

A Convenient Procedure for the Synthesis of 1-Tetralone Derivatives Using a Suzuki Coupling-Friedel-Crafts Acylation Sequence

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Abstract. The reported 1-tetralone derivatives have been synthesized from arylbromides using as key steps a Suzuki coupling followed by intramolecular Friedel-Crafts acylation. © 1997 Elsevier Science Ltd. All rights reserved.

In recent reports concerning the enantio and diastereoselective approach to substituted hydrophenalene derivatives related to the bioactive diterpenes helioporin E (1) and the aglycon part of pseudopterosin G (2), Schmalz *et al*¹ have developed an elegant methodology based on the use of chromocarbene chemistry, starting from the 6,7-dimethoxy-1-tetralone (3). A related procedure has been used by the same group for the synthesis of funcionalized hydronaphthalene derivatives related to the aglycon part of *seco*-pseudopterosins (4) from 5,6-dimethoxy-1-tetralone (5) (Figure 1).²



Figure 1

0040-4020/98/\$19.00 © 1997 Elsevier Science Ltd. All rights reserved. PII: S0040-4020(97)10270-8 In the reported cases the final product has been obtained lacking in the aromatic methyl group, or else, the final aromatic methylation gave also "significative amounts of the mono-O-demethylated (phenolic) byproducts".^{1a} On the other hand, introduction of a benzodioxole unit (present in compounds such as 1) from the related dimethoxy derivative is usually problematic.³ In this report we wish to account for a convenient synthesis of the four tetralones 6 and 7 starting from the commercially available catechol derivatives 8 and 9 using a three-step procedure involving regiocontrolled bromination, followed by Suzuki coupling to give the related 4-arylbutanoic acids. Final intramolecular Friedel-Crafts acylation will afford compounds 6 and 7 (Scheme 1).



i) Regiocontrolled bromination step.

ii) Suzuki coupling.

iii) Intramolecular Friedel-Crafts acylation.

Scheme 1

The synthesis of the bromoderivatives 10a and 10b (Scheme 2) was achieved from compounds 14 (prepared from 8 in 75% yield using the system $CH_2Cl_2/NaOH$ in DMSO)⁴ and 9, respectively, by reaction with Br₂ in CCl₄ at rt.^{5,6} The synthesis of the bromide 11b was performed by a sequence of metalationbromination of 9.7 In this way, 12b has been obtained in 62% isolated yield. Bromination of 14 using this procedure was unsuccessful.⁸ Thus, we have prepared compound 11a by bromination of 8^{9,10} (Br₂, 0.5 eq./CCl₄) followed by methylenation of the resulting bromoderivative 15 (Scheme 2).

The synthesis of the 4-arylbutanoic acids 12 and 13 were achieved using a protocol¹¹ by reaction of the bromoderivatives 10 and 11 with the borane¹² derived from the reaction of 9-BBN and methyl but-3-enoate¹³ in the presence of 1,1'-bis-(diphenylphosphino)ferrocene palladium (II)-chloride followed by hydrolysis with KOH in ethanol. Finally, intramolecular Friedel-Crafts acylations were accomplished by reaction of compounds 12 and 13 with PPE (polyphosphonate ester) (Scheme 3).¹⁴



Key i) CH₂Cl₂-MeOH, DMSO, Δ. 75% for 14; 84% for 11a. ii) Br₂, CCl₄,0°C to rt, 70%. iii) Br₂ (0.5 eq.), CCl₄, 0° to rt, 42%.

Key i) Br₂, CCl₄, 0°C to rt, 88%. ii) a) nBuLi, Et₂O, TMEDA, 0°C to rt. b) Br₂, -78°C to rt, 65%.





Key i) 9-BBN-(CH₂)₃CO₂CH₃, PdCl₂(dppf) (3%), MeONa, THF, rt. 72% for 16a; 87% for 16b.
ii) KOH/EtOH, rt. 96% for 12a ; 82% for 12b.

iii) PPE, CHCl3, rt. 87% for 6a; 95% for 6b.



Key The same procedures as above were employed. Isolated yields: 70% for 17a;
 68% for 17b; 80% for 13a; 85% for 13b; 81% for 7a; 89% for 7b.

Scheme 3

In view of these results we have extended the above methodology (Suzuki coupling followed by intramolecular Friedel-Crafts acylation) to the synthesis of other tetralone derivatives. The results are summarized in Table 1.

Entry ^a	Starting bromideb	4-Arylbutanoic acid	Product
1	or Br	0 CO ₂ H 18 (61%)	۲۹ (87%)
2	20 (92%)	от СО ₂ н СН ₃ 21 (63%)	о СН ₃ 22 (78%)
3	Br	CO ₂ H 23 (67%)	24 (72%)
4	Br	25 (66%)	
			27 Ratio 26/27 = 1:3.7 (80 %)

Table 1. Synthesis of 1-tetralone derivatives (Isolated yields).



- ^a All starting bromides, except 20, were commercial products.
- ^b Overall yield for the two-step procedure, namely Suzuki coupling and methyl ester hydrolysis.
- ^c Minor amount of the third possible cyclization product **35** was detected in the reaction mixture.



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In summary, a convenient procedure has been developed for the synthesis of aryl and polycyclic 1tetralones using as key step the Suzuki coupling between the aromatic bromoderivative and the appropriate alkylborane, followed by Friedel-Crafts cyclization. The method appears to be quite general and compatible with different substitution patterns in the aromatic moiety.

EXPERIMENTAL SECTION

General. The reactions were carried out under a positive pressure of dry argon using freshly distilled solvents under anhydrous conditions. Reagents and solvents were handled by using standard syringe techniques. IR espectra were recorded on a Perkin-Elmer 297 spectrophotometer. Tetrahydrofurane and diethylether were distilled over sodium/benzophenone; dichloromethane, DMSO, and TMEDA were distilled over CaH₂ before use. 3-Methylcatechol was purified by distillation and the remaining chemicals and solvents were commercial and used as received. ¹H NMR and ¹³C NMR were obtained on Varian XL-300, Bruker AM-250 and Bruker AM-300 spectrometers. Chemical shifts (δ) are reported in ppm from internal (CH₃)₄Si. Silica gel Merck 60 (230-400 mesh) and Merck 60F₂₅₄ plates were used for conventional and analytical (TLC) chromatography respectively. Melting points were determined on a Gallenkamp instrument and are uncorrected. Elemental analyses were performed at the Universidad Complutense of Madrid.

Synthesis of Arylbromides.

2,3-Methylenedioxytoluene (14). To a solution of 3-methylcatechol (2.75 g, 22 mmol) in anhydrous DMSO (35 ml) at rt under argon, powdered sodium hydroxide (1.85 g, 46 mmol) and anhydrous CH₂Cl₂ (1.70 ml, 20 mmol) were added. The resulting mixture was refluxed for 3.5 h, and then it was cooled at rt. After adding distilled water (50 ml), the resulting azeotrope was distilled off. The aqueous distillate was extracted with Et₂O (4x5 ml) and the combined organic layers were washed with brine and dried (MgSO4). The solvent was removed *in vacuo* and the desired product was obtained as a yellowish oil (2.27 g, 75 %) which was used without further purification. ¹H NMR (CDCl₃, 300 MHz): δ 2.20 (s, 3H, CH₃), 5.90 (s, 2H, OCH₂O), 6.60-6.80 (m, 3H, 3xCH).¹³C NMR (CDCl₃, 75 MHz): δ 14.7, 100.5 (OCH₂O), 106.2, 119.3, 121.4, 123.6, 145.8, 146.9. IR (KBr): v 2780, 1180, 930 (O-C-O) cm⁻¹. Anal. Calcd for C₈H₈O₂: C, 70.58; H, 5.92. Found: C, 70.44; H, 5.98.

