Synthesis of Thiophene-Substituted 3*H*-Naphtho[2,1-*b*]pyrans, Precursors of Photomodulated Materials

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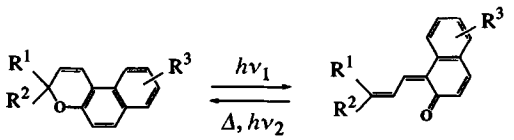
The synthesis of 3*H*-naphtho[2,1-*b*]pyrans **9**–**21** linked to a thiophene moiety is described. Two different synthetic approaches were applied to prepare these novel functionalized compounds, and their spectrokinetic properties in solution are reported.

Introduction. – In the last decade, research in the area of photochromic compounds has increased significantly, due to their promising applications in optical technology as well as in the design of photomodulated materials [1–6].

In previous publications, we showed that the introduction of a thiophene moiety into spiro[indoline-naphthoxazines] [7][8] allows subsequent preparation of photochromic and photoelectronic materials through electrochemical polymerization or copolymerization [9][10]. In the present work, the same type of approach is extended to the 3*H*-naphtho[2,1-*b*]pyran series, showing interesting photochromic behavior (good fatigue resistance, wide range of absorption in the visible region) [11][12].

The photochromic properties of the 2*H*-chromene structure [13][14] and, hence, 3*H*-naphtho[2,1-*b*]pyrans are based on a reversible color change observed upon ultraviolet irradiation. There are two interconvertible isomers: the colorless or closed form (CF), and the colored or open form (OF) (*Scheme 1*). The reverse reaction, OF → CF, can be induced by irradiation (VIS) or by heating.

Scheme 1



Closed form (CF) Open form (OF)

These systems, working through an external light stimulus, can be the basis for photomolecular switches [15][16]. Then, under appropriate light irradiation, changes of geometry and polarity of the photochromic entity can lead to a topologic change of an

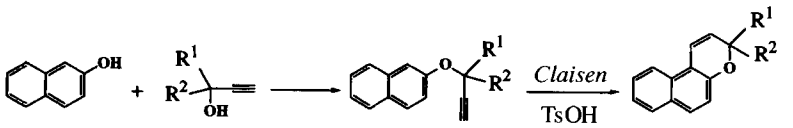
attached molecular system, modifying in turn the physical properties of the material under design.

In this paper, the synthesis and the spectrokinetic properties in solution of a variety of 3*H*-naphtho[2,1-*b*]pyrans with thiophene moieties are reported. These molecular systems are good candidates for promoting photomodulated materials.

To investigate the influence of the position and nature of the linkage, the thiophene nucleus has been directly attached to the sp^3-C-atom, or to the naphthopyran part of the photochromic skeleton. Compounds in which the thiophene moiety has been attached to the chromene part through an ester function have also been prepared.

Results and Discussion. – *Synthesis.* Two strategies were considered for the synthesis of photochromic compounds. *Procedure A* is based on a 'one-pot reaction' starting from a suitable naphthol and an alkynol [17][18]. This condensation reaction takes place in an apolar solvent under acid catalysis [19][20]. TsOH is currently used. For this kind of reaction, toluene is generally used as solvent, but in our case, CH_2Cl_2 turned out to be the better choice, leading to higher yields due to the suppression of competitive reactions. The reaction proceeds *via* a *Claisen* rearrangement of alkynyl aryl ethers resulting from naphthol '*O*-alkylation', followed by an H-shift and electrocyclic ring closure (*Scheme 2*).

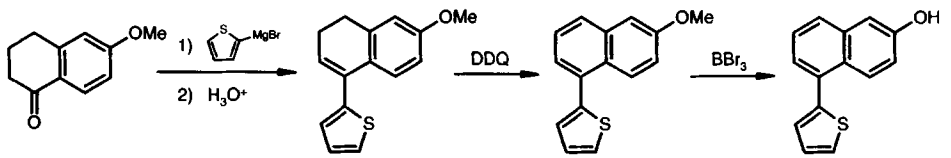
Scheme 2



R^1, R^2 = Aryl, thienyl, fluorenyl

Two naphthols have been used: the commercially available naphthalen-2-ol and the 2-(6-hydroxynaphthalen-1-yl)thiophene **3** (*Scheme 3*).

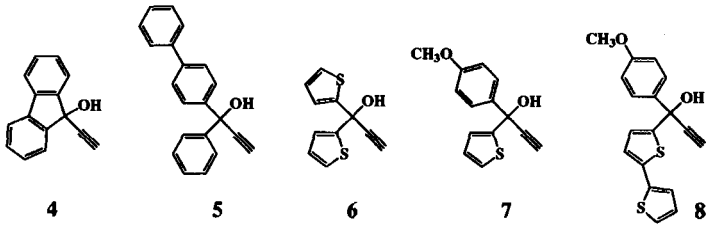
Scheme 3



1 **2** **3**

The reaction of (thiophen-2-yl)magnesium bromide [21] with 1,2,3,4-tetrahydro-6-methoxynaphthalen-1-one, followed by acid hydrolysis [22], afforded **1** (82%). Oxidation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [23][24] converts **1** to its aromatic parent compound **2**. According to the literature, different solvents can be used for the aromatization [25]. The best yield was obtained with benzene (74%). Demethylation of **2** was performed by reaction with BBr_3 [26] in refluxing CH_2Cl_2 to give the naphthol **3** (63%).

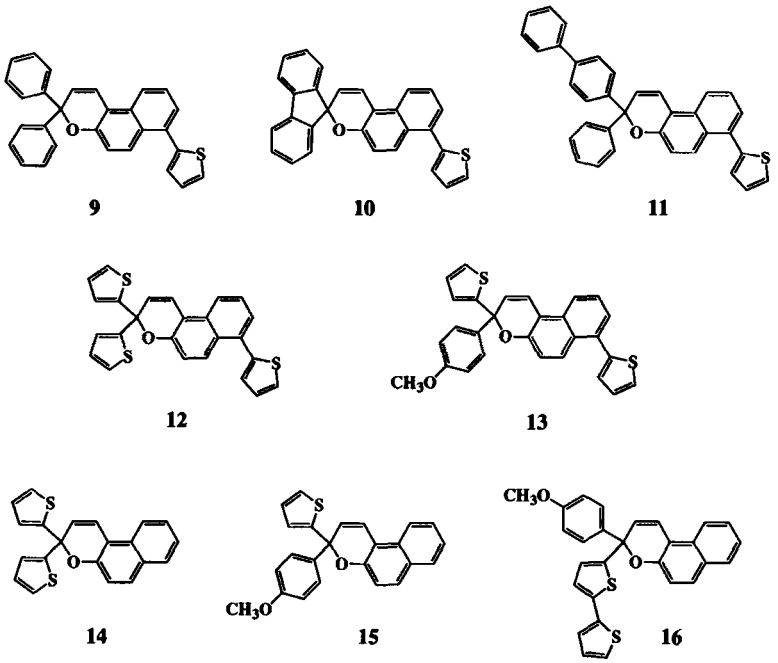
On the other hand, in addition to the commercially available 1,1-diphenylprop-2-yn-1-ol, alcohols **4**–**8** have been used.



