New Synthetic Approach to Naphtho[1,2-*b*]furan and 4′-Oxo-Substituted Spiro[cyclopropane-1,1′(4′*H*)-naphthalene] Derivatives

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A one-step synthesis of ethyl 2,3-dihydronaphtho[1,2-*b*]furan-2-carboxylate and/or ethyl 4′-oxospiro[cyclopropane-1,1′(4′*H*)-naphthalene]-2′-carboxylate derivatives **2** and **3**, respectively, from substituted naphthalen-1-ols and ethyl 2,3-dibromopropanoate is described (*Scheme 1*). Compounds **2** were easily aromatized (*Scheme 2*). In the same way, 3,4-dibromobutan-2-one afforded the corresponding 1-(2,3-dihydronaphtho[1,2-*b*]furan-2-yl)ethanone and/or spiro derivatives **8** and **9**, respectively (*Scheme 6*). A mechanism for the formation of the dihydronaphtho[1,2-*b*]furan ring and of the spiro compounds **3** is proposed (*Schemes 3* and *4*). The structures of spiro compounds **3a** and **3f** were established by X-ray structural analysis. The reactivity of compound **3a** was also briefly examined (*Scheme 9*).

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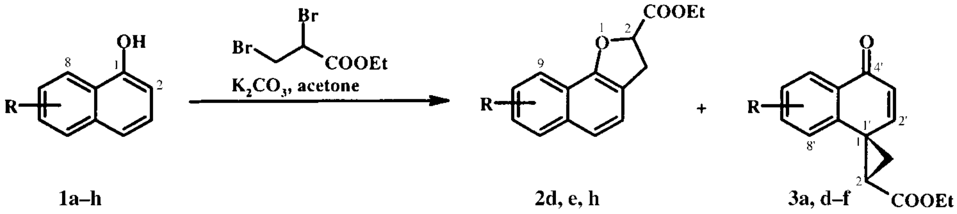
1. Introduction. – As part of our investigation to find new antihypertensive drugs, we recently reported a convenient and versatile synthesis of 1,2-dihydronaphtho[2,1-*b*]furan derivatives [1] by direct condensation of substituted naphthalen-2-ols with ethyl 2,3-dibromopropanoate in the presence of K_2CO_3 in refluxing acetone. In this paper, we wish now to report first how naphthalen-1-ols behave in the presence of ethyl 2,3-dibromopropanoate and 3,4-dibromobutan-2-one derivatives, and also the synthesis of the analogous compounds, *i.e.* 2,3-dihydronaphtho[1,2-*b*]furans **2**.

2. Synthesis. – Treatment of naphthalen-1-ol (**1a**) with ethyl 2,3-dibromopropanoate in the presence of K_2CO_3 in refluxing acetone in analogy to [1] did not afford the expected ethyl 2,3-dihydronaphtho[1,2-*b*]furan-2-carboxylate (**2a**), but only the unexpected ethyl 4′-oxospiro[cyclopropane-1,1′(4′*H*)-naphthalene]-2-carboxylate (**3a**) as a single diastereoisomer in 30% yield, besides starting material **1a** (*Scheme 1*). A longer reaction time did not improve the yield of **3a**. Unsubstituted spiro derivatives possessing the same framework as **3a** were described earlier as being formed in a two-step procedure from naphthalen-1-ol and oxirane [2]. Condensation of various commercially or easily available substituted naphthalen-1-ols **1b**–**h** [3–5] was attempted (*Scheme 1*). Thus naphthalen-1-ols substituted with an amino or protected amino group at C(5) (see **1b** and **1c**) did not give spiro compounds, but yielded only decomposition products. The use of 5-methoxynaphthalen-1-ol (**1d**) afforded two compounds, 2,3-dihydronaphtho[1,2-*b*]furan **2d** and spiro derivative **3d** in 20 and 17% yield, respectively. The 7-methoxy analog **1e** had the same behavior, giving compounds **2e** and **3e** in 31 and 33% yield, respectively. We succeeded in improving the yield of formation of spiro compound **3** by using a 2-substituted naphthalen-1-ol such as 2-methyl derivative **1f**; thus, spiro compound **3f** was obtained in 71% yield. But condensation of 2-carboxaldehyde **1g** resulted in the decomposition of the mixture. Likewise, when we used 4-chloronaphthalen-1-ol (**1h**) to improve the yield of the 2,3-dihydronaphtho[1,2-*b*]furan derivative by impeding the formation of spiro compound **3h**, the result was disappointing, **2h** being obtained in only 21% yield.

Scheme 1



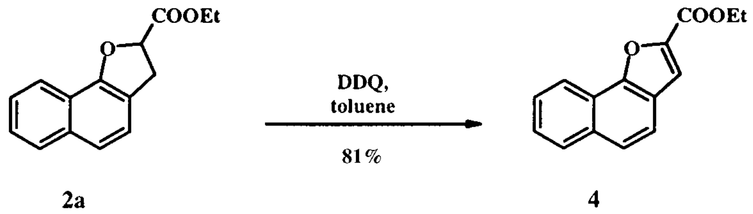
	R in **1**	**2** (Yield [%])	**3**(Yield [%])	**1** (Recovery [%])
a	H	0	30	50
a	H	27[a])	25[a])	15[a]
b	5-NH_2	0	0	dec.
c	5-AcNH	0	0	dec.
d	5-OMe	20	17	29
e	7-OMe	31	33	19
f	2-Me	0	71	–
g	2-CHO	0	0	dec.
h	Cl	21	0	39

[a]) Obtained from **1a** and ethyl 2-bromoprop-2-enoate in refluxing methyl isobutyl ketone (MIBK).

The reaction of naphthalen-1-ol **1a** with ethyl 2-bromoprop-2-enoate instead of ethyl 2,3-dibromopropanoate in the presence of K_2CO_3 in refluxing acetone generated spiro derivative **3a** in a lower yield (23%), besides 50% recovered **1a**. After different attempts, we finally succeeded in obtaining compound **2a** [6] by using refluxing methyl isobutyl ketone (MIBK) instead of acetone. The higher boiling point of this solvent allowed us to generate a mixture of products **2a** and **3a** in 27 and 25% yield, respectively (*Scheme 1*).

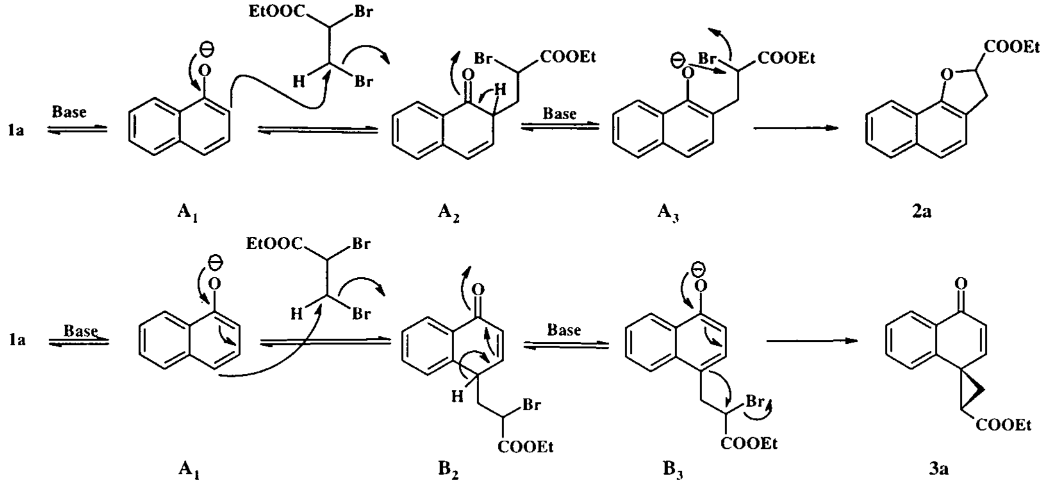
Aromatization of ethyl 2,3-dihydronaphtho[1,2-*b*]furan-2-carboxylate (**2a**) was easily achieved. As described earlier [1], dehydrogenation of **2a** with 4,5-dichloro-3,6-dioxobenzene-1,2-dicarbonitrile (=2,3-dichloro-5,6-dicyanobenzoquinone; DDQ) in refluxing toluene gave naphtho[1,2-*b*]furan-2-carboxylate **4** [7] in good yield (81%) (*Scheme 2*).

Scheme 2



We propose the following mechanism as an effective one for the formation of dihydronaphtho[1,2-*b*]furans **2** and spiro derivatives **3** (*Scheme 3*). First, the formation of naphthalen-1-olate anion $\mathbf{A_1}$ with a base, followed by the displacement of the Br-atom of the ethyl 2,3-dibromopropanoate generates the C−C bond of intermediate $\mathbf{A_2}$. A subsequent aromatization reaction gives the naphthalen-1-olate anion $\mathbf{A_3}$, which undergoes an intramolecular nucleophilic substitution at the Br-bearing C-atom, affording the dihydrofuran moiety of compound **2a**. Intermediate $\mathbf{A_1}$ can also form a C−C bond with the ethyl 2,3-dibromopropanoate to give intermediate $\mathbf{B_2}$, which is transformed to $\mathbf{B_3}$ in the same way as $\mathbf{A_2}$ is into $\mathbf{A_3}$. The latter then generates the cyclopropane moiety of **3a** by an intramolecular nucleophilic substitution.

