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TETRAHEDRON

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

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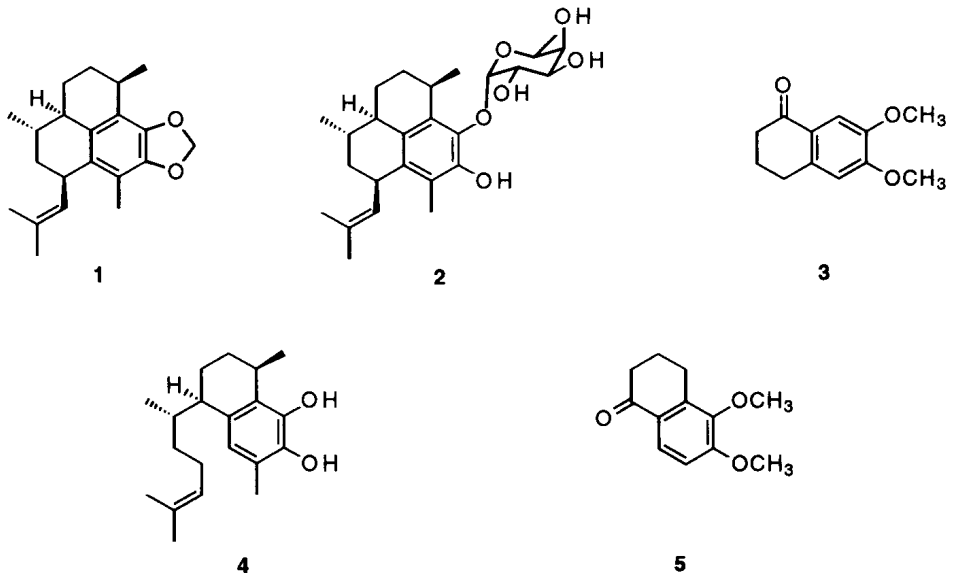
Abstract. The reported 1-tetralone derivatives have been synthesized from arylbromides using as key steps a Suzuki coupling followed by intramolecular Friedel-Crafts acylation. © 1997 Elsevier Science Ltd. All rights reserved.

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]



1 2 3

4 5

Figure 1

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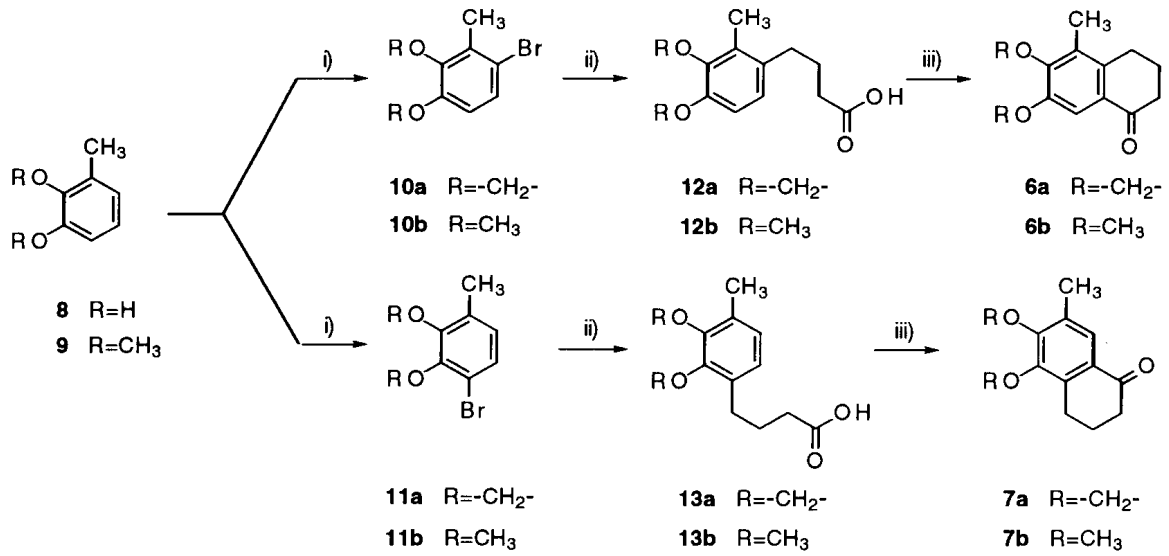
In the reported cases the final product has been obtained lacking in the aromatic methyl group, or else, the final aromatic methylation gave also "significative amounts of the mono-O-demethylated (phenolic) byproducts".[1a] On the other hand, introduction of a benzodioxole unit (present in compounds 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.