4 **5** **6** **7** **8**

Compounds **4**–**7** were obtained with yields varying from 31 to 90%, through nucleophilic addition of sodium acetylide onto commercially available ketones, and **8** was obtained in 36% yield, following the same procedure. In this case, the 2,2′-bithiophen-5-yl 4-methoxyphenyl ketone, precursor of **8**, was isolated in good yield (83%) from the reaction of 2,2′-bithiophene [27] with 4-methoxybenzoyl chloride in presence of $SnCl_4$ [28].

The photochromic compounds **9**–**13** resulted from the condensation of **3** with the different alcohols. Yields after purification varied from 28 to 58%. Compounds **14**–**16** were obtained by reaction of naphthalen-2-ol with the alkynols **6**–**8** in 28, 33, and 71% yields, respectively.



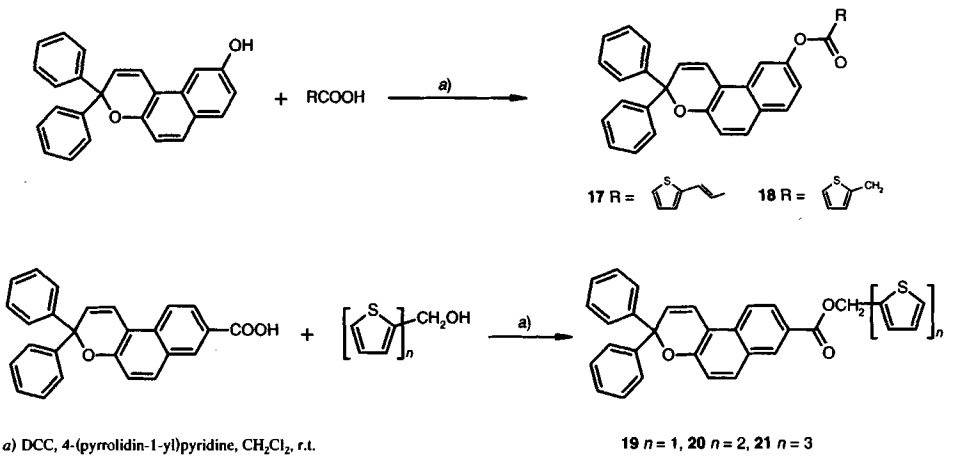
9 **10** **11** **12** **13** **14** **15** **16**

It is noteworthy that degradation by-products are formed during the preparation of **16** (the reaction was monitored by TLC (pentane/Et_2O 1:1)). The use of pyridinium *para*-toluenesulfonate (PPTS) [29] instead of TsOH allows to overcome this problem.

Thus, the condensation of **8** with naphthalen-2-ol in CH_2Cl_2, at room temperature, with catalytic amount of PPTS, leads to **16** in excellent yield (71%).

Procedure B is based on a mild 'one-pot esterification' [30] of a preformed naphthopyran functionalized by an OH or a CH_2OH group. This reaction occurs at room temperature under neutral conditions. Then, the condensation of 3,3-diphenyl-9-hydroxy-3*H*-naphtho[2,1-*b*]pyran with a carboxylic acid possessing a thiophene moiety gave the compounds **17** and **18** in 47 and 52% yields, respectively (*Scheme 4*).

Scheme 4



In the same way, the reaction of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran-8-carboxylic acid [31] with thiophene-, bithiophene-, or terthiophene-methanols [32][33] affords the compounds **19**–**21** in yields over 50%.

Photochromic Properties. All described compounds exhibit photochromic behavior at room temperature in toluene. The λ_{max} values and the rate constants (k_Δ) of thermal bleaching (ring closure) were determined using flash photolysis coupled to a fast-scanning spectro-photometer [34]. The 'colorability', which is a function of the quantum yield of photocoloration and of the molar absorptivity of the colored species [35], has been evaluated from the absorbance measured at λ_{max} and immediately after the flash (A_0). The experimental conditions used are reported in the corresponding section.

Photochromic characteristics of compounds **9**–**21** are listed in the *Table* and are compared to those previously obtained for the 3,3-diphenylnaphtho[2,1-*b*]pyran **22** [12] without any substituent.

From a general point of view, two phases of kinetics of fading are observed, which probably correspond to different isomers of the open form. This behavior was observed for a large majority of compounds in the chromene series [36] except for the reference compound **22** which exhibits only a single kinetic phase.

The slow fading rate can be attributed to the most stable s-*trans*-isomer as represented in *Scheme 1*. Variation in the absorption and 'colorability' of the open form will be discussed according to the position of the substituents.

Introduction of a thiophene moiety in the 'naphtho' part of a 3,3-diphenylnaphtho[2,1-*b*]pyran leads to a weak bathochromic shift of the λ_{max} (from 4 to 16 nm)

Table. *Fading Rates* (k_d), *Absorption Wavelengths* (λ_{max}), *and 'Colorability'* (initial absorbance A_0) of *Naphtho-[2,1-b]pyrans Measured by Flash Photolysis in Toluene at 25°* (2.5×10^{-5} M)

Compound	**9**	**10**	**11**	**12**	**13**	**14**	**15**
λ_{max} [nm]	445	472	460	483	483	472	476
A_0	1.6	1.1	1.3	1.3	1.68	0.6	0.5
k_d [s^{-1}]	0.25	0.25	0.31	0.63	0.86	0.42	0.41
	0.028	0.027	0.047	0.12	0.28	0.16	0.19
Compound	**16**	**17**	**18**	**19**	**20**	**21**	**22**[a])
λ_{max} [nm]	511	440	436	448	441	438	432
A_0	2.16	0.3	0.73	1.01	1.94	0.8	0.84
k_d [s^{-1}]	0.44	0.23	0.21	0.35	0.38	0.40	0.09
	0.15	0.024	0.028	0.054	0.069	0.07	

[a]) From [12].

independent of the type of the junction: conjugated (**9**) or nonconjugated (**17**–**21**). In contrast, the replacement of one or two Ph groups at C(3) by one or two thiophene moieties induces a strong bathochromic shift of the λ_{max}. The more pronounced effect is obtained with **16** in which a bithiophenyl has replaced a Ph group: the unusual shift of λ_{max} (+ 79 nm, with respect to the reference compound **22**) is certainly enhanced by the donor substituent (MeO) in *p*-position of the Ph group [12]. It is also interesting to note that this compound shows an exceptional enhancement of the 'colorability' (A_0 is *ca.* three times higher than that measured for **22**). This could be due to the hyperchromic effect when the π-electron system of the bithiophenyl is conjugated with the delocalized electron system of the naphthopyran part in the open form.

