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Thermochromic Furofurans. IV[1]

Approach to the Synthesis of Bridgehead Substituted Furo[3,2-b]furans and Side Products of McMurry Reactions

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Abstract. Substituted dihydroxystilbenes **2** are suitable starting materials for the synthesis of photochromic systems derived from **3/4**. Attempts to couple the naphthones **8a–8e** by the McMurry reaction with $TiCl_3/LiAlH_4$ yielded mainly reduction products such as **8f, g** or **9**. However, the furofuran **3b** was isolated when using the zinc–copper couple for reduction. The helicene **11** was formed as an unexpected by-product in the McMurry reaction of the pivaloylnaphthalene **8d**.

Dimethoxynaphthofuro[3,2-b]naphthofuran (**3a**) isomerizes in most solvents under UV light or upon heating to blue violet **4a**, which recyclizes thermally or photochemically back to **3a** [2]. Both compounds form a novel photochromic system, whose dependence on steric and electronic factors claims our interest.

Both the stilbene **2a** and furan **3a** are easily accessible by thermolysis of the spiroquinol ether **1a** [3]. Previous investigations [4] have shown, however, that spiroquinol ethers **1**, which are disubstituted in the dihydropyran ring (R = Me, Alkyl, Ph), fragmentate differently and are thus not suitable for the synthesis of bridgehead substituted **3a**-derivatives.

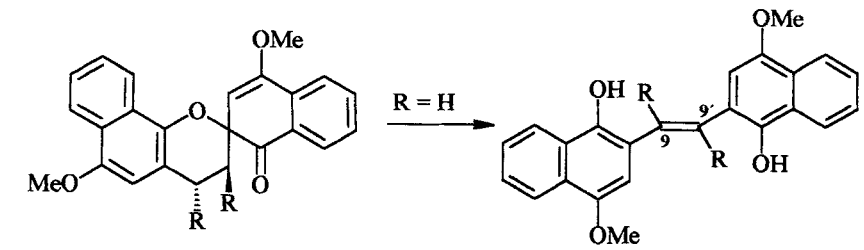
Only few other methods of synthesis for compounds of type **3** are known. In contrast to earlier reports [5], the pinacol reduction and the dehydration of substituted *o*-hydroxy- naphthaldehydes does not deliver **3**, but yield mainly acetals **5** [6]. Furthermore, [3,2-b]furofurans **3** should be accessible e.g. by Claisen rearrangement of 1,4-bisaryloxy-2-butynes such as **6**, following a procedure of Ramah and Laude [7]. However, due to the instability of **3a** under these drastic reaction conditions (12 h 200 °C, protic catalysis), side reactions should predominate.

On the other hand, the methide **4a** is easily accessible by oxidation of **2a**. Therefore, it was more promising to direct the synthesis of **3b** and of related compounds to stilbenes like **2b** which should be formed by McMurry coupling [8] of the corresponding naphthones. Oxidation of **2b** should yield *E/Z*-**4b** which delivers **3b** by thermal cyclization. Herein we report the first synthesis of **3b** using this approach, and on various side products of these reactions.

McMurry Reactions with Naphthones

As Castedo [9] has reported, the *p*-toluenesulfonyl group is well suited for protection of *o*-acyl phenols in the McMurry reaction. For the synthesis of **2b** we therefore started from the tosylate **8e** which was synthesized in dichloromethane from 2-acetyl-4-methoxy-1-naphthol (**8a**) and *p*-toluenesulfonyl chloride in almost quantitative yield. However, the reaction with $TiCl_3/LiAlH_4$ gave only a very complex reaction mixture, from which solely the compounds **8g**, **9d**, **12** (from intermediately produced thiocresol and THF according to earlier reports [10, 11]) and **13** [12, 13] along with **8a** and the remaining starting material, could be isolated. Those structures were ascertained by high resolution mass and NMR spectra, and by elemental analyses.

Under the conditions of the McMurry reaction, the *p*-toluenesulfonyl group is more stable, if the zinc/copper couple is used for the preparation of the low-valent



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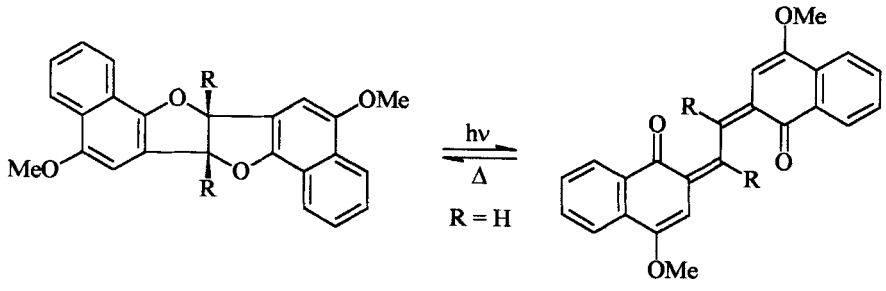
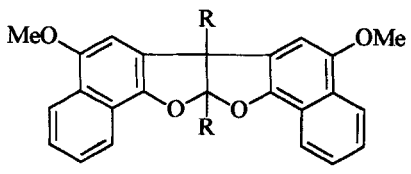