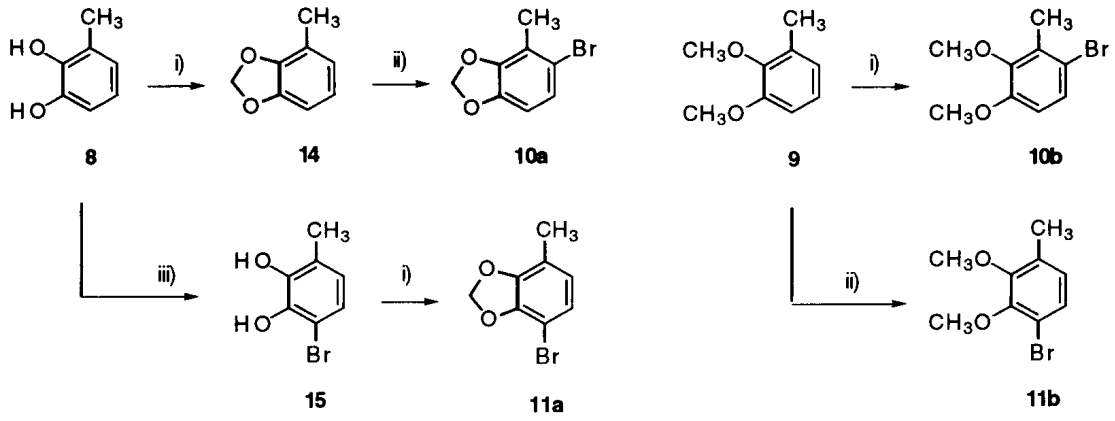
ii) Suzuki coupling.

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 Br_2 in CCl_4 at rt.[5,6] The synthesis of the bromide **11b** was performed by a sequence of metalation-bromination 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] (Br_2, 0.5 eq./CCl_4) followed by methylenation of the resulting bromoderivative **15** (Scheme 2).

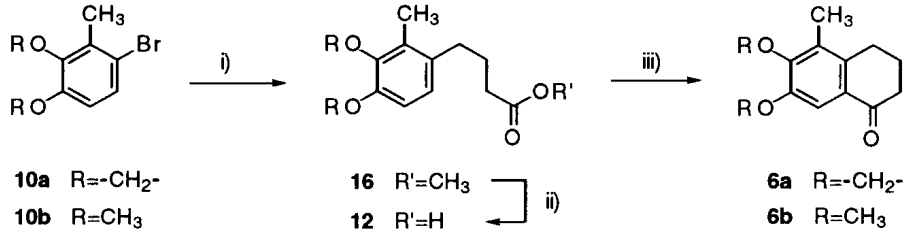
The synthesis of the 4-arylbutanoic acids **12** and **13** were achieved using a protocol[11] by reaction of the bromoderivatives **10** and **11** with the borane[12] derived from the reaction of 9-BBN and methyl but-3-enoate[13] in the presence of 1,1'-bis-(diphenylphosphino)ferrocene palladium (II)-chloride 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) CH_2Cl_2-MeOH, DMSO, Δ. 75% for **14**; 84% for **11a**. ii) Br_2, CCl_4, 0°C to rt, 70%. iii) Br_2 (0.5 eq.), CCl_4, 0° to rt, 42%.

Key i) Br_2, CCl_4, 0°C to rt, 88%. ii) a) nBuLi, Et_2O, TMEDA, 0°C to rt. b) Br_2, -78°C to rt, 65%.

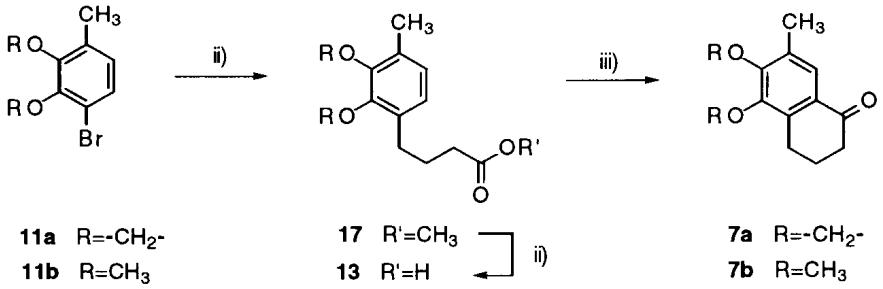
Scheme 2



Key i) 9-BBN-$(CH_2)_3CO_2CH_3$, $PdCl_2$(dppf) (3%), MeONa, THF, rt. 72% for **16a**; 87% for **16b**.

ii) KOH/EtOH, rt. 96% for **12a** ; 82% for **12b**.

iii) PPE, $CHCl_3$, rt. 87% for **6a**; 95% for **6b**.

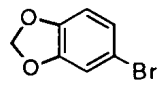
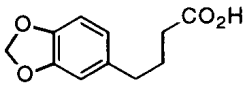
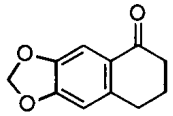
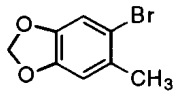
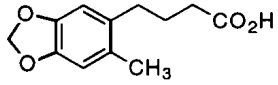
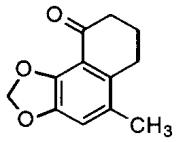
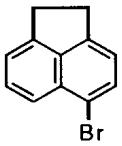
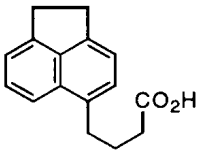
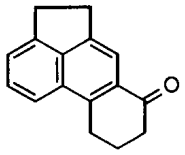
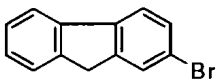
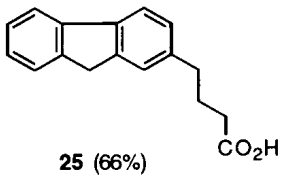
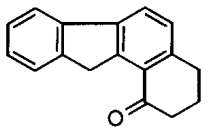
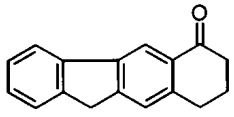