Conclusion. – It has been shown that the synthesis of thiophenyl-substituted 3*H*-naphtho[2,1-*b*]pyrans can be achieved by usual methods. The thermal stability of colored forms is not modified when a thiophene nucleus is linked to the naphthopyran structure. In contrast, λ_{max} of absorption and colorability are especially improved, when C(3) is substituted by one or two thiophenyl groups. These compounds will be good precursors for the design of new photomodulated materials.

Experimental Part

General. Solvents were dried by distillation on drying agents as follows: THF and Et_2O were freshly distilled from sodium benzophenone ketyl, CH_2Cl_2 (CaH_2). Benzene was purchased from *S.D.S. Co.* Column chromatography (CC): on silica gel *60* (*Merck 7734*). M.p.: in capillary tubes on a *Büchi 510* apparatus, uncorrected. *Fourier* transform (FT) IR spectra: *Matson Polaris* spectrophotometer, $\tilde{\nu}$ in cm^{-1}. NMR Spectra: in $CDCl_3$ soln. on a *Bruker AC 250* spectrometer, chemical shifts δ in ppm downfield from Me_4Si, coupling constants J in Hz. Photochromic measurements were performed in toluene solns. of spectrophotometric grade (*UCB*) at 25° (± 0.2°), using cylindrical cells with a 100-mm pathlength and a 10-mm section. The fading rate constants, k_d, were measured at the λ_{max} of absorption of the colored form generated after flash photolysis (Xe tube, 50 µs, 60 J). Initial absorbances (A_0) were given for a standard concentration of 2.5×10^{-5} M.

Preparation of **3**. *2-(6-Methoxy-3,4-dihyronaphthalene-1-yl)thiophene* (**1**). To a flask equipped with a magnetic stirrer and a reflux condenser under Ar, Mg turnings (2.54 g, 0.1 mol) in dry Et_2O (15 ml) were introduced.

2-Bromothiophene (15.54 g, 0.09 mol) in dry Et_2O (25 ml) was slowly added to maintain the reflux of the mixture. The resulting soln. was stirred at r.t. for 1 h. The *Grignard* soln. was transferred to the dropping funnel of a second apparatus *via* cannula and was added dropwise to a soln. of 1,2,3,4-tetrahydro-6-methoxynaphthalen-1-one (12 g, 0.06 mol) in dry Et_2O (200 ml). The mixture was refluxed for 3 h under Ar. After cooling (ice bath), an aq. soln. of H_2SO_4 (0.1N, 100 ml) was slowly added. The aq. layer was extracted with Et_2O (3 × 100 ml). The combined org. layer was dried ($MgSO_4$). The solvent was removed under reduced pressure. The crude product was purified by CC (silica gel, pentane/Et_2O 100:0 to 80:20): 13.46 g (82%) of **1**. IR (film): 3104, 3027, 2998, 2830, 1652, 1606, 1454, 1279, 1022. ^{1}H-NMR (250 MHz): 7.28 (*d*, *J* = 8.5, 1 H); 7.22 (*dd*, *J* = 2.7, 3.5, 1 H); 7.06–7.01 (*m*, 2 H); 6.76 (*d*, *J* = 2.7, 1 H); 6.68 (*dd*, *J* = 2.7, 8.5, 1 H); 6.14 (*t*, *J* = 4.8, 1 H); 3.80 (*s*, 3 H); 2.79 (*dd*, *J* = 7.6, 8.1, 2 H); 2.39–2.31 (*m*, 2 H). ^{13}C-NMR (62.5 MHz): 23.38 (CH_2); 28.53 (CH_2); 55.19 (MeO); 110.76 (CH); 113.80 (CH); 123.84 (CH); 125.36 (CH); 126.46 (CH); 126.51 (CH); 126.96 (CH); 127.47 (C); 132.43 (C); 138.54 (C); 142.90 (C); 158.76 (C). Anal. calc. for $C_{15}H_{14}OS$: C 74.35, H 5.82, S 13.2; found: C 74.30, H 5.93, S 13.2.

2-(6-Methoxynaphthalen-1-yl)thiophene (**2**). In a flask equipped with a magnetic stirred and a reflux condenser under Ar, DDQ (8.44 g, 0.03 mol) in dry benzene (100 ml) was introduced. A soln. of **1** (3 g, 0.01 mol) in dry benzene (30 ml) was added dropwise. The mixture was refluxed for 5 h, cooled to r.t., and filtered through silica gel. The silica gel was washed with Et_2O. The solvents were removed under reduced pressure. The residue was purified by CC (silica gel, pentane/Et_2O 100:0 to 80:20): 2.20 g (74%) of **2**. IR (film): 3104, 3001, 2956, 2834, 1594, 1507, 1272, 1027. ^{1}H-NMR (250 MHz): 8.12 (*dd*, *J* = 0.4, 8.9, 1 H); 7.73 (*dd*, *J* = 2.8, 6.6, 1 H); 7.50–7.35 (*m*, 3 H); 7.25–7.05 (*m*, 4 H); 3.91 (*s*, 3 H). ^{13}C-NMR (62.5 MHz): 55.26 (MeO); 106.18 (CH); 119.02 (CH); 125.52 (CH); 125.86 (CH); 125.98 (CH); 127.20 (2 CH); 127.24 (CH); 127.39 (CH); 127.50 (C); 132.38 (C); 135.19 (C); 141.96 (C); 157.59 (C). Anal. calc. for $C_{15}H_{12}OS$: C 74.96, H 5.03, S 13.3; found: C 74.82, H 5.07, S 13.3.

