Novel Concepts in Directed Biaryl Synthesis, IX[1]

Synthesis and Structure of Benzonaphthopyranones, Useful Bridged Model Precursors for Stereoselective Biaryl Syntheses☆

Gerhard Bringmann*[a], Thomas Hartung[a], Lothar Göbel[a], Olaf Schupp[a], Christian L. J. Ewers[a], Bernd Schöner[a], Rainer Zagst[a], Karl Peters[b], Hans Georg von Schnering[b], and Christian Burschka[c]

Institut für Organische Chemie der Universität Würzburg[a], Am Hubland, W-8700 Würzburg, Germany

Max-Planck-Institut für Festkörperforschung[b], Heisenbergstraße 1, W-7000 Stuttgart 80, Germany

Institut für Anorganische Chemie der Universität Würzburg[c], Am Hubland, W-8700 Würzburg, Germany

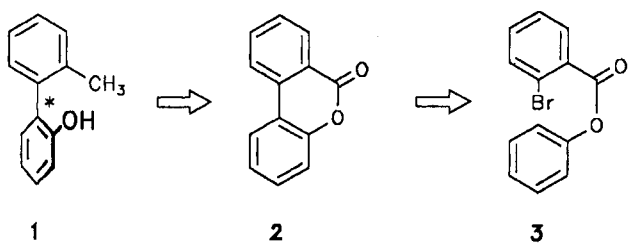
Received November 14, 1991

Key Words: Aryl coupling, intramolecular / Biaryls, ester-type bridged, preparation and stereostructure of

A practicable two-step procedure for the preparation of a series of lactone-type bridged biaryls **7** as favorable substrates for subsequent atropisomer-selective ring-opening reactions is described. Due to the efficiency of the coupling step, which tolerates even a *tert*-butyl group next to the biaryl axis and avoids problems of regioselectivity, a variety of differently substituted representatives is prepared. These cover a broad range of steric hindrance and thus molecular distortion. The structures are investigated mainly by NMR spectroscopy and X-ray diffraction, showing the lactones **7** to be helically distorted, depending on the size of the residues R.

The regio- and stereoselective construction of natural and unnatural hindered biaryl systems is a synthetic challenge that has successfully been approached only very recently[2-4]. Exemplarily for the substitution pattern as in **1**, which is found in many naturally occurring biaryls[5], we have developed a useful procedure in which the two formal partial goals of stereoselective biaryl synthesis are attained *consecutively*[6-11]: The CC bond formation is performed by intramolecular aryl coupling of the ester-type prefixed aromatics as in **3**, and the asymmetric induction at this biaryl axis is achieved by an atropdiastereo- or enantioselective ring opening of the resulting lactones **2**. Hence, such bridged biaryls **2** play a crucial role in this concept: Although they already possess the biaryl axis, most of them are axially prostereogenic[6,7,12,13], i.e. they do not occur as stable atropisomers (helimers) at the synthetically relevant temperatures. Apparently, the rotational barrier of **2** is drastically lower than that of the open-chain final target biaryls **1** and thus allows rapid helimerization (e.g. at room temperature).

For a thorough investigation of the structures of such bridged biaryls, of their isomerization mechanism, and especially of the unprecedented stereocontrolled ring opening process, there is a great need of appropriately substituted representatives of this stereochemically interesting class of bridged biaryls. In this paper, we describe a practicable synthetic pathway to a series of benzonaphthopyranones of the general type **7**, with a broad variety of substituents of most different sizes next to the biaryl axis. Part of this work has recently been reported in preliminary form[9,10].



1 **2** **3**

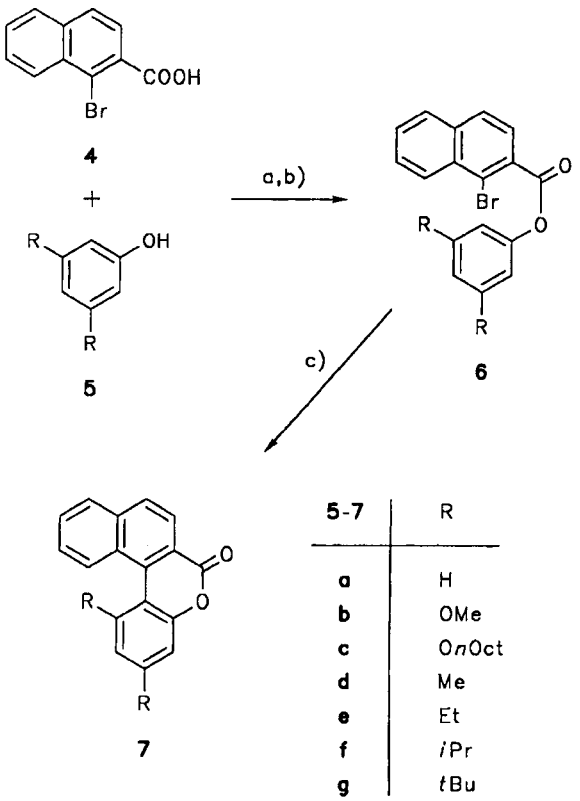
The structural type **7** was chosen for different reasons: On the one hand, its substitution pattern (alkyl groups and oxygen functions in *ortho*-positions with respect to the axis) is similar to that of many naturally occurring biaryls. Also, the symmetrical structure of the variable phenolic component helps to avoid additional problems of regioselectivity in the intramolecular aryl coupling step. A further advantage of the lactones **7** was their supposed tendency to afford crystals suitable for X-ray structure analysis (see below). By contrast, the long-chain *O*-substituted derivative **7c** was prepared because of its expected favorable solubility properties, e.g. for recording EXAFS spectra of the corresponding metal complexes[14] and for the eventual preparation of liquid crystalline phases.

The required phenols **5a**, **b**, **d**, and **g** are commercially available. **5c**, a new compound, was synthesized from phloroglucinol by acid-catalyzed *O*-alkylation with *n*-octanol and hydrochloric acid (see Experimental). **5e**[15,16] and **5f**[17,18] were prepared according to known procedures.

The naphthalene part of **7** was chosen because of the ready availability of the known[19] 1-bromo-2-naphthalenecarboxylic acid (**4**), whose halogenation site guarantees ex-

  0170–2041/92/0303–0225 $ 3.50+.25/0

Scheme 1. Reaction conditions: a) Activation of the acid [$(COCl)_2$, DMF, dichloromethane]. – b) Esterification (5, Et_3N, DMAP, dichloromethane). – c) Aryl coupling [Pd$(OAc)_2$, PPh_3, NaOAc, DMA, 120°C; or $(Ph_3P)_2PdCl_2$, NaOAc, DMA, 130°C]



5-7	R
a	H
b	OMe
c	O*n*Oct
d	Me
e	Et
f	*i*Pr
g	*t*Bu

clusive coupling in this *peri*-position, and because of the expected higher efficiency of the intramolecular coupling of naphthalene components[12,13,20], compared with monocyclic aromatics[21,22].

The benzonaphthopyranones **7a–g** were synthesized in two steps: The carboxylic acid **4**, after its transformation to the acyl chloride, was linked to the phenols **5a–g** to give the corresponding bromo esters **6a–g**, which were then transformed into the target lactones **7a–g** by palladium-catalyzed intramolecular aryl coupling[21] with elimination of hydrogen bromide (Scheme 1). The efficiency of this procedure can be seen by the very practicable yields, which, though distinctly diminished for **7g**, show that even this highly hindered biaryl, with the bulky *tert*-butyl group next to the rigid naphthalene part, can still be synthesized in this way. This clearly contrasts with similar intermolecular reactions, which do not tolerate such sterically demanding *ortho*-substituents[3,23].