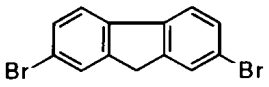
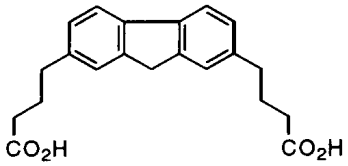
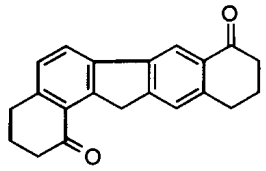
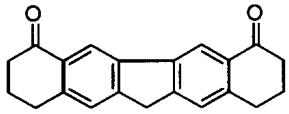
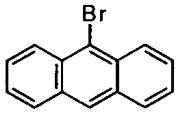
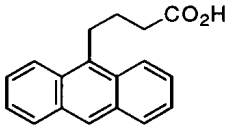
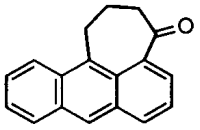
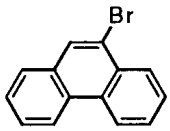
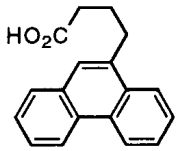
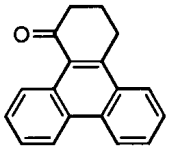
Key The same procedures as above were employed. Isolated yields: 70% for **17a**; 68% for **17b**; 80% for **13a**; 85% for **13b**; 81% for **7a**; 89% for **7b**.

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.

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

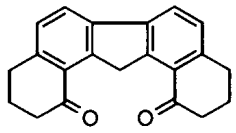
Entry[a]	Starting bromide[b]	4-Arylbutanoic acid	Product
1		 **18** (61%)	 **19** (87%)
2	 **20** (92%)	 **21** (63%)	 **22** (78%)
3		 **23** (67%)	 **24** (72%)
4		 **25** (66%)	 **26**  **27** Ratio **26/27**= 1:3.7 (80 %)

Entry[a]	Starting bromide[b]	4-Arylbutanoic acid	Product
5		 **28** (56%)	 **29**  **30** Ratio **29/30**=1:4 (68 %)
6		 **31** (95%)	 **32** (63 %)
7		 **33** (65%)	 **34** (81%)

[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.



35

In summary, a convenient procedure has been developed for the synthesis of aryl and polycyclic 1-tetralones using as key step the Suzuki coupling between the aromatic bromoderivative and the appropiate

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 CaH_2 before use. 3-Methylcatechol was purified by distillation and the remaining chemicals and solvents were commercial and used as received. ^1H NMR and ^{13}C NMR were obtained on Varian XL-300, Bruker AM-250 and Bruker AM-300 spectrometers. Chemical shifts (δ) are reported in ppm from internal $(CH_3)_4Si$. Silica gel Merck 60 (230-400 mesh) and Merck $60F_{254}$ 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 CH_2Cl_2 (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 Et_2O (4x5 ml) and the combined organic layers were washed with brine and dried ($MgSO_4$). 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 ($CDCl_3$, 300 MHz): δ 2.20 (s, 3H, CH_3), 5.90 (s, 2H, OCH_2O), 6.60-6.80 (m, 3H, 3xCH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.7, 100.5 (OCH_2O), 106.2, 119.3, 121.4, 123.6, 145.8, 146.9. IR (KBr): ν 2780, 1180, 930 (O-C-O) cm^{-1}. Anal. Calcd for $C_8H_8O_2$: 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 CCl_4 (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 $CHCl_3$. The combined organic layers were washed with aqueous 10% $NaHSO_3$, aqueous saturated $NaHCO_3$, water and brine, dried ($MgSO_4$) 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 ($CDCl_3$, 300 MHz): δ 2.23 (s, 3H, CH_3), 5.94 (s, 2H, OCH_2O), 6.53 (d, 1H, J = 8.4 Hz, CH), 6.99 (d, 1H, J = 8.4 Hz, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.4, 101.4 (OCH_2O), 107.3, 116.7, 119.9, 124.7, 146.3, 146.9. IR (KBr): ν 2790, 940 (O-C-O) cm^{-1}. Anal. Calcd for $C_8H_7O_2Br$: 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 ($CDCl_3$, 300 MHz): δ 2.34 (s, 3H, CH_3), 3.78 (s,