6-Bromo-2,3-methylenedioxytoluene (10a). Bromine (10 mmol) was added dropwise to a solution of 2,3-methylenedioxytoluene (14) (1.36 g, 10 mmol) in CCl₄ (20 ml) at 0°C. The resulting mixture was stirred at rt for 3 h and then poured into ice/water. The aqueous layer was extracted with CHCl₃. The combined organic layers were washed with aqueous 10% NaHSO₃, aqueous saturated NaHCO₃, water and brine, dried (MgSO₄) and concentrated *in vacuo*. The monobrominated product was obtained as a white crystalline solid (1.51 g, 70 %) after recrystallization from hexane. Mp=52-53°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.23 (s, 3H, CH₃), 5.94 (s, 2H, OCH₂O), 6.53 (d, 1H, J = 8.4 Hz, CH), 6.99 (d, 1H, J = 8.4 Hz, CH). ¹³C NMR (CDCl₃, 75 MHz): δ 15.4, 101.4 (OCH₂O), 107.3, 116.7, 119.9, 124.7, 146.3, 146.9. IR (KBr): v 2790, 940 (O-C-O) cm⁻¹. Anal. Calcd for C₈H₇O₂Br: C, 44.68; H, 3.28. Found: C, 44.44; H, 3.31.

6-Bromo-2,3-dimethoxytoluene (10b). Following the procedure described for the synthesis of **10a**, from 2,3-dimethoxytoluene after 2.5 h of reaction, a white solid which was purified by recrystallization from hexane was obtained (88 %). Mp=51-52°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.34 (s, 3H, CH₃), 3.78 (s,

3H, OCH₃), 3.84 (s, 3H, OCH₃), 6.66 (d, 1H, J = 7.3 Hz, CH), 7.24 (d, 1H, J = 7.3 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 16.2, 55.9 (OCH₃), 60.5 (OCH₃), 111.0, 116.1, 127.4, 132.4, 148.1, 152.2. IR (KBr): v 3000-2835, 1270, 1230 (C-O), 830-800, 690 (C-Br) cm⁻¹. Anal. Calcd for C₉H₁₁O₂Br: C, 46.78; H, 4.80. Found: C, 46.64; H, 4.24.

3-Bromo-6-methylcatechol (15). Following the procedure described for the synthesis of 10a, using 0.5 eq. of bromine, from 3-methylcatechol after 2 h of reaction and purification by column chromatography (Hexane/AcOEt 8:1) a white solid (42 % based in bromine) was obtained. Mp= 68-69°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.22 (s, 3H, CH₃), 5.45 (br s, 2H, 2xOH), 6.63 (d, 1H, J = 8.2 Hz, CH), 6.90 (d, 1H, J = 8.2 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 15.4, 106.4, 122.0, 123.5, 124.5, 139.5, 142.8. IR (KBr): v 3520 (O-H), 1260 (C-O), 1035 cm⁻¹. Anal. Calcd for C₇H₇O₂Br: C, 41.41; H, 3.48. Found: C, 41.74; H, 3.32.

4-Bromo-2,3-methylenedioxytoluene (11a). Following the procedure described for the synthesis of 14, from 15 after 3 h of reaction and purification by recrystallization from hexane a pale yellow solid (84 %) was obtained. Mp= 66-67°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.18 (s, 3H, CH₃), 6.01 (s, 2H, OCH₂O), 6.56 (d, 1H, J = 8.4 Hz, CH), 6.57 (d, 1H, J = 8.4 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 14.3, 97.9 (OCH₂O), 100.9, 118.3, 124.4, 124.6, 144.9, 146.2. IR (KBr): v 2790, 940 (O-C-O) cm⁻¹. Anal. Calcd for C₈H₇O₂Br: C, 44.68; H, 3.28. Found: C, 44.34; H, 3.35.

4-Bromo-2,3-dimethoxytoluene (11b). BuLi 1.6 M in hexane (1.88 ml, 3 mmol) was added dropwise, at 0°C under argon, to a solution of 2,3-dimethoxytoluene (304 mg, 2 mmol) and TMEDA (0.44 ml, 3 mmol) in anhydrous Et₂O (5 ml). After stirring the resulting yellow suspension at rt for 2 h, it was cooled at -78°C and bromine (0.11 ml, 2 mmol) was added. The resulting mixture was stirred at rt for 15 h and then water (5ml) was added. The aqueous layer was extracted with Et₂O and the combined organic phase was washed with aqueous saturated NaHSO₃, water and brine and dried (MgSO₄). After concentrating under reduced pressure, the product was obtained after purification by column chromatography (Hexane/AcOEt 10:1) a colorless oil (65 %). ¹H NMR (CDCl₃, 300 MHz): δ 2.22 (s, 3H, CH₃), 3.85 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 6.63 (d, 1H, J = 8.2 Hz, CH), 6.90 (d, 1H, J = 8.2 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 15.7, 60.3 (OCH₃), 60.4 (OCH₃), 114.6, 126.6, 127.4, 132.0, 150.3, 152.5. IR (KBr): v 2950, 1475-1390, 1240, 1215 (C-O), 695 (C-Br) cm⁻¹. Anal. Calcd for C₉H₁₁O₂Br: C, 46.78; H, 4.80. Found: C, 47.16; H, 4.91.

2-Bromo-4,5-methylenedioxytoluene (20). From 3,4-dimethoxytoluene following the procedure described for the synthesis of 10a, after 5 h of reaction and purification by recrystallization from ethanol a white solid (92%) was obtained. Mp=35-36°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.30 (s, 3H, CH₃), 5.93 (s, 2H, OCH₂O), 6.71 (s, 1H, CH), 6.99 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 22.9, 101.6 (OCH₂O), 110.5, 112.5, 114.8, 130.7, 146.5, 147.2. IR (KBr): v 3080, 2900, 1870, 1045, 940 (O-C-O), 860-830, 670 (C-Br) cm⁻¹. Anal. Calcd for C₈H₇O₂Br: C, 44.68; H, 3.28. Found: C, 44.34; H, 3.35.

Synthesis of 4-Arylbutanoic acids.

Methyl but-3-enoate. Vinylacetic acid (1.6 g, 19 mmol) was added to a suspension of K₂CO₃ (3.20 g, 23 mmol) in acetone (30 ml). After stirring the resulting mixture at rt for some minutes, it was cooled at 0°C and methyl iodide (2.64 g, 29 mmol) was added. The reaction mixture was refluxed for 6 h and then it was cooled at rt. The resulting suspension was filtered *in vacuo* over a short path of celite. After concentrating the filtrate, the product was obtained as a colorless liquid wich was purified by destilation to yield 1.43 g (77 %) of the desired ester as a colorless liquid. Bp=104-106°C (760 mm Hg). ¹H NMR (CDCl₃, 300 MHz): δ 3.11 (dt, 2H, J = 6.9, 1.3 Hz, CH₂), 3.72 (s, 3H, CO₂CH₃), 5.18 (m, 2H, =CH₂), 5.82-6.02 (m, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 18.6, 51.5 (CO₂CH₃), 118.1 (CH₂=), 130.7 (=CH), 171.5 (C=O). IR (CHCl₃): v 1745 (C=O), 1650 (C=C) cm⁻¹.