Table 1. Preparation of the lactones **7** by Pd-catalyzed intramolecular aryl coupling

Phenol	Ester	Yield[a] (%)	Lactone	Yield[a] (%)
5a	**6a**	91	**7a**	70
5b	**6b**	92	**7b**	77
5c	**6c**	72	**7c**	81
5d	**6d**	91	**7d**	72
5e	**6e**	88	**7e**	71
5f	**6f**	90	**7f**	72
5g	**6g**	87	**7g**	31[b]

[a] Yield of isolated pure products. – [b] In addition, hydrodehalogenation (35%) was found to occur, as well as formation of the known 2-methyl-4*H*-naphtho[2,1-*c*]pyran-4-one (14%)[24].

The biaryl lactones **7** thus prepared are not only synthetically important, but are, above all, stereochemically intriguing: on the one hand, especially the representatives **7a–c** are axially prostereogenic, i.e. not yet configurationally defined, since they can be ring-opened with high stereoselectivities, to give any desired atropoenantiomer or -diastereomer[11] – on the other hand, they are not planar at all, but rather exist as helicene-like distorted conformers. The chirality of these molecules within the NMR time scale can clearly be seen for the derivatives **7e** and **7f**, which both contain diastereotopic hydrogen atoms (2 × 2 H's for **7e** and 2 × 2 CH_3's for **7f**) that should become enantiotopic on rapid interconversion of the two helimers at higher temperatures. Due to their proximity to the molecular dissymmetry, especially the two methyl groups of the isopropyl residue next to the biaryl axis of **7f** exhibit a highly diastereotopic character: their signals appear at δ = 0.66 and 1.58, respectively. Exemplarily for this compound, these two methyl groups could be stereochemically assigned, relative to the configuration at the biaryl axis, by selective NOE experiments, thus permitting to establish a rough stereomodel of **7f**, as sketched in Figure 1. This stereochemical representation is in accordance with the structure in the crystal (see below).

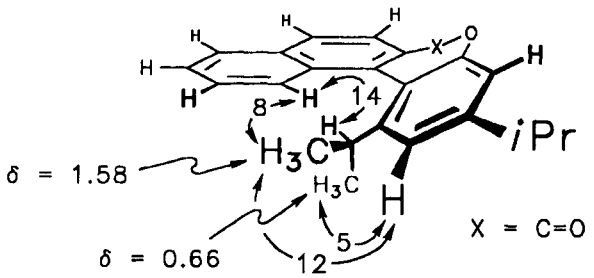


Figure 1. Selected NOE interactions (in %) and proposed stereostructure of **7f** in solution ($CDCl_3$)

Independent of the presence of diastereotopic/enantiotopic units, the screw-shaped character of the molecules can best be seen by X-ray crystallography. Figure 2 shows the crystal structures of the lactones **7b, d, e,** and **f**. In contrast to other helicene-like compounds[25], these substances crystallize as racemates. Figure 2 reveals the structures of only one of the two respective helimeric enantiomers.

Regrettably, no X-ray-structure analysis could be achieved for **7a** and **7g**, i.e. the least and the most hindered representatives of this series. Nonetheless, some stereochemical features can already be deduced from the crystal structures of **7b, d, e,** and **f**: As anticipated, the helical distortion of the biaryl lactones depends on the steric demand of the substituents R. As Table 2 reveals, the extent of this distor-

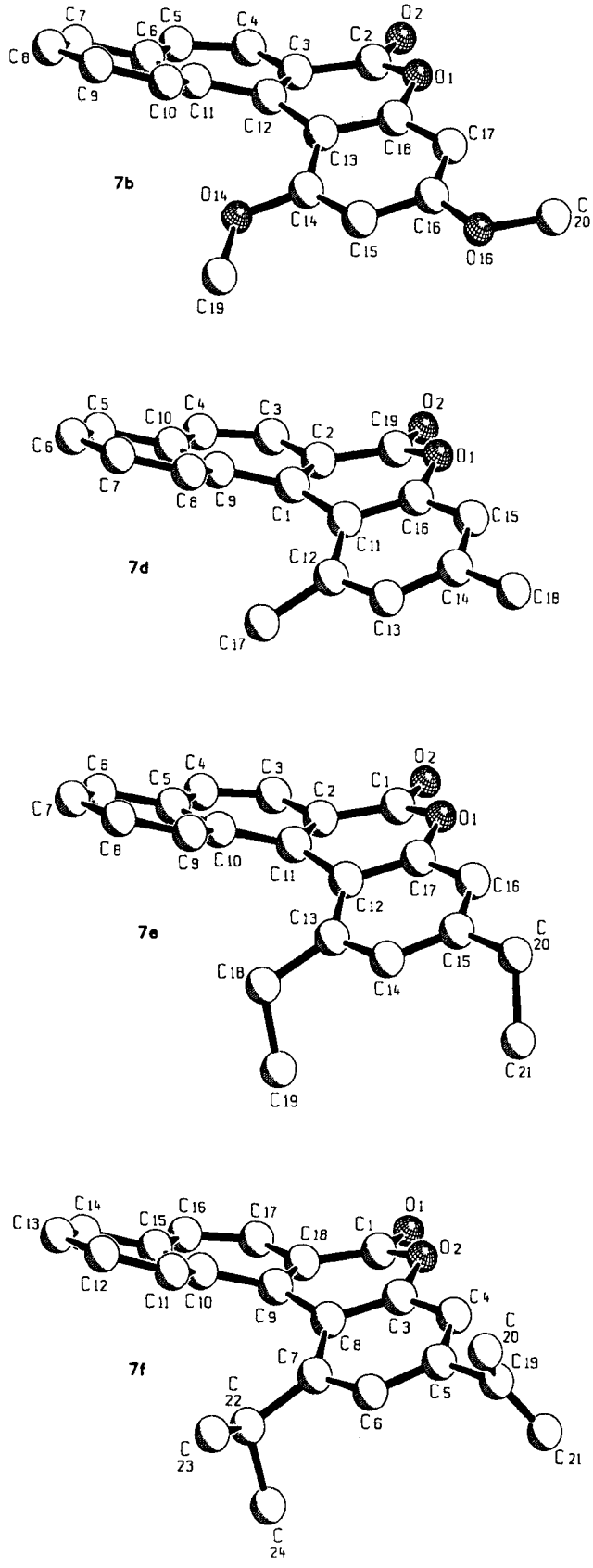
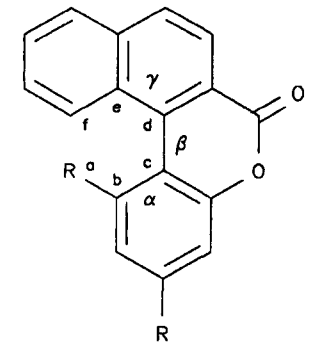


Figure 2. Structures of **7b**, **7d**, **7e**, and **7f**, as determined by X-ray diffraction

tion is only insufficiently described by regarding the dihedral angle β at the axis alone, because the *entire molecule* is concerned. A useful measure for the helical character is the sum of all the dihedral angles α to γ, thus considering the whole inner spiral loop[26]. The single values show only little changes for the axis-near part of this helix (e.g. for the angles β and γ), which is embedded into the relatively rigid ring system, whereas the outer part of the loop (as represented e.g. by the angle α), which largely lacks such a ring framework support, is more drastically distorted and thus greatly contributes to the global helicity of the system.

Table 2. Dihedral angles α(abcd), β(bcde), and γ(cdef) of the lactones **7**, as determined by X-ray diffraction. Σ = total sum of the dihedral angles α, β, and γ



	α	β	γ	Σ[a]
7b	6.01	32.22	17.22	55.45
7d	12.38	34.08	15.00	61.46
7e	14.45	34.02	14.22	62.91
7f	18.06	34.12	14.36	66.54

The relative steric differences between the lactones **7** are best visualized by superimposing the crystal structures of those lactones with the smallest and the largest residues R, i.e. **7b** and **7f** (see Figure 3).