3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.66 (d, 1H, J = 7.3 Hz, CH), 7.24 (d, 1H, J = 7.3 Hz, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.2, 55.9 (OCH_3), 60.5 (OCH_3), 111.0, 116.1, 127.4, 132.4, 148.1, 152.2. IR (KBr): ν 3000-2835, 1270, 1230 (C-O), 830-800, 690 (C-Br) cm^{-1}. Anal. Calcd for $C_9H_{11}O_2Br$: 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 ($CDCl_3$, 300 MHz): δ 2.22 (s, 3H, CH_3), 5.45 (br s, 2H, 2xOH), 6.63 (d, 1H, J = 8.2 Hz, CH), 6.90 (d, 1H, J = 8.2 Hz, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.4, 106.4, 122.0, 123.5, 124.5, 139.5, 142.8. IR (KBr): ν 3520 (O-H), 1260 (C-O), 1035 cm^{-1}. Anal. Calcd for $C_7H_7O_2Br$: 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 ($CDCl_3$, 300 MHz): δ 2.18 (s, 3H, CH_3), 6.01 (s, 2H, OCH_2O), 6.56 (d, 1H, J = 8.4 Hz, CH), 6.57 (d, 1H, J = 8.4 Hz, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.3, 97.9 (OCH_2O), 100.9, 118.3, 124.4, 124.6, 144.9, 146.2. IR (KBr): ν 2790, 940 (O-C-O) cm^{-1}. Anal. Calcd for $C_8H_7O_2Br$: 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 Et_2O (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 Et_2O and the combined organic phase was washed with aqueous saturated $NaHSO_3$, water and brine and dried ($MgSO_4$). After concentrating under reduced pressure, the product was obtained after purification by column chromatography (Hexane/AcOEt 10:1) a colorless oil (65 %). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.22 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.63 (d, 1H, J = 8.2 Hz, CH), 6.90 (d, 1H, J = 8.2 Hz, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.7, 60.3 (OCH_3), 60.4 (OCH_3), 114.6, 126.6, 127.4, 132.0, 150.3, 152.5. IR (KBr): ν 2950, 1475-1390, 1240, 1215 (C-O), 695 (C-Br) cm^{-1}. Anal. Calcd for $C_9H_{11}O_2Br$: 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 ($CDCl_3$, 300 MHz): δ 2.30 (s, 3H, CH_3), 5.93 (s, 2H, OCH_2O), 6.71 (s, 1H, CH), 6.99 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.9, 101.6 (OCH_2O), 110.5, 112.5, 114.8, 130.7, 146.5, 147.2. IR (KBr): ν 3080, 2900, 1870, 1045, 940 (O-C-O), 860-830, 670 (C-Br) cm^{-1}. Anal. Calcd for $C_8H_7O_2Br$: 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 K_2CO_3 (3.20 g, 23 mmol) in acetone (30 ml). After stirring the resulting mixture at rt for some minutes, it was cooled at 0ºC 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=104-106ºC (760 mm Hg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.11 (dt, 2H, J = 6.9, 1.3 Hz, CH_2), 3.72 (s, 3H, CO_2CH_3), 5.18 (m, 2H, $=CH_2$), 5.82-6.02 (m, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.6, 51.5 (CO_2CH_3), 118.1 (CH_2=), 130.7 (=CH), 171.5 (C=O). IR ($CHCl_3$): ν 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-3-enoate, 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 Et_2O and the combined organic layers were washed with brine, dried ($MgSO_4$) 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 (CH_2Cl_2) a colorless oil (72 %) was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.84 (q, 2H, J = 7.2 Hz, CH_2), 2.17 (s, 3H, CH_3), 2.35 (t, 2H, J = 7.2 Hz, CH_2), 2.56 (t, 2H, J = 7.2 Hz, CH_2), 3.67 (s, 3H, CO_2CH_3), 5.91 (s, 2H, OCH_2O), 6.59 (s, 2H, 2xCH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.7, 26.1, 32.3, 33.8, 51.9 (CO_2CH_3), 100.9 (OCH_2O), 105.9, 118.1, 121.9, 134.2, 145.4, 146.6, 174.3 (C=O). IR ($CHCl_3$): ν 2785 (O-C-O), 1745 (C=O) cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_4$: 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 (CH_2Cl_2) a colorless oil (87 %) was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.87 (q, 2H, J = 7.6 Hz, CH_2), 2.23 (s, 3H, CH_3), 2.37 (t, 2H, J = 7.6 Hz, CH_2), 2.58 (t, 2H, J = 7.6 Hz, CH_2), 3.68 (s, 3H, CO_2CH_3), 3.78 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.70 (d, 1H, J = 8.4 Hz, CH), 6.84 (d, 1H, J = 8.4 Hz, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.8, 25.7, 32.5, 33.7, 51.6 (CO_2CH_3), 55.8 (OCH_3), 60.3 (OCH_3), 109.4, 124.3, 130.4, 133.0, 147.4, 151.1, 172.1 (C=O). IR ($CHCl_3$): ν 1255 (C-O), 1740 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_4$: 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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.94 (q, 2H, J = 6.3 Hz, CH_2), 2.19 (s, 3H, CH_3), 2.34 (t, 2H, J =

6.3 Hz, CH_2), 2.59 (t, 2H, J = 6.3 Hz, CH_2), 3.66 (s, 3H, CO_2CH_3), 5.91 (s, 2H, OCH_2O), 6.56 (s, 1H, CH), 6.57 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.4, 24.8, 28.6, 33.3, 51.4 (CO_2CH_3), 100.3 (OCH_2O), 116.9, 120.1, 122.1, 123.2, 144.9, 145.2, 173.9 (C=O). IR ($CHCl_3$): ν 2800 (O-C-O), 1745 (C=O) cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.21; H, 6.99.