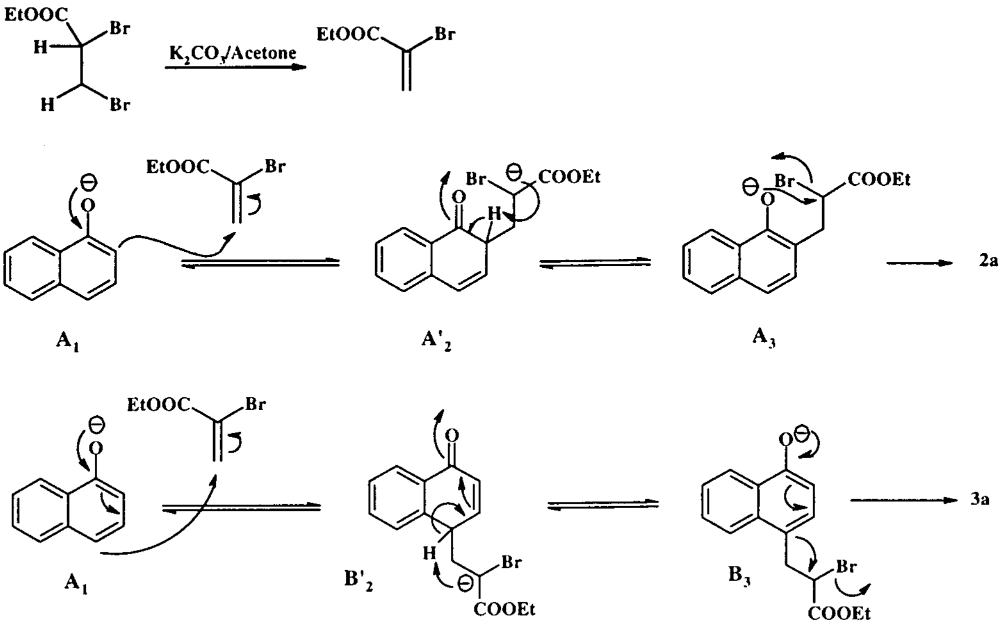
Scheme 3



In basic medium, the ethyl 2,3-dibromopropanoate could generate ethyl 2-bromoprop-2-enoate [8] (*Scheme 4*). Thus, intermediates $\mathbf{A_3}$ or $\mathbf{B_3}$ could also be obtained by a *Michael*-type addition of naphthalenolate $\mathbf{A_1}$ to the ethyl 2-bromoprop-2-enoate *via* intermediates $\mathbf{A'_2}$ or $\mathbf{B'_2}$, respectively.

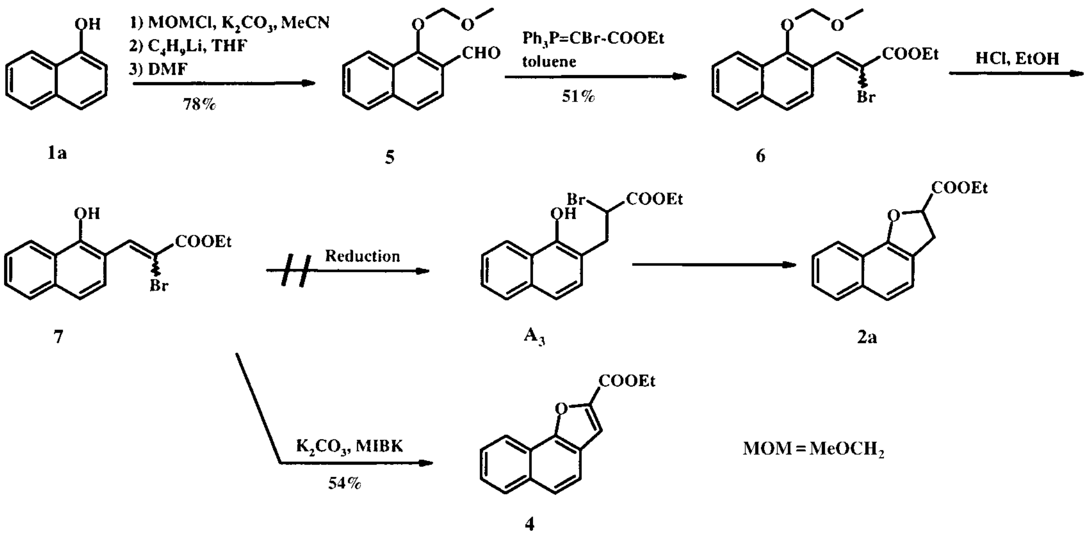
No reaction occurred when naphthalen-1-ol (**1a**) was treated with ethyl prop-2-enoate instead of ethyl 2-bromoprop-2-enoate, which indicates the need of a leaving group such as the Br-atom to generate the dihydrofuran or the cyclopropane ring. To support this mechanism, we tried to synthesize intermediate $\mathbf{A_3}$ from **1a** (*Scheme 5*). Thus, **1a** was converted into its methoxymethyl (MOM) ether, which was selectively lithiated at the *ortho*-position to the MOMO group, and then reacted with dimethylformamide to give aldehyde **5** [9]. Subsequent reaction with ethyl bromo-(triphenylphosphoranylidene)acetate [10] afforded compound **6**. The MOMO group of **6** was hydrolyzed with aqueous ethanolic hydrochloric acid to give derivative **7**. Different attempts to selectively reduce the C=C bond of this compound were made (catalytic hydrogenation over Pd/C in EtOH [11] or with *Raney*-Ni in EtOH [12], reduction with Mg/MeOH [13]); however, only the saturated compound that had lost its Br-atom was obtained. Nevertheless, we succeeded in cyclizing compound **7** by

Scheme 4



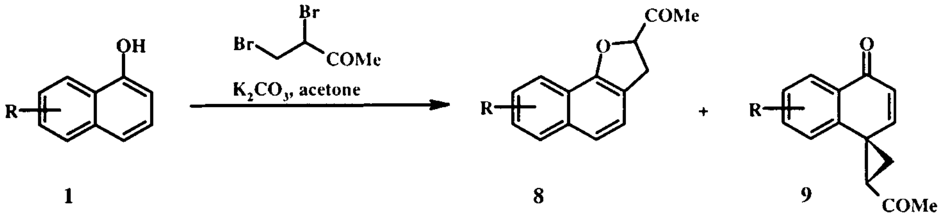
heating in refluxing methyl isobutyl ketone (MIBK) in the presence of K_2CO_3 to obtain naphtho[1,2-*b*]furan-2-carboxylate **4**, which was identical to compound **4** obtained by aromatization of **2a** (see above).

Scheme 5



To broaden the scope of these reactions, we investigated the reactivity of the naphthalen-1-ols **1** with 3,4-dibromobutan-2-one and 2,3-dibromopropanenitrile by applying the same methodology as described above. Thus, the reaction of substituted naphthalen-1-ols **1** with 3,4-dibromobutan-2-one afforded 2,3-dihydronaphtho[1,2-*b*]furan-2-yl ketones **8** and spiro derivatives **9** (*Scheme 6*). In the case of **1a**, only spiro structure **9a** was obtained. Naphthalenols **1d** and **1e** afforded a mixture of spiro derivatives **9d** (16% yield) and **9e** (32% yield), respectively, and naphthofuran derivatives **8d** (21% yield) and **8e** (25% yield), respectively (*Scheme 6*). Compounds **9a**,**d**–**f** were obtained as single diastereoisomers with the same spatial disposition for the ethanone moiety as for the ester group of **3a**.

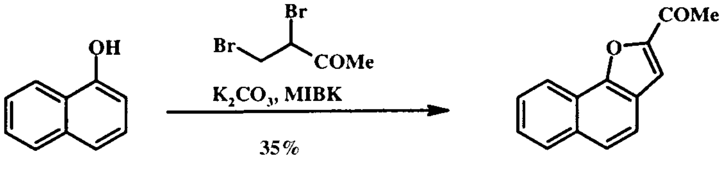
Scheme 6



	R in **1**	**8** (Yield [%])	**9** (Yield [%])
a	H	0	18
d	5-MeO	21	16
e	7-MeO	25	32
f	2-Me	0	29

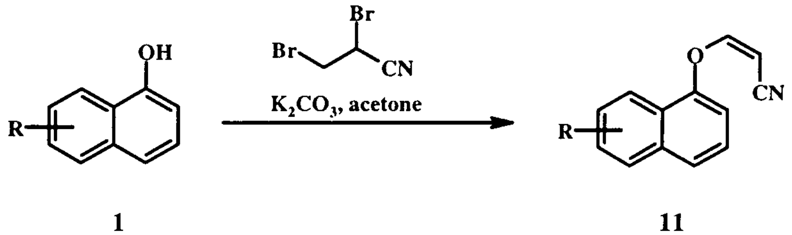
The same reaction of naphthalen-1-ol **1a** and 3,4-dibromobutan-2-one in refluxing MIBK instead of acetone did not afford the 2,3-dihydronaphtho[1,2-*b*]furan-2-yl ketone, but directly the fully aromatized naphtho[1,2-*b*]furanyl ketone **10** in a yield of 35% (*Scheme 7*). No spiro derivative **9** was observed under these conditions.

Scheme 7



When 2,3-dibromopropanenitrile was used instead of ethyl 2,3-dibromopropanoate, neither naphthofuran nor spiro derivative was generated; only the noncyclized compounds **11** were obtained (45–58% yield, *Scheme 8*). Compounds **11** were (*Z*)-isomers [14][15]. This configuration is the result of a naphthalenolate addition to the intermediate ethynecarbonitrile; this intermediate is generated from 2,3-dibromopropanenitrile by elimination of two molecules of HBr in basic medium. This behavior was different from that of the naphthalen-2-ols, which gave 1,2-dihydronaphtho[2,1-*b*]furan derivatives [1].

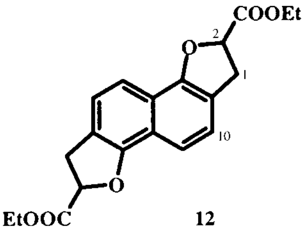
Scheme 8



1 **11**

	R	**11** (Yield [%])
a	H	45
d	5-MeO	58
e	7-MeO	47
f	2-Me	67

The use of naphthalen-1,5-diol instead of naphthalen-1-ol (**1a**) in the condensation reaction with ethyl 2,3-dibromopropanoate in refluxing acetone afforded compound **12** in 41% yield; the both OH groups reacted to give **12** in diasteromer ratio of *ca.* 26 : 74; the major diastereoisomer was isolated by semipreparative HPLC.