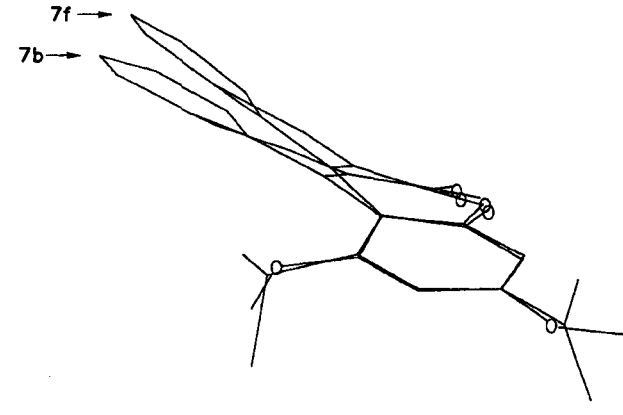


Figure 3. Structures of **7b** and **7f** in the crystal, matched with respect to the previously phenolic part (hydrogen atoms omitted for reasons of clarity)

Work to predict the atropisomerization barrier of **7a–g** by semiempirical or ab initio calculations as well as the experimental determination and thus rescaling of these energies by DNMR for **7e** and **7f** is in progress. Furthermore, the enantioselective preparation of the more hindered representatives of this class and the systematic preparative and mechanistic investigation of atropoenantioselective biaryl syntheses via **7** are under investigation.

This work was supported by the *Deutsche Forschungsgemeinschaft* (Sonderforschungsbereich No. 347 "Selective Reactions by Metal-Activated Molecules") and by the *Fonds der Chemischen Industrie*. We are indebted to Mrs. *L. Kinzinger*, Mrs. *M. Schäffer*, and Mr. *G. Kickelbick* for valuable technical assistance. A generous gift of palladium(II) acetate by the *Degussa AG*, Hanau, Germany, is gratefully acknowledged.

Experimental

Melting points (corrected): Kofler hot-stage. – IR: Perkin-Elmer 1420 spectrophotometer. – ^1H and ^{13}C NMR [δ values relative to the solvent $CDCl_3$: δ = 7.26 (^1H) and 77.0 (^{13}C)]: Bruker AC 200, AC 250, and WM 400 instruments. – MS: Electron ionization, Finnigan MAT MS 8200 apparatus. – Microanalyses: Microanalytical laboratory of the University of Würzburg, Carlo-Erba M 1106 apparatus. – Reactions were monitored by thin-layer chromatography (TLC) using TLC aluminium sheets silica gel 60 F_{254} (Merck). – For column chromatography: silica gel (0.063–0.200 mm, Merck). – The petroleum ether used had a boiling range of 30–70 C. – The phenols **5a**, **b**, **d**, and **g** were purchased from Aldrich. *N,N*-Dimethylacetamide (DMA) was purified by distillation from calcium hydride and stored over 3-Å molecular sieves under argon. All chemicals used for the aryl coupling reactions were dried in vacuo at 60 C prior to use.

3,5-Dioctoxyphenol (**5a**): Into a suspension of 5.00 g (30.8 mmol) of phloroglucinol dihydrate in 1-octanol (75 ml) dry HCl is bubbled over a period of 30 min. The mixture is then warmed to 70 C and the resulting solution stirred for 3 h. The solvent is distilled off and the residue purified by column chromatography on silica gel, using dichloromethane/methanol (100:1) as an eluent, to give 1.43 g (4.08 mmol, 13%) of **5c** as an oil. – IR (neat): $\tilde{\nu}$ = 3360 cm^{-1} (m, OH), 2920, 2840 (s, CH aliph.), 1590 (s, C=C), 1155 (s, C–O). – ^1H NMR (200 MHz): δ = 0.83–0.94 (t, *J* = 6.8 Hz, 6H, 2 $O[CH_2]_7CH_3$), 1.27–1.44 (m, 20H, 2 $OCH_2CH_2[CH_2]_5CH_3$), 1.66–1.79 (m, 4H, 2 $OCH_2CH_2[CH_2]_5CH_3$), 3.87 (t, *J* = 6.4 Hz, 4H, 2 $OCH_2[CH_2]_6CH_3$), 4.85 (br. s, 1H, OH), 5.97 (d, *J* = 2.1 Hz, 2H, 2- and 6-H), 6.04 (t, *J* = 2.1 Hz, 1H, 4-H). – MS (70 eV): *m/z* (%) = 350 (11) [M^+], 238 (22) [$M^+ - C_8H_{16}$], 127 (78) [$M^+ + H - 2\,C_8H_{16}$], 126 (100) [$M^+ - 2\,C_8H_{16}$].

$C_{22}H_{38}O_3$ (350.5) Calcd. C 75.38 H 10.93
Found C 75.58 H 11.21

General Procedure for the Preparation of the Esters **6a–g**: To a suspension of 1 equivalent of 1-bromo-2-naphthalenecarboxylic acid (**4**)[19] in dry dichloromethane (10 ml per 0.75 mmol acid) and some drops of DMF as catalyst, 1.1 equivalents of oxalyl chloride are added at 0 C. The mixture is stirred at 0 C for 1 h and at room temp. for 3 h. This solution is added dropwise to a solution of 1 equivalent of phenol and 1.5 equivalents of triethylamine dissolved in dichloromethane (10 ml per 0.75 mmol acid), to which have been added some crystals of DMAP as an acylation catalyst. Then the mixture is stirred at room temp. for 3 h. After evaporation of the solvent under reduced pressure, the residue is chromatographed to give the ester **6**.

Phenyl 1-Bromo-2-naphthoate (**6a**): According to the general procedure 7.53 g (30.0 mmol) of **4** is esterified with 2.83 g (30.0 mmol) of phenol. Chromatography with dichloromethane yields **6a** as colorless crystals. Yield 8.93 g (27.3 mmol, 91%), m.p. 87–88 C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w, CH arom.), 1725 (s, C=O), 1585, 1575 (m, C=C), 1185 (s, C–O), 960, 755, 745 (s). – ^1H NMR (250 MHz): δ = 7.29–7.48 (m, 5H, Ph), 7.66 (m_c, 2H, 6- and 7-H), 7.88 (m_c, 3H, 4-, 5-, and 8-H), 8.50 (m_c, 1H, 3-H). – MS (70 eV): *m/z* (%) = 328/326 (6/6) [M^+], 235/233 (100/100) [$M^+ - C_6H_5O$], 207/205 (24/23) [$C_{10}H_6Br^+$], 126 (73) [$C_{10}H_6^+$].

$C_{17}H_{11}BrO_2$ (327.2) Calcd. C 62.40 H 3.39
Found C 62.65 H 3.41

3,5-Dimethoxyphenyl 1-Bromo-2-naphthoate (**6b**): According to the general procedure, 7.53 g (30.0 mmol) of **4** is esterified with 4.63 g (30.0 mmol) of 3,5-dimethoxyphenol. Chromatography with dichloromethane gives **6b** as colorless crystals. Yield 10.7 g (27.6 mmol, 92%), m.p. 84–85 C. – IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1} (w, CH aliph.), 1730 (s, C=O), 1610, 1580 (m, C=C), 1100 (s). – ^1H NMR (250 MHz): δ = 3.82 (s, 6H, 2 OCH_3), 6.41 (t, *J* = 2.2 Hz, 1H, 4'-H), 6.51 (d, *J* = 2.2 Hz, 2H, 2'- and 6'-H), 7.66 (m_c, 2H, 6- and 7-H), 7.88 (m_c, 3H, 4-, 5-, and 8-H), 8.50 (m_c, 1H, 3-H). – MS (70 eV): *m/z* (%) = 388/386 (2/2) [M^+], 307 (53) [M^+ – Br], 235/233 (97/100) [$M^+ - C_8H_9O_3$], 207/205 (17/18) [$C_{10}H_6Br^+$], 126 (37) [$C_{10}H_6^+$].