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 ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.91 (q, 2H, J = 7.6 Hz, CH_2), 2.23 (s, 3H, CH_3), 2.36 (t, 2H, J = 7.6 Hz, CH_2), 2.62 (t, 2H, J = 7.6 Hz, CH_2), 3.67 (s, 3H, CO_2CH_3), 3.82 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.82 (s, 1H, CH), 6.81 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.7, 25.9, 29.1, 33.6, 51.5 (CO_2CH_3), 59.9 (OCH_3), 60.4 (OCH_3), 124.5, 125.4, 130.2, 133.0, 151.1, 151.3, 174.0 (C=O). IR ($CHCl_3$): ν 1750 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.77; H, 7.72.

Methyl 4-(3,4-methylenedioxy)phenylbutanoate. From 1-bromo-3,4-methylenedioxybenzene after 5 h of reaction and purification by column chromatography (CH_2Cl_2) a colorless oil (65 %) was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.88 (q, 2H, J = 7.5 Hz, CH_2), 2.29 (t, 2H, J = 7.5 Hz, CH_2), 2.55 (t, 2H, J = 7.5 Hz, CH_2), 3.64 (s, 3H, CO_2CH_3), 5.90 (s, 2H, OCH_2O), 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).^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.8, 33.3, 34.9, 51.6 (CO_2CH_3), 100.9 (OCH_2O), 108.2, 109.0, 121.3, 135.3, 145.8, 147.7, 174.0 (C=O). IR ($CHCl_3$): ν 3040, 2690, 1740 (C=O), 1450, 1150 (C-O), 950 (C-O-C), 865, 675 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_4$: 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 (CH_2Cl_2) a pale yellow oil was obtained (73 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.86 (q, 2H, J = 7.5 Hz, CH_2), 2.22 (s, 3H, CH_3), 2.36 (t, 2H, J = 7.5 Hz, CH_2), 2.54 (t, 2H, J = 7.5 Hz, CH_2), 3.57 (s, 3H, CO_2CH_3), 5.77 (s, 2H, OCH_2O), 6.51 (s, 1H, CH), 6.52 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.2, 25.7, 32.5, 33.6, 51.6 (CO_2CH_3), 100.7 (OCH_2O), 109.3, 110.5 (2C), 128.8, 132.6, 145.7, 174.0 (C=O). IR ($CHCl_3$): ν 2960, 1740 (C=O), 1170, 925 (O-C-O) cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_4$: 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 (CH_2Cl_2) a yellow oil (68 %) was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.09 (q, 2H, J = 7.5 Hz, CH_2), 2.42 (t, 2H, J = 7.5 Hz, CH_2), 3.06 (t, 2H, J = 7.5 Hz, CH_2), 3.34-3.45 (m, 4H, 2xCH_2), 3.70 (s, 3H, CO_2CH_3), 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).^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.0 , 30.0, 30.7, 31.5, 33.8, 51.6 (CO_2CH_3), 119.1, 119.2, 119.4, 127.7 (2C), 130.5, 133.4, 139.7, 144.5, 146.6, 174.2 (C=O). IR ($CHCl_3$): ν 2950 , 1740 (C=O), 1450, 1165 (C-O), 850 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2$: 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 (CH_2Cl_2) a yellow solid (76 %) was obtained. Mp = 64-65°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.00 (q, 2H, J = 7.5 Hz, CH_2), 2.36 (t, 2H, J = 7.5 Hz, CH_2), 2.72 (t, 2H, J = 7.5 Hz, CH_2), 3.66 (s, 3H, CO_2CH_3), 3.86 (s, 2H, CH_2), 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).^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.7, 33.4, 35.3, 36.8, 51.5 ($CO_2\mathit{CH_3}$), 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 ($CHCl_3$): ν 2960 , 1740 (C=O), 1160 (C-O), 845 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_2$: 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 = 78-80ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.00 (q, 4H, J = 7.5 Hz, 2xCH_2), 2.36 (t, 4H, J = 7.5 Hz, 2xCH_2), 2.72 (t, 4H, J = 7.5 Hz, 2xCH_2), 3.67 (s, 6H, 2x$CO_2\mathit{CH_3}$), 3.83 (s, 2H, CH_2), 7.17 (d, 2H, J = 7.5 Hz, 2xCH), 7.34 (s, 2H, 2xCH), 7.65 (d, 2H, J = 7.5 Hz, 2xCH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.7 (2C), 33.4 (2C), 35.2 (2C), 36.7, 51.5 (2x$CO_2\mathit{CH_3}$), 119.4 (2C), 125.1 (2C), 127.0 (2C), 139.6 (2C), 139.7 (2C), 143.5 (2C), 174.0 (2xC=O). IR ($CHCl_3$): ν 3000-2920, 2860, 1735 (C=O), 1440, 1175 (C-O), 825 cm^{-1}. Anal. Calcd for $C_{23}H_{26}O_4$: 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 (CH_2Cl_2) a yellow solid (95 %) was obtained. Mp = 73-75ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.07-2.18 (m, 2H, CH_2), 2.51 (t, 2H, J = 7.2 Hz, CH_2), 3.60-3.66 (m, 2H, CH_2), 3.70 (s, 3H, $CO_2\mathit{CH_3}$), 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).