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The structures of the spiro derivatives **3** obtained were unambiguously established by spectroscopic means and confirmed by the X-ray crystal-structure analyses of **3a** and **3f** (*Figs. 1* and *2*, *Table*).

The ^{1}H-NMR spectrum of **3a** indicated the presence of olefinic H-atoms (J = 10.3 Hz) and ^{13}C-NMR data that of a quaternary spiro C-atom (δ 30.8) and of a keto moiety (δ 184.9). NOESY Experiments showed connectivities that allowed us to determine the spatial position of the ester group with respect to the rings (see *Fig. 3*). Compound **3a** was obtained as a single diastereoisomer with the ester group next to the cyclic olefinic bond. The coupling constant of the olefinic H-atoms of the 8′-MeO-substituted spiro compound **3d** was identical to that of **3a** (10.3 Hz). The chemical shift of the quaternary spiro C-atom of **3d** was observed at 31.5 and that of the keto group at 184.5 ppm. NOESY Experiments indicated again the spatial position of the ester group (see *Fig. 3*). The ^{1}H-NMR spectrum of **9f** showed the presence of only one olefinic H-atom (*s* at 6.77 ppm), and the ^{13}C-NMR spectrum confirmed the presence of a quaternary spiro C-atom (δ 32.3) and the presence of two keto groups (δ 185.0 and 203.0). NOESY Experiments showed also here the position of the ethanone moiety relative to the rings (see *Fig. 3*).

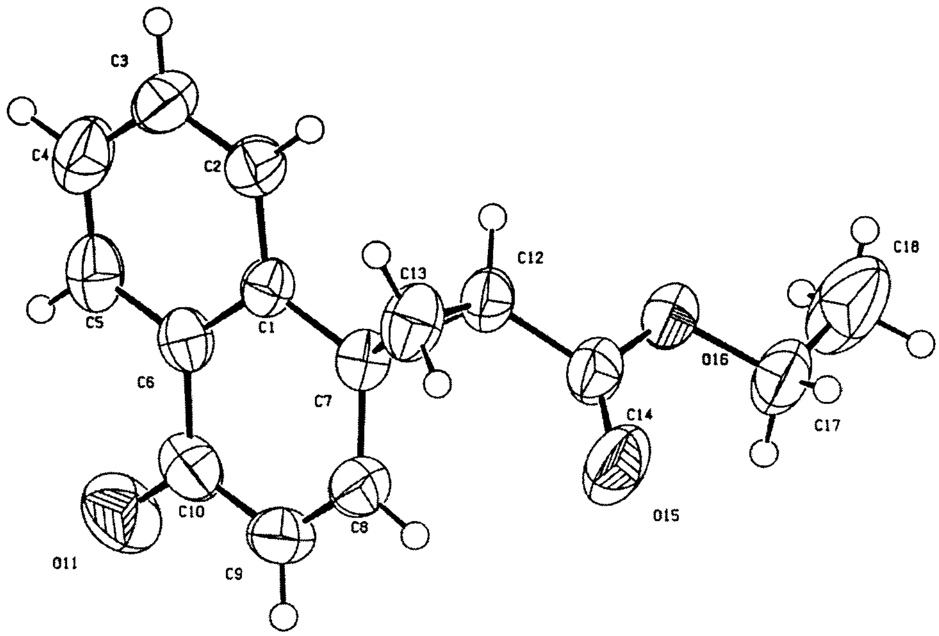


Fig. 1. *ORTEP Drawing of the crystal structure of compound* **3a** *with atom numbering* (ellipsoids at 50% probability)

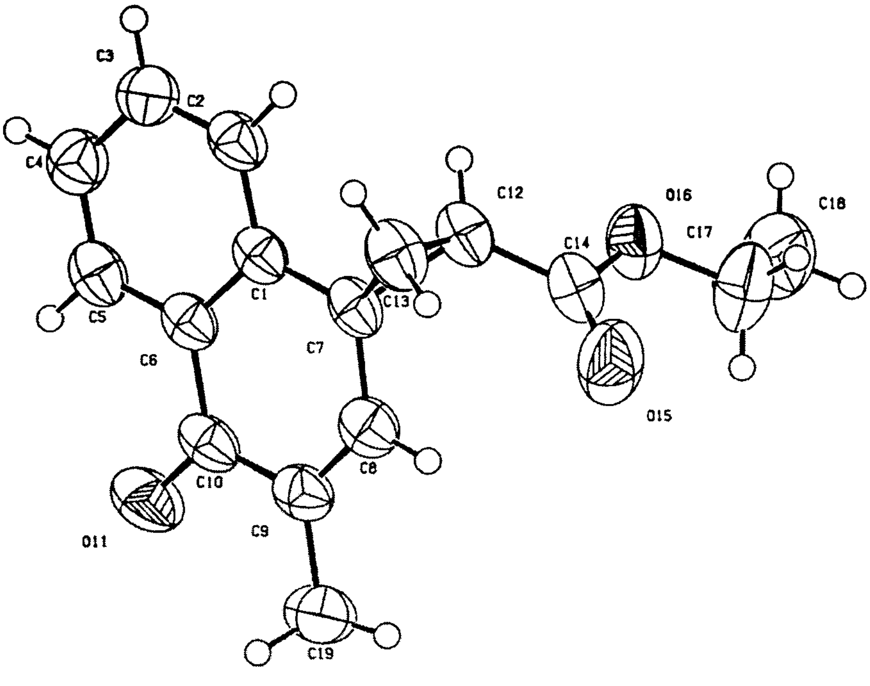
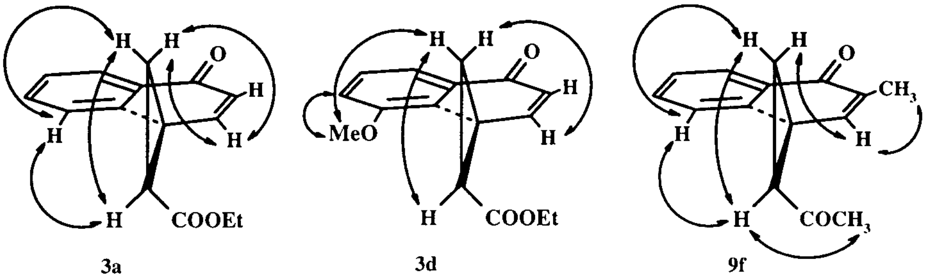


Fig. 2. *ORTEP Drawing of the crystal structure of compound* **3f** *with atom numbering* (ellipsoids at 50% probability)

Table. *Crystal Data and Parameters Pertaining to Structural Analyses of* **3a** *and* **3f**

	3a	**3f**
Crystallization solvent	CH_2Cl_2	CH_2Cl_2
Chemical formula	$C_{15}H_{14}O_3$	$C_{16}H_{16}O_3$
Temperature [K]	296(2)	296(2)
Wavelength [Å]	1.54178	1.54178
Crystal system, space group	triclinic, *P*-1	monoclinic, $P2_1/c$
Unit-cell dimensions	$a = 7.5010(1)$ Å, $\alpha = 92.46(2)°$ $b = 7.859(3)$ Å, $\beta = 97.990(1)°$ $c = 10.698(2)$ Å, $\gamma = 96.35(2)°$	$a = 11.278(1)$ Å $b = 15.798(2)$ Å, $\beta = 98.24(2)°$ $c = 7.518(3)$ Å
Volume	619.6(3) $Å^3$	1325.7(6) $Å^3$
Z	2	4
Calculated density	1.299 Mg/m^3	1.284 Mg/m^3
Absorption coefficient	0.733 mm^{-1}	0.712 mm^{-1}
F(000)	256	544
Crystal size	0.50 × 0.35 × 0.12 mm	0.30 × 0.15 × 0.10 mm
θ Range for data collectioin	5.67 – 65.02°	3.96 – 59.91°
Index ranges	$-8 < h < 8, 0 < k < 9, -12 < l < 12$	$-12 < h < 12, 0 < k < 17, 0 < 1 < 8$
Reflections collected/unique	2052/2045 (R(int) = 0.0027)	1918
Completeness to 2θ	65.03, 97.2%	59.91, 93.5%
Max. and min. transmission	0.9172 and 0.7108	0.9322 and 0.8147
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data, restraints, parameters	2045, 0, 164	1918, 0, 174
Goodness-of-fit on F^2	1.064	1.243
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0413$, $wR_2 = 0.1249$	$R_1 = 0.0692$, $wR_2 = 0.2786$
R indices (all data)	$R_1 = 0.0447$, $wR_2 = 0.1286$	$R_1 = 0.0901$, $wR_2 = 0.2973$
Extinction coefficient	0.060(6)	0.0054(18)
Largest diff. peak and hole	0.159 and -0.140 e · A^{-3}	0.326 and -0.316 e · A^{-3}