5-(Thiophen-2-yl)naphthalen-2-ol (**3**). To a 150-ml flask, fitted with a side arm and capped by a rubber septum, a soln. of **2** (3.5 g, 0.01 mol) in dry CH_2Cl_2 (25 ml) was introduced. After cooling to 0° (ice bath), 18.5 ml of 1.0M soln. of Br_3B in CH_2Cl_2 was added. The mixture was refluxed for 15 h, cooled to r.t., and hydrolyzed with an aq. NaOH soln. (5%). The mixture was filtered through *Celite*. *Celite* was washed with CH_2Cl_2. The aq. layer was extracted with Et_2O (3 × 100 ml). The combinated org. layer was dried ($MgSO_4$). The solvent was removed under reduced pressure, and the crude product was purified by CC (silica gel, pentane/Et_2O 100:0 to 50:50): 2.05 g (63%) of **3**. M.p. 84–85°. IR (KBr): 3623, 3500, 2900, 3105, 1599, 1586, 1209. ^{1}H-NMR (250 MHz): 8.14 (*d*, *J* = 9.1, 1 H); 7.65 (*t*, *J* = 4.7, 1 H); 7.50–7.35 (*m*, 3 H); 7.28–7.14 (*m*, 3 H); 7.10 (*dd*, *J* = 2.4, 9.1, 1 H); 5.54 (br. *s*, 1 H). ^{13}C-NMR (62.5 MHz): 109.98 (CH); 118.05 (CH); 125.56 (CH); 126.02 (CH); 126.05 (CH); 126.84 (CH); 127.26 (2 CH); 127.94 (CH); 132.45 (C); 135.15 (C); 141.84 (C); 153.25 (C). Anal. calc. for $C_{14}H_{10}OS$: C 74.30, H 4.45, S 14.1; found: C 74.25, H 4.44, S 14.1.

Preparation of the Alcohols **4**–**8**. *General Procedure*. In a three-necked flask fitted with a condenser, a dropping funnel, and an Ar inlet, sodium acetylide (3*x* mol, 18 wt-% slurry, 95% purity) in xylene was introduced. The ketone (*x* mol) was added dropwise at 0°. The mixture was stirred at r.t. under Ar. The mixture was concentrated to 2/3 and hydrolyzed with H_2O (50 ml). A sat. aq. NH_4Cl soln. was added to the resulting mixture until pH 7 was reached. The mixture was extracted with Et_2O (3 × 100 ml). The combined org. layer was dried ($MgSO_4$), concentrated, and eluted on silica gel with pentane/Et_2O 100:0 to 50:50 to obtain the alcohol.

9-Ethynyl-9H-fluoren-9-ol (**4**): reaction time 4 d, yield 69%. M.p. 108°. IR (KBr): 3550, 3100, 1605, 1585, 1450, 1196, 732. ^{1}H-NMR (250 MHz): 7.70 (*dd*, *J* = 1.5, 6.5, 2 H); 7.61 (*dd*, *J* = 1.3, 6.6, 2 H); 7.41 (*dt*, *J* = 1.3, 7.4, 2 H); 7.35 (*dt*, *J* = 1.3, 7.4, 2 H); 2.58 (*s*, 1 H); 2.47 (*s*, 1 H). ^{13}C-NMR (62.5 MHz): 71.36 (≡CH); 74.51 (C); 83.84 (C); 120.20 (2 CH); 124.24 (2 CH); 128.58 (2 CH); 129.79 (2 CH); 139.05 (2 C); 146.56 (2 C).

1-(1,1'-Biphenyl-4-yl)-1-phenylprop-2-yn-1-ol (**5**): reaction time 2 d, yield 53%. M.p. 94°. IR (KBr): 3556, 3280, 1448, 1158, 834, 768, 696. ^{1}H-NMR (250 MHz): 7.80–7.15 (*m*, 14 H); 2.90 (*s*, 1 H); 2.86 (*s*, 1 H). ^{13}C-NMR (62.5 MHz): 74.36 (C); 75.84 (≡CH); 86.53 (C); 126.18 (2 CH); 126.61 (2 CH); 127.25 (2 CH); 127.30 (2 CH); 127.58 (CH); 128.13 (CH); 128.55 (2 CH); 128.95 (2 CH); 140.77 (C); 140.94 (C); 143.61 (C); 144.50 (C).

1,1-Di(thiophen-2-yl)prop-2-yn-1-ol (**6**): reaction time 2 d, yield 31%. ^{1}H-NMR (250 MHz): 7.28 (*dd*, *J* = 1.2, 5.0, 2 H); 7.19 (*dd*, *J* = 1.2, 3.6, 2 H); 6.94 (*dd*, *J* = 3.6, 5.0, 2 H); 3.18 (*s*, 1 H); 2.91 (*s*, 1 H). ^{13}C-NMR (62.5 MHz): 69.57 (C); 75.03 (≡CH); 85.37 (C); 125.97 (2 CH); 126.47 (2 CH); 126.88 (2 CH); 148.85 (2 C).

1-(4-Methoxyphenyl)-1-(thiophen-2-yl)prop-2-yn-1-ol (**7**): reaction time 2 d, yield 90%. Oil. IR (film): 3435, 3284, 3104, 3073, 2956, 2932, 2114, 1607, 1585, 1509, 1462, 1441, 1351, 1249, 1175, 1033, 966, 827, 706. ^{1}H-NMR (250 MHz): 2.79 (*s*, 1 H); 3.32 (br. *s*, 1 H); 3.69 (*s*, 3 H); 6.79 (*m*, 2 H); 6.82 (*dd*, *J* = 3.6, 5.1, 1 H); 7.00 (*dd*, *J* = 0.9, 3.6, 1 H); 7.16 (*dd*, *J* = 0.9, 5.1, 1 H); 7.52 (*m*, 2 H). ^{13}C-NMR (62.5 MHz): 55.42 (MeO); 71.49 (*q*); 74.99 (≡CH); 86.12 (*q*); 113.71 (2 CH); 125.57 (CH); 126.11 (CH); 126.59 (CH); 127.25 (2 CH); 136.24 (*q*); 150.05 (*q*); 159.43 (*q*).