General Procedure for the Synthesis of Methyl 4-Arylbutanoates by Suzuki Coupling. A solution of methyl 4-(9-BBN)butanoate (1.1 mmol of 9-BBN 0.5 N in THF, 1.1 mmol of methyl but-3enoate, 3 h at rt under argon) was added dropwise to a mixture of the arylbromide (1 mmol), dichloro[1,1'bis(diphenylphosfino)ferrocene]palladium(II) (0.03 mmol) and sodium methoxyde (3 mmol) in 3 ml of anhydrous THF, at rt and under argon. The resulting mixture was refluxed until complete disappearance of the starting material (TLC). The mixture was cooled at rt and distilled water (5 ml) was added. The aqueous phase was extracted with Et₂O and the combined organic layers were washed with brine, dried (MgSO₄) and concentrated *in vacuo*. The corresponding methyl 4-arylbutanoates were obtained after purification by column chromatography.

Methyl 4-(2-methyl-3,4-methylenedioxyphenyl)butanoate (16a). From 10a after 5 h of reaction and purification by column chromatography (CH₂Cl₂) a colorless oil (72 %) was obtained. ¹H NMR (CDCl₃, 300 MHz): δ 1.84 (q, 2H, J = 7.2 Hz, CH₂), 2.17 (s, 3H, CH₃), 2.35 (t, 2H, J = 7.2 Hz, CH₂), 2.56 (t, 2H, J = 7.2 Hz, CH₂), 3.67 (s, 3H, CO₂CH₃), 5.91 (s, 2H, OCH₂O), 6.59 (s, 2H, 2xCH).¹³C NMR (CDCl₃, 75 MHz): δ 11.7, 26.1, 32.3, 33.8, 51.9 (CO₂CH₃), 100.9 (OCH₂O), 105.9, 118.1, 121.9, 134.2, 145.4, 146.6, 174.3 (C=O). IR (CHCl₃): v 2785 (O-C-O), 1745 (C=O) cm⁻¹. Anal. Calcd for C₁₃H₁₆O₄: C, 66.09; H, 6.83. Found: C, 65.86; H, 6.76.

Methyl 4-(2-methyl-3,4-dimethoxyphenyl)butanoate (16b). From 10b after 4.5 h of reaction and purification by column chromatography (CH₂Cl₂) a colorless oil (87 %) was obtained. ¹H NMR (CDCl₃, 300 MHz): δ 1.87 (q, 2H, J = 7.6 Hz, CH₂), 2.23 (s, 3H, CH₃), 2.37 (t, 2H, J = 7.6 Hz, CH₂), 2.58 (t, 2H, J = 7.6 Hz, CH₂), 3.68 (s, 3H, CO₂CH₃), 3.78 (s, 3H, OCH₃), 3.84 (s, 3H, OCH₃), 6.70 (d, 1H, J = 8.4 Hz, CH), 6.84 (d, 1H, J = 8.4 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 11.8, 25.7, 32.5, 33.7, 51.6 (CO₂CH₃), 55.8 (OCH₃), 60.3 (OCH₃), 109.4, 124.3, 130.4, 133.0, 147.4, 151.1, 172.1 (C=O). IR (CHCl₃): v 1255 (C-O), 1740 (C=O) cm⁻¹. Anal. Calcd for C₁₄H₂₀O₄: C, 66.65; H, 7.99. Found: C, 66.56; H, 7.84.

Methyl 4-(4-methyl-2,3-methylenedioxyphenyl)butanoate (17a). From 11a after 3.5 h of reaction and purification by column chromatography (Hexane/AcOEt 5:1) a pale yellow oil (70 %) was obtained. ¹H NMR (CDCl₃, 300 MHz): δ 1.94 (q, 2H, J = 6.3 Hz, CH₂), 2.19 (s, 3H, CH₃), 2.34 (t, 2H, J =

6.3 Hz, CH₂), 2.59 (t, 2H, J = 6.3 Hz, CH₂), 3.66 (s, 3H, CO₂CH₃), 5.91 (s, 2H, OCH₂O), 6.56 (s, 1H, CH), 6.57 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 14.4, 24.8, 28.6, 33.3, 51.4 (CO₂CH₃), 100.3 (OCH₂O), 116.9, 120.1, 122.1, 123.2, 144.9, 145.2, 173.9 (C=O). IR (CHCl₃): v 2800 (O-C-O), 1745

Methyl 4-(4-methyl-2,3-dimethoxyphenyl)butanoate (17b). From 11b after 3 h of reaction and purification by column chromatography (Hexane/AcOEt 4:1) a colorless oil (68 %) was obtained ¹H NMR (CDCl₃, 300 MHz): δ 1.91 (q, 2H, J = 7.6 Hz, CH₂), 2.23 (s, 3H, CH₃), 2.36 (t, 2H, J = 7.6 Hz, CH₂), 2.62 (t, 2H, J = 7.6 Hz, CH₂), 3.67 (s, 3H, CO₂CH₃), 3.82 (s, 3H, OCH₃), 3.84 (s, 3H, OCH₃), 6.82 (s, 1H, CH), 6.81 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 15.7, 25.9, 29.1, 33.6, 51.5 (CO₂CH₃), 59.9 (OCH₃), 60.4 (OCH₃), 124.5, 125.4, 130.2, 133.0, 151.1, 151.3, 174.0 (C=O). IR (CHCl₃): v 1750 (C=O) cm⁻¹. Anal. Calcd for C₁₄H₂₀O₄: C, 66.65; H, 7.99. Found: C, 66.77; H, 7.72.

 $(C=O) \text{ cm}^{-1}$. Anal. Calcd for C₁₃H₁₆O₄: C, 66.09; H, 6.83. Found: C, 66.21; H, 6.99.

Methyl 4-(3,4-methylenedioxy)phenylbutanoate. From 1-bromo-3,4-methylenedioxybenzene after 5 h of reaction and purification by column chromatography (CH₂Cl₂) a colorless oil (65 %) was obtained. ¹H NMR (CDCl₃, 300 MHz): δ 1.88 (q, 2H, J = 7.5 Hz, CH₂), 2.29 (t, 2H, J = 7.5 Hz, CH₂), 2.55 (t, 2H, J = 7.5 Hz, CH₂), 3.64 (s, 3H, CO₂*CH*₃), 5.90 (s, 2H, OCH₂O), 6.59 (dd, 1H, J = 7.8, 1.5 Hz, CH), 6.65 (d, 1H, J = 1.5 Hz, CH), 6.70 (d, 1H, J = 7.8 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 26.8, 33.3, 34.9, 51.6 (CO₂*CH*₃), 100.9 (OCH₂O), 108.2, 109.0, 121.3, 135.3, 145.8, 147.7, 174.0 (C=O). IR (CHCl₃): v 3040, 2690, 1740 (C=O), 1450, 1150 (C-O), 950 (C-O-C), 865, 675 cm⁻¹. Anal. Calcd for C₁₂H₁₄O₄: C, 64.85; H, 6.35. Found: C, 64.81; H, 6.42.