$C_{19}H_{15}BrO_4$ (387.2) Calcd. C 58.94 H 3.91
Found C 58.97 H 3.99

3,5-Dioctoxyphenyl 1-Bromo-2-naphthoate (**6c**): The acid **4** (393 mg, 1.57 mmol) is esterified with 549 mg (1.57 mmol) of **5c** to give 654 mg (1.12 mmol, 72%) of **6c** as an oil after chromatography with dichloromethane/petroleum ether (1:3). – IR (neat): $\tilde{\nu}$ = 2980 cm^{-1} (s, CH aliph.), 1740 (m, C=O), 1610, 1580 (m, C=C), 1450 (m), 1160, 1125 (s, C–O). – ^1H NMR (200 MHz): δ = 0.80–0.88 (m, 6H, 2 $O[CH_2]_7CH_3$), 1.27–1.51 (m, 20H, 2 $OCH_2CH_2[CH_2]_5CH_3$), 1.69–1.79 (m, 4H, 2 $OCH_2CH_2[CH_2]_5CH_3$), 3.93 (t, *J* = 6.5 Hz, 4H, $OCH_2[CH_2]_6CH_3$), 6.38 (d, *J* = 2.2 Hz, 1H, 4'-H), 6.45 (d, *J* = 2.2 Hz, 2H, 2'- and 6'-H), 7.59–7.72 (m, 2H, aromatic H), 7.85–7.96 (m, 3H, aromatic H), 8.46–8.51 (m, 1H, aromatic H). – MS (70 eV): *m/z* (%) = 584/582 (0.8/0.7) [M^+], 503 (54) [M^+ – Br], 235/233 (100/95) [$M^+ - C_{22}H_{37}O_3$].

$C_{33}H_{43}BrO_4$ (583.6) Calcd. C 67.92 H 7.43
Found C 68.21 H 7.68

3,5-Dimethylphenyl 1-Bromo-2-naphthoate (**6d**): According to the general procedure, the acid **4** is esterified with 3.66 g (30.0 mmol) of 3,5-dimethylphenol to give **6d** as colorless crystals after chromatography with dichloromethane. Yield 9.68 g (27.3 mmol, 91%), m.p. 86 C. – IR (KBr): $\tilde{\nu}$ = 2910 cm^{-1} (w, CH aliph.), 1730 (s, C=O), 1605, 1580 (m, C=C), 1270 (s), 1140 (s, C–O). – ^1H NMR (250 MHz): δ = 2.38 (s, 6H, 2 CH_3), 6.95 (s, 3H, 2'-, 4'-, and 6'-H), 7.67 (m_c, 2H, 6- and 7-H), 7.88 (m_c, 3H, 4-, 5-, and 8-H), 8.50 (m_c, 1H, 3-H). – MS (70 eV): *m/z* (%) = 356/354 (7/7) [M^+], 275 (4) [M^+ – Br], 235/233 (98/100) [$M^+ - C_8H_9O$], 207/205 (17/18) [$C_{10}H_6Br^+$], 126 (46) [$C_{10}H_6^+$].

$C_{19}H_{15}BrO_2$ (355.2) Calcd. C 64.25 H 4.26
Found C 64.08 H 4.14

3,5-Diethylphenyl 1-Bromo-2-naphthoate (**6e**): According to the general procedure 702 mg (2.79 mmol) of **4** and 420 mg (2.79 mmol) of **5e** gave 945 mg (2.46 mmol, 88%) of **6e** as colorless crystals after chromatography with diethyl ether/petroleum ether (1:3), m.p. 58 C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (w, CH arom.), 2960, 2920, 2860 (m, CH aliph.), 1735 (s, C=O), 1100 (s, C–O), 760 (m). – ^1H NMR (200 MHz): δ = 1.30 (t, 6H, *J* = 7.6 Hz, 2 CH_3), 2.72 (q, *J* = 7.6 Hz, 4H, 2 CH_2), 7.01 (s, 3H, 2'-, 4'-, and 6'-H), 7.67 (m_c, 2H, 6- and

7-H), 7.90 (m_c, 3H, 4-, 5-, and 8-H), 8.54 (m_c, 1H, 3-H). – MS (70 eV): *m/z* (%) = 384/382 (5/5) [M^+], 303 (4) [$M^+ - Br$], 235/233 (100/97) [$M^+ - C_{10}H_{13}O$], 126 (46) [$C_{10}H_6^+$].

$C_{21}H_{19}BrO_2$ (383.4) Calcd. C 65.79 H 4.99
Found C 65.87 H 5.01

3,5-Diisopropylphenyl 1-Bromo-2-naphthoate (**6f**): According to the general procedure 473 mg (1.96 mmol) of **4** and 350 mg (1.96 mmol) of **5f** gave 725 mg (1.76 mmol, 90%) of **6f** as colorless crystals after chromatography with diethyl ether/petroleum ether (1:2), m.p. 86–88°C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w, CH arom.), 2940, 2920, 2860 (m, CH aliph.), 1730 (s, C=O), 1600, 1560 (m, C=C), 1100 (s, C–O). – ^1H NMR (200 MHz): δ = 1.30 [t, *J* = 6.9 Hz, 12H, 2 CH(CH_3)$_2$], 2.96 [sept, *J* = 6.9 Hz, 2H, 2 $CH(CH_3)_2$], 7.02 (m_c, 2H, 2'- and 6'-H), 7.03 (m_c, 1H, 4'-H), 7.59–7.73 (m, 2H, 6- and 7-H), 7.84–7.91 (m, 3H, 4-, 5-, and 8-H), 8.50–8.55 (m, 1H, 3-H). – MS (70 eV): *m/z* (%) = 412/410 (4/5) [M^+], 235/233 (97/100) [$M^+ - C_{12}H_{17}O$], 126 (78) [$C_{10}H_6^+$].

$C_{23}H_{23}BrO_2$ (411.3) Calcd. C 67.17 H 5.64
Found C 67.28 H 5.81

3,5-Di-tert-butylphenyl 1-Bromo-2-naphthoate (**6g**): According to the general procedure 5.02 g (20.0 mmol) of **4** and 4.13 g (20.0 mmol) of **5g** gave 7.64 g (17.4 mmol, 87%) of **6g** as colorless crystals after chromatography with diethyl ether/petroleum ether (1:15), m.p. 115.5–116.5°C. – IR (KBr); $\tilde{\nu}$ = 3050 cm^{-1} (w, CH arom.), 2940 (s, CH aliph.), 2890, 2860 (m, CH aliph.), 1730 (s, C=O), 1600, 1580 (m, C=C), 1105 (s, C–O). – ^1H NMR (250 MHz): δ = 1.35 (s, 18H, 6 CH_3), 7.11 (d, *J* = 1.7 Hz, 2H, 2'- and 6'-H), 7.34 (d, *J* = 1.7 Hz, 1H, 4'-H), 7.59–7.72 (m_c, 2H, 6- and 7-H), 7.88 (m_c, 3H, 4-, 5-, and 8-H), 8.52 (m_c, 1H, 3-H). – MS (70 eV): *m/z* (%) = 440/438 (5/4) [M^+], 235/233 (98/100) [$M^+ - C_{14}H_{21}O$], 207/205 (18/17) [$C_{10}H_6Br^+$], 126 (55) [$C_{10}H_6^+$], 57 (15) [$C_4H_9^+$].

$C_{25}H_{27}BrO_2$ (439.4) Calcd. C 68.34 H 6.19
Found C 68.38 H 6.06

General Procedure for the Synthesis of the Benzonaphthopyranones **7a–g**

Method A: A mixture of 1 equivalent of ester **6**, 2 equivalents of sodium acetate, 0.6 equivalents of triphenylphosphane, and 0.2 equivalents of palladium(II) acetate in dry DMA (10–15 ml per mmol ester) is heated to 120°C and stirred at this temp. for 15 h. The coupling reaction can easily be followed by TLC, because of the brilliant fluorescence of **7** upon UV excitation (366 nm). The solvent is evaporated under reduced pressure and the residue filtered over Celite (dichloromethane). After removal of the solvent in vacuo, the residue is chromatographed to give the pure lactone **7**.