3 4

1, 3, 4
a: R = H; **b:** R = Me

2a: R = H
2b: R =Me

2c: R = Me, OMe instead of OH
2d: *t*-Bu, OMe instead of OH



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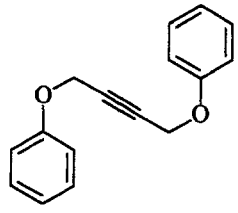

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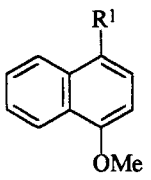
titanium, rather than lithium aluminum hydride as reducing agent [7]. However, under these conditions, the transformation of **8e** produced a complex mixture containing starting material and compounds **8a**, **8g**, **9d**, and **13**. The desired dihydroxystilbene **2b** was not observed, but upon prolonged standing of the reaction mixture, the furofuran **3b** was formed, presumabely via oxidation of **2b** and cyclization of the intermediate **4b**. The yield was reproducibly low and could not be improved by saponification of the crude product and/or oxidation with silver oxide.

In the furofuran **3a**, the *cis*-anellation of the fused rings was determined by a ^{13}C-H coupling of J = 7,5 Hz [2], and for **3b** the less strained *cis*-arrangement was expected as well. Crystals of derivative **3b** were suitable for x-ray analysis: As shown in figure 1, the methyl groups are indeed on the same side.

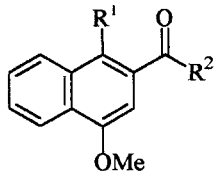
All attempts to open the furofuran **3b** to the methide **4b**, like the parent compound **3a**, by irradiation with UV light (254 or 366 nm) in the temperature range between –100 and 30 °C or thermally in boiling dimethyl sulfoxide solution were unsuccessful. This is difficult to explain on the basis of an antarafacial [4+4]cycloreversion [3], because PM3 calculations gave nearly identical results for the photochromic reaction **3a** → **4a** and for **3b** → **4b** [14].

The low yield of **2b/3b** seems not only due to a loss of the protecting group in **8e**, for with 1,4-dimethoxynaphthalenes yields were low or other side products were also formed: By reaction of **8c** with the McMurry reagent $(TiCl_3)_2LiAlH_4$, **2c** was obtained as an *E*/*Z*-mixture, from which only *E*-**2c** could be isolated in pure state. The moderate yield (40%) could not be improved by longer reaction times, under reflux or by keeping the reaction mixture at 0 °C.

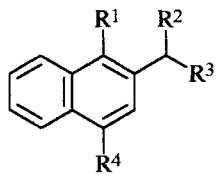
By reductive coupling of 2-pivaloyl-1,4-dimethoxynaphthalene (**8d**) with $(TiCl_3)_2LiAlH_4$, a complex reaction mixture was obtained, which again did not contain the stilbene **2d**. Surprisingly, along with **8b**, the naphthol ethers **8f**, **9a** and **9b** as well as 2-neopentyl-naphthalene [15] (**9c**) were formed, the latter four by cleavage of aryl oxygen bonds.In the same reaction, presum-



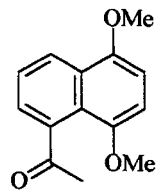
7	R
a	OH
b	OMe
c	OAc



8	R^1	R^2
a	OH	Me
b	OH	*t*-Bu
c	OMe	Me
d	OMe	*t*-Bu
e	OTs	Me
f	H	*t*-Bu
g	H	Me



9	R^1	R^2	R^3	R^4
a	H	OH	*t*-Bu	OMe
b	H	H	*t*-Bu	OMe
c	H	H	*t*-Bu	H
d	OTs	OH	Me	OMe



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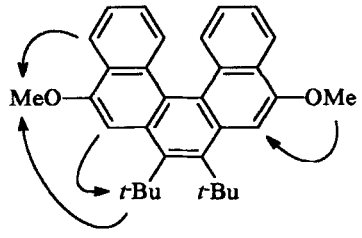
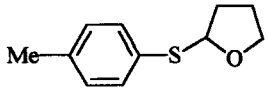
ably via dealkylation and double McMurry coupling, the yellow dibenzo[c,g]phenanthrene **11** was formed in 1,8% yield. The structure of **11** was confirmed by the mass and NMR spectrum with its expected Overhauser effects. The mechanism of this novel reaction and its application to the synthesis of other helicenes will be discussed elsewhere.