1-(2,2'-Bithiophen-5-yl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (**8**): reaction time 1 h, yield 36%. Oil. IR (film): 3519, 3435, 3300, 3106, 3071, 3003, 2957, 2933, 2115, 1607, 1584, 1510, 1424, 1304, 1250, 1175, 1033, 962, 893,

863, 829, 699. ^{1}H-NMR (250 MHz): 2.74 (*s*, 1 H); 2.97 (*s*, 1 H); 3.64 (*s*, 3 H); 6.74 (*m*, 2 H); 6.78–6.86 (*m*, 3 H); 6.95 (*dd*, *J* = 1.1, 3.6, 1 H); 7.03 (*dd*, *J* = 1.1, 5.1, 1 H); 7.47 (*m*, 2 H). ^{13}C-NMR (62.5 MHz): 55.37 (MeO); 71.45 (*q*); 75.14 (≡CH); 85.68 (*q*); 113.72 (2 CH); 123.00 (CH); 123.88 (CH); 124.65 (CH); 126.12 (CH); 127.19 (2 CH); 127.88 (CH); 135.76 (*q*); 137.20 (*q*); 138.09 (*q*); 148.67 (*q*); 159.54 (*q*).

2,2′-Bithiophen-5-yl 4-methoxyphenyl ketone, precursor of **8**, was prepared as follows: To a three-necked 50-ml flask protected by a $CaCl_2$ drying tube, a soln. of 4-methoxybenzoyl chloride (2.72 g, 16 mmol) and 2,2′-bithiophene (2 g, 12 mmol) in dry benzene (15 ml) was introduced and cooled to −2°. A soln. of $SnCl_4$ (1.41 ml, 12 mmol) in dry benzene (8 ml) was added at such a rate as to keep the temp. at 4°. After addition was completed, the resulting soln. was stirred at r.t. for 15 min. The dark mixture was poured onto a slurry of ice (20 ml), and an aq. soln. of HCl (1N, 20 ml) was added slowly. The layers were separated and the aq. layer was extracted with benzene (3 × 15 ml). The benzene soln. was washed with H_2O (3 × 10 ml), an aq. soln. of NaOH (1N, 3 × 10 ml), H_2O (3 × 10 ml), and brine (3 × 15 ml). The org. layer was dried ($MgSO_4$) and concentrated under reduced pressure. The precipitated ketone was filtered, washed with small portions of pentane, and dried to give 3 g (83%) of ketone. M.p. 119–120°. IR (KBr): 3092, 3069, 3008, 2981, 2939, 2842, 1625, 1600, 1511, 1505, 1447, 1412, 1336, 1320, 1293, 1264, 1226, 1175, 1021, 873, 853, 842, 809, 756, 696. ^{1}H-NMR (250 MHz): 3.98 (*s*, 3 H); 7.08 (*m*, 2 H); 7.15 (*dd*, *J* = 3.6, 5.1, 1 H); 7.28 (*d*, *J* = 3.9, 1 H); 7.37–7.46 (*m*, 2 H); 7.62 (*d*, *J* = 3.9, 1 H); 7.98 (*m*, 2 H). ^{13}C-NMR (62.5 MHz): 55.48 (MeO); 113.73 (2 CH); 123.97 (CH); 125.58 (CH); 126.38 (CH); 128.24 (CH); 130.59 (*q*); 131.42 (2 CH); 134.92 (CH); 136.41 (*q*); 141.90 (*q*); 145.43 (*q*); 163.06 (*q*); 186.42 (C=O). Anal. calc. for $C_{16}H_{12}O_2S_2$: C 63.98, H 4.03, S 21.3; found: C 63.96, H 4.05, S 20.7.

Preparation of the Photochromic Compounds: Procedure A: General Procedure for Compounds **9**–**16**. A soln. of the appropriate naphthol (2.2 mmol), alcohol (2.2 mmol), and TsOH (cat. amount) in dry CH_2Cl_2 (15 ml) was stirred at r.t. under Ar (the disappearance of the alcohol was monitored by TLC (pentane/AcOEt 1:1)). The solvent was removed under reduced pressure, and the residue was purified by CC (silica gel, CH_2Cl_2) to give the corresponding naphthopyran. Recrystallization from pentane/CH_2Cl_2 gave crystalline material.

Procedure B: General Procedure for Compounds **17**–**21**. a) *For* **17** *and* **18**. A soln. of carboxylic acid (11 mmol), *N,N*-dicyclohexylcarbodiimide (DCC, 11 mmol), 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran-9-ol (10 mmol), and 4-(pyrrolidin-1-yl)pyridine (1 mmol) in CH_2Cl_2 (30–40 ml) was stirred at r.t. until esterification was complete (the disappearance of the alcohol was monitored by TLC (pentane/AcOEt 1:1)). The *N,N*-dicyclohexylurea was filtered and the filtrate washed with CH_2Cl_2. The solvent was removed under reduced pressure, and the residue was purified by CC (silica gel, pentane/Et_2O 100:0 to 60:40) to yield the corresponding ester. Recrystallization from cyclohexane/Et_2O gave crystalline material.

a) *For* **19**–**21**. A soln. of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran-8-carboxylic acid (10 mmol), DCC (11 mmol), and 4-(pyrrolidin-1-yl)pyridine (1 mmol) in CH_2Cl_2 (30–40 ml) was stirred at r.t. until esterification was complete (the disappearance of the alcohol was monitored by TLC (pentane/AcOEt 1:1)). The *N,N*-dicyclohexylurea was filtered and the filtrate washed with CH_2Cl_2. The solvent was removed under reduced pressure, and the residue was purified by CC (silica gel, pentane/Et_2O 100:0 to 50:50) to afford the corresponding ester. Recrystallization from pentane/Et_2O gave crystalline material.

*3,3-Diphenyl-7-(thiophen-2-yl)-3*H*-naphtho[2,1-b]pyran* (**9**): reaction time 17 h, yield 57%. M.p. 82°. IR (KBr): 3100, 3000, 1585, 1446, 1435, 1252, 1082, 1066, 903, 849, 831, 763, 698. ^{1}H-NMR (250 MHz): 6.29 (*d*, *J* = 10.0, 1 H); 7.10–7.58 (*m*, 17 H); 7.98 (*d*, *J* = 8.3, 1 H); 8.02 (*d*, *J* = 9.2, 1 H). ^{13}C-NMR (62.5 MHz): 82.51 (C); 114.15 (C); 118.57 (CH); 119.65 (CH); 121.61 (CH); 125.60 (CH); 126.00 (CH); 126.12 (CH); 126.99 (4 CH); 127.17 (CH); 127.43 (CH); 127.55 (2 CH); 127.78 (C); 127.82 (CH); 127.96 (CH); 128.10 (4 CH); 130.31 (C); 133.04 (C); 141.83 (C); 144.75 (2 C); 150.58 (C). Anal. calc. for $C_{29}H_{20}OS$: C 83.62, H 4.84, S 7.7; found: C 83.64, H 4.84, S 7.6.