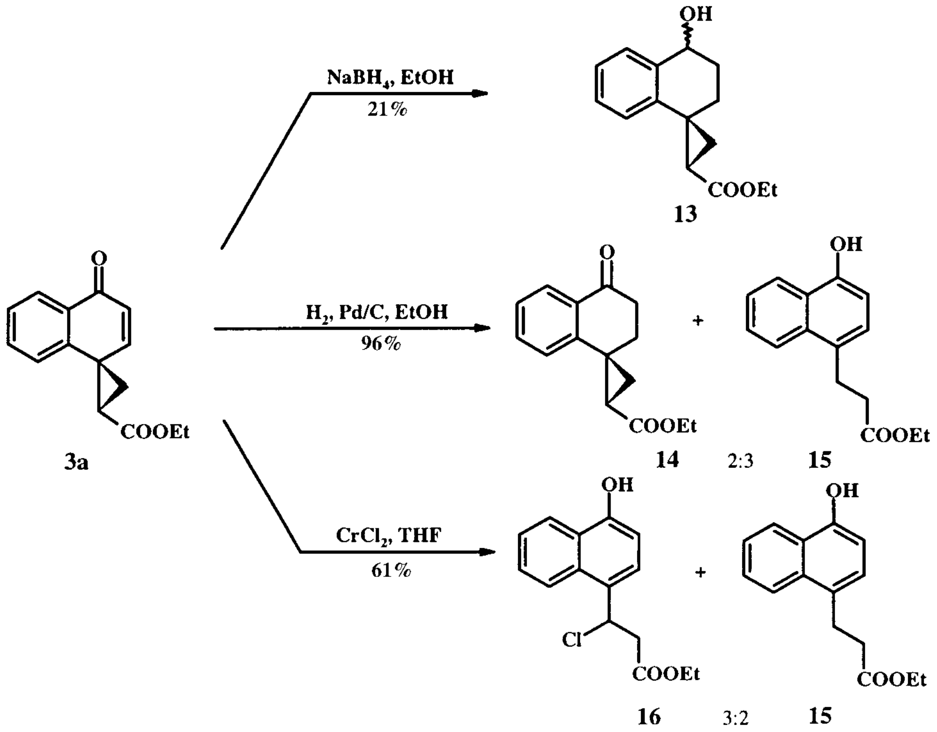


3a **3d** **9f**

Fig. 3. *Relative configurations of* **3a**, **3d**, *and* **9f**, *as established by NOESY data*

The chemistry of the highly functionalized compound **3a** was briefly investigated. Reduction with $NaBH_4$ in EtOH gave saturated alcohol **13** (21% yield) in a diastereoisomer ratio of 3:2 (*Scheme 9*). The use of $NaBH_4/CeCl_3$ did not yield the expected unsaturated alcohol, but only a product mixture resulting from decomposition. Hydrogenation of **3a** over Pd/C in EtOH at atmospheric pressure afforded, in 96% total yield, ketone **14** and naphthalenol **15** in a 2:3 ratio. Reaction of **3a** with chromium(II) chloride [16] at room temperature in THF gave a mixture of the unstable chloro-hydroxy ester **16** and hydroxy ester **15** in 61% total yield and in a 3:2 ratio. *Diels-Alder* reactions with dienophile **3a** are still under investigation.

Scheme 9



3. Conclusion. – In an efficient one-pot synthesis, functionalized 2,3-dihydronaphtho[1,2-*b*]furan derivatives and spiro[cyclopropane-1,1′(4′*H*)-naphthalene] derivatives were obtained from available naphthalen-1-ols.

Experimental Part

1. *General.* THF was freshly distilled from Na/benzophenone. The solvents were HPLC grade and used without further purification. TLC: SiO$_2$-*60F$_{254}$*-precoated plates from *Merck*; UV detection at 254 or 366 nm. Flash chromatography (FC): SiO$_2$ *60* (230–400 mesh, 0.040–0.063 mm) from *Merck*. M.p.: *Kofler* hot-stage apparatus; uncorrected. IR Spectra: thin film on NaCl plates for oils and KBr pellet for solids; *Perkin-Elmer* spectrometer *FT PARAGON 1000 PC*; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker* instrument *Avance DPX-250* (250 MHz) with solvent peak as reference; chemical shifts δ in ppm and coupling constants *J* in Hz. MS: *Perkin-Elmer* mass spectrometer *SCIEX API-300* (ion spray or heat nebulizer). The naphthalenols **1c**–**e** were prepared according to [3–5].

2. *2,3-Dihydronaphtho[1,2-*b*]furan-2-carboxylates* **2a**,**d**,**e**,**h** *and/or Spiro[cyclopropane-1,1′-(4′*H*)-2-carboxylates* **3a**,**d**–**f**: *General Procedure* (*G.P.*). To a soln. of substituted naphthalen-1-ol **1** (2.76 mmol) in anh. acetone (10 ml), K$_2$CO$_3$ (1.072 g, 7.76 mmol) and ethyl 2,3-dibromopropanoate (0.44 ml, 3.06 mmol) were added. The mixture was refluxed for 28 h and cooled to r.t. The salts were filtered off and washed with acetone. The filtrate was evaporated and the residue poured into H$_2$O (30 ml) and extracted with AcOEt (3 × 40 ml). The combined extracts were dried (MgSO$_4$) and evaporated. FC (SiO$_2$, AcOEt/petroleum ether 1:3) gave **2d,e,h** and/or **3a**,**d**–**f**.

Similarly, **2a** was obtained from **1a** and ethyl 2-bromoprop-2-enoate by refluxing in MIBK instead of acetone.

*Ethyl 2,3-Dihydronaphtho[1,2-*b*]furan-2-carboxylate* (**2a**) [6]: M.p. 140°. IR (KBr): 1656*m*, 1719*s*. ^{1}H-NMR (CDCl$_3$): 1.25 (*t*, *J* = 7.1, *Me*CH$_2$O); 3.45 (*dd*, *J* = 15.6, 7.1, 1 H, CH$_2$(3)); 3.62 (*dd*, *J* = 15.6, 10.6, 1 H, CH$_2$(3));

4.20 (*q*, $J = 7.1$, MeC*H*$_2$O); 5.32 (*dd*, $J = 10.6$, 7.1, H–C(2)); 7.24 (*d*, $J = 8.3$, 1 arom. H); 7.36 (*d*, $J = 8.3$, 1 arom. H); 7.38–7.43 (*m*, 2 arom. H); 7.76 (*dd*, $J = 7.0$, 2.3, 1 arom. H); 7.53 (*td*, $J = 7.0$, 2.3, 1 arom. H). ^{13}C-NMR (CDCl$_3$): 14.2 (Me); 34.8 (CH$_2$); 61.6 (CH$_2$); 79.7 (CH); 118.0 (C); 120.4 (C); 121.1 (CH); 121.5 (CH); 122.3 (CH); 125.6 (CH); 125.9 (CH); 127.8 (CH); 134.1 (C); 154.6 (C); 171.3 (C=O). MS: 243 ([M + H]$^+$). Anal. calc. for $C_{15}H_{14}O_3$ (242.28): C 74.36, H 5.82; found: C 74.69, H 5.70.

*Ethyl 6-Methoxy-2,3-dihydronaphtho[1,2-*b*]furan-2-carboxylate* (**2d**): Gum. IR (NaCl): 1406*s*, 1519*s*, 1598*m*, 1745*s*. ^{1}H-NMR (CDCl$_3$): 1.28 (*t*, $J = 7.2$, *Me*CH$_2$O); 3.52 (*dd*, $J = 15.7$, 6.9, 1 H, CH$_2$(3)); 3.71 (*dd*, $J = 15.7$, 10.7, 1 H, CH$_2$(3)); 3.99 (*s*, MeO); 4.26 (*q*, $J = 7.2$, MeC*H*$_2$O); 5.36 (*dd*, $J = 10.7$, 6.9, H–C(2)); 6.77 (*d*, $J = 7.5$, 1 arom. H); 7.26 (*d*, $J = 8.4$, 1 arom. H); 7.36 (*dd*, $J = 8.4$, 7.8, 1 arom. H); 7.60 (*d*, $J = 8.4$, 1 arom. H); 7.80 (*d*, $J = 7.5$, 1 arom. H). ^{13}C-NMR (CDCl$_3$): 16.3 (Me); 23.2 (CH$_2$); 37.0 (MeO); 63.7 (CH$_2$); 81.7 (CH); 106.1 (CH); 116.0 (CH); 117.4 (CH); 121.0 (C); 123.5 (C); 123.6 (CH); 127.9 (CH); 128.3 (C); 156.6 (C); 157.6 (C); 173.5 (C=O). MS: 273 ([M + H]$^+$). Anal. calc. for $C_{16}H_{16}O_4$ (272.30): C 70.58, H 5.92; found: C 70.97, H 6.03.

*Ethyl 8-Methoxy-2,3-dihydronaphtho[1,2-*b*]furan-2-carboxylate* (**2e**): Gum. IR (NaCl): 1255*s*, 1467*m*, 1605*s*, 1756*s*. ^{1}H-NMR (CDCl$_3$): 1.31 (*t*, $J = 7.2$, *Me*CH$_2$O); 3.55 (*dd*, $J = 15.7$, 7.3, 1 H, CH$_2$(3)); 3.71 (*dd*, $J = 15.7$, 10.7, 1 H, CH$_2$(3)); 3.92 (*s*, MeO); 4.28 (*q*, $J = 7.2$, CH$_2$); 5.37 (*dd*, $J = 10.7$, 7.3, H–C(2)); 7.08 (*dd*, $J = 9.2$, 2.5, 1 arom. H); 7.15 (*d*, $J = 8.2$, 1 arom. H); 7.25 (*d*, $J = 2.5$, 1 arom. H); 7.34 (*d*, $J = 8.2$, 1 arom. H); 7.69 (*d*, $J = 9.1$, 1 arom. H). ^{13}C-NMR (CDCl$_3$): 14.6 (Me); 35.3 (CH$_2$); 55.9 (MeO); 62.0 (CH$_2$); 79.9 (CH); 99.6 (CH); 118.9 (C); 119.4 (CH); 120.1 (CH); 121.4 (CH); 122.2 (C); 129.6 (CH); 130.4 (C); 154.1 (C); 158.0 (C); 171.8 (C=O). MS: 273 ([M + H]$^+$). Anal. calc. for $C_{16}H_{16}O_4$ (272.30): C 70.58, H 5.92; found: C 70.24, H 5.85.