^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.0, 27.1, 33.9, 51.6 ($CO_2\mathit{CH_3}$), 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 ($CHCl_3$): ν 3030, 1735 (C=O), 1450, 1165 (C-O), 930-890, 745 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_2$: 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 (CH_2Cl_2), a white solid (72 %) was obtained. Mp = 87-88ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (q, 2H, J = 7.5 Hz, CH_2), 2.44 (t, 2H, J = 7.5 Hz, CH_2), 3.12 (t, 2H, J = 7.5 Hz, CH_2), 3.66 (s, 1H, $CO_2\mathit{CH_3}$), 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).^{13}C NMR (DMSO, 75 MHz): δ 25.2, 32.7, 33.7, 51.6 ($CO_2\mathit{CH_3}$), 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 ($CHCl_3$): ν 2950, 1740 (C=O), 1435, 1150, 860 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_2$: 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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.84 (q, 2H, J = 7.2 Hz, CH_2), 2.15 (s, 3H, CH_3), 2.37 (t, 2H, J = 7.2 Hz, CH_2), 2.57 (t, 2H, J = 7.2 Hz, CH_2), 5.90 (s, 2H, OCH_2O), 6.58 (s, 2H, 2xCH), 10.3 (s, 1H, CO*OH*).^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.5, 25.5, 31.9, 33.6, 100.7 (OCH_2O), 105.7, 117.9, 121.7, 133.7, 145.2, 146.4, 180.1 (C=O). IR (KBr): ν 3400-3100 (COO-H), 2790, 1720 (C=O), 945 (O-C-O) cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_4$: 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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.83 (q, 2H, J = 6.3 Hz, CH_2), 2.19 (s, 3H, CH_3), 2.36 (t, 2H, J = 6.3 Hz, CH_2), 2.56 (t, 2H, J = 6.3 Hz, CH_2), 3.73 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.65 (d, 1H, J = 7.0 Hz, CH), 6.79 (d, 1H, J = 7.0, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.8, 25.4, 32.4, 33.7, 55.7 (OCH_3), 60.3 (OCH_3), 109.4, 124.4, 130.4, 132.8, 147.4, 151.1, 180.0 (C=O). IR ($CHCl_3$): ν 2990 (COO-H), 1760 (C=O) cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_4$: 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%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.95 (q, 2H, J = 7.3 Hz, CH_2), 2.20 (s, 3H, CH_3), 2.38 (t, 2H, J = 7.3 Hz, CH_2), 2.61 (t, 2H, J = 7.3 Hz, CH_2), 5.92 (s, 2H, OCH_2O), 6.58 (s, 2H, 2xCH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.4, 24.5, 28.5, 33.2, 100.3 (OCH_2O), 117.0, 119.9, 122.1, 123.2, 144.9, 145.2, 179.7 (C=O). IR (KBr): ν 2980-2940, 1740 (C=O), 1430, 1260 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_4$: 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 H_2O a white solid was obtained (85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.92 (q, 2H, J = 7.5 Hz, CH_2), 2.23 (s, 3H, CH_3), 2.39 (t, 2H, J = 7.5 Hz, CH_2), 2.64 (t, 2H, J = 7.6 Hz, CH_2), 3.82 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.79 (d, 1H, CH), 6.83 (d, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.7, 24.7, 29.1, 33.6, 59.9 (OCH_3), 60.3 (OCH_3), 124.6, 125.5, 130.3, 132.9, 151.2, 151.3, 179.6 (C=O). IR (KBr): ν 2960 (COO-H), 1775 (C=O) cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_4$: C, 63.53; H, 7.61. Found: C, 63.29; H, 7.88.

4-(3,4-Methylenedioxy)phenylbutanoic acid (18). From methyl 4-(3,4-methylenedioxy)phenylbutanoate after 2 h of reaction a white solid which was used without further purification was obtained (94 %). Mp = 81-83°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.88 (q, 2H, J = 7.5 Hz, CH_2), 2.32 (t, 2H, J = 7.5 Hz, CH_2), 2.56 (t, 2H, J = 7.5 Hz, CH_2), 5.90 (s, 2H, OCH_2O), 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, CO*OH*).^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.6, 33.5, 34.7, 100.7 (OCH_2O), 108.1, 108.8, 121.2, 135.1, 145.7, 147.5, 179.8 (C=O). IR (KBr): ν 2940 (COO-H), 1725 (C=O), 1160, 945 (O-C-O), 930-820 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_4$: 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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.88 (q, 2H, J = 7.5 Hz, CH_2), 2.23