7′-(Thiophen-2-yl)spiro[fluorene-9,3′-[3′*H]naphtho[2,1-b]pyran]* (**10**): reaction time 24 h, yield 44%. M.p. 204–205°. IR (KBr): 3104, 3022, 1604, 1584, 1508, 1449, 1436, 1319, 1249, 1236, 1081, 1064, 851, 736. ^{1}H-NMR (250 MHz): 5.74 (*d*, *J* = 10.0, 1 H); 7.04 (*d*, *J* = 9.2, 1 H); 7.17 (*dd*, *J* = 3.6, 5.0, 1 H); 7.20–7.54 (*m*, 9 H); 7.57 (*m*, *J* = 7.5, 2 H); 7.66 (*d*, *J* = 7.5, 2 H); 8.04 (*d*, *J* = 9.2, 1 H); 8.11 (*d*, *J* = 8.3, 1 H). ^{13}C-NMR (62.5 MHz): 85.62 (C); 113.27 (C); 118.79 (CH); 120.28 (2 CH); 120.54 (CH); 121.60 (CH); 125.26 (CH); 125.37 (2 CH); 125.83 (CH); 126.29 (CH); 126.33 (CH); 127.40 (CH); 127.63 (CH); 127.66 (CH); 128.05 (C); 128.54 (2 CH); 130.12 (2 CH); 130.52 (C); 133.38 (C); 139.20 (2 C); 142.03 (C); 147.59 (2 C); 152.31 (C). Anal. calc. for $C_{29}H_{18}OS$: C 84.02, H 4.38, S 7.7; found: C 84.05, H 4.40, S 7.7.

*3-(1,1′-Biphenyl-4-yl)-3-phenyl-7-(thiophen-2-yl)-3*H*-naphtho[2,1-b]pyran* (**11**): reaction time 21 h, yield 39%. M.p. 92°. IR (KBr): 3100, 3027, 1599, 1446, 1435, 1371, 1249, 1230, 1085, 1065, 908, 836, 760, 696. ^{1}H-NMR (250 MHz): 6.33 (*d*, *J* = 10.0, 1 H); 7.10–7.60 (*m*, 21 H); 7.99 (*d*, *J* = 8.3, 1 H); 8.04 (*d*, *J* = 9.3, 1 H). ^{13}C-NMR (62.5 MHz): 82.68 (C); 114.39 (C); 118.82 (CH); 119.97 (CH); 121.86 (CH); 125.85 (CH); 126.27 (CH); 126.40

(CH); 127.09 (CH); 127.12 (CH); 127.22 (2 CH); 127.33 (2 CH); 127.41 (2 CH); 127.55 (CH); 127.66 (CH); 127.69 (CH); 127.85 (CH); 128.11 (CH); 128.38 (CH); 128.40 (2 CH); 128.93 (C); 128.95 (2 CH); 130.57 (C); 133.31 (C); 140.66 (C); 140.88 (C); 142.07 (C); 144.02 (C); 144.93 (C); 150.83 (C). Anal. calc. for $C_{35}H_{24}OS$: C 85.33, H 4.91, S 6.5; found: C 85.29, H 4.99, S 6.4.

*3,3,7-Tri(thiophen-2-yl)-3*H*-naphtho[2,1-*b*]pyran* (**12**): reaction time 4 h, yield 28%. M.p. 150°. IR (KBr): 3101, 3066, 1757, 1585, 1433, 1374, 1252, 1228, 1085, 1068, 1042, 904, 847, 800, 761, 696. ^{1}H-NMR (250 MHz): 6.31 (*d*, *J* = 9.9, 1 H); 6.94 (*dd*, *J* = 3.6, 5.0, 2 H); 7.07 (*dd*, *J* = 1.2, 3.6, 2 H); 7.10–7.20 (*m*, 3 H); 7.29 (*dd*, *J* = 1.2, 5.0, 2 H); 7.35 (*d*, *J* = 9.9, 1 H); 7.37–7.55 (*m*, 3 H); 8.00 (*d*, *J* = 8.4, 1 H); 8.05 (*d*, *J* = 9.4, 1 H). ^{13}C-NMR (62.5 MHz): 78.73 (C); 113.86 (C); 118.64 (CH); 120.13 (CH); 121.72 (CH); 125.81 (CH); 126.14 (2 CH); 126.30 (CH); 126.34 (2 CH); 126.49 (CH); 126.59 (2 CH); 127.12 (CH); 127.34 (CH); 127.62 (CH); 128.19 (C); 128.27 (CH); 130.40 (C); 133.28 (C); 141.87 (C); 148.61 (2 C); 150.17 (C). Anal. calc. for $C_{25}H_{16}OS_3$: C 70.06, H 3.76, S 22.4; found: C 70.09, H 3.76, S 22.3.

*3-(4-Methoxyphenyl)-3,7-di(thiophen-2-yl)-3*H*-naphtho[2,1-*b*]pyran* (**13**): reaction time 13 h, yield 58%. M.p. 119–120°. IR (KRr): 3099, 3070, 3000, 2953, 2930, 1626, 1609, 1583, 1511, 1463, 1435, 1253, 1236, 1175, 1081, 1028, 980, 850, 829, 801, 760, 701. ^{1}H-NMR (250 MHz): 3.82 (*s*, 3 H); 6.32 (*d*, *J* = 9.9, 1 H); 6.85–7.02 (*m*, 4 H); 7.15–7.27 (*m*, 3 H); 7.32 (*dd*, *J* = 1.4, 4.9, 1 H); 7.37 (*d*, *J* = 9.9, 1 H); 7.42–7.57 (*m*, 5 H); 8.06 (*d*, *J* = 8.4, 1 H); 8.08 (*d*, *J* = 9.4, 1 H). ^{13}C-NMR (62.5 MHz): 55.33 (MeO); 80.31 (*q*); 113.54 (2 CH); 114.11 (*q*); 118.68 (CH); 119.77 (CH); 121.72 (CH); 125.74 (CH); 126.18 (CH); 126.32 (CH); 126.36 (CH); 126.46 (CH); 127.30 (CH); 127.57 (2 CH); 127.79 (CH); 127.90 (2 CH); 127.99 (*q*); 128.04 (CH); 130.40 (*q*); 133.19 (*q*); 136.58 (*q*); 141.91 (*q*); 149.65 (*q*); 150.46 (*q*); 159.29 (*q*). Anal. calc. for $C_{28}H_{20}O_2S_2$: C 74.30, H 4.45, S 6.4; found: C 74.73, H 5.01, S 6.5.