*Ethyl 5-Chloro-2,3-dihydronaphtho[1,2-*b*]furan-2-carboxylate* (**2h**): Gum. IR (NaCl): 1722*s*. ^{1}H-NMR (CDCl$_3$): 1.28 (*t*, $J = 7.0$, *Me*CH$_2$O); 3.46 (*dd*, $J = 15.7$, 6.9, 1 H, CH$_2$(3)); 3.63 (*dd*, $J = 15.7$, 10.3, 1 H, CH$_2$(3)); 4.24 (*q*, $J = 7.0$, MeC*H*$_2$O); 5.33 (*dd*, $J = 10.3$, 6.9, H–C(2)); 7.34 (*s*, 1 arom. H); 7.44–7.57 (*m*, 2 arom. H); 8.01 (*m*, 1 arom. H); 8.15 (*m*, 1 arom. H). ^{13}C-NMR (CDCl$_3$): 14.6 (Me); 35.0 (CH$_2$); 62.1 (CH$_2$); 80.2 (CH); 118.6 (C); 121.4 (C); 122.4 (CH); 122.9 (CH); 124.0 (C); 125.1 (CH); 126.7 (CH); 127.4 (CH); 131.0 (C); 154.2 (C); 171.3 (C=O). MS: 277 and 279 ([M + H]$^+$). Anal. calc. for $C_{15}H_{13}ClO_3$ (272.30): C 65.11, H 4.74; found: C 65.46, H 4.63.

*Ethyl 4′-Oxospiro[cyclopropan-1,1′(4′*H*)-naphthalene]-2-carboxylate* (**3a**): M.p. 67°. IR (KBr): 1195*m*, 1655*s*, 1718*s*. ^{1}H-NMR (CDCl$_3$): 1.24 (*t*, $J = 7.1$, *Me*CH$_2$O); 2.13 (*dd*, $J = 7.5$, 5.4, 1 H, CH$_2$(3)); 2.36 (*dd*, $J = 7.5$, 5.4, 1 H, CH$_2$(3)); 2.79 (br. *t*, $J = 7.5$, H–C(2)); 4.19 (*q*, $J = 7.1$, MeC*H*$_2$O); 6.61 (*d*, $J = 10.3$, 1 olef. H); 6.91 (*d*, $J = 7.7$, 1 arom. H); 7.15 (*d*, $J = 10.3$, 1 olef. H); 7.41 (*td*, $J = 7.7$, 1.2, 1 arom. H); 7.53 (*td*, $J = 7.7$, 1.2, 1 arom. H); 8.23 (*dd*, $J = 7.7$, 1.2, 1 arom. H). ^{13}C-NMR (CDCl$_3$): 14.4 (Me); 26.7 (CH$_2$); 30.8 (C); 36.4 (CH); 62.0 (CH$_2$); 121.6 (CH); 127.4 (2 CH); 130.4 (CH); 133.1 (C); 133.1 (CH); 143.3 (C); 148.0 (CH); 169.9 (C=O, ester); 184.9 (C=O). MS: 243 ([M + H]$^+$). Anal. calc. for $C_{15}H_{14}O_3$ (242.28): C 74.36, H 5.82; found: C 74.55, H 5.92.

*Ethyl 8′-Methoxy-4′-oxospiro[cyclopropane-1,1′(4′*H*)-naphthalene]-2-carboxylate* (**3d**): Gum. IR (NaCl): 1596*s*, 1651*s*, 1744*s*. ^{1}H-NMR (CDCl$_3$): 1.25 (*t*, $J = 7.1$, *Me*CH$_2$O); 2.04 (*dd*, $J = 7.3$, 5.3, 1 H, CH$_2$(3)); 3.05 (*dd*, $J = 7.9$, 5.3, 1 H, CH$_2$(3)); 3.84 (*s*, MeO); 3.86 (*t*, $J = 7.7$, H–C(2)); 4.15 (*q*, $J = 7.1$, MeC*H*$_2$O); 6.57 (*d*, $J = 10.3$, 1 olef. H); 7.05 (*d*, $J = 10.3$, 1 olef. H); 7.08 (*dd*, $J = 8.1$, 1.2, 1 arom. H); 7.39 (*t*, $J = 8.1$, 1 arom. H); 7.97 (*dd*, $J = 8.1$, 1.2, 1 arom. H). ^{13}C-NMR (CDCl$_3$): 14.3 (Me); 23.1 (CH$_2$); 30.8 (CH); 31.5 (C); 55.7 (MeO); 61.5 (CH$_2$); 114.5 (CH); 120.1 (CH); 127.7 (CH); 128.3 (olef. CH); 129.7 (C); 135.7 (C); 151.0 (olef. CH); 156.7 (C); 171.2 (C=O, ester), 184.5 (C=O). MS: 273 ([M + H]$^+$). Anal. calc. for $C_{16}H_{16}O_4$ (272.30): C 70.58, H 5.92; found: C 70.32, H 5.88.

*Ethyl 6′-Methoxy-4′-oxospiro[cyclopropane-1,1′-(4′*H*)-naphthalene]-2-carboxylate* (**3e**): Gum. IR (NaCl): 1032*m*, 1191*m*, 1725*s*. ^{1}H-NMR (CDCl$_3$): 1.26 (*t*, $J = 7.1$, *Me*CH$_2$O); 2.12 (*dd*, $J = 7.9$, 5.3, 1 H, CH$_2$(3)); 2.78 (*t*, $J = 7.8$, H–C(2)); 3.05 (*dd*, $J = 7.5$, 5.3, 1 H, CH$_2$(3)); 3.88 (*s*, MeO); 4.20 (*q*, $J = 7.1$, CH$_2$); 6.64 (*d*, $J = 10.2$, 1 olef. H); 6.85 (*d*, $J = 10.2$, 1 olef. H); 7.12–7.19 (*m*, 2 arom. H); 7.72 (*d*, $J = 2.9$, 1 arom. H). ^{13}C-NMR (CDCl$_3$): 14.3 (Me); 26.0 (CH$_2$); 30.6 (C); 35.6 (CH); 55.7 (Me); 61.7 (CH$_2$); 108.4 (CH); 122.0 (CH); 122.9 (CH); 129.9 (olef. CH); 133.9 (C); 135.8 (C); 148.2 (olef. CH); 158.8 (C); 169.7 (C=O); 184.8 (C=O). MS: 273 ([M + H]$^+$). Anal. calc. for $C_{16}H_6O_4$ (272.30): C 70.58, H 5.92; found: C 70.84, H 5.76.

*Ethyl 3′-Methyl-4′-oxospiro[cyclopropane-1,1′(4′*H*)-naphthalene]-2-carboxylate* (**3f**): Solid. M.p. 118°. IR (KBr): 1179*s*, 1649*s*, 1721*s*. ^{1}H-NMR (CDCl$_3$): 1.26 (*t*, $J = 7.1$, *Me*CH$_2$O); 2.07 (*s*, Me–C(3′)); 2.10 (*dd*, $J = 7.8$, 5.3, 1 H, CH$_2$(3)); 2.32 (*dd*, $J = 7.4$, 5.3, 1 H, CH$_2$(3)); 2.77 (*t*, $J = 7.7$, H–C(2)); 4.20 (*q*, $J = 7.1$, MeC*H*$_2$O); 6.92 (*d*, $J = 8.1$, 1 arom. H); 6.95 (*s*, 1 olef. H); 7.42 (*td*, $J = 7.9$, 0.8, 1 arom. H); 7.52 (*td*, $J = 7.5$, 1.5, 1 arom. H); 8.26 (*dd*, $J = 7.9$, 1.5, 1 arom. H). ^{13}C-NMR (CDCl$_3$): 14.2 (Me); 16.7 (Me); 25.9 (CH$_2$); 30.0 (C); 35.5 (CH); 61.5 (CH$_2$); 121.1 (CH); 126.9 (CH); 127.1 (CH); 132.3 (CH); 132.4 (C); 136.6 (C); 142.8 (CH); 143.2 (C); 169.7

(C=O); 184.9 (C=O). MS: 257 ([*M* + H]$^+$). Anal. calc. for $C_{16}H_{16}O_3$ (256.30): C 74.98, H 6.29; found: C 75.30, H 6.15.

3. *Ethyl Naphtho[1,2-*b*]furan-2-carboxylate* (**4**) [7] via *Oxidation of* **2a**. DDQ (238 mg, 1.05 mmol) was added to a soln. of **2a** (243 mg, 1 mmol) in toluene (6 ml). The mixture was refluxed for 5 h and then cooled to r.t. The soln. was hydrolyzed and neutralized with 5% aq. NaOH soln., the mixture extracted with AcOEt (3 × 75 ml), and the combined extract dried ($MgSO_4$) and evaporated. FC (SiO_2, AcOEt/petroleum ether 1:2) gave pale yellow solid **4** (195 mg, 81%). M.p. 87–89°. IR (KBr): 1556*m*, 1729*s*. ^{1}H-NMR ($CDCl_3$): 1.43 (*t*, *J* = 7.1, *Me*CH$_2$O); 4.45 (*q*, *J* = 7.1, MeC*H*$_2$O); 7.45–7.63 (*m*, 4 arom. H); 7.60 (*s*, H–C(3)); 7.88 (*d*, *J* = 7.3, 1 arom. H); 8.43 (*d*, *J* = 7.7, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 14.4 (Me); 61.4 (CH_2); 114.9 (CH); 119.9 (CH); 121.0 (CH); 121.5 (C); 122.9 (C); 124.8 (CH); 126.6 (CH); 126.9 (CH); 128.4 (CH); 133.0 (C); 145.2 (C); 152.3 (C); 159.5 (C=O). MS: 241 ([*M* + H]$^+$). Anal. calc. for $C_{15}H_{12}O_3$ (240.26): C 74.99, H 5.03; found: C 74.64, H 5.09.