Methyl 4-(2-methyl-4,5-methylenedioxy)phenylbutanoate. From 20 after 2.5 h of reaction and purification by column chromatography (CH₂Cl₂) a pale yellow oil was obtained (73 %). ¹H NMR (CDCl₃, 300 MHz): δ 1.86 (q, 2H, J = 7.5 Hz, CH₂), 2.22 (s, 3H, CH₃), 2.36 (t, 2H, J = 7.5 Hz, CH₂), 2.54 (t, 2H, J = 7.5 Hz, CH₂), 3.57 (s, 3H, CO₂CH₃), 5.77 (s, 2H, OCH₂O), 6.51 (s, 1H, CH), 6.52 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 19.2, 25.7, 32.5, 33.6, 51.6 (CO₂CH₃), 100.7 (OCH₂O), 109.3, 110.5 (2C), 128.8, 132.6, 145.7, 174.0 (C=O). IR (CHCl₃): v 2960, 1740 (C=O), 1170, 925 (O-C-O) cm⁻¹. Anal. Calcd for C₁₃H₁₆O₄: C, 66.09; H, 6.83. Found: C, 66.12; H, 7.01.

Methyl 4-(5-acenaphthenyl)butanoate. From 5-bromoacenaphthene after 2.5 h of reaction and purification by column chromatography (CH₂Cl₂) a yellow oil (68 %) was obtained. ¹H NMR (CDCl₃, 300 MHz): δ 2.09 (q, 2H, J = 7.5 Hz, CH₂), 2.42 (t, 2H, J = 7.5 Hz, CH₂), 3.06 (t, 2H, J = 7.5 Hz, CH₂), 3.34-3.45 (m, 4H, 2xCH₂), 3.70 (s, 3H, CO₂CH₃), 7.22 (d, 1H, J = 6.9 Hz, CH), 7.24 (d, 1H, J = 8.4 Hz, CH), 7.29 (d, 1H, J = 8.4 Hz, CH), 7.48 (dd, 1H, J = 8.4, 6.9 Hz, CH), 7.73 (d, 1H, J = 8.4 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 26.0, 30.0, 30.7, 31.5, 33.8, 51.6 (CO₂CH₃), 119.1, 119.2, 119.4, 127.7 (2C), 130.5, 133.4, 139.7, 144.5, 146.6, 174.2 (C=O). IR (CHCl₃): v 2950, 1740 (C=O), 1450, 1165 (C-O), 850 cm⁻¹. Anal. Calcd for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 79.96; H, 7.32.

Methyl 4-(2-fluorenyl)butanoate. From 2-bromofluorene after 4.5 h of reaction and purification by column chromatography (CH₂Cl₂) a yellow solid (76 %) was obtained. Mp = $64-65^{\circ}$ C. ¹H NMR (CDCl₃, 300 MHz): δ 2.00 (q, 2H, J = 7.5 Hz, CH₂), 2.36 (t, 2H, J = 7.5 Hz, CH₂), 2.72 (t, 2H, J = 7.5 Hz, CH₂), 3.66 (s, 3H, CO₂CH₃), 3.86 (s, 2H, CH₂), 7.17 (d, 1H, J = 7.2 Hz, CH), 7.26 (t, 1H, J = 7.2 Hz, CH),

7.35 (s, 1H, CH), 7.32-7.37 (m, 1H, CH), 7.51 (d, 1H, J = 7.2 Hz, CH), 7.68 (d, 1H, J = 7.2 Hz, CH), 7.74 (d, 1H, J = 7.5 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 26.7, 33.4, 35.3, 36.8, 51.5 (CO₂CH₃), 119.6, 119.7, 125.0, 125.1, 126.3, 126.7, 127.1, 139.7, 140.1, 141.6, 143.1, 143.5, 174.0 (C=O). IR (CHCl₃): v 2960, 1740 (C=O), 1160 (C-O), 845 cm⁻¹. Anal. Calcd for C₁₈H₁₈O₂: C, 81.17; H, 6.81. Found: C, 81.25; H, 6.93.

Dimethyl 2,7-fluorenedibutanoate. From 2,7-dibromofluorene after 4 h of reaction and purification by column chromatography (Hexane/AcOEt 10:1) a yellowish solid (70 %) was obtained. Mp = 78-80°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.00 (q, 4H, J = 7.5 Hz, 2xCH₂), 2.36 (t, 4H, J = 7.5 Hz, 2xCH₂), 2.72 (t, 4H, J = 7.5 Hz, 2xCH₂), 3.67 (s, 6H, 2xCO₂CH₃), 3.83 (s, 2H, CH₂), 7.17 (d, 2H, J = 7.5 Hz, 2xCH), 7.34 (s, 2H, 2xCH), 7.65 (d, 2H, J = 7.5 Hz, 2xCH).¹³C NMR (CDCl₃, 75 MHz): δ 26.7 (2C), 33.4 (2C), 35.2 (2C), 36.7, 51.5 (2xCO₂CH₃), 119.4 (2C), 125.1 (2C), 127.0 (2C), 139.6 (2C), 139.7 (2C), 143.5 (2C), 174.0 (2xC=O). IR (CHCl₃): v 3000-2920, 2860, 1735 (C=O), 1440, 1175 (C-O), 825 cm⁻¹. Anal. Calcd for C₂₃H₂₆O₄: C, 75.38; H, 7.15. Found: C, 75.86; H, 7.12.

Methyl 4-(9-anthracenyl)butanoate. From 9-bromoanthracene after 6 h of reaction and purification by column chromatography (CH₂Cl₂) a yellow solid (95 %) was obtained. Mp = 73-75°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.07-2.18 (m, 2H, CH₂), 2.51 (t, 2H, J = 7.2 Hz, CH₂), 3.60-3.66 (m, 2H, CH₂), 3.70 (s, 3H, CO₂CH₃), 7.43 (ddd, 2H, J = 8.1, 6.6, 1.5 Hz, 2xCH), 7.50 (ddd, 2H, J = 8.7, 6.9, 1.5 Hz, 2xCH), 7.97 (d, 1H, J = 8.1 Hz, CH), 8.25 (s, 1H, CH), 8.30 (d, 1H, J = 8.7 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 26.0, 27.1, 33.9, 51.6 (CO₂CH₃), 124.3 (2C), 124.9 (2C), 125.6 (2C), 126.0, 129.2 (2C), 129.7 (2C), 131.6 (2C), 133.9, 173.9 (C=O). IR (CHCl₃): v 3030, 1735 (C=O), 1450, 1165 (C-O), 930-890, 745 cm⁻¹. Anal. Calcd for C₁₉H₁₈O₂: C, 81.99; H, 6.52. Found: C, 81.86; H, 6.62.

Methyl 4-(9-phenanthrenyl)butanoate. From 9-bromophenanthrene after 10 h of reaction and purification by column chromatography (CH₂Cl₂), a white solid (72 %) was obtained. Mp = 87-88°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.13 (q, 2H, J = 7.5 Hz, CH₂), 2.44 (t, 2H, J = 7.5 Hz, CH₂), 3.12 (t, 2H, J = 7.5 Hz, CH₂), 3.66 (s, 1H, CO₂CH₃), 7.55 (s, 1H, CH), 7.56-7.64 (m, 4H, 4xCH), 7.78-7.81(m, 1H, CH), 8.09-8.12 (m, 1H, CH), 8.60-8.72 (m, 2H, 2xCH).¹³C NMR (DMSO, 75 MHz): δ 25.2, 32.7, 33.7, 51.6 (CO₂CH₃), 122.5, 123.3, 124.4, 126.1, 126.2, 126.4, 126.7 (2C), 128.1, 129.8, 130.8, 131.1, 131.8, 135.6, 174.5 (C=O). IR (CHCl₃): v 2950, 1740 (C=O), 1435, 1150, 860 cm⁻¹. Anal. Calcd for C₁₉H₁₈O₂: C, 81.99; H, 6.52. Found: C, 82.15; H, 6.67.