*3,3-Di(thiophen-2-yl)-3*H*-naphtho[2,1-*b*]pyran* (**14**): reaction time 2 d, yield 28%. M.p. 138–139°. IR (KBr): 3098, 3078, 3067, 1633, 1586, 1586, 1517, 1461, 1433, 1225, 1202, 1091, 1084, 1038, 987, 932, 848, 831, 807, 751, 707, 694. ^{1}H-NMR (250 MHz): 6.21 (*d*, *J* = 9.8, 1 H); 6.85 (*dd*, *J* = 3.6, 4.9, 2 H); 6.99 (*dd*, *J* = 1.0, 3.6, 2 H); 7.09–7.50 (*m*, 6 H); 7.59 (*d*, *J* = 8.9, 1 H); 7.64 (*d*, *J* = 8.1, 1 H); 7.89 (*d*, *J* = 8.4, 1 H). ^{13}C-NMR (62.5 MHz): 78.75 (*q*); 118.69 (*q*); 118.39 (CH); 119.99 (CH); 121.42 (CH); 123.97 (CH); 126.08 (2 CH); 126.28 (2 CH); 126.56 (2 CH); 126.88 (CH); 126.91 (CH); 128.69 (CH); 129.68 (*q*); 129.85 (*q*); 130.25 (CH); 148.70 (2*q*); 150.10 (*q*). Anal. calc. for $C_{21}H_{14}OS_2$: C 72.80, H 4.07, S 18.5; found: C 72.88, H 4.12, S 17.8.

*3-(4-Methoxyphenyl)-3-(thiophen-2-yl)-3*H*-naphtho[2,1-*b*]pyran* (**15**): reaction time 2 d, yield 33%. M.p. 126°. IR (KBr): 3103, 3061, 3010, 2962, 2931, 2834, 1629, 1609, 1584, 1510, 1460, 1251, 1234, 1217, 1175, 1088, 1078, 1034, 1000, 850, 826, 817, 805, 753, 701. ^{1}H-NMR (250 MHz): 3.58 (*s*, 3 H); 6.08 (*d*, *J* = 9.8, 1 H); 6.60–7.40 (*m*, 11 H); 7.48 (*d*, *J* = 8.8, 1 H); 7.53 (*d*, *J* = 8.0, 1 H); 7.78 (*d*, *J* = 8.4, 1 H). ^{13}C-NMR (62.5 MHz): 55.39 (MeO); 80.38 (*q*); 113.56 (2 CH); 113.98 (*q*); 118.48 (CH); 119.69 (CH); 121.47 (CH); 123.84 (CH); 126.30 (CH); 126.35 (CH); 126.48 (CH); 126.83 (CH); 127.57 (CH); 127.95 (2 CH); 128.68 (CH); 129.58 (*q*); 129.92 (*q*); 130.08 (CH); 136.73 (*q*); 149.81 (*q*); 150.46 (*q*); 159.31 (*q*). Anal. calc. for $C_{24}H_{18}O_2S$: C 77.80, H 4.90, S 8.6; found: C 77.76, H 4.98, S 8.6.

*3-(2,2'-Bithiophen-5-yl)-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran* (**16**): reaction time 24 h, yield 71%. M.p. 134°. IR (KBr): 3107, 3064, 2931, 2836, 1631, 1607, 1583, 1510, 1460, 1225, 1384, 1250, 1228, 1085, 1001, 906, 832, 754, 694. ^{1}H-NMR (250 MHz): 3.68 (*s*, 3 H); 6.15 (*d*, *J* = 9.8, 1 H); 6.70–6.90 (*m*, 5 H); 6.99 (*dd*, *J* = 1.0, 3.6, 1 H); 7.06 (*dd*, *J* = 1.0, 5.1, 1 H); 7.11 (*d*, *J* = 8.8, 1 H); 7.18–7.50 (*m*, 5 H); 7.58 (*d*, *J* = 8.8, 1 H); 7.63 (*d*, *J* = 8.3, 1 H); 7.87 (*d*, *J* = 8.3, 1 H). ^{13}C-NMR (62.5 MHz): 55.34 (MeO); 80.33 (*q*); 113.58 (2 CH); 113.91 (*q*); 118.41 (CH); 119.90 (CH); 121.41 (CH); 122.95 (CH); 123.82 (2 CH); 124.55 (CH); 126.82 (CH); 127.06 (CH); 127.13 (CH); 127.88 (3 CH); 128.65 (CH); 129.56 (*q*); 129.86 (*q*); 130.12 (CH); 136.27 (*q*); 137.35 (*q*); 138.33 (*q*); 148.54 (*q*); 150.34 (*q*); 159.32 (*q*). Anal. calc. for $C_{28}H_{20}O_2S_2$: C 74.31, H 4.45, S 14.1; found: C 74.49, H 4.47, S 14.2.

*3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran-9-yl* (E)*-3-(thiophen-2-yl)prop-2-enoate* (**17**): reaction time 18 h, yield 47%. M.p. 167–168°. IR (KBr): 3109, 3026, 1730, 1620, 1591, 1513, 1449, 1425, 1377, 1237, 1135, 1173, 1094, 1056, 928, 858, 699, 733. ^{1}H-NMR (250 MHz): 6.24 (*d*, *J* = 9.9, 1 H); 6.46 (*d*, *J* = 15.6, 1 H); 7.00–7.50 (*m*, 16 H); 7.64 (*d*, *J* = 8.9, 1 H); 7.70 (*s*, 1 H); 7.72 (*d*, *J* = 8.9, 1 H); 7.99 (*d*, *J* = 15.6, 1 H). ^{13}C-NMR (62.5 MHz): 82.61 (C); 112.69 (CH); 113.95 (C); 115.79 (CH); 118.09 (CH); 118.73 (CH); 119.35 (CH); 126.94 (4 CH); 127.29 (C); 127.50 (2 CH); 127.73 (CH); 128.05 (4 CH); 128.21 (CH); 129.16 (CH); 129.60 (CH); 129.93 (CH); 130.48 (C); 131.59 (CH); 139.00 (CH); 139.25 (C); 144.61 (2 C); 149.42 (C); 151.09 (C); 165.40 (C=O). Anal. calc. for $C_{32}H_{22}O_3S$: C 78.98, H 4.56, S 6.5; found: C 78.97, H 4.57, S 6.3.