Method B: A mixture of 1 equivalent of ester **6**, 2 equivalents of sodium acetate, and 0.2 equivalents of bis(triphenylphosphane)palladium dichloride in DMA (10–15 ml per mmol ester) is heated at 130°C for 0.5–7 h. Concerning workup cf. method A.

6H-Benzo[b]naphtho[1,2-d]pyran-6-one (**7a**)[27]: According to the general procedure A 4.91 g (15.0 mmol) of **6a** gave 2.61 g (10.6 mmol, 70%) of **7a** as colorless crystals after chromatography with *tert*-butyl methyl ether/petroleum ether (1:15), m.p. 126 to 127°C. – IR[28] (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w, CH arom.), 1715 (s, C=O), 1605, 1585 (m, C=C), 1080 (m, C–O), 750 (m). – ^1H NMR (250 MHz): δ = 7.37–7.58 (m, 3H, 2-, 3-, and 4-H), 7.72 (m_c, 2H, 10- and 11-H), 7.98 (m_c, 2H, 8- and 9-H), 8.32 (d, *J* = 8.6 Hz, 1H, 7-H), 8.52 (m_c, 1H, 1-H), 8.87 (m_c, 1H, 12-H). – MS (70 eV): *m/z* (%) = 246 (100) [M^+], 218 (60) [$M^+ - CO$], 126 (19) [$C_{10}H_6^+$], 94 (25) [$C_6H_6O^+$].

$C_{17}H_{10}O_2$ (246.3) Calcd. C 82.90 H 4.09
Found C 83.19 H 4.31

1,3-Dimethoxy-6H-benzo[b]naphtho[1,2-d]pyran-6-one (**7b**): According to the general procedure A 5.81 g (15.0 mmol) of **6b** gave 3.53 g (11.5 mmol, 77%) of **7b** as yellow crystals after chromatography with *tert*-butyl methyl ether/petroleum ether (1:15), m.p. 180–181°C. – IR (KBr): $\tilde{\nu}$ = 2830 cm^{-1} (w, CH aliph.), 1700 (s, C=O), 1605, 1585, 1565 (m, C=C), 1195, 1155, 1095 (m, C–O), 745 (m). – ^1H NMR (250 MHz): δ = 3.81 and 3.91 (2 s, 3H each, 2 OCH_3), 6.50 and 6.65 (2 d, *J* = 2.5 Hz, 1H each, 2- and 4-H), 7.49 (m, 1H, 10- or 11-H), 7.64 (m, 1H, 10- or 11-H), 7.89 (m_c, 2H, 8- and 9-H), 8.04 (m_c, 1H, 12-H), 8.32 (d, *J* = 8.5 Hz, 1H, 7-H). – MS (70 eV): *m/z* (%) = 306 (100) [M^+], 291 (8) [$M^+ - CH_3$], 263 (9) [291 – CO], 262 (9) [$M^+ - CO_2$].

$C_{19}H_{14}O_4$ (306.3) Calcd. C 74.50 H 4.61
Found C 74.35 H 4.75

1,3-Dioctoxy-6H-benzo[b]naphtho[1,2-d]pyran-6-one (**7c**): According to the general procedure B 394 mg (675 μmol) of **6c** gave 276 mg (549 μmol, 81%) of **7c** as pale yellow crystals after chromatography with dichloromethane/petroleum ether (3:1), m.p. 72–74°C. – IR (KBr): $\tilde{\nu}$ = 2910 cm^{-1} (m, CH aliph.), 1715 (s, C=O), 1605 (s, C=C), 1165 (m, C–O), 750 (m). – ^1H NMR (200 MHz): δ = 0.78–1.58 (m, 26H, 2 O[CH_2]$_2$[CH_2]$_5CH_3$), 1.75–1.89 (m, 4H, 2 $OCH_2CH_2[CH_2]_5CH_3$), 3.94 (t, *J* = 6.6 Hz, 2H, 3-$OCH_2[CH_2]_6CH_3$), 4.03 (t, *J* = 6.5 Hz, 2H, 1-$OCH_2[CH_2]_6CH_3$), 6.46 and 6.59 (2 d, *J* = 2.4 Hz, 1H each, 2- and 4-H), 7.44 (ddd, *J* = 8.4, *J'* = 6.9, *J''* = 1.4 Hz, 1H, 10- or 11-H), 7.60 (ddd, *J* = 8.1, *J'* = 6.9, *J''* = 1.3 Hz, 1H, 10- or 11-H), 7.85 (d, *J* = 8.5 Hz, 2H, 9- and 12-H), 8.11 (dd, *J* = 8.6, *J'* = 0.6 Hz, 1H, 8-H), 8.20 (d, *J* = 8.5 Hz, 1H, 7-H). – MS (70 eV): *m/z* (%) = 503 (26) [$M^+ + H$], 502 (78) [M^+], 391 (11) [$M^+ + H - C_8H_{16}$], 390 (23) [$M^+ - C_8H_{16}$], 279 (21) [391 – C_8H_{16}], 278 (100) [390 – C_8H_{16}].

$C_{33}H_{42}O_4$ (502.7) Calcd. C 78.85 H 8.42
Found C 79.21 H 8.50

1,3-Dimethyl-6H-benzo[b]naphtho[1,2-d]pyran-6-one (**7d**): According to the general procedure A 5.33 g (15.0 mmol) of **6d** gave 2.96 g (10.8 mmol, 72%) of **7d** as pale yellow crystals after chromatography with *tert*-butyl methyl ether/petroleum ether (1:15), m.p. 154–155°C. – IR (KBr):$\tilde{\nu}$ = 2900 cm^{-1} (w, CH alip.), 1705 (s, C=O), 1600, 1585 (m, C=C), 1100 (m, C–O), 755 (m). – ^1H NMR (250 MHz): δ = 2.25 and 2.46 (2 s, 3H each, 2 CH_3), 7.08 (s, 1H, 2-H), 7.15 (s, 1H, 4-H), 7.56 (m, 1H, 11-H), 7.66 (m, 1H, 10-H), 7.96 (d, *J* = 8.5 Hz, 3H, 8-, 9-, and 12-H), 8.27 (d, *J* = 8.5 Hz, 1H, 7-H)[29]. – MS (70 eV): *m/z* (%) = 274 (100) [M^+], 259 (19) [$M^+ - CH_3$], 246 (13) [$M^+ - CO$], 231 (16) [246 – CH_3], 215 (13) [231 – O].

$C_{19}H_{14}O_2$ (274.3) Calcd. C 83.20 H 5.14
Found C 83.50 H 5.05

1,3-Diethyl-6H-benzo[b]naphtho[1,2-d]pyran-6-one (**7e**): According to the general procedure B 850 mg (2.22 mmol) of **6e** gave 455 mg (1.58 mmol, 71%) of **7e** as colorless crystals after chromatography with diethyl ether/petroleum ether (1:10), m.p. 104–105°C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w, CH arom.), 2950, 2920, 2860 (m, CH aliph.), 1710 (s, C=O), 1085 (s, C–O), 755 (m). – ^1H NMR (400 MHz): δ = 0.92 (t, 3H, *J* = 7.6 Hz, 1-CH_2CH_3), 1.34 (t, 3H, *J* = 7.4 Hz, 3-CH_2CH_3), 2.59 [m_c, J_{gem} = 14.6, J_{vic} = 7.4 Hz (as established by decoupling experiments), 1H, 1-C*H*HCH$_3$], 2.79 (q, 2H, *J* = 7.6 Hz, 3-CH_2CH_3), 2.84 (m_c, J_{gem} = 14.6, J_{vic} = 7.4 Hz, 1H, 1-C*H*HCH$_3$), 7.16 (s, 1H, 2-H), 7.19 (s, 1H, 4-H), 7.55 (t, *J* = 7.6 Hz, 1H, 11-H), 7.66 (t, *J* = 7.6 Hz, 1H, 10-H), 7.95 (d, *J* = 8.4 Hz, 2H, 8- and 9-H), 8.06 (d, *J* = 8.5 Hz, 1H, 12-H), 8.28 (d, *J* = 8.5 Hz, 1H, 7-H)[29]. – MS (70 eV): *m/z* (%) = 302 (100) [M^+], 287 (49) [$M^+ - CH_3$], 273 (12) [$M^+ - C_2H_5$].