General Procedure for the Hydrolysis of the Methyl Esters. To a suspension of potasium hydroxide (4 mmol for the synthesis of 28 and 2 mmol for all the rest) in distilled ethanol (4 ml), at rt, the corresponding methyl 4-aryl-butanoate (1 mmol) was added. The reaction mixture was stirred until the hydrolysis was complete (TLC). After removing the solvent *in vacuo* a solid was obtained, which was disolved in distilled water. This solution was acidulated with glacial acetic acid until appearance of a pale yellow solid which was filtered off and washed with distilled water. Most of the produts were used without further purification.

4-(2-Methyl-3,4-methylenedioxyphenyl)butanoic acid (12a). From 16a after 2.5 h of reaction a white solid which was identified without further purification was obtained (96 %). Mp = 123-124°C. ¹H NMR (CDCl₃, 300 MHz): δ 1.84 (q, 2H, J = 7.2 Hz, CH₂), 2.15 (s, 3H, CH₃), 2.37 (t, 2H, J = 7.2 Hz, CH₂), 2.57 (t, 2H, J = 7.2 Hz, CH₂), 5.90 (s, 2H, OCH₂O), 6.58 (s, 2H, 2xCH), 10.3 (s, 1H, CO*OH*).¹³C NMR (CDCl₃, 75 MHz): δ 11.5, 25.5, 31.9, 33.6, 100.7 (OCH₂O), 105.7, 117.9, 121.7, 133.7, 145.2, 146.4, 180.1 (C=O). IR (KBr): v 3400-3100 (COO-H), 2790, 1720 (C=O), 945 (O-C-O) cm⁻¹. Anal. Calcd for C₁₂H₁₄O₄ : C, 64.85; H, 6.35. Found: C, 64.65; H, 6.41.

4-(2-Methyl-3,4-dimethoxyphenyl)butanoic acid (12b). From 16b after 2.5 h of reaction a white solid which was used without further purification was obtained (82 %). Mp = 87-88°C. ¹H NMR (CDC1₃, 300 MHz): δ 1.83 (q, 2H, J = 6.3 Hz, CH₂), 2.19 (s, 3H, CH₃), 2.36 (t, 2H, J = 6.3 Hz, CH₂), 2.56 (t, 2H, J = 6.3 Hz, CH₂), 3.73 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 6.65 (d, 1H, J = 7.0 Hz, CH), 6.79 (d, 1H, J = 7.0, CH).¹³C NMR (CDCl₃, 75 MHz): δ 11.8, 25.4, 32.4, 33.7, 55.7 (OCH₃), 60.3 (OCH₃), 109.4, 124.4, 130.4, 132.8, 147.4, 151.1, 180.0 (C=O). IR (CHCl₃): v 2990 (COO-H), 1760 (C=O) cm⁻¹. Anal. Calcd for C₁₃H₁₈O₄: C, 65.53; H, 7.61. Found: C, 65.65; H, 7.41.

4-(4-Methyl-2,3-methylenedioxyphenyl)butanoic acid (13a). From **17a** after 2.5 h of reaction a white solid which was used without further purification was obtained (80%). ¹H NMR (CDCl₃, 300 MHz): δ 1.95 (q, 2H, J = 7.3 Hz, CH₂), 2.20 (s, 3H, CH₃), 2.38 (t, 2H, J = 7.3 Hz, CH₂), 2.61 (t, 2H, J = 7.3 Hz, CH₂), 5.92 (s, 2H, OCH₂O), 6.58 (s, 2H, 2xCH).¹³C NMR (CDCl₃, 75 MHz): δ 14.4, 24.5, 28.5, 33.2, 100.3 (OCH₂O), 117.0, 119.9, 122.1, 123.2, 144.9, 145.2, 179.7 (C=O). IR (KBr): v 2980-2940, 1740 (C=O), 1430, 1260 cm⁻¹. Anal. Calcd for C₁₂H₁₄O4: C, 64.85; H, 6.35. Found: C, 65.00; H, 6.24.

4-(4-Methyl-2,3-dimethoxyphenyl)butanoic acid (13b). From 17b after 4 h of reaction and purification by recrystallization from H₂O a white solid was obtained (85%). ¹H NMR (CDCl₃, 300 MHz): δ 1.92 (q, 2H, J = 7.5 Hz, CH₂), 2.23 (s, 3H, CH₃), 2.39 (t, 2H, J = 7.5 Hz, CH₂), 2.64 (t, 2H, J = 7.6 Hz, CH₂), 3.82 (s, 3H, OCH₃), 3.84 (s, 3H, OCH₃), 6.79 (d, 1H, CH), 6.83 (d, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 15.7, 24.7, 29.1, 33.6, 59.9 (OCH₃), 60.3 (OCH₃), 124.6, 125.5, 130.3, 132.9, 151.2, 151.3, 179.6 (C=O). IR (KBr): v 2960 (COO-H), 1775 (C=O) cm⁻¹. Anal. Calcd for C₁₃H₁₈O4: C, 63.53; H, 7.61. Found: C, 63.29; H, 7.88.

4-(3,4-Methylenedioxy)phenylbutanoic acid (18). From methyl 4-(3,4methylenedioxy)phenylbutanoate after 2 h of reaction a white solid which was used without further purification was obtained (94 %). Mp = 81-83°C. ¹H NMR (CDCl₃, 300 MHz): δ 1.88 (q, 2H, J = 7.5 Hz, CH₂), 2.32 (t, 2H, J = 7.5 Hz, CH₂), 2.56 (t, 2H, J = 7.5 Hz, CH₂), 5.90 (s, 2H, OCH₂O), 6.45 (dd, 1H, J = 7.8, 1.2 Hz, CH), 6.66 (d, 1H, J = 1.2 Hz, CH), 6.71 (d, 1H, J = 7.8 Hz, CH), 9.60 (s br, 1H, COOH).¹³C NMR (CDCl₃, 75 MHz): δ 26.6, 33.5, 34.7, 100.7 (OCH₂O), 108.1, 108.8, 121.2, 135.1, 145.7, 147.5, 179.8 (C=O). IR (KBr): v 2940 (COO-H), 1725 (C=O), 1160, 945 (O-C-O), 930-820 cm⁻¹. Anal. Calcd for C₁₁H₁₂O₄: C, 63.45; H, 5.81. Found: C, 63.49; H, 5.71.

4-(2-Methyl-4,5-methylenedioxy)butanoic acid (21). From methyl 4-(2-methyl-4,5-methylenedioxy)phenylbutanoate after 3 h of reaction a white solid which was used without further purification was obtained (86 %). Mp = 108-110°C. ¹H NMR (CDCl₃, 300 MHz): δ 1.88 (q, 2H, J = 7.5 Hz, CH₂), 2.23

(s, 3H, CH₃), 2.42 (t, 2H, J = 7.5 Hz, CH₂), 2.53 (t, 2H, J = 7.5 Hz, CH₂), 5.89 (s, 2H, OCH₂O), 6.64 (s, 2H, 2xCH).¹³C NMR (CDCl₃, 75 MHz): δ 19.2, 25.4, 32.4, 33.5, 100.7 (OCH₂O), 109.3, 110.5, 128.9, 132.4, 145.7 (2C), 179.8 (C=O). IR (KBr): v 2950 (COO-H), 1720 (C=O), 1500, 925 (O-C-O) cm⁻¹. Anal. Calcd for C₁₂H₁₄O₄: C, 64.85; H, 6.35. Found: C, 64.97; H, 6.56.