We thank Mr. R. Machinek (Göttingen) for detailed NMR measurements, and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.



11



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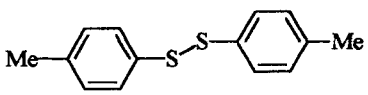

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Experimental

Material and methods as in Lit. [1]. ^{1}H NMR spectra were measured at 200 MHz, if not otherwise stated.

Synthesis of Naphthones

2-Acetyl-4-methoxy-1-naphthol (**8a**)

22,4 g (0,286 mol) of acetyl chloride and 38,2 g (0,286 mol) of $AlCl_3$ were dissolved at 0 °C in 200 ml of 1,2-dichloroethane (1 l round-bottom flask), cooled to –78 °C, and mixed with a 60 °C solution of 42,5 g (0,244 mol) of **7a** in 200 ml of 1,2-dichloroethane. After 3 h at 0 °C, 35,2 g (0,264 mol) of $AlCl_3$ was added at –78 °C and the mixture kept for 12 h at 0 °C. The mixture was finally poured into 1 l of cold water and extracted repeatedly with CH_2Cl_2. Column chromatography (80×8 cm) with petroleum ether/CH_2Cl_2 (5:1 in the beginning, 3:1 after separation of less polar impurities) followed by crystallization from pentane/MeOH (8:2) and sublimation in a high vacuum at 120 °C gave 42,6 g (80,6%) of **8a** as thin yellow needles (R_f = 0,60, CH_2Cl_2) with m.p. 118–119 °C. Solutions of **8a** showed a strong yellow-green fluorescence under UV light at 366 nm. – ^{1}H-NMR ($CDCl_3$): δ = 13,75 (s, 1 H, OH), 8,42, 8,16 (2 d br, J = 6 Hz, each 1 H, 5-, 8-H), 7,66, 7,58 (2 t, J = 6 Hz, each 1 H, 6-, 7-H), 6,77 (s, 1 H, 3-H), 3,96 (s, 3 H, OMe), 2,65 (s, 3 H, Ac). – ^{13}C-NMR ($CDCl_3$): δ = 203,7, 157,2 (s), 147,2 (s), 130,1 (s), 129,6 (d), 126,5 (d), 125,8 (s), 124,2 (d), 121,8 (d), 111,8 (s), 100,6 (d), 55,5 (OMe), 26,9 (Me).

$C_{13}H_{12}O_3$ (216,2) calcd. C 72,21 H 5,59
found C 72,07 H 5,64

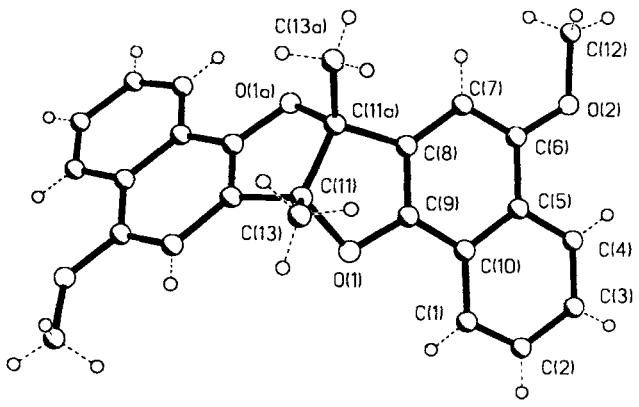

Fig. 1 Crystal structure of *cis*-6b,13b-Dimethyl-5,12-dimethoxydinaphtho[2',1'-d:2",1"-4,5]furo[3,2-b]furan (**3b**)

2-Acetyl-4-methoxy-1-naphthol (**8a**), *2-Acetyl-1,4-di-methoxynaphthalene* (**8c**) *and 5-Acetyl-1,4-dimethoxynaphthalene* (**10**)

To a solution of 30,0 g (0,159 mol) of 1,4-dimethoxy-naphthalene (**7b**) in 200 ml of 1,2-dichloroethane, 23,4 g

(0,175 mol) of $AlCl_3$ and 13,1 g (0,167 mol) of acetyl chloride were added successively at 0 °C. The mixture was stirred vigorously for some minutes, kept for 6 h at 0 °C under moisture protection, and then poured into 400 ml of cold 2 N HCl. The mixture was worked up as described above, giving four fractions. Their constituents were purified by sublimation in a high vacuum at 120 °C.

Fraction 1 contained 9,20 g of starting material **7b** (R_f = 0,47).