$C_{21}H_{18}O_2$ (302.4) Calcd. C 83.42 H 6.00
Found C 83.18 H 5.79

1,3-Diisopropyl-6H-benzo[b]naphtho[1,2-]pyran-6-one (**7f**): According to the general procedure B 240 mg (580 μmol) of **6f** gave 140 mg (420 μmol, 72%) of **7f** as colorless crystals after chromatography with diethyl ether/petroleum ether (1:2), m.p. 143–144 C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w, CH arom.), 2940, 2910, 2860 (m, CH aliph.), 1710 (s, C=O), 1590, 1575 (m, C=C), 1080 (m, C–O), 760 (m). – ^{1}H NMR (400 MHz): δ = 0.66 (d, *J* = 6.7 Hz, 3H, 1-CHC*H*$_3$), 1.34 (d, *J* = 6.9 Hz, 3H, 3-CHC*H*$_3$), 1.36 (d, *J* = 6.9 Hz, 3H, 3-CHC*H*$_3$), 1.58 (d, *J* = 6.7 Hz, 3H, 1-CHC*H*$_3$), 3.04 [sept, *J* = 6.9 Hz, 1H, 3-C*H*(CH$_3$)$_2$], 3.30 [sept, *J* = 6.7 Hz, 1H, 1-C*H*(CH$_3$)$_2$], 7.17 (d, $J_{4,2}$ = 1.8 Hz, 1H, 4-H), 7.27 (d, $J_{2,4}$ = 1.8 Hz, 1H, 2-H), 7.55 (ddd, $J_{11,12}$ = 8.3, $J_{11,10}$ = 6.9, $J_{11,9}$ = 1.4 Hz, 1H, 11-H), 7.66 (ddd, $J_{10,9}$ = 8.1, $J_{10,11}$ = 6.9, $J_{10,12}$ = 1.2 Hz, 1H, 10-H), 7.94 (d, $J_{8,7}$ = 8.6 Hz, 1H, 8-H), 7.95 (dd, $J_{9,10}$ = 8.1, $J_{9,11}$ = 1.4 Hz, 1H, 9-H), 8.17 (dd, $J_{12,11}$ = 8.3, $J_{12,10}$ = 1.2 Hz, 1H, 12-H), 8.27 (d, $J_{7,8}$ = 8.6 Hz, 1H, 7-H); assignment of the aromatic protons was attained by means of NOE experiments. – ^{13}C NMR (50 MHz): δ = 20.7 (q, 1-CH*C*H$_3$), 23.7 (q, 3-CH*C*H$_3$), 23.8 (q, 3-CH*C*H$_3$), 27.8 (q, 1-CH*C*H$_3$), 31.7 [d, 3-*C*H(CH$_3$)$_2$], 34.1 [d, 1-*C*H(CH$_3$)$_2$], 111.9, 113.9, 121.1, 121.3, 124.2, 125.6, 128.1, 128.4, 128.8, 128.9, 135.6, 136.2, 148.6, 151.7 and 152.0 (C-arom.), 162.0 (C=O). – MS (70 eV): *m/z* (%) = 330 (100) [M^+], 315 (33) [M^+ – CH_3], 273 (66) [M^+ – C_4H_9].

$C_{23}H_{22}O_2$ (330.4) Calcd. C 83.60 H 6.71
Found C 83.73 H 6.82

1,3-Di-tert-butyl-6H-benzo[b]naphtho[1,2-d]pyran-6-one (**7g**): According to the general procedure B 5.24 g (11.9 mmol) of **6g** gave 1.33 g (3.71 mmol, 31%) of **7g** as an amorphous solid after chro-

Table 4. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters *U*(eq) (× 10^{-1}) [pm^2] for **7b** (standard deviations in parentheses). Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
O(1)	7067(2)	1040(1)	2142(2)	47(1
C(2)	6746(3)	1809(2)	3379(3)	47(1
O(2)	5168(2)	1767(1)	2986(3)	66(1
C(3)	8342(3)	2675(2)	4937(3)	42(1
C(4)	7991(3)	3554(2)	6028(3)	50(1
C(5)	9369(3)	4456(2)	7272(3)	52(1
C(6)	11119(3)	4564(2)	7343(3)	45(1
C(7)	12468(3)	5564(2)	8395(3)	54(1
C(8)	14076(3)	5715(2)	8296(3)	57(1)
C(9)	14386(3)	4882(2)	7095(3)	52(1)
C(10)	13143(3)	3888(2)	6108(3)	44(1)
C(11)	11491(2)	3685(1)	6252(3)	39(1)
C(12)	10105(2)	2668(1)	5192(3)	37(1)
C(13)	10356(2)	1634(1)	4292(3)	37(1)
C(14)	11992(2)	1259(1)	4997(3)	38(1)
O(14)	13413(2)	1897(1)	6794(2)	46(1)
C(15)	12065(3)	274(2)	3981(3)	42(1)
C(16)	10487(3)	-410(2)	2293(3)	41(1)
O(16)	10732(2)	-1365(1)	1438(2)	51(1)
C(17)	8822(3)	-131(2)	1658(3)	41(1)
C(18)	8808(2)	862(2)	2717(3)	39(1)
C(19)	15089(3)	1555(2)	7571(3)	54(1)
C(20)	9125(3)	-2173(2)	-93(3)	59(1)

Table 3. Experimental details and results of crystal structure determinations of **7b**, **7d**, **7e**, and **7f**

compound	**7b**	**7d**	**7e**	**7f**
empirical formula	$C_{19}H_{14}O_4$	$C_{19}H_{14}O_2$	$C_{21}H_{18}O_2$	$C_{23}H_{22}O_2$
molecular mass	306.32	274.32	302.38	330.43
a [pm]	833.2(3)	854.7(1)	1152.8(5)	1853.5(4)
b [pm]	1293.0(4)	1145.0(2)	1427.8(8)	1270.8(2)
c [pm]	769.7(3)	820.4(3)	1031.8(4)	799.1(1)
α [deg]	101.52(3)	107.31(2)		
β [deg]	115.59(2)	118.42(2)	114.48(3)	90.21(2)
γ [deg]	97.64(3)	76.21(2)		
V [pm^3] × 10^6	709.9(4)	669.6(2)	1546(1)	1882(1)
Z	2	2	4	4
d (calcd) [g × cm^{-3}]	1.43	1.36	1.18	1.166
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	P -1	P -1	P 2_1/n	P2_1/a
crystal size [mm]	0.4 × 0.6 × 0.2	0.2 × 0.2 × 0.3	0.8 × 1.5 × 0.3	0.4 × 0.8 × 0.2
Θ range [deg]	1.75 - 27.5	2.0 - 26.0	1.75 - 27.5	1.75 -27.5
recip. latt. segment	h = - 10 - 9	h = -10 - 9	h = 0 - 14	h = 0 - 24
	k = -16 - 16	k = -14 - 14	k = 0 - 18	k = 0 - 16
	l = 0 - 10	l = 0 - 10	l = -13 - 12	l = - 10 - 10
no. refl. measd.	3280	2623	3879	4843
no. unique refl.	3280	2623	3562	4304
no. refl. F > 3σ(F)	2791	2022	3108	3173
lin. abs. coeff. [mm^{-1}]	0.08	0.08	0.08	0.07
F_0/parameter ratio	13.42	10.6	14.94	13.28
largest pos. diff. peak [eÅ^{-3}]	0.24	0.33	0.22	0.42
largest neg. diff. peak [eÅ^{-3}]	0.18	0.24	0.21	0.35
R, R_W	0.045, 0.044	0.052, 0.057	0.048, 0.046	0.089, 0.086