(s, 3H, CH_3), 2.42 (t, 2H, J = 7.5 Hz, CH_2), 2.53 (t, 2H, J = 7.5 Hz, CH_2), 5.89 (s, 2H, OCH_2O), 6.64 (s, 2H, 2xCH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.2, 25.4, 32.4, 33.5, 100.7 (OCH_2O), 109.3, 110.5, 128.9, 132.4, 145.7 (2C), 179.8 (C=O). IR (KBr): ν 2950 (COO-H), 1720 (C=O), 1500, 925 (O-C-O) cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_4$: 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 ($CDCl_3$, 300 MHz): δ 2.08 (q, 2H, J = 7.5 Hz, CH_2), 2.44 (t, 2H, J = 7.5 Hz, CH_2), 3.07 (t, 2H, J = 7.5 Hz, CH_2), 3.31-3.46 (m, 4H, 2xCH_2), 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). ^{13}C NMR ($CDCl_3$, 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): ν 3030-2900 (COO-H), 1730 (C=O), 1450-1430, 950 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_2$: 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 ($CDCl_3$, 300 MHz): δ 1.99 (q, 2H, J = 7.2 Hz, CH_2), 2.37 (t, 2H, J = 7.2 Hz, CH_2), 2.73 (t, 2H, J = 7.2 Hz, CH_2), 3.85 (s, 2H, CH_2), 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). ^{13}C NMR ($CDCl_3$, 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): ν 3060-2850 (COO-H), 1700 (C=O), 1440, 1465, 950, 750 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_2$: 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, 2xCH_2), 2.24 (t, 4H, J = 7.3 Hz, 2xCH_2), 2.65 (t, 4H, J = 7.3 Hz, 2xCH_2), 3.85 (s, 2H, CH_2), 7.18 (d, 2H, J = 7.8, 2xCH), 7.38 (s, 2H, 2xCH), 7.74 (d, 2H, J = 7.8, 2xCH). ^{13}C 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): ν 3040-2850 (COO-H), 1700 (C=O), 1425, 1465, 1180, 830 cm^{-1}. Anal. Calcd for $C_{21}H_{22}O_4$: 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 ($CDCl_3$, 300 MHz): δ 2.17 (q, 2H, J = 7.2 Hz, CH_2), 2.61 (t, 2H, J = 7.2 Hz, CH_2), 3.67-3.72 (m, 2H, CH_2), 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). ^{13}C 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): ν 3080, 2970-2850 (COO-H), 1715 (C=O), 1260, 950-840 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2$: 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°C. ^1H

NMR (DMSO, 300 MHz): δ 1.97 (q, 2H, J = 7.4 Hz, CH_2), 2.39 (t, 2H, J = 7.4 Hz, CH_2), 3.11 (t, 2H, J = 7.4 Hz, CH_2), 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).^{13}C 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): ν 3060, 2980 (COO-H), 1720 (C=O), 1200, 835 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2$: 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 $CHCl_3$, 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 $CHCl_3$ and the combined organic layers were washed with aqueous 5% $NaHCO_3$, water and brine, and dried ($MgSO_4$). 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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.09 (q, 2H, J = 6.4 Hz, CH_2), 2.16 (s, 3H, CH_3), 2.57 (t, 2H, J = 6.4 Hz, CH_2), 2.77 (t, 2H, J = 6.4 Hz, CH_2), 5.98 (s, 2H, OCH_2O), 7.38 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.5, 23.0, 26.4, 38.4, 101.3 (OCH_2O), 104.1, 116.7, 127.5, 140.1, 145.8, 150.6, 197.3 (C=O). IR (KBr): ν 1660 (C=O), 1610, 935 (O-C-O) cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_3$: 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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (q, 2H, J = 5.3 Hz, CH_2), 2.22 (s, 3H, CH_3), 2.61 (t, 2H, J = 5.3 Hz, CH_2), 2.80 (t, 2H, J = 5.3 Hz, CH_2), 3.84 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 7.42 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.0, 23.0, 26.5, 38.5, 55.8 (OCH_3), 60.5 (OCH_3), 107.5, 128.8, 130.1, 137.5, 151.3, 151.9, 198.2 (C=O). IR (KBr): ν 1690 (C=O), 1250, 1225 (C-O), 1095 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: 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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.10 (q, 2H, J = 5.3 Hz, CH_2), 2.23 (s, 3H, CH_3), 2.60 (t, 2H, J = 5.3 Hz, CH_2), 2.82 (t, 2H, J = 5.3 Hz, CH_2), 6.06 (s, 2H, OCH_2O), 7.54 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.4, 22.7, 22.8, 38.9, 101.8 (OCH_2O), 117.5, 123.0, 124.3, 127.1, 143.9, 149.7, 197.0 (C=O). IR (KBr): ν 2785, 1670 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_3$: 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°C. ^{1}H NMR ($CDCl_3$,