Fraction 2 (R_f = 0,24) contained 2,8 g (11,7%, calculated on consumed 7b) of 2-acetyl-4-methoxy-1-naphthol (8a).

Fraction 3 (R_f = 0,32, CH_2Cl_2) contained 11,5 g (45,2%) of 2-acetyl-1,4-dimethoxynaphthalene (**8c**) which crystallized from CH_2Cl_2/MeOH as colorless hairlike needles with m.p. 59–60 °C ([16] 59–60,5 °C). – ^{1}H-NMR ($CDCl_3$, 80 MHz): δ = 8,31–7,98 (m, 2 H), 7,64–7,40 (m, 2 H), 7,03 (s, 1 H, 3-H), 3,99 (s, 3 H, 4-OMe), 3,94 (s, 3 H, 1-OMe), 2,78 (s, 3 H, CH_3).

Fraction 4 gave 9,24 g (38,7%) of 5-acetyl-1,4-dimethoxynaphthalene [17] (**10**) which crystallized from CH_2Cl_2/MeOH as colorless prisms with m.p. 58–59 °C. – ^{1}H-NMR ($CDCl_3$, 80 MHz): δ = 8,19 (dd, J = 11 Hz, J' = 2 Hz, 1 H, 6-H), 7,51–7,20 (m, 2 H), 6,71 (s, 2 H, 2-H, 3-H), 3,93, 3,84 (2 s, 3 H each, OMe), 2,46 (s, 3 H, Ac).

4-Methoxy-2-pivaloyl-1-naphthol (**8b**)

a) In nitrogen atmosphere, under moisture protection and at –78 °C, a solution of 31,3 g (0,18 mol) of **7a** in 200 ml of 1,2-dichloroethane was added to a solution of 24,2 g (0,2 mol) of pivalic acid chloride and 65,2 g (0,25 mol) of freshly distilled $SnCl_4$ in 200 ml of 1,2-dichloroethane. The reaction mixture was stirred for 15 min and then kept at room temp. for additional 2 h. The reaction mixture was slowly poured into 500 ml of ice water and extracted repeatedly with dichloromethane. The combined extracts were washed with saturated $NaHCO_3$ solution, dried with Na_2SO_4, and evaporated to dryness in vacuo. Column chromatography on silica gel (100 × 8 cm, petroleum ether/CH_2Cl_2, 1:1) gave 4,51 g (9,7%) of **8b** from the main fraction, which fluoresced yellow-green under UV light at 366 nm. Upon sublimation in a high vacuum (120 °C) the naphthol gave sulfur colored prisms with m.p. 103–104 °C (R_f = 0,76). – ^{1}H-NMR ($CDCl_3$, 100 MHz): δ = 14,34 (s, 1 H, OH), 8,54–8,40 (m, 1 H), 8,22–8,08 (m, 1 H), 7,76–7,48 (m, 2 H), 7,22 (s, 1 H), 3,98 (s, 3 H, OMe), 1,52 (s, 9 H, 3 CH_3).

$C_{16}H_{18}O_3$ (258,3) calcd. C 74,39 H 6,95
found C 74,29 H 6,95

Mol.weight calcd. 258,12558; found 258,1254 (HR-MS).

1,4-Dimethoxy-2-pivaloylnaphthalene (**8d**)

5,0 g (0,026 mol) of **7b** were dissolved under a nitrogen atmosphere and moisture protection in 20 ml of dry THF; 16,2 ml of 1,6 M *n*-butyllithium in hexane was then added at 0 °C, and the mixture stirred at room temperature for 5 h. In nitrogen atmosphere and at –78 °C, the reaction mixture was added to 9,4 g (0,078 mol) of pivalic acid chloride in 30 ml of dry THF. After 30 min stirring, the mixture was slowly brought to room temperature. Column chromatography (silica gel 50 × 3 cm, CH_2Cl_2) of the reaction product gave 4,15 g (58,6%) of **8d** as the main product, as well as 1,05 g (5,6 mmol) of starting material. After sublimation in a high vacuum at 120 °C, **8d** formed colorless prisms with m.p. 93–94 °C (R_f = 0,53, CH_2Cl_2). – ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8,26 (dd, J = 6, J' = 2 Hz, 1 H, *peri*-H), 8,04 (dd, J = 6, J' = 2 H, 1 H, *peri*-H), 7,53 (m, 2 H, 6-, 7-H), 6,42 (s, 1 H, 3-H), 3,93 (s, 3 H, 4-OMe), 3,83 (s, 3 H, 1-OMe), 1,28 (s, 9 H, 3 CH_3). – ^{13}C-NMR ($CDCl_3$): δ = 214,4 (CO), 151,7 (s), 144,9 (s), 130,4 (s), 128,4 (s), 127,0 (d), 126,6 (s), 126,1 (d), 122,5 (d), 122,0 (d), 101,0 (d), 63,5 (OMe), 55,7 (OMe), 45,2 (s), 27,1 (Me).