matography with *tert*-butyl methyl ether/petroleum ether (1:30), m.p. 105–107°C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w, CH arom.), 2950 (s, CH aliph.), 2890, 2760 (m, CH aliph.), 1725 (s, C=O), 1590 (m, C=C), 1075 (s, C–O), 760 (s). – ^1H NMR (250 MHz): δ = 1.05 and 1.42 [2 s, 9H each, 2 $C(CH_3)_3$], 7.22 and 7.60 (2 d, J = 2.0 Hz, 1H each, 2- and 4-H), 7.46–7.67 (m, 2H, 10- and 11-H), 7.86 (m_c, 2H, 8- and 9-H), 8.17 (d, J = 8.5 Hz, 1H, 7-H), 8.23 (d, J = 8.5 Hz, 1H, 12-H). – MS (70 eV): m/z (%) = 358 (92) [M^+], 343 (65) [$M^+ - CH_3$], 328 (47) [343 – CH_3], 313 (25) [328 – CH_3], 302 (69) [$M^+ - C_4H_8$], 287 (63) [302 – CH_3], 272 (14) [287 – CH_3], 57 (100) [$C_4H_9^+$], 41 (68) [C_3H_5].

$C_{25}H_{26}O_2$ (358.5) Calcd. C 83.76 H 7.31
Found C 83.87 H 7.38

Crystal Structure Determination[30] of Lactones **7b**, **7d**, **7e**, *and* **7f**: Suitable crystals were grown from THF (for **7b**), dichloromethane/petroleum ether (for **7d**), and diethyl ether/petroleum ether (for **7e** and **7f**). Measurements of the diffraction intensities were performed on a Siemens 3m/V diffractometer (for **7d**, **7e**, and **7f**) or an Enraf-Nonius CAD4 diffractometer (for **7b**) by using Mo-K_α radiation (0.7107 Å). Cell parameters were determined by least-squares refinement of 25 reflections. The structures were solved with Siemens SHELXTL PLUS (for **7d**, **7e**, and **7f**) or Nonius SDP package (for **7b**) by using direct methods. All non-hydrogen atoms could be refined anisotropically except for the isopropyl group *para* to the biaryl axis, which appears nearly planar. The hydrogen positions were calculated by using a riding model and were considered fixed with isotropic U(eq) in all refinements. The final residual values R and R_w and other crystal data are given in Table 3, atomic coordinates and U(eq) values in Tables 4–7.

Table 5. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters U(eq) (×10^{-1}) [pm^2] for **7d** (standard deviations in parentheses) [U(eq) see Table 4]

	x	y	z	U(eq)
C(1)	5031(3)	7260(2)	-366(3)	33(1)
C(2)	6642(3)	7170(3)	1246(4)	38(1)
C(3)	7961(4)	6146(3)	1285(4)	47(1)
C(4)	7623(4)	5186(3)	-219(4)	49(1)
C(5)	5467(4)	4069(3)	-3229(4)	48(1)
C(6)	3780(4)	3977(3)	-4641(4)	50(1)
C(7)	2422(4)	4952(3)	-4641(4)	46(1)
C(8)	2797(4)	6023(3)	-3286(4)	39(1)
C(9)	4567(3)	6175(2)	-1850(3)	34(1)
C(10)	5907(4)	5144(3)	-1777(4)	40(2)
C(11)	3900(3)	8450(2)	-351(3)	33(1)
C(12)	2704(3)	8982(3)	-1932(4)	35(1)
C(13)	1628(4)	10073(3)	-1652(4)	41(1)
C(14)	1722(4)	10682(3)	130(4)	42(1)
C(15)	3025(4)	10239(3)	1703(4)	43(1)
C(16)	4115(3)	9172(3)	1427(4)	38(1)
C(17)	2664(4)	8515(3)	-3876(4)	42(1)
C(18)	489(4)	11846(3)	354(5)	57(1)
C(19)	6947(4)	8056(3)	3040(4)	43(2)
O(1)	5510(3)	8871(2)	3090(3)	45(1)
O(2)	8291(3)	8061(2)	4505(3)	58(1)

Table 6. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters U(eq) (×10^{-1}) [pm^2] for **7e** (standard deviations in parentheses) [U(eq) see Table 4]

	x	y	z	U(eq)
O(1)	4184(1)	2115(1)	528(1)	46(1)
O(2)	2533(2)	2600(1)	894(2)	63(1)
C(1)	3183(2)	2713(2)	242(2)	46(1)
C(2)	3069(2)	3494(1)	-719(2)	42(1)
C(3)	2195(2)	4210(2)	-814(2)	52(1)
C(4)	2204(2)	5028(2)	-1472(2)	53(1)
C(5)	3175(2)	5206(1)	-1954(2)	45(1)
C(6)	3317(2)	6106(1)	-2451(2)	54(1)
C(7)	4299(2)	6297(2)	-2818(2)	59(1)
C(8)	5207(2)	5606(1)	-2662(2)	55(1)
C(9)	5103(2)	4724(1)	-2201(2)	45(1)
C(10)	4053(2)	4484(1)	-1881(2)	39(1)
C(11)	3905(2)	3571(1)	-1380(2)	37(1)
C(12)	4609(2)	2729(1)	-1433(2)	35(1)
C(13)	5041(2)	2476(1)	-2496(2)	36(1)
C(14)	5791(2)	1687(1)	-2292(2)	40(1)
C(15)	6097(2)	1083(1)	-1136(2)	39(1)
C(16)	5553(2)	1271(1)	-185(2)	42(1)
C(17)	4804(2)	2056(1)	-374(2)	38(1)
C(18)	4571(2)	2950(1)	-3945(2)	45(1)
C(19)	3888(2)	2280(2)	-5151(2)	65(1)
C(20)	6922(2)	232(1)	-959(2)	49(1)
C(21)	6608(2)	-335(2)	-2305(2)	60(1)

Table 7. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters U(eq) (×10^{-1}) [pm^2] for **7f** (standard deviations in parentheses [U(eq] see Table 4]

	x	y	z	U(eq)
O(1)	4221(1)	7336(2)	5359(4)	109(1)
C(1)	3861(2)	6705(3)	4599(5)	74(1)
O(2)	4177(1)	5757(2)	4259(3)	80(1)
C(3)	3888(2)	5099(3)	3047(5)	66(1)
C(4)	4344(2)	4316(3)	2518(6)	89(2)
C(5)	4146(2)	3676(3)	1216(7)	102(2)
C(6)	3506(2)	3911(3)	412(6)	89(2)
C(7)	3028(2)	4696(3)	915(4)	65(1)
C(8)	3189(2)	5257(2)	2394(4)	53(1)
C(9)	2747(2)	6035(2)	3269(3)	50(1)
C(10)	1973(2)	6001(2)	3374(3)	50(1)
C(11)	1565(2)	5105(3)	2968(4)	60(1)
C(12)	833(2)	5083(3)	3158(5)	78(1)
C(13)	472(2)	5978(4)	3756(5)	85(1)
C(14)	847(2)	6842(3)	4209(4)	79(1)
C(15)	1605(2)	6875(3)	4101(4)	61(1)
C(16)	2005(2)	7715(3)	4766(4)	79(1)
C(17)	2730(2)	7664(3)	4852(5)	78(1)
C(18)	3100(2)	6810(3)	4161(4)	57(1)
C(19)	4633(3)	2801(4)	621(10)	180(4)
C(20)	4365(3)	1800(3)	893(6)	111(2)
C(21)	5208(3)	3099(4)	-266(9)	156(3)
C(22)	2434(2)	5033(3)	-289(4)	78(1)
C(23)	1964(3)	4122(4)	-887(7)	128(2)
C(24)	2773(3)	5601(4)	-1767(5)	125(2)