4. *Attempted Synthesis of Intermediate* $\mathbf{A_3}$ *by* Wittig *Reaction and Cyclization. Ethyl 2-Bromo-3-[1-(methoxymethoxy)naphthalen-2-yl]prop-2-enoate* (**6**). To a soln. of **5** [9] (432 mg, 2 mmol) in toluene (10 ml), ethyl bromo(triphenylphosphosphoranylidene)acetate [10] (1.29 g, 3 mmol) was added. After stirring in refluxing toluene for 5 h and evaporation, H_2O (15 ml) was added and the mixture extracted with AcOEt (3 × 30 ml). The combined org. layer was dried ($MgSO_4$) and evaporated. FC (SiO_2, AcOEt/petroleum ether 2:8) gave **6** (372 mg, 51%). Yellow oil. IR (NaCl): 1317*m*, 1626*s*, 1723*m*. ^{1}H-NMR ($CDCl_3$): 1.40 (*t*, *J* = 7.2, *Me*CH$_2$O); 3.67 (*s*, MeO); 4.38 (*q*, *J* = 7.2, MeC*H*$_2$O); 5.18 (*s*, MeOC*H*$_2$O); 7.52–7.56 (*m*, 2 arom. H); 7.68 (*d*, *J* = 8.7, 1 arom. H); 7.85 (*t*, *J* = 4.5, 1 arom. H); 7.08 (*d*, *J* = 8.7, 1 arom. H); 8.16 (*t*, *J* = 4.5, 1 arom. H); 8.68 (*s*, H–C(3)). ^{13}C-NMR ($CDCl_3$): 14.4 (Me); 58.2 (Me); 62.9 (CH_2); 101.3 (CH_2); 114.7 (C); 122.9 (CH); 123.9 (CH); 125.7 (CH); 126.0 (CH); 127.7 (CH); 128.1 (CH); 135.6 (C); 138.0 (C); 153.9 (C); 163.4 (C). MS: 366–368 ([*M* + H]$^+$). Anal. calc. for $C_{17}H_{17}BrO_4$ (365.23): C 55.91, H 4.69; found: C 60.22, H 4.75.

Ethyl 2-Bromo-3-(1-hydroxynaphthalen-2-yl)prop-2-enoate (**7**). Compound **6** (365 mg, 1 mmol) was added to 3N HCl (1 ml) in EtOH (10 ml) and stirred for 1 h at 40°. After evaporation of the EtOH, H_2O (12 ml) was added and the mixture extracted with CH_2Cl_2 (3 × 15 ml). The combined org. layers were dried ($MgSO_4$) and evaporated. FC (SiO_2, AcOEt/petroleum ether 2:8) gave **7** (270 mg, 84%). Yellow oil. IR (NaCl): 1214*s*, 1269*s*, 1676*s*, 3405*m*. ^{1}H-NMR ($CDCl_3$): 1.39 (*t*, *J* = 7.2, *Me*CH$_2$O); 4.37 (*q*, *J* = 7.2, MeC*H*$_2$O); 7.43 (*d*, *J* = 8.8, 1 arom. H); 7.49–7.55 (*m*, 2 arom. H); 7.76–7.85 (*m*, 2 arom. H); 8.18–8.23 (*m*, 1 arom. H); 8.58 (*s*, H–C(3)). ^{13}C-NMR ($CDCl_3$): 14.3 (Me); 63.2 (CH_2); 115.5 (C); 115.6 (C); 120.4 (CH); 122.0 (CH); 124.5 (C); 125.6 (CH); 126.1 (CH); 127.8 (CH); 128.0 (CH); 135.3 (C); 137.2 (CH); 150.3 (C); 163.5 (CO). MS: 322–324 ([*M* + H]$^+$). Anal. calc. for $C_{17}H_{17}BrO_4$ (321.17): C 56.10, H 4.08; found: C 56.34, H 4.27.

*Ethyl Naphtho[1,2-*b*]furan-2-carboxylate* (**4**) [7]. A soln. of **7** (321 mg, 1 mmol) and K_2CO_3 (276 mg, 2 mmol) in methyl isobutyl ketone (10 ml) was stirred at 100° for 10 h and cooled to r.t. The salts were filtered off and washed with acetone. The filtrate was evaporated, the residue poured into H_2O (15 ml) and then extracted with AcOEt (3 × 20 ml), and the combined extract dried ($MgSO_4$) and evaporated. FC (SiO_2, AcOEt/petroleum ether 1:2) gave **4** (151 mg, 45%). Yellow oil. Data of **4**: see *Exper. 3.*

5. *1-(2,3-Dihydronaphtho[1,2-*b*]furan-2-yl)ethan-1-ones* **8d**,**e** *and/or 2-Acetylspiro[cyclopropane-1,1′(4′*H*)-naphthalene]-4′-one]* **9a**,**d**–**f**). According to the *G.P.* of *Exper. 2*, with 3,4-dibromobutan-2-one instead of ethyl 2,3-dibromopropanoate. FC (SiO_2, AcOEt/petroleum ether 1:3) gave **8d**,**e** and/or **9a**,**d**–**f**.

*1-(2,3-Dihydro-6-methoxynaphtho[1,2-*b*]furan-2-yl)ethan-1-one* (**8d**): Solid. M.p. 110°. IR (KBr): 1407*s*, 1520*m*, 1597*s*, 1714*s*. ^{1}H-NMR ($CDCl_3$): 2.32 (*s*, MeCO); 3.98 (*s*, MeO); 3.47 (*dd*, *J* = 15.8, 6.6, CH$_2$(3)); 3.64 (*dd*, *J* = 15.8, 10.9, 1 H, CH$_2$(3)); 5.20 (*dd*, *J* = 10.9, 6.6, H–C(2)); 6.79 (*d*, *J* = 7.6, 1 arom. H); 7.25–7.39 (*m*, 2 arom. H); 7.58 (*d*, *J* = 8.3, 1 arom. H); 7.82 (*d*, *J* = 8.3, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 26.3 (Me); 33.9 (CH_2); 55.6 (MeO); 86.4 (CH); 104.1 (CH); 113.5 (CH); 115.5 (CH); 119.3 (C); 121.5 (C); 121.8 (CH); 125.0 (CH); 126.1 (C); 154.3 (C); 155.7 (C); 209.5 (C=O). MS: 243 ([*M* + H]$^+$). Anal. calc. for $C_{15}H_{14}O_3$ (242.28): C 74.36, H 5.82; found: C 74.03, H 5.72.

*1-(2,3-Dihydro-8-methoxynaphtho[1,2-*b*]furan-2-yl)ethan-1-one* (**8e**): Solid. M.p. 84°. IR (KBr): 1222*s*, 1607*m*, 1726*s*. ^{1}H-NMR ($CDCl_3$): 2.34 (*s*, MeCO); 3.45 (*dd*, *J* = 16.0, 6.6, 1 H, CH$_2$(3)); 3.67 (*dd*, *J* = 16.0, 10.8, 1 H, CH$_2$(3)); 3.94 (*s*, MeO); 5.22 (*dd*, *J* = 10.8, 6.6, H–C(2)); 7.11 (*dd*, *J* = 9.1, 2.8, 1 arom. H); 7.16 (*d*, *J* = 6.2, 1 arom. H); 7.25 (*s*, 1 arom. H); 7.35 (*d*, *J* = 8.2, 2 arom. H); 7.72 (*d*, *J* = 9.1, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 26.5 (Me); 34.4 (CH_2); 55.5 (MeO); 86.3 (CH); 99.2 (CH); 119.0 (CH); 119.1 (C); 120.1 (CH); 121.2 (CH); 121.3 (C); 129.7 (CH); 129.7 (C); 153.5 (C); 157.8 (C)); 209.4 (C=O). MS: 243 ([*M* + H]$^+$). Anal. calc. for $C_{15}H_{14}O_3$ (242.28): C 74.36, H 5.82; found: C 74.14, H 5.79.

*2-Acetylspiro[cyclopropane-1,1′(4′*H*)-naphthalen]-4′-one* (**9a**): Gum. IR (NaCl): 1260*s*, 1644*m*, 1695*s*. ^{1}H-NMR ($CDCl_3$): 2.29 (*s*, MeCO); 2.16 (*dd*, *J* = 7.9, 5.1, 1 H, CH$_2$(3)); 2.99 (*dd*, *J* = 7.5, 5.1, 1 H, CH$_2$(3)); 3.10 (*t*, *J* = 7.7, H–C(2)); 6.59 (*d*, *J* = 10.4, 1 olef. H); 6.97 (*d*, *J* = 10.4, 1 olef. H); 7.00 (*d*, *J* = 7.7, 1 arom. H); 7.47

(*td*, *J* = 8.1, 1.3, 1 arom. H); 7.59 (*td*, *J* = 7.8, 1.5, 1 arom. H); 8.25 (*dd*, *J* = 7.7, 1.2, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 26.9 (CH_2); 32.5 (CH); 33.2 (C); 43.6 (Me); 121.6 (CH); 127.5 (CH); 127.6 (CH); 130.3 (CH); 133.1 (CH); 133.2 (C); 143.5 (C); 147.6 (CH); 185.0 (C=O); 203.0 (C=O). MS: 213 ($[M+H]^+$). Anal. calc. for $C_{14}H_{12}O_2$ (212.25): C 73.23, H 5.70; found: C 73.58, H 5.89.