4-(9-Acenaphthenyl)butanoic acid (23). From methyl 4-(5-acenaphthenyl)butanoate after 3.5 h of reaction a white solid which was used without further purification was obtained (98 %). Mp = 140-141°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.08 (q, 2H, J = 7.5 Hz, CH₂), 2.44 (t, 2H, J = 7.5 Hz, CH₂), 3.07 (t, 2H, J = 7.5 Hz, CH₂), 3.31-3.46 (m, 4H, 2xCH₂), 7.19 (d, 1H, J = 6.9 Hz, CH), 7.25 (d, 1H, J = 6.5 Hz, CH), 7.27 (d, 1H, J = 6.5 Hz, CH), 7.45 (dd, 1H, J = 8.4, 6.9 Hz, CH), 7.70 (d, 1H, J = 8.4 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 25.6, 29.8, 30.5, 31.2, 33.5, 118.9, 119.0, 119.1, 127.6 (2C), 130.3, 133.0, 139.6, 144.4, 146.5, 179.7 (C=O). IR (KBr): v 3030-2900 (COO-H), 1730 (C=O), 1450-1430, 950 cm⁻¹. Anal. Calcd for C₁₆H₁₆O₂: C, 79.97; H, 6.71. Found: C, 79.62; H, 6.86.

4-(2-Fluorenyl)butanoic acid (25). From methyl 4-(2-fluorenyl)butanoate) after 6 h of reaction a white solid which was used without further purification was obtained (87 %). Mp = 150-152°C. ¹H NMR (CDC1₃, 300 MHz): δ 1.99 (q, 2H, J = 7.2 Hz, CH₂), 2.37 (t, 2H, J = 7.2 Hz, CH₂), 2.73 (t, 2H, J = 7.2 Hz, CH₂), 3.85 (s, 2H, CH₂), 7.18 (d, 1H, J = 7.8 Hz, CH), 7.27 (t, 1H, J = 7.2 Hz, CH), 7.32-7.37 (m, 1H, CH), 7.35 (s, 1H, CH), 7.51 (d, 1H, J = 7.2 Hz, CH), 7.68 (d, 1H, J = 7.2 Hz, CH), 7.74 (d, 1H, J = 7.5 Hz, CH).¹³C NMR (CDC1₃, 75 MHz): δ 26.4, 33.4, 35.2, 36.8, 119.6, 119.7, 125.0, 125.2, 126.4, 126.7, 127.1, 139.8, 139.9, 141.6, 143.1, 143.6, 180.0 (C=O). IR (KBr): v 3060-2850 (COO-H), 1700 (C=O), 1440, 1465, 950, 750 cm⁻¹. Anal. Calcd for C₁₇H₁₆O₂: C, 80.93; H, 6.39. Found: C, 80.84; H, 6.53.

2,7-Fluorenedibutanoic acid (28). From dimethyl 2,7-fluorenedibutanoate after 3 h of reaction a white solid which was used without further purification was obtained (80 %). Mp = 231-232°C. ¹H NMR (DMSO, 300 MHz): δ 1.83 (q, 4H, J = 7.3 Hz, 2xCH₂), 2.24 (t, 4H, J = 7.3 Hz, 2xCH₂), 2.65 (t, 4H, J = 7.3 Hz, 2xCH₂), 3.85 (s, 2H, CH₂), 7.18 (d, 2H, J = 7.8, 2xCH), 7.38 (s, 2H, 2xCH), 7.74 (d, 2H, J = 7.8, 2xCH).¹³C NMR (DMSO, 75 MHz): δ 21.4 (2C), 28.0 (2C), 29.4 (2C), 31.0, 114.4 (2C), 119.9 (2C), 121.8 (2C), 133.9 (2C), 134.8 (2C), 138.0 (2C), 169.2 (2xC=O). IR (KBr): v 3040-2850 (COO-H), 1700 (C=O), 1425, 1465, 1180, 830 cm⁻¹. Anal. Calcd for C₂₁H₂₂O₄: C, 74.54; H, 6.55. Found: C, 74.45; H, 6.40.

4-(9-Anthracenyl)butanoic acid (31). From methyl 4-(9-anthracenyl)butanoate after 3.5 h of reaction a white solid which was used without further purification was obtained (100 %). Mp = 154-156°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.17 (q, 2H, J = 7.2 Hz, CH₂), 2.61 (t, 2H, J = 7.2 Hz, CH₂), 3.67-3.72 (m, 2H, CH₂), 7.43-7.54 (m, 4H, 4xCH), 8.01 (d, 2H, J = 8.4 Hz, 2xCH), 8.27 (d, 2H, J = 8.7 Hz, 2xCH), 8.35 (s, 1H, CH).¹³C NMR (DMSO, 75 MHz): δ 26.3, 26.6, 33.5, 124.4 (2C), 125.1 (2C), 125.5 (2C), 125.8 (2C), 129.0 (2C), 129.2, 131.1 (2C), 134.4, 174.6 (C=O). IR (KBr): v 3080, 2970-2850 (COO-H), 1715 (C=O), 1260, 950-840 cm⁻¹. Anal. Calcd for C₁₈H₁₆O₂: C, 81.79; H, 6.10. Found: C, 81.82; H, 6.31.

4-(9-Phenanthrenyl)butanoic acid (33). From methyl 4-(9-phenanthrenyl)butanoate after 15 h of reaction a white solid which was used without further purification was obtained (90 %). Mp = $168-170^{\circ}$ C. ¹H

NMR (DMSO, 300 MHz): δ 1.97 (q, 2H, J = 7.4 Hz, CH₂), 2.39 (t, 2H, J = 7.4 Hz, CH₂), 3.11 (t, 2H, J = 7.4 Hz, CH₂), 3.40 (br s, 1H, CO*OH*), 7.61-7.71 (m, 4H, 4xCH), 7.67 (s, 1H, CH), 7.89-7.92 (m, 1H, CH), 8.20 (t, 1H, J = 5.0 Hz, CH), 8.78 (d, 1H, J = 8.4 Hz, CH), 8.85 (m, 1H, CH).¹³C NMR (DMSO, 75 MHz): δ 25.3, 32.0, 33.4, 122.7, 123.5, 124.4, 126.0, 126.3, 126.5, 126.8, 126.9, 128.0, 129.1, 130.2, 130.6, 131.4, 135.9, 174.4 (C=O). IR (KBr): v 3060, 2980 (COO-H), 1720 (C=O), 1200, 835 cm⁻¹. Anal. Calcd for C₁₈H₁₆O₂: C, 81.79; H, 6.10. Found: C, 81.91; H, 5.99.

Synthesis of 1-Tetralone Derivatives.

General Procedure for the Friedel-Crafts Acylations. To the 4-arylbutanoic acid (1 mmol), at rt, a freshly prepared solution of PPE (4 ml) (1.5 g of P_2O_5 , 10 ml of anhydrous Et_2O and 20 ml of CHCl₃, refluxed for 6 h under argon) was added. The resulting mixture was stirred at rt for some hours, until complete disappearance of the starting material, and then it was poured into ice/water. The aqueous layer was extracted with CHCl₃ and the combined organic layers were washed with aqueous 5% NaHCO₃, water and brine, and dried (MgSO₄). After removing the solvent in *vacuo*, the products were obtained in most cases as solids which were purified by chromatography and/or recrystallization.