$C_{17}H_{20}O_3$ (272,3) calcd. C 74,97 H 7,40
found C 74,99 H 7,32.

2-Acetyl-4-methoxy-1-naphthol-p-tosylate (**8e**)

A solution of 10,81 g (50 mmol) of **8a**, 5,05 g (50 mmol) of triethylamine, 9,53 g (50 mmol) of *p*-toluenesulfonyl chloride and 50 mg of 4-(dimethylamino)pyridine was dissolved in 150 ml of dichloromethane under moisture protection, refluxed for 12 h and stirred at room temp. for an additional 20 h. The mixture was poured into 200 ml of water and the organic layer filtered over 100 g of silica gel. The residue obtained upon evaporation of the solvent yielded, after triplicate recrystallization from methanol, 17,2 g (92,8%) of **8e** as colorless prisms (R_f = 0,55, CH_2Cl_2) with m. p. 165 °C. – ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8,20 (dd, J = 8, J' = 1,5 Hz, 1 H, 8-H), 7,70 (dd, J = 8, J' = 1,5 Hz, 1 H, 5-H), 7,64, 7,22 (AB pattern, 4 H, MePh), 7,48, 7,34 (2 td, J = 8, J' = 1,5 Hz, 1H each, 6-, 7-H), 6,94 (s, 1 H, 3-H), 4,04 (s, 3 H, OMe), 2,64 (s, 3 H, Ac), 2,40 (s, 3 H, CH_3). – ^{13}C NMR ($CDCl_3$): d = 154,0 (s), 145,9 (s), 137,4 (s), 131,7 (s), 131,3 (s), 129,8 (d, Tos), 128,7 (d, Tos), 128,3 (s), 127,6 (s), 127,4 (d), 127,3 (d), 123,0 (s), 121,9 (s), 102,2 (s), 55,9 (q, OMe), 30,3 (q, MePhe), 21,7 (q, Me).

$C_{20}H_{18}O_5S$ (370,4) calcd. C 64,85 H 4,89
found C 64,92 H 4,98.

McMurry-Reactions

E/Z-2,2'-(1,2-Dimethyl-1,2-ethendiyl)-bis(1,4-dimethoxynaphthalene) (**2c**)

Into a 100 ml two-necked round bottom flask with condenser, magnetic stirring bar and septum, under nitrogen atmosphere (glove box), 5,0 g (14,4 mmol) of $(TiCl_3)_2LiAlH_4$ (Aldrich) were weighted. Through the septum, 50 ml of dry THF was added slowly at –78 °C. The suspension was warmed up to room temperature, and a solution of 3,0 g (0,013 mol) of **8c** in 20 ml of dry THF was added dropwise. The mixture was refluxed for 3 h, poured into 100 ml of cold water and extracted 5 times with 100 ml portions of pentane/CH_2Cl_2 (3:1). The combined organic layers were washed with saturated $NaHCO_3$ solution, dried with Na_2SO_4 and evaporated to dryness at 40 °C in vacuo. Column chromatography (silica gel 0,05–0,2 mm, 4 × 100 cm, CH_2Cl_2) of the crude product (2,1 g) gave 1,15 g (41,3%) of brownish **2c** as an *E/Z*-mixture. The slightly less mobile *E*-**2c** was separated by flash-chromatography (silica gel 0,04–0,063 mm, petroleum ether/CH_2Cl_2 5:1); *Z*-**2c** was characterized from the mixture.

$C_{28}H_{28}O_4$ calcd. 428,19875,
found 428,1976 (HR-MS).

E-**2c**: R_f = 0,62, CH_2Cl_2, – ^{1}H-NMR ($CDCl_3$, 80 MHz): δ = 8,30–7,95 (m, 4 H), 7,63–7,32 (m, 4 H), 6,58 (s, 2 H), 4,01, 3,97 (2 s, 6 H each, OMe), 1,95 (s, 6 H, CH_3).
Z-**2c**: R_f = 0,68, CH_2Cl_2, – ^{1}H-NMR ($CDCl_3$, 100 MHz): δ = 8,36–7,91 (m, 4 H), 7,66–7,23 (m, 4 H), 6,55, 6,43 (2 s, 1 H each), 4,00, 3,98 (2 s, 3 H each, 2 OMe), 2,36–2,25 (m, 6 H, 2 CH_3).