*2-Acetyl-8′-methoxyspiro[cyclopropane-1,1′(4′*H*)-naphthalen]-4′-one* (**9d**): Gum. IR (NaCl): 1604*m*, 1649*s*, 1703*s*. ^{1}H-NMR ($CDCl_3$): 2.25 (*s*, MeCO); 2.17 (*dd*, *J* = 7.6, 4.1, 1 H, CH_2(3)); 2.99 (*dd*, *J* = 7.5, 4.1, 1 H, CH_2(3)); 3.87 (*s*, MeO); 4.01 (*t*, *J* = 7.6, H–C(2)); 6.53 (*d*, *J* = 10.3, 1 olef. H); 6.81 (*d*, *J* = 10.3, 1 olef. H); 7.10 (*dd*, *J* = 8.1, 0.9, 1 arom. H); 7.41 (*t*, *J* = 8.1, 1 arom. H); 7.98 (*dd*, *J* = 7.8, 0.9, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 23.5 (CH_2); 32.4 (CH); 33.8 (C); 38.4 (Me); 56.1 (Me); 114.8 (CH); 120.5 (CH); 128.1 (CH); 128.5 (CH); 130.0 (C); 135.6 (C); 150.8 (CH); 157.0 (C); 184.6 (C=O); 205.2 (C=O). MS: 243 ($[M+H]^+$). Anal. calc. for $C_{14}H_{12}O_2$ (242.28): C 74.36, H 5.82; found: C 74.65, H 5.63.

*2-Acetyl-6′-methoxyspiro[cyclopropane-1,1′(4′*H*)-naphthalen]-4′-one* (**9e**): Gum. IR (NaCl): 1595*m*, 1651*s*, 1702*s*. ^{1}H-NMR ($CDCl_3$): 2.29 (*s*, MeCO); 3.89 (*s*, MeO); 2.09 (*dd*, *J* = 7.8, 5.3, 1 H, CH_2(3)); 2.49 (*dd*, *J* = 7.5, 5.3, 1 H, CH_2(3)); 3.06 (*t*, *J* = 7.6, H–C(2)); 6.59 (*d*, *J* = 10.3, 1 olef. H); 7.00 (*d*, *J* = 8.8, 1 arom. H); 6.95 (*d*, *J* = 10.3, 1 olef. H); 7.17 (*dd*, *J* = 8.8, 2.8, 1 arom. H); 7.72 (*d*, *J* = 2.8, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 26.4 (CH_2); 32.4 (CH); 33.2 (C); 43.1 (Me); 56.0 (Me); 108.6 (CH); 122.2 (CH); 123.1 (CH); 130.1 (CH); 134.2 (C); 136.0 (C); 147.7 (CH); 159.1 (C); 184.7 (C=O); 203.0 (C=O). MS: 243 ($[M+H]^+$). Anal. calc. for $C_{14}H_{12}O_2$ (242.28): C 74.36, H 5.82; found: C 74.71, H 5.69.

*2-Acetyl-3′-methylspiro[cyclopropane-1,1′(4′*H*)-naphthalen]-4′-one* (**9f**): Gum. IR (NaCl): 1177*s*, 1635*s*, 1648*s*, 1697*s*. ^{1}H-NMR ($CDCl_3$): 2.03 (*s*, Me–C(3′)); 2.29 (*s*, MeCO); 2.08 (*dd*, *J* = 7.5, 5.1, 1 H, CH_2(3)); 2.45 (*dd*, *J* = 7.7, 5.1, 1 H, CH_2(3)); 3.06 (*t*, *J* = 7.7, H–C(2)); 6.77 (*s*, 1 olef. H); 7.00 (*d*, *J* = 7.9, 1 arom. H); 7.45 (*td*, *J* = 8.1, 0.9, 1 arom. H); 7.57 (*td*, *J* = 7.5, 1.5, 1 arom. H); 8.28 (*dd*, *J* = 7.5, 1.5, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 16.7 (Me); 26.0 (CH_2); 32.3 (CH); 32.3 (C); 42.8 (Me); 121.2 (CH); 127.1 (CH); 127.3 (CH); 132.4 (CH); 132.5 (C); 136.7 (C); 142.2 (olef. CH); 143.4 (C); 185.0 (C=O); 203.0 (C=O). MS: 227 ($[M+H]^+$). Anal. calc. for $C_{14}H_{14}O_2$ (226.28): C 79.62, H 6.24; found: C 79.94, H 6.40.

6. *1-(Naphtho[1,2-*b*]furan-2-yl)ethan-1-one* (**10**). According to the *G.P.* of *Exper. 2*, with 3,4-dibromobutan-2-one instead of ethyl 2,3-dibromopropanoate and MIBK in place of acetone. FC (SiO_2, AcOEt/petroleum ether 1 : 3) gave **10** (148 mg, 35%). M.p. 66–68°. IR (KBr): 1550*m*, 1672*s*. ^{1}H-NMR ($CDCl_3$): 2.41 (*s*, MeCO); 7.32–7.41 (*m*, 4 arom. H); 7.37 (*s*, 1 olef. H); 7.67 (*dd*, *J* = 7.2, 2.2, 1 arom. H); 8.16 (*d*, *J* = 7.8, 1.9, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 26.4 (Me); 114.2 (CH); 120.1 (CH); 120.9 (CH); 121.4 (C); 123.0 (C); 124.9 (CH); 126.9 (CH); 127.0 (CH); 128.5 (CH); 133.4 (C); 152.3 (C); 152.4 (C); 188.0 (C=O). MS: 211 ($[M+H]^+$). Anal. calc. for $C_{14}H_{10}O_2$ (210.23): C 79.98, H 4.79; found: C 80.14, H 4.65.

7. *Noncyclized Carbonitriles* **11a,d,e,f**. According to the *G.P.* of *Exper. 2*, with 2,3-dibromopropanenitrile instead of ethyl 2,3-dibromopropanoate. FC (SiO_2, AcOEt/petroleum ether 1 : 4) gave **11a,d,e,f**.

*(*Z*)-3-[(Naphthalen-1-yl)oxy]prop-2-enenitrile* (**11a**) [14]: Solid. M.p. 73°. IR (KBr): 1260*s*, 1644*m*, 2225*m*. ^{1}H-NMR ($CDCl_3$): 4.78 (*d*, *J* = 6.2, 1 olef. H); 6.96 (*dd*, *J* = 7.8, 0.8, 1 arom. H); 7.18 (*d*, *J* = 6.2, 1 olef. H); 7.35 (*t*, *J* = 7.8, 1 arom. H); 7.47–7.54 (*m*, 2 arom. H); 7.63 (*d*, *J* = 7.8, 1 arom. H); 7.80 (*m*, 1 arom. H); 8.15 (*m*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 79.1 (olef. CH); 111.2 (CH); 114.6 (CN); 121.3 (CH); 125.2 (C); 125.3 (2 CH); 126.7 (CH); 127.2 (CH); 127.7 (CH); 134.6 (C); 151.9 (C); 159.4 (CH). MS: 196 ($[M+H]^+$). Anal. calc. for $C_{13}H_9NO$ (195.22): C 79.98, H 4.65, N 7.17; found: C 80.26, H 4.80, N 7.01.

*(*Z*)-3-[(5-Methoxynaphthalen-1-yl)oxy]prop-2-enenitrile* (**11d**): Gum. IR (NaCl): 1397*s*, 1641*s*, 2220*m*. ^{1}H-NMR ($CDCl_3$): 3.96 (*s*, MeO); 4.78 (*d*, *J* = 6.3, 1 olef. H); 6.85 (*d*, *J* = 7.8, 1 arom. H); 7.01 (*d*, *J* = 7.5, 1 arom. H); 7.19 (*d*, *J* = 6.3, 1 olef. H); 7.35 (*d*, *J* = 7.5, 1 arom. H); 7.43 (*d*, *J* = 7.8, 1 arom. H); 7.73 (*d*, *J* = 8.5, 1 arom. H); 8.08 (*d*, *J* = 8.5, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 55.6 (MeO); 78.9 (CH); 105.1 (CH); 112.1 (CH); 113.4 (CH); 114.7 (CN); 119.6 (CH); 124.5 (CH); 126.4 (C); 126.8 (C); 127.0 (CH); 151.8 (C); 155.2 (C); 159.7 (CH). MS: 226 ($[M+H]^+$). Anal. calc. for $C_{14}H_{11}NO_2$ (225.25): C 74.65, H 4.92, N 6.22; found: C 75.00, H 4.78, N 6.36.

*(*Z*)-3-[(7-Methoxynaphthalen-1-yl)oxy]prop-2-enenitrile* (**11e**): Solid. M.p. 61°. IR (KBr): 1251*s*, 1635*s*, 2218*m*. ^{1}H-NMR ($CDCl_3$): 3.94 (*s*, MeO); 4.82 (*d*, *J* = 6.1, 1 olef. H); 7.01 (*d*, *J* = 7.5, 1 arom. H); 7.18 (*dd*, *J* = 9.0, 2.5, 1 arom. H); 7.21 (*d*, *J* = 6.1, 1 olef. H); 7.25 (*d*, *J* = 8.0, 1 arom. H); 7.40 (*d*, *J* = 2.5, 1 arom. H); 7.61 (*d*, *J* = 8.0, 1 arom. H); 7.74 (*d*, *J* = 9.0, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 55.9 (MeO); 79.5 (CH); 99.6 (CH); 112.4 (CH); 115.0 (CN); 120.6 (CH); 123.2 (CH); 125.5 (CH); 126.9 (C); 129.8 (CH); 130.6 (C); 151.6 (C); 158.8 (C); 160.1 (CH). MS: 226 ($[M+H]^+$). Anal. calc. for $C_{14}H_{11}NO_2$ (225.25): C 74.65, H 4.92, N 6.22; found: C 74.87, H 4.77, N 6.15.