5-Methyl-6,7-methylenedioxy-1-tetralone (6a). From **12a** after 2.5 h of reaction a yellowish solid which was purified by recrystallization from EtOH (87 %) was obtained. Mp = 114-115°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.09 (q, 2H, J = 6.4 Hz, CH₂), 2.16 (s, 3H, CH₃), 2.57 (t, 2H, J = 6.4 Hz, CH₂), 2.77 (t, 2H, J = 6.4 Hz, CH₂), 5.98 (s, 2H, OCH₂O), 7.38 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 11.5, 23.0, 26.4, 38.4, 101.3 (OCH₂O), 104.1, 116.7, 127.5, 140.1, 145.8, 150.6, 197.3 (C=O). IR (KBr): v 1660 (C=O), 1610, 935 (O-C-O) cm⁻¹. Anal. Calcd for C₁₂H₁₂O₃: C, 70.58; H, 5.92. Found: C, 70.30; H, 6.09.

5-Methyl-6,7-dimethoxy-1-tetralone (6b). From 12b after 6.5 h of reaction and purification by recrystallization from EtOH a yellowish solid was (95 %) obtained. Mp = 72-73°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.13 (q, 2H, J = 5.3 Hz, CH₂), 2.22 (s, 3H, CH₃), 2.61 (t, 2H, J = 5.3 Hz, CH₂), 2.80 (t, 2H, J = 5.3 Hz, CH₂), 3.84 (s, 3H, OCH₃), 3.89 (s, 3H, OCH₃), 7.42 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 12.0, 23.0, 26.5, 38.5, 55.8 (OCH₃), 60.5 (OCH₃), 107.5, 128.8, 130.1, 137.5, 151.3, 151.9, 198.2 (C=O). IR (KBr): v 1690 (C=O), 1250, 1225 (C-O), 1095 cm⁻¹. Anal. Calcd for C₁₃H₁₆O₃: C, 70.89; H, 7.32. Found: C, 70.79; H, 7.43.

7-Methyl-5,6-methylenedioxy-1-tetralone (7a). From 13a after 2.5 h of reaction and purification by recrystallization from hexane a yellowish solid was obtained (81 %). Mp = 100-101°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.10 (q, 2H, J = 5.3 Hz, CH₂), 2.23 (s, 3H, CH₃), 2.60 (t, 2H, J = 5.3 Hz, CH₂), 2.82 (t, 2H, J = 5.3 Hz, CH₂), 6.06 (s, 2H, OCH₂O), 7.54 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 14.4, 22.7, 22.8, 38.9, 101.8 (OCH₂O), 117.5, 123.0, 124.3, 127.1, 143.9, 149.7, 197.0 (C=O). IR (KBr): \vee 2785, 1670 (C=O) cm⁻¹. Anal. Calcd for C₁₂H₁₂O₃: C, 70.58; H, 5.92. Found: C, 70.45; H, 6.01.

7-Methyl-5,6-dimethoxy-1-tetralone (7b). From 13b after 7 h of reaction a yellowish solid which was purified by recrystallization from EtOH was obtained (89 %). Mp = $72-73^{\circ}$ C. ¹H NMR (CDCl₃,

300 MHz): δ 2.10 (q, 2H, J = 5.3 Hz, CH₂), 2.26 (s, 3H, CH₃), 2.59 (t, 2H, J = 5.3 Hz, CH₂), 2.91 (t, 2H, J = 5.3 Hz, CH₂), 3.83 (s, 3H, OCH₃), 3.90 (s, 3H, OCH₃), 7.67 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 15.9, 23.0, 23.2, 38.8, 60.1 (OCH₃), 60.2 (OCH₃), 124.8, 128.6, 130.5, 137.6, 149.5, 156.0, 197.9 (C=O). IR (KBr): v 2920, 1685 (C=O) cm⁻¹. Anal. Calcd for C₁₃H₁₆O₃: C, 70.89; H, 7.32. Found: C, 71.05; H, 7.41.

6,7-Methylenedioxy-1-tetralone (19). From **18** after 5 h of reaction a yellow solid which was which was purified by recrystallization from EtOH was obtained (87 %). Mp = 74-75°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.07 (q, 2H, J = 6.3 Hz, CH₂), 2.57 (t, 2H, J = 6.3 Hz, CH₂), 2.85 (t, 2H, J = 6.3 Hz, CH₂), 5.97 (s, 2H, OCH₂O), 6.34 (s, 1H, CH), 7.44 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 23.5, 30.0, 38.6, 101.6 (OCH₂O), 106.2, 107.9, 127.4, 141.4, 146.9, 152.0, 196.7 (C=O). IR (KBr): v 2950-2880, 1675 (C=O), 1270-1250 (C-O-C), 940 (O-C-O) cm⁻¹. Anal. Calcd for C₁₁H₁₀O₃: C, 69.46; H, 5.30. Found: C, 69.68; H, 5.37.

5-Methyl-7,8-methylenedioxy-1-tetralone (22). From 21 after 14 h of reaction and purification by column chromatography (Hexane/AcOEt 4:1), a yellow solid (78 %) was obtained. Mp = $132-133^{\circ}$ C. ¹H NMR (CDCl₃, 300 MHz): δ 2.09 (q, 2H, J = 6.3 Hz, CH₂), 2.22 (s, 3H, CH₃), 2.61 (t, 2H, J = 6.3 Hz, CH₂), 2.75 (t, 2H, J = 6.3 Hz, CH₂), 6.06 (s, 2H, OCH₂O), 6.83 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 19.6, 22.5, 26.3, 39.3, 101.9 (OCH₂O), 114.6, 117.2, 128.3, 134.1, 145.7, 146.3, 187.1 (C=O). IR (KBr): v 2950, 1680 (C=O), 1050, 925 (O-C-O) cm⁻¹. Anal. Calcd for C₁₂H₁₂O₃: C, 70.58; H, 5.92. Found: C, 70.37; H, 5.94.

4,5,7,8,9,10-Hexahydro-7-oxo-cyclopenta[j,k]phenanthrene (24). From 23 after 9 h of reaction and purification by column chromatography (Hexane/AcOEt 5:1), a yellowish solid (72 %) was obtained. Mp = 138-140°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.26 (q, 2H, J = 6.4 Hz, CH₂), 2.74 (t, 2H, J = 6.4 Hz, CH₂), 3.29 (t, 2H, J = 6.4 Hz, CH₂), 3.21-3.42 (m, 4H, 2xCH₂), 7.42 (d, 1H, J = 6.9 Hz, CH), 7.53 (dd, 1H, J = 8.4, 6.9 Hz, CH), 7.85 (d, 1H, J = 8.4 Hz, CH), 7.91 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 22.9, 25.0, 29.8, 30.5, 38.9, 116.1, 120.5, 122.2, 128.3, 129.7, 131.5, 139.7, 141.3, 144.2, 146.4, 199.4 (C=O). IR (KBr): v 2970, 1660 (C=O), 1435-1400, 790-765 cm⁻¹. Anal. Calcd for C₁₆H₁₄O: C, 86.45; H, 6.35. Found: C, 86.66; H, 6.11.