1-Methoxy-3-pivaloyl-naphthalene (**8f**), *3-(1-Hydroxy-2,2-dimethyl)propyl-1-methoxynaphthalene* (**9a**),*4-Methoxy 2-neopentyl-naphthalene* (**9b**), *2-Neopentylnaphthalene* (**9c**), *and 3,4-Di-tert-butyl-1,6-dimethoxy-dibenzo[c,g]phenanthrene* (**11**)

The reaction mixture (2,9 g) obtained from 3,0 g (11 mmol) of **8d**, 3,77 g (24 mmol) of $TiCl_3$ and 0,46 g (12 mmol) of $LiAlH_4$ in 100 ml of THF under conditions as for the synthesis of **2c** was separated by column chromatography (silica gel 4× 30 cm, CH_2Cl_2). Three main fractions [A (300 mg), B (110 mg) and C (1,7 g)] were obtained together with mixed fractions containing several minor components.
Repeated column chromatography (petroleum ether) of *fraction A* yielded a yellow zone (R_f = 0,92, CH_2Cl_2) containing 44 mg (1,8%) of **11** and two slower moving colorless fractions containing 95 mg (3,8%) of **9b** (R_f = 0,90, CH_2Cl_2; 0,40, petroleum ether) and 21 mg (1,0%) of **9c** (R_f = 0,90, CH_2Cl_2; 0,60, petroleum ether).

11: Readily soluble in CH_2Cl_2, from CH_2Cl_2/CH_3OH thin lemon-yellow needles with m. p. 292–296 °C. In solution, **11** showed only a weak, in solid state an intense blue-green fluorescence. – UV ($CHCl_3$): λ_{max} (lg ε) = 438–408 (3,27), 345 sh (4,26), 327 (4,48), 285 (4,44), 248 nm (4,65). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8,29 (dd, J = 8,3, J' = 1,2 Hz, 2 H, 7-, 14-H), 8,18 (d br, J = 8,6 Hz, 2 H, 10-, 11-H), 7,71 (s, 2 H, 2-, 5-H), 7,40 (td, J = 8,3, J' = 1,2 Hz, 2 H, 9-, 12-H), 7,19 (td, J = 8,6, J' = 1,4 Hz, 2 H, 8-, 13-H), 4,19 (s, 6 H, 2 OMe), 1,72 (18 H, 2 *t*-Bu). – MS (70 eV): *m/z* (%) = 451 (17) [M+1], 450,2556 (45) [M$^+$, calcd. 450,25588 for $C_{32}H_{34}O_2$], 435 (5) [M – Me], 393 (17) [M – *t*-Bu], 361 (10), 111 (20), 97 (37), 85 (35), 83 (38), 71 (52), 69 (49), 57 (100) [*t*-Bu], 55 (53), (75).

9b: Colorless oil. – ^{1}H NMR ($CDCl_3$): δ = 8,20 (dd, J = 6, J' = 2 Hz, 1 H, 5/8-H), 7,72 (dd, J = 6, J' = 2 Hz, 8/5-H), 7,42 (m, 2 H), 7,15 (s br, 1 H, 1-H), 6,61 (d, J = 2 Hz, 1 H, 3-H), 3,97 (s, 3 H, OMe), 2,62 (s, 2 H, CH_2), 0,98 (s, 9 H, *t*-Bu). – MS (70 eV): *m/z* (%) = 228 (71) [M$^+$], 172 (100), 171 (66), 157 (12), 128 (19).

$C_{16}H_{20}O$ (218,3)	calcd.	C 84,16 H 8,83
	found	C 84,05 H 8,73

9c [6]: Colorless needles with m.p. 71–72 °C. – ^{1}H NMR ($CDCl_3$): δ = 7,8 (m, 2 H, 5-, 8-H), 7,74 (d, J = 6 Hz, 1 H, 4-H), 7,57 (s br, 1 H, 1-H), 7,43 (m, 2 H, 6-, 7-H), 7,29 (dd, J = 6,2 Hz, 1 H, 3-H), 2,65 (s, 2 H, CH_2), 0,98 (s, 9 H, *t*-Bu). – MS (70 eV): *m/z* (%) = 198,1408 (83) [M$^+$, calcd. 198,14085 for $C_{15}H_{18}$], 142 (58), 141 (100), 139 (20), 128 (10), 115 (54).

Separation of *fraction B* by flash chromatography [silica gel, petroleum ether/diethyl ether (75/25 vol%)] gave 19 mg (0,7 %) of **8f** as a colorless oil with R_f = 0,70, CH_2Cl_2, – ^{1}H NMR ($CDCl_3$): δ = 8,24 (m, 1 H, *peri*-H), 7,89 (s br, 1 H, 1-H), 7,84 (m, 1 H, *peri*-H), 7,55 (m, 2 H), 4,03 (s, 3 H, OMe), 1,45 (s, 9 H, *t*-Bu). – MS (70 eV): *m/z* (%) = 242,1306 (30) [M$^+$, calcd. 242,13068 for $C_{16}H_{18}O_2$], 185 (74), 157 (100), 142 (26), 128 (18), 113 (23).

