.4 (dd, J = 8.6 and 1.5 Hz), 105.5 (dd, J = 21.0 and 4.0 Hz), 90.6 (dq, J = 198 and 33 Hz); ^{19}F NMR (acetone-d_6) δ −78.34 (q, J = 9.8 Hz, 3 F), −112.57 (br s, 1 F), −115.84 (m, 1 F), −169.19 (br s, 1 F); IR ($CHCl_3$) ν_{max} 3300−1944 (br), 3036, 2930−2855, 1756, 1640, 1302, 1200 cm^{-1}. Elem anal. calcd for $C_{17}H_8F_6O_2$: C, 57.00; H, 2.25. Found: C, 56.84; H, 2.17.

2-(8-Bromo-1,3-difluorophenanthr-2-yl)-2,3,3,3-tetrafluoropropionic acid (5b): (88%); mp 207 °C dec; ^{1}H NMR (acetone-d_6) δ 8.56 (d, J = 8.6 Hz, 1 H), 8.35 (d, J = 13.7 Hz, 1 H), 8.00 (d, J = 9.5 Hz, 1 H), 7.93 (dd, J = 7.6 and 0.9 Hz, 1 H), 7.89 (d, J = 9.5 Hz, 1 H), 7.51 (dd, J = 8.2 and 7.8 Hz, 1 H); ^{13}C NMR (acetone-d_6) δ 162.7 (d, J = 22.0 Hz), 158.0 (ddd, J = 250, 7.0, and 3.3 Hz), 157.2 (ddd, J = 259, 7.3, and 3.9 Hz), 133.1 (dd, J = 11.1 and 6.6 Hz), 132.8, 130.9, 129.6 (dd, J = 4.3 and 2.7 Hz), 128.1, 125.9 (t, J = 2.4 Hz), 123.5, 123.0, 121.6 (qt, J = 283 and 29.2 Hz), 119.0 (dd, J = 8.7 and 1.6 Hz), 118.1 (dd, J = 16.3 and 1.9 Hz), 105.9 (dd, J = 24.6 and 4.1 Hz), 105.8 (m), 90.4 (dq, J = 199 and 37.5 Hz); ^{19}F NMR (acetone-d_6) δ −78.33 (q, J = 10.0 Hz, 3 F), −111.7 (sept, J = 11.3 Hz, 1 F), −115.36 (sext, J = 12.1 Hz, 1 F), 169.59 (m, 1 F); IR (KBr) ν_{max} 3447, 3300−2000 (br), 3068, 1759, 1643, 1214, 1191, 1128, 997, 758 cm^{-1}. Elem anal. calcd for $C_{17}H_7BrF_6O_2$: C, 46.71; H, 1.61. Found: C, 46.57; H, 1.56.

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Supporting Information Available: ^{1}H, ^{13}C, and ^{19}F NMR spectra of all the reported new products. This material is available free of charge via the Internet at http://pubs.acs.org.

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