300 MHz): δ 2.10 (q, 2H, J = 5.3 Hz, CH_2), 2.26 (s, 3H, CH_3), 2.59 (t, 2H, J = 5.3 Hz, CH_2), 2.91 (t, 2H, J = 5.3 Hz, CH_2), 3.83 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 7.67 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.9, 23.0, 23.2, 38.8, 60.1 (OCH_3), 60.2 (OCH_3), 124.8, 128.6, 130.5, 137.6, 149.5, 156.0, 197.9 (C=O). IR (KBr): ν 2920, 1685 (C=O) cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: 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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.07 (q, 2H, J = 6.3 Hz, CH_2), 2.57 (t, 2H, J = 6.3 Hz, CH_2), 2.85 (t, 2H, J = 6.3 Hz, CH_2), 5.97 (s, 2H, OCH_2O), 6.34 (s, 1H, CH), 7.44 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.5, 30.0, 38.6, 101.6 (OCH_2O), 106.2, 107.9, 127.4, 141.4, 146.9, 152.0, 196.7 (C=O). IR (KBr): ν 2950-2880, 1675 (C=O), 1270-1250 (C-O-C), 940 (O-C-O) cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_3$: 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°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.09 (q, 2H, J = 6.3 Hz, CH_2), 2.22 (s, 3H, CH_3), 2.61 (t, 2H, J = 6.3 Hz, CH_2), 2.75 (t, 2H, J = 6.3 Hz, CH_2), 6.06 (s, 2H, OCH_2O), 6.83 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.6, 22.5, 26.3, 39.3, 101.9 (OCH_2O), 114.6, 117.2, 128.3, 134.1, 145.7, 146.3, 187.1 (C=O). IR (KBr): ν 2950, 1680 (C=O), 1050, 925 (O-C-O) cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_3$: 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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.26 (q, 2H, J = 6.4 Hz, CH_2), 2.74 (t, 2H, J = 6.4 Hz, CH_2), 3.29 (t, 2H, J = 6.4 Hz, CH_2), 3.21-3.42 (m, 4H, 2xCH_2), 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).^{13}C NMR ($CDCl_3$, 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): ν 2970, 1660 (C=O), 1435-1400, 790-765 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.66; H, 6.11.

1,2,3,4-Tetrahydro-1-oxo-[11*H*]-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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.18 (q, 2H, J = 6.3 Hz, CH_2), 2.72 (t, 2H, J = 6.3 Hz, CH_2), 3.06 (t, 2H, J = 6.3 Hz, CH_2), 4.29 (s, 2H, CH_2), 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).^{13}C NMR ($CDCl_3$, 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): ν 2930, 1680 (C=O), 1470-1385, 770-760 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.99; H, 6.15.

1,2,3,4-Tetrahydro-1-oxo-[6*H*]-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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.16 (q, 2H, J = 6.3 Hz,

CH_2), 2.69 (t, 2H, J = 6.3 Hz, CH_2), 3.01 (t, 2H, J = 6.3 Hz, CH_2), 3.89 (s, 2H, CH_2), 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).^{13}C NMR ($CDCl_3$, 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): ν 3080-2830, 2925, 1685 (C=O), 1410, 835 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O$: 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 (CH_2Cl_2), **29** was obtained as a yellowish solid from a mixture **29/30**=1:4 (68 %). Mp = 244-245°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.18 (q, 4H, J = 6.3 Hz, 2xCH_2), 2.69-2.74 (m, 4H, 2xCH_2), 3.04-3.09 (m, 4H, 2xCH_2), 4.29 (s, 2H, CH_2), 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).^{13}C NMR ($CDCl_3$, 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): ν 2930, 1735 (C=O), 1675 (C=O), 1410, 1290-1185, 835 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_2$: 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-[12*H*]-dibenzo[b,h]fluorene (30). From **28** after 15 h of reaction and purification by column chromatography (CH_2Cl_2), **30** was obtained as a pale orange solid from a separable mixture **29/30**=1:4 (68 %). Mp = 222-223°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.17 (q, 4H, J = 6.3 Hz, 2xCH_2), 2.70 (t, 4H, J = 6.3 Hz, 2xCH_2), 3.03 (t, 4H, J = 6.3 Hz, 2xCH_2), 3.93 (s, 2H, CH_2), 7.40 (s, 2H, 2xCH), 8.48 (s, 2H, 2xCH).^{13}C NMR ($CDCl_3$, 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): ν 2940, 1685 (C=O), 1620, 1140, 900-835 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.70; H, 5.79.

1,2,3,4-Tetrahydro-4-oxo-cyclohepta[k,l]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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.55 (q, 2H, J = 7.1 Hz, CH_2), 2.80 (t, 2H, J = 7.1 Hz, CH_2), 3.59 (t, 2H, J = 7.1 Hz, CH_2), 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).^{13}C NMR ($CDCl_3$, 75 MHz): δ 27.5, 28.7, 41.9, 123.9, 124.1, 125.5, 126.5, 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): ν 2940, 1710 (C=O), 1610, 1040, 940, 865 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O$: 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. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.30 (q, 2H, J = 6.5 Hz, CH_2), 2.84 (t, 2H, J = 6.5 Hz, CH_2), 3.42 (t, 2H, J = 6.5 Hz, CH_2), 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).^{13}C NMR ($CDCl_3$, 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): ν 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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