Fraction C contained pure **9a**: R_f = 0,40, CH_2Cl_2; yield 1,7 g (63%), crystallized slowly at 4 °C as off-white needles with m.p. 66–67 °C. – ^{13}C NMR ($CDCl_3$): δ = 154,7 (s), 140,1 (s), 133,7 (s), 127,5 (d), 126,5 (d), 125,0 (s + d) (signals separated in C_6D_6) , 121,8 (d), 118,9 (d), 104,0 (d), 82,8 (CHOH), 55,5 (OMe), 32,8 (s), 26,2 (*t*-Bu). – ^{1}H NMR ($CDCl_3$): δ = 8,0 (dd, J = 6, J' = 1 Hz, 1 H, 5-H), 7,55 (dd, J = 6, J' = 1 Hz, 1 H, 8-H), 7,23 (m, 2 H, 6-, 7-H), 7,08 (s, 1 H, 1-H), 6,60 (d, 1 Hz, 1 H, 3-H), 4,28 (s, 1 H, CH), 3,78 (s, 3 H, OMe), 1,82 (s br, 1 H, OH), 0,76 (s, 9 H, *t*-Bu). – MS (70 eV): *m/z* (%) = 244 (34) [M$^+$], 188 (16), 187 (100), 159 (53), 144 (30), 115 (14).

$C_{16}H_{20}O_2$ (244,3)	calcd.	C 78,65 H 8,25
	found	C 78,82 H 8,10

3-Acetyl-1-methoxynaphthalene (**8g**), *2(1-Hydroxyethyl)-4-methoxy-1-naphthol tosylate* (**9d**), *(4-Methylphenyl)-2-oxolanyl sulfide* (**12**), *and Bis(methylphenyl)disulfide* (**13**)

2,5 g (6,8 mmol) of **8e**, 2,81 g (15,0 mmol) of $TiCl_3$ and 0,28 g (8,0 mmol) of $LiAlH_4$ in 80 ml of THF gave 2,48 g of crude product under the reaction conditions stated above. Separation on silica gel (column 4 × 30 cm, CH_2Cl_2) gave six fractions [A, 230 mg; B, 160 mg; C, 170 mg; D 860 mg; E, 380 mg, and F, 360 mg]. An additional fraction G (300 mg) was obtained when the column was eluted with diethyl ether. All fractions contained mixtures of several compounds.

50 mg of *fraction A* was separated by preparative TLC (CH_2Cl_2) and gave 20 mg (1,2%) of **13** [10–12] as a colorless liquid, R_f = 0,90, CH_2Cl_2, – ^{1}H-NMR ($CDCl_3$): δ = 7,38, 7,08 (AB pattern, J = 8 Hz, 8 Ar-H), 2,32 (s, 6 H, 2 Me). – MS (70 eV): *m/z* (%) = 246 (100) [M$^+$], 186 (46), 171 (23), 123 (62).

Upon separation by flash chromatography (silica gel, CH_2Cl_2), *fraction D* (860 mg) gave the constituents **12**, **8g**, **9d**, and starting material **8e**, listed in the order of decreasing R_f-values.

The zone with R_f = 0,70 (CH_2Cl_2) gave 23 mg (1,7%) of **12** [8,9] as a light yellow oil. – ^{1}H NMR ($CDCl_3$): δ = 7,42, 7,12 (AB pattern, 4 H, MePh), 5,58 (m, 1 H), 3,96 (m, 2 H, OCH_2), 2,10–1,55 (m, 4 H, 2 CH_2). – MS (70 eV): *m/z* (%) = 194 (10) [M$^+$], 124 (20), 71 (59), 49 (78).

The zone with R_f = 0,50 (CH_2Cl_2) gave 5,3 mg (0,4%) of **8g** as a colorless oil. – ^{1}H NMR ($CDCl_3$): δ = 8,28 (dd, J = 6, J' = 2 Hz, 1 H, *peri*-H), 8,07 (s, 1 H, 1-H), 7,92 (dd, J = 6, J' = 2 Hz, 1 H, peri-H), 7,61-7,48 (m, 2 H, 6-, 7-H), 7,40 (s, 1 H, 3-H), 4,06 (s, 3 H, OMe), 2,23 (s, 3 H, Me). – MS (70 eV): *m/z* (%) = 200,0837 (18) [M$^+$, calcd. 200,08373 for $C_{13}H_{12}O_2$], 185 (26), 165 (8), 157 (13), 149 (18), 147 (30), 128 (8), 122 (13), 94 (18), 91 (100).