CAS Registry Numbers

4: 20717-79-7 / **5a**: 108-95-2 / **5b**: 500-99-2 / **5c**: 102944-30-9 / **5d**: 108-68-9 / **5e**: 1197-34-8 / **5f**: 26886-05-5 / **5g**: 1138-52-9 / **6a**: 129667-82-9 / **6b**: 138435-64-0 / **6c**: 138435-65-1 / **6d**: 138435-66-2 / **6e**: 138435-67-3 / **6f**: 138435-68-4 / **6g**: 138435-69-5 / **7a**: 5724-44-7 / **7b**: 138435-70-8 / **7c**: 138435-71-9 / **7d**: 138435-72-0 / **7e**: 138435-73-1 / **7f**: 138435-74-2 / **7g**: 138435-75-3 / 2-methyl-4*H*-naphtho[2,1-*c*]pyran-4-one: 126743-63-3 / phloroglucinol: 108-73-6 / 1-octanol: 111-87-5 / palladium(II) acetate: 3375-31-3 / bis-(triphenylphosphine)palladium dichloride: 13965-03-2

Dedicated to Professor Dr. Dr. h. c. mult. *Karl Heinz Büchel*, on the occasion of his 60th birthday.
[1] For Part VIII see ref.[11]
[2] H. J. Altenbach, *Nachr. Chem. Tech. Lab.* **1988**, *36*, 1324–1327.
[3] G. Bringmann, R. Walter, R. Weirich, *Angew. Chem.* **1990**, *102*, 1006–1019; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 977–991.
[4] G. Bringmann, R. Walter, R. Weirich, *Methods of Organic Chemistry (Houben-Weyl)*, E **22**, C2, in press.
[5] For some selected naturally occurring biaryls, e.g. in the fields of carbazols, isoquinolines, and sesquiterpens, see [5a] H. Furukawa, T. S. Wu, T. Ohta, *Chem. Pharm. Bull.* **1983**, *31*, 4202 to 4205. – [5b] G. Bringmann in *The Alkaloids* (Ed.: A. Brossi), Academic Press, New York, **1986**, vol. 29, p. 141–184. – [5c] L. Huang, Y.-K. Si, G. Snatzke, D.-K. Zheng, J. Zhon, *Collect. Czech. Chem. Commun.* **1988**, *53*, 2664–2666.
[6] G. Bringmann, H. Reuscher, *Angew. Chem.* **1989**, *101*, 1725–1726; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1672–1673.
[7] G. Bringmann, J. R. Jansen, *Synthesis* **1991**, 825–827.
[8] G. Bringmann, R. Walter, Ch. L. J. Ewers, *Synlett* **1991**, 581–583.
[9] G. Bringmann, Ch. L. J. Ewers, L. Göbel, T. Hartung, L. Kinzinger, M. Schäffer, B. Schöner, O. Schupp in *Selective Reactions of Metal-Activated Molecules* (Eds.: H. Werner, A. G. Griesbeck, W. Adam, G. Bringmann, W. Kiefer), Vieweg, Braunschweig, **1992**, p. 175–178.
[10] G. Bringmann, H. Busse, S. Güssregen, B. Schöner, R. Zagst, Ch. Burschka, in *Selective Reactions of Metal-Activated Molecules* (Eds.: H. Werner, A. G. Griesbeck, W. Adam, G. Bringmann, W. Kiefer), Vieweg, Braunschweig, **1992**, p. 179–182.
[11] G. Bringmann, Ch. L. J. Ewers, L. Göbel, T. Hartung, B. Schöner, O. Schupp, R. Walter in *Selective Reactions of Metal-Activated Molecules* (Eds.: H. Werner, A. G. Griesbeck, W. Adam, G. Bringmann, W. Kiefer), Vieweg, Braunschweig, **1992**, p. 183–186.
[12] G. Bringmann, H. Reuscher, *Tetrahedron Lett.* **1989**, *30*, 5249–5252.
[13] G. Bringmann, J. R. Jansen, H. Reuscher, M. Rübenacker, K. Peters, H. G. von Schnering, *Tetrahedron Lett.* **1990**, *31*, 643–646.
[14] [14a] T. Ertel, S. Hückmann, H. Bertagnolli, G. Bringmann, Ch. L. J. Ewers, G. Erker, I. Hart, Ch. Sarter in *X-Ray Absorption Fine Structure* (Ed.: S. S. Hasnain), Ellis Horwood Publishers, New York **1991**, p. 562–565. – [14b] T. S. Ertel, D. Peter, S. Hückmann, U. Kolb, R. Grüsemann, H. Bertagnolli in *Selective Reactions of Metal-Activated Molecules* (Eds.: H. Werner, A. G. Griesbeck, W. Adam, G. Bringmann, W. Kiefer), Vieweg, Braunschweig, **1992**, p. 213–220.
[15] G. Baddeley, *J. Chem. Soc.* **1943**, 527–531.
[16] Slightly better yields were obtained when performing the reaction with 1-ethoxy-4-ethyl-benzene instead of 4-ethylphenol, the substrate used in ref.[15]
[17] R. Adams, N. Kornblum, *J. Am. Chem. Soc.* **1941**, *63*, 188–200.
[18] M. F. Hawthorne, *J. Org. Chem.* **1957**, *22*, 1001.
[19] [19a] R. Adams, L. O. Binder, *J. Am. Chem. Soc.* **1941**, *63*, 2773–2776. – [19b] E. Weber, J. Csöregh, B. Stensland, M. Czugler, *J. Am. Chem. Soc.* **1984**, *106*, 3297–3306. – [19c] J. Smith, P. W. Dibble, R. E. Sandborn, *J. Org. Chem.* **1986**, *51*, 3762–3768.
[20] G. Bringmann, J. R. Jansen, *Angew. Chem.* **1986**, *98*, 917–919; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 913–915.
[21] D. E. Ames, A. Opalko, *Tetrahedron* **1984**, *40*, 1919–1925.
[22] G. Bringmann, M. Berndsen, Ch. L. J. Ewers, R. Walter, T. Hartung, B. Schöner, unpublished results.
[23] W. J. Thompson, J. Gaudino, *J. Org. Chem.* **1984**, *49*, 5237–5242.
[24] R. G. R. Bacon, J. C. F. Murray, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1267–1272.
[25] [25a] R. H. Martin, *Angew. Chem.* **1974**, *86*, 727–738; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649–660. – [25b] B. S. Green, M. Knossow, *Science* **1981**, *214*, 795–797.
[26] This seemed more reasonable than following the definition of an "(interplanar) angle" between the "planes" of the terminal rings[25a], since these are *not* planar, but part of the helix, themselves!
[27] Compound **7a** has already been described in the literature (P. S. Dewar, A. R. Forrester, R. H. Thomson, *J. Chem. Soc. C* **1971**, 3950–3959), yet with distinctly different physical and spectroscopical properties, so it should be considered as a new compound.
[28] For a more detailed vibrational analysis of this "parent" lactone, see A. Ellebracht, Th. Grimm, W. Kiefer in *Selective Reactions of Metal-Activated Molecules* (Eds.: H. Werner, A. G. Griesbeck, W. Adam, G. Bringmann, W. Kiefer), Vieweg, Braunschweig, **1992**, p. 221–224.
[29] Assignment of the aromatic protons by analogy with compound **7f**.
[30] Further details of the structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany, on quoting the depository number CSD-55917, the names fo the authors, and the journal citation.

[257/91]