1,2,3,4-Tetrahydro-1-oxo-[11H]-benzo[a]fluorene (26). From **25** after 10 h of reaction and purification by column chromatography (Hexane/AcOEt 10:1), **26** was obtained as a pale yellow solid from a mixture **26/27=**1:3.7 (80 %). Mp = 120-121°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.18 (q, 2H, J = 6.3 Hz, CH₂), 2.72 (t, 2H, J = 6.3 Hz, CH₂), 3.06 (t, 2H, J = 6.3 Hz, CH₂), 4.29 (s, 2H, CH₂), 7.31 (d, 1H, J = 6.9 Hz, CH), 7.33-7.40 (m, 2H, 2xCH), 7.61 (d, 1H, J = 6.9 Hz, CH), 7.77 (d, 1H, J = 7.5 Hz, CH), 7.79 (d, 1H, J = 7.5 Hz, CH).¹³C NMR (CDCl₃, 75 MHz): δ 23.7, 30.6, 39.6, 40.6, 119.7, 124.6, 125.3, 126.8, 127.2, 128.1, 129.5, 140.4, 141.6, 143.9, 144.7, 145.2, 185.4 (C=O). IR (KBr): v 2930, 1680 (C=O), 1470-1385, 770-760 cm⁻¹. Anal. Calcd for C₁₇H₁₄O: C, 87.15; H, 6.02. Found: C, 86.99; H, 6.15.

1,2,3,4-Tetrahydro-1-oxo-[6H]-benzo[b]fluorene (27). From 25 after 10 h of reaction and purification by column chromatography (Hexane/AcOEt 10:1), 27 was obtained as a pale yellow solid from a mixture 26/27=1:3.7 (80 %). Mp = 150-151°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.16 (q, 2H, J = 6.3 Hz,

CH₂), 2.69 (t, 2H, J = 6.3 Hz, CH₂), 3.01 (t, 2H, J = 6.3 Hz, CH₂), 3.89 (s, 2H, CH₂), 7.31 (td, 1H, J = 7.2, 1.2 Hz, CH), 7.39 (s, 1H, CH), 7.39 (t, 1H, J = 7.2 Hz, CH), 7.51 (d, 1H, J = 7.2 Hz, CH), 7.82 (d, 1H, J = 7.2 Hz, CH), 8.42 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 23.4, 30.1, 37.0, 39.2, 118.2, 120.3, 124.9, 125.2, 127.0, 127.1, 131.5, 140.6, 140.8, 142.7, 143.3, 149.0, 186.1 (C=O). IR (KBr): v 3080-2830, 2925, 1685 (C=O), 1410, 835 cm⁻¹. Anal. Calcd for C₁₇H₁₄O: C, 87.15; H, 6.02. Found: C, 87.22; H, 6.19.

1,2,3,4,8,9,10,11-Octahydro-1,8-dioxo-[13*H*]-dibenzo[a,h]fluorene (29). From 28 after 15 h of reaction and purification by column chromatography (CH₂Cl₂), 29 was obtained as a yellowish solid from a mixture 29/30=1:4 (68 %). Mp = 244-245°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.18 (q, 4H, J = 6.3 Hz, 2xCH₂), 2.69-2.74 (m, 4H, 2xCH₂), 3.04-3.09 (m, 4H, 2xCH₂), 4.29 (s, 2H, CH₂), 7.31 (d, 1H, J = 7.6 Hz, CH), 7.47 (s, 1H, CH), 7.93 (d, 1H, J = 7.6 Hz, CH), 8.41 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 23.4 (2C), 30.3 (2C), 39.3, 39.5, 40.2, 118.0 (2C), 124.8, 125.2, 128.3, 131.5, 139.1, 140.6, 143.7, 144.1, 144.4, 150.2, 198.8 (C=O), 199.7 (C=O). IR (KBr): v 2930, 1735 (C=O), 1675 (C=O), 1410, 1290-1185, 835 cm⁻¹. Anal. Calcd for C_{21H18}O₂: C, 83.42; H, 6.00. Found: C, 83.23; H, 6.35.

1,2,3,4,7,8,9,10-Octahydro-4,7-dioxo-[12H]-dibenzo[b,h]fluorene (30). From 28 after 15 h of reaction and purification by column chromatography (CH₂Cl₂), 30 was obtained as a pale orange solid from a separable mixture 29/30=1:4 (68 %). Mp = 222-223°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.17 (q, 4H, J = 6.3 Hz, 2xCH₂), 2.70 (t, 4H, J = 6.3 Hz, 2xCH₂), 3.03 (t, 4H, J = 6.3 Hz, 2xCH₂), 3.93 (s, 2H, CH₂), 7.40 (s, 2H, 2xCH), 8.48 (s, 2H, 2xCH).¹³C NMR (CDCl₃, 75 MHz): δ 23.4 (2C), 30.2 (2C), 37.1 (2C), 39.2, 118.8 (2C), 125.2 (2C), 131.9 (2C), 139.8 (2C), 143.7 (2C), 148.4 (2C), 198.2 (2xC=O). IR (KBr): v 2940, 1685 (C=O), 1620, 1140, 900-835 cm⁻¹. Anal. Calcd for C₂₁H₁₈O₂: C, 83.42; H, 6.00. Found: C, 83.70; H, 5.79.

1,2,3,4-Tetrahydro-4-oxo-cyclohepta[k,1]anthracene (32). From 31 after 2.5 h of reaction and purification by column chromatography (Hexane/AcOEt 10:1), a pale orange solid (63 %) was obtained. Mp= 84-85°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.55 (q, 2H, J = 7.1 Hz, CH₂), 2.80 (t, 2H, J = 7.1 Hz, CH₂), 3.59 (t, 2H, J = 7.1 Hz, CH₂), 7.46 (dd, 1H, J = 8.7, 6.3 Hz, CH), 7.53 (d, 1H, J = 8.1 Hz, CH), 7.57 (d, 1H, J = 8.4 Hz, CH), 7.83 (d, 1H, J = 6.3 Hz, CH), 8.05 (dd, 2H, J = 8.4, 8.1 Hz, 2xCH), 8.32 (d, 1H, J = 8.7 Hz, CH), 8.40 (s, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 27.5, 28.7, 41.9, 123.9, 124.1, 125.5, 126.6, 127.2, 128.1, 129.1, 130.8, 131.1, 132.1, 132.6, 133.8, 139.5, 206.4 (C=O). IR (KBr): v 2940, 1710 (C=O), 1610, 1040, 940, 865 cm⁻¹. Anal. Calcd for C₁₈H₁₄O: C, 87.78; H, 5.73. Found: C, 87.54; H, 5.89.

1,2,3,4-Tetrahydro-1-oxo-benzo[l]phenanthrene (34). From **33** after 14 h of reaction and purification by column chromatography (Hexane/AcOEt 5:1), the product was obtained as a yellowish solid (81%). Mp = 76-77°C. ¹H NMR (CDCl₃, 300 MHz): δ 2.30 (q, 2H, J = 6.5 Hz, CH₂), 2.84 (t, 2H, J = 6.5 Hz, CH₂), 3.42 (t, 2H, J = 6.5 Hz, CH₂), 7.61-7.68 (m, 3H, 3xCH), 7.76 (ddd, 1H, J = 8.1, 7.5, 1.2 Hz, CH), 8.19 (d, 1H, J = 7.5 Hz, CH), 8.64-8.68 (m, 1H, CH), 8.69 (d, 1H, J = 8.1 Hz, CH), 9.24-9.27 (m, 1H, CH).¹³C NMR (CDCl₃, 75 MHz): δ 22.2, 27.2, 40.4, 122.4, 123.2, 125.5, 126.6, 127.1, 127.6, 127.8,

128.8, 129.2, 129.9, 132.4, 137.0, 144.2, 144.4, 200.8 (C=O). IR (KBr): v 3080, 2925, 1660 (C=O), 1385, 1180, 750 cm⁻¹. Anal. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73. Found: C, 88.01; H, 5.67.

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