Purification of *fraction G* by flash chromatography (silica gel, diethyl ether) gave 150 mg (5,9%) of **9d** as a brownish resin, R_f = 0,10, CH_2Cl_2; 0,5, Et_2O. – ^{1}H NMR ($CDCl_3$): δ = 8,18 (d br, J = 8 Hz, 1 H, *peri*-H), 7,80, 7,30 (AB pattern, J = 8 Hz, 2 H each, MePh), 7,50 (d br, J = 8 Hz, 1 H, *peri*-H), 7,40–7,20

(m, 2 H, 6-, 7-H), 7,0 (s, 1 H, 3-H), 5,46 (q, J = 6 Hz, 1 H, CHOH), 4,04 (s, 3 H, OMe), 2,46 (s, 3 H, PhMe), 1,54 (d, J = 6 Hz, 3 H, Me). – MS (70 eV): *m/z* (%) = 372,1034 (18) [M+], calcd. 372,10314 for $C_{20}H_{20}SO_5$], 217 (100), 202 (24), 175 (52), 159 (22), 128 (19).

Fractions B, C, E and *F* contained mixtures of compounds which were also obtained from A, D and G. These mixtures were not further separated.

cis-6b,13b-Dimethyl-5,12-dimethoxydinaphtho[2',1'-d:2'',1''-4,5]furo[3,2-b]furan (**3b**)

100 ml of dry THF was added to 9,2 g (60 mmol) of $TiCl_3$ and 15.4 g of Zn/Cu [18] under nitrogen atmosphere and refluxed with stirring for 1 h. 11,2 g (30 mmol) of **8e** in 50 ml dry THF was added rapidly and refluxing continued for 16 h. The tightly closed flask was kept at room temp. for 4 weeks. 150 g of silica gel was then added, the mixture evaporated to dryness and the solid washed repeatedly with CH_2Cl_2. Chromatography (silica gel, cyclohexane/ethyl acetate) afforded a crude yield of **3b** from a fraction with R_f = 0.7–0.8, which was recrystallized from cyclohexane as beige needles with m.p. 232–233 °C (yield 214 mg, 3,5%). – IR (KBr): ν = 2944 cm^{-1}, 2920, 1633, 1592, 1450, 1398, 1280, 1200, 818, 755, – ^{13}C NMR ($CDCl_3$): δ = 150,4, 148,0, 127,2, 126,1, 122,5, 122,0, 121,4, 120,6, 99,2, 98,2, 56,0, 20,8. – ^1H-NMR ($CDCl_3$, 200 MHz): δ = 8,24–8,12 (m, 2 H), 8,03–7,91 (m, 2 H), 7,54–7,46 (m, 4 H) 6,93 (s, 2 H, 6-H, 13-H), 4,04 (s, 6 H, 2 OMe), 1,93 (s, 6 H, 2 CH_3). – MS (70 eV): *m/z* (%) = 398,1513 (76) [M+, calcd. 398,15188 for $C_{26}H_{22}O_4$], 383 (100), 246 (37), 226 (24), 119 (32).

Crystal Structure of cis-6b,13b-Dimethyl-5,12-dimethoxydinaphtho[2',1'-d:2'',1''-4,5]furo[3,2-b]furan (**3b**, $C_{26}H_{22}O_4$)

Upon slow evaporation of a dichloromethane/cyclohexane solution, **3b** crystallized as monoclinic needles, M_r = 398,44, space group C2/c, a = 1800,1(4), b = 987,5(2), c = 1121,7(2) pm, α = 90°, b = 102,54(3)°, g = 90°, V = 1,9464(7) nm^3, Z = 4, d_{calc} = 1,360 g×cm^{-3}, μ = 0,091 mm^{-1}, 2496 data in a range of 3,72 £ 2Q £ 22,53° were collected on a STOE four circle diffractometer with Mo-Kα radiation at room temperature from a crystal measuring 0,8 × 0,8 × 0,6 mm. Thereof 1272 independent reflections remained for structure solution (SHELXS-90 [19]) and refinement against F2 (SHELXL-93 [20]). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and treated as riding. Final residual values were wR2 = 0,0927, R1 = 0,0348 [I > 2s(I)] and R1 = 0,0362, wR2 = 0,0970 for all data.The rest electron density was 102 and –180 e.nm^{-3}.

Further details on the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshausen 2, (FRG) on quoting the depository number CSD 59231, the names of the authors, and the journal citation.

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