*(*Z*)-3-[(2-Methylnaphthalen-1-yl)oxy]prop-2-enenitrile* (**11f**): Gum. IR: 1244*s*, 1630*s*, 2216*m*. ^{1}H-NMR ($CDCl_3$): 2.41 (*s*, Me–C(2)); 4.68 (*d*, *J* = 6.3, 1 olef. H); 6.85 (*d*, *J* = 6.3, 1 olef. H); 7.01 (*d*, *J* = 8.4, 1 arom. H);

7.44 – 7.56 (*m*, 2 arom. H); 7.65 (*d*, $J = 8.5$, 1 arom. H); 7.80 – 7.89 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 16.4 (Me); 78.0 (CH); 114.9 (CN); 121.0 (CH); 125.9 (C); 126.2 (CH); 126.5 (CH); 126.7 (C); 127.5 (CH); 128.3 (CH); 129.3 (CH); 133.7 (C); 149.8 (C); 163.1 (CH). MS: 210 ($[M+H]^+$). Anal. calc. for $C_{14}H_{11}NO$ (209.25): C 80.36, H 5.30, N 6.69; found: C 80.64, H 5.43, N 6.88.

8. *Diethyl 1,2,6,7-Tetrahydronaphtho[1,2-*b*:5,6-*b*′]difuran-2,7-dicarboxylate* (**12**). According to the *G.P.* of *Exper. 2*, with naphthalene-1,5-diol and 2.2 equiv. of ethyl 2,3-dibromopropanoate. Purification by FC (SiO_2, AcOEt/petroleum ether 1:3): 41% of **12**. M.p. 149 – 151°. IR (KBr): 1200, 1403, 1748*s*. MS: 357 ($[M+H]^+$).

The two diastereoisomers (ratio 26:74) of **12** can be separated by semi-prep. HPLC (*UP5ODB-25K* column, H_2O/MeCN 40:60): minor diastereoisomer at t_R 7.340 and major diastereoisomer at t_R 7.843).

Major diastereoisomer: ^{1}H-NMR (400 MHz, C_6D_6): 0.85 (*t*, $J = 7.0$, *Me*CH_2O); 3.06 (*dd*, $J = 15.8$, 6.8, 1 H, CH_2); 3.20 (*dd*, $J = 15.8$, 10.7, 1 H, CH_2); 3.87 (*q*, $J = 7.0$, MeC*H*$_2$O); 4.98 (*dd*, $J = 10.7$, 6.9, 1 H, CHO); 6.93 (*d*, $J = 8.1$, 2 arom. H); 7.88 (*d*, $J = 8.1$, 2 arom. H). Minor diastereoisomer: 0.84 (*t*, $J = 7.0$, *Me*CH_2O); 3.06 (*dd*, $J = 15.8$, 6.8, 1 H, CH_2); 3.20 (*dd*, $J = 15.8$, 10.7, 1 H, CH_2); 3.87 (*q*, $J = 7.0$, MeC*H*$_2$O); 4.97 (*dd*, $J = 10.7$, 6.9, 1 H, CHO); 6.94 (*d*, $J = 8.1$, 2 arom. H); 7.88 (*d*, $J = 8.1$, 2 arom. H). Anal. calc. for $C_{20}H_{20}O_6$ (356.38): C 67.41, H 5.66; found: C 67.03; H 5.48.

9. *Transformations of* **3a**. *Ethyl 3′,4′-Dihydro-4′-hydroxyspiro[cyclopropane-1,1′(2′*H*)-naphthalene]-2-carboxylate* (**13**). To a soln. of **3a** (243 mg, 1 mmol) in EtOH (15 ml), $NaBH_4$ (42 mg, 1.1 mmol) was added. After 30 min, the mixture was hydrolyzed, the EtOH evaporated, the residue extracted with CH_2Cl_2 (3×15 ml), and the combined extract dried ($MgSO_4$) and evaporated. FC (SiO_2, AcOEt/petroleum ether 1:2) gave **13** (52 mg, 21%). Brown gum. IR (NaCl): 1399*s*, 1581*s*, 1732*s*, 3406*m*. ^{1}H-NMR ($CDCl_3$): 1.24 (*t*, $J = 7.1$, *Me*CH_2O); 1.49 – 1.60 (*m*, 2 H, CH_2); 1.78 – 2.13 (*m*, 5 H, CH, 2 CH_2); 4.17 (*q*, $J = 7.1$, MeC*H*$_2$O); 4.82 (br. *s*, CH); 6.68 – 6.76 (*m*, 1 arom. H); 7.18 – 7.24 (*m*, 2 arom. H); 7.46 – 7.51 (*m*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 15.5 (Me); 24.5 (CH_2); 25.3 (CH_2); 29.9 (C); 32.7 (CH_2); 33.0 (CH); 62.0 (CH_2O); 70.2 (CH); 123.0 (CH); 128.0 (CH); 129.7 (CH); 129.9 (CH); 130.3 (C); 140.4 (C); 172.5 (C=O). MS: 269 ($[M+Na]^+$). Anal. calc. for $C_{15}H_{18}O_3$ (246.31): C 73.15, H 7.37; found: C 73.40, H 7.29.

*Ethyl 3′,4′-Dihydro-4′-oxospiro[cyclopropane-1,1′(2′*H*)-naphthalene]-2-carboxylate* (**14**) *and Ethyl 4-Hydroxynaphthalene-1-propanoate* (**15**). To a soln. of **3a** (243 mg, 1 mmol) in EtOH (5 ml) 10% Pd/C (24 mg) was added and the mixture stirred under H_2 (1 atm) for 15 min. After filtration, EtOH was removed. FC (SiO_2, AcOEt/petroleum ether 1:2) gave **14** (93 mg, 38%) as a pale yellow solid and **15** (142 mg, 58%) as a yellow oil.

Data of **14**: M.p. 130 – 132°. IR (KBr): 1188*m*, 1680*s*, 1717*s*. ^{1}H-NMR ($CDCl_3$): 1.26 (*t*, $J = 7.1$, *Me*CH_2O); 1.61 – 1.69 (*m*, CH); 1.75 – 1.81 (*m*, CH); 1.99 – 2.05 (*m*, CH); 2.27 – 2.41 (*m*, CH_2); 2.56 – 2.77 (*m*, CH_2); 4.18 (*q*, $J = 7.1$, MeC*H*$_2$O); 6.90 (*d*, $J = 7.8$, 1 arom. H); 7.32 (*t*, $J = 7.8$, 1 arom. H); 7.50 (*td*, $J = 7.8$, 1.0, 1 arom. H); 8.03 (*d*, $J = 7.6$, 1.2, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 14.3 (Me); 20.3 (CH_2); 26.2 (CH_2); 28.9 (C); 30.4 (CH); 31.9 (CH_2); 61.0 (CH_2); 122.0 (CH); 126.9 (CH); 127.6 (CH); 133.0 (C); 134.1 (CH); 145.3 (C); 171.0 (C=O); 197.9 (C=O). MS: 245 ($[M+H]^+$). Anal. calc. for $C_{15}H_{16}O_3$ (244.29): C 73.75, H 6.60; found: C 73.54, H 6.76.

Data of **15**: IR (NaCl): 1589*s*, 1731*s*, 3401*m*. ^{1}H-NMR ($CDCl_3 + D_2O$): 1.25 (*t*, $J = 7.1$, *Me*CH_2O); 2.73 (*t*, $J = 8.3$, CH_2); 3.46 (*t*, $J = 8.3$, CH_2); 4.15 (*q*, $J = 7.1$, MeC*H*$_2$O); 6.69 (*d*, $J = 7.6$, H–C(2)); 7.14 (*d*, $J = 7.6$, H–C(3)); 7.45 – 7.57 (*m*, 2 arom. H); 7.95 (*dd*, $J = 7.1$, 1.7, 1 arom. H); 8.19 – 8.25 (*m*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 14.3 (Me); 27.9 (CH_2); 35.6 (CH_2); 60.8 (CH_2); 108.2 (CH); 122.6 (CH); 123.5 (CH); 125.0 (C); 125.0 (CH); 126.0 (CH); 126.7 (CH); 128.8 (C); 129.1 (C); 150.7 (C); 173.7 (C=O). MS: 245 ($[M+H]^+$). Anal. calc. for $C_{15}H_{16}O_3$ (244.29): C 73.75, H 6.60; found: C 73.52, H 6.48.

Ethyl 4-Hydroxynaphthalene-1-propanoate (**15**) *and Ethyl β-Chloro-4-hydroxynaphthalene-1-propanoate* (**16**). To a soln. of **3a** (243 mg, 1 mmol) in THF (5 ml), chromium(II) chloride (123 mg, 1 mmol) was added, and the mixture was stirred for 8 h at 50°. After cooling, the THF was evaporated. FC (SiO_2, CH_2Cl_2/EtOH 9:1) gave **16** (103 mg, 37%) as an orange oil and **15** (59 mg, 24%) as a yellow oil.

Data of **16**: IR (KBr): 3444*s*, 1736*s*, 1685*s*, 1519*m*. ^{1}H-NMR ($CDCl_3$): 1.22 (*t*, $J = 7.1$, *Me*CH_2O); 3.72 (*dd*, $J = 6.4$, 4.6, 1 H, CH_2); 4.20 (*dd*, $J = 6.4$, 5.9, 1 H, CH_2); 4.21 (*q*, $J = 7.1$, MeC*H*$_2$O); 4.70 (*dd*, $J = 5.9$, 4.6, CH), 6.48 (br. *s*, OH); 6.70 (*d*, $J = 7.8$, 1 arom. H); 7.26 (*d*, $J = 7.8$, 1 arom. H); 7.45 – 7.62 (*m*, 2 arom. H); 8.04 (*d*, $J = 8.3$, 1 arom. H); 8.27 (*d*, $J = 7.8$, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 14.2 (Me); 44.6 (CH_2); 49.5 (CH); 61.9 (CH_2); 108.0 (CH); 122.5 (CH); 123.0 (CH); 123.7 (C); 125.1 (CH); 125.3 (CH); 127.4 (CH); 132.3 (C); 152.3 (C); 172.8 (C=O). MS: ($[M+H]^+$), 279 – 281.

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