*3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran-9-yl Thiophen-2-acetate* (**18**): reaction time 23 h, yield 52%. M.p. 116–117°. IR (KBr): 3107, 3021, 2850, 3000, 1756, 1635, 1590, 1450, 1443, 1376, 1241, 1076, 942, 881, 840, 813, 761, 699. ^{1}H-NMR (250 MHz): 4.00 (*s*, 2 H); 6.12 (*d*, *J* = 9.9, 1 H); 6.80–7.25 (*m*, 12 H); 7.34 (*d*, *J* = 7.5, 4 H);

7.51 (*d*, *J* = 8.8, 1 H); 7.53 (*s*, 1 H); 7.58 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (62.5 MHz): 35.78 (CH_2); 82.83 (C); 112.78 (CH); 114.19 (C); 118.44 (CH); 118.58 (CH); 119.53 (CH); 125.55 (CH); 127.15 (5 CH); 127.40 (CH); 127.56 (C); 127.74 (2 CH); 128.00 (CH); 128.28 (4 CH); 129.82 (CH); 130.20 (CH); 130.60 (C); 134.45 (C); 144.79 (2 C); 149.47 (C); 151.35 (C); 169.22 (C=O). Anal. calc. for $C_{31}H_{22}O_3S$: C 78.45, H 4.67, S 6.7; found: C 78.24, H 4.74, S 6.6.

*(Thiophen-2-yl)methyl 3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran-8-carboxylate* (**19**): reaction time 3 d, yield 61%. M.p. 136–137°. IR (KBr): 3086, 3026, 2956, 2921, 1712, 1629, 1590, 1465, 1445, 1206, 1248, 1184, 1079, 1055, 950, 815, 754, 696. ^{1}H-NMR (250 MHz): 5.70 (*s*, 2 H); 6.44 (*d*, *J* = 10.0, 1 H); 7.17 (*dd*, *J* = 3.5, 5.1, 1 H); 7.30–7.70 (*m*, 15 H); 7.89 (*d*, *J* = 8.9, 1 H); 8.10 (*d*, *J* = 8.9, 1 H); 8.20 (*dd*, *J* = 1.7, 8.9, 1 H). ^{13}C-NMR (62.5 MHz): 61.09 (CH_2O); 83.02 (C); 113.92 (C); 119.07 (CH); 119.21 (CH); 121.55 (CH); 124.91 (C); 126.18 (CH); 126.89 (2 CH); 127.01 (4 CH); 127.72 (2 CH); 128.03 (CH); 128.21 (5 CH); 128.31 (C); 131.42 (CH); 131.90 (CH); 132.23 (C); 138.19 (C); 144.61 (2 C); 152.62 (C); 166.42 (C=O). Anal. calc. for $C_{31}H_{22}O_3S$: C 78.45, H 4.67, S 6.8; found: C 78.41, H 4.72, S 6.9.

*(2,2'-Bithiophen-5-yl)methyl 3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran-8-carboxylate* (**20**): reaction time 3 d, yield 54%. M.p. 111–112°. IR (KBr): 3059, 3027, 2951, 1714, 1628, 1589, 1492, 1467, 1447, 1381, 1275, 1248, 1207, 1186, 1091, 1080, 1008, 951, 839, 806, 755, 697. ^{1}H-NMR (250 MHz): 5.30 (*s*, 2 H); 6.08 (*d*, *J* = 10.0, 1 H); 6.70–7.40 (*m*, 17 H); 7.55 (*d*, *J* = 8.9, 1 H); 7.80 (*AB*, J_{AB} = 8.8, $\Delta\nu$ = 22.7, 2 H); 8.28 (br. *s*, 1 H). ^{13}C-NMR (62.5 MHz): 61.27 (CH_2O): 83.05 (*q*); 113.95 (*q*); 119.10 (CH); 119.26 (CH); 121.62 (CH); 123.32 (CH); 124.05 (CH); 124.76 (CH); 124.84 (*q*); 126.19 (CH); 127.03 (4 CH); 127.75 (2 CH); 127.89 (CH); 128.05 (CH); 128.24 (4 CH); 128.35 (*q*); 129.07 (CH); 131.47 (CH); 131.97 (CH); 132.29 (*q*); 137.09 (*q*); 137.14 (*q*); 139.04 (*q*); 144.63 (2*q*); 152.67 (*q*); 166.47 (C=O). Anal. calc. for $C_{35}H_{24}O_3S_2$: C 75.51, H 4.34, S 11.5; found: C 75.28, H 4.32, S 11.4.

*(2,2':5',2''-Terthiophen-2-yl)methyl 3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran-8-carboxylate* (**21**): reaction time 3 d, yield 63%. M.p. 138–139°. IR (KBr): 3065, 3029, 2926, 1715, 1627, 1492, 1468, 1447, 1380, 1275, 1247, 1208, 1186, 1091, 1081, 1007, 950, 837, 796, 756, 699. ^{1}H-NMR (250 MHz): 5.32 (br. *s*, 2 H); 6.11 (*d*, *J* = 10.0, 1 H); 6.80–7.40 (*m*, 19 H); 7.58 (*d*, *J* = 8.9, 1 H); 7.83 (*AB*, J_{AB} = 8.9, $\Delta\nu$ = 20.0, 2 H); 8.30 (br. *s*, 1 H). ^{13}C-NMR (62.5 MHz): 61.48 (CH_2O); 83.23 (*q*): 114.20 (*q*); 119.34 (CH); 119.49 (CH); 121.87 (CH); 123.47 (CH); 124.07 (CH); 124.62 (CH); 124.85 (CH); 124.88 (CH); 125.04 (*q*); 126.42 (CH); 127.27 (4 CH); 128.00 (2 CH); 128.20 (CH); 128.29 (4 CH); 128.49 (CH); 128.58 (*q*); 129.38 (CH); 131.71 (CH); 132.22 (CH); 132.53 (CH); 136.09 (*q*); 136.82 (*q*); 137.29 (*q*); 137.44 (*q*); 138.96 (*q*); 144.88 (2*q*); 152.92 (*q*); 166.70 (C=O). Anal. calc. for $C_{39}H_{26}O_3S_3$: C 73.32, H 4.10, S 15.0; found: C 73.25, H 4.13, S 14.7.

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