Synthesis of New Thiophene-Substituted 3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyrans by Cross-Coupling Reactions, Precursors of Photomodulated Materials

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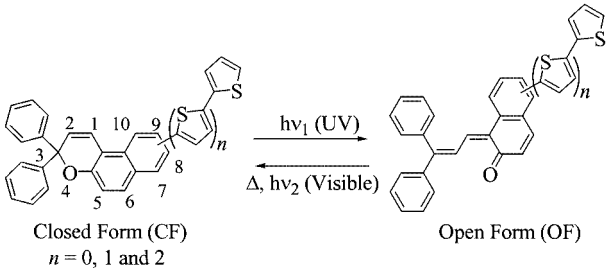
3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyrans linked to one, two, or three thiophene nuclei in different positions of the naphthalene moiety (5, 6, 8, and 9) by a covalent bond have been prepared in good yields. A Suzuki cross-coupling reaction was used with two possible strategies: chromenization before the coupling with oligothiophenes or chromenization after the coupling, the main intermediates being the diphenyl propargylic alcohol, the functionalized naphthol derivatives, and the thiophenic boronates. The overall yields for obtaining such photochromic compounds are generally quite satisfying. For the 7-position, the coupling reaction has been realized using a Grignard reaction between a tetralone derivative and a thiophenic bromo magnesium intermediate.

Introduction

In the last decade, the design and synthesis of organic molecular materials, whose structure and macroscopic properties can be controlled by external triggers, has become a challenging topic of multidisciplinary research. This considerable research effort is justified by the potential applications of these materials in emerging opto-electronic and photonic technologies.[1] In this context, a photochromic system, working through an external light stimulus, can be the basic unit for a molecular switch.[2] Then, under appropriate light irradiation, intrinsic changes of the geometry and polarity of the chromophoric entity can lead to a topological change of an attached molecular system, modifying in turn the physical properties of the material under consideration.[3−5] So, our attention has been focused on the synthesis of 3*H*-naphtho[2,1-*b*]pyrans (or, 2*H*-chromenes) linked to a thiophene moiety, because first, this family of organic pigments exhibits interesting photochromic properties[6,7] (good fatigue resistance, wide range of absorption in the visible region) and then, oligothiophenes are well known for their fascinating electronic properties.[8,9] These individual molecules are attractive building blocks for the design of molecular switches on a meso- or macroscopic scale.

Exposure of these naphthopyrans to UV irradiation, either in liquid solution or in a rigid polymer matrix, results in a drastic color change. The naphthopyran closed form absorbs in the UV region and, through excited intermediates, gives cleavage of the Csp^3-O bond and isomerization, leading to a set of quasi-planar open colored forms (photomerocyanines), highly conjugated, absorbing in the visible range. The molecule reverts to its original colorless form either thermally or photochemically[10,11] as depicted in Scheme 1.



Scheme 1. Photochromic equilibrium between Closed Form (CF) and Open Form (OF) (the most stable stereoisomer)

The change from the closed form to open forms results in the expansion of π-electron delocalization over the whole skeleton. The reverse reaction, the closing of the chromene ring, leads to the interruption of conjugation between the left and right sides. This concomitant electronic change can be used to control and modulate the intrinsic electrical conductivity of the molecular system, which depends on the conjugation state. Thus, the tetrahedral carbon atom, which changes its hybridization reversibly from sp^3 to sp^2, allowing or stopping the electron flow between the different parts of the molecular system, plays the role of a switch. Our molecular switches based on oligothiophenes operate at a molecular level, where the photo-switching occurs, in turn resulting in a macroscopic change of the electrical and optical properties.

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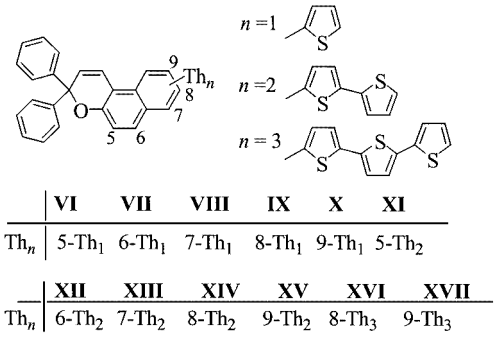
In the present work, we report the synthesis of a series of thiophene-substituted 3*H*-naphtho[2,1-*b*]pyrans, in which the thiophene moiety is linked directly to the naphthopyran photochromic skeleton. The participation of the thiophene entity in the π-electronic delocalization, depending on its linkage to positions 5 to 9 of the naphthalenic nucleus, has been investigated (Scheme 2).



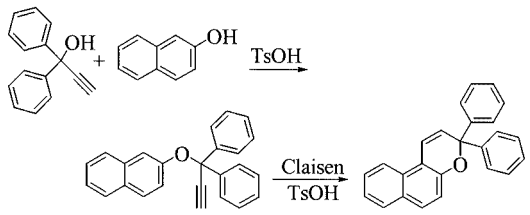
	VI	VII	VIII	IX	X	XI
Th$_n$	5-Th$_1$	6-Th$_1$	7-Th$_1$	8-Th$_1$	9-Th$_1$	5-Th$_2$

	XII	XIII	XIV	XV	XVI	XVII
Th$_n$	6-Th$_2$	7-Th$_2$	8-Th$_2$	9-Th$_2$	8-Th$_3$	9-Th$_3$

Scheme 2. Structures of the target molecules **VI** to **XVII**

Results and Discussion

The building of the 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans can be achieved by a "one-pot reaction" starting from a suitable naphthol and the commercially available 1,1-diphenyl-2-yn-1-ol.[12,13] This condensation reaction takes place in an apolar solvent (toluene, CH_2Cl_2) under acid catalysis[14,15] (Scheme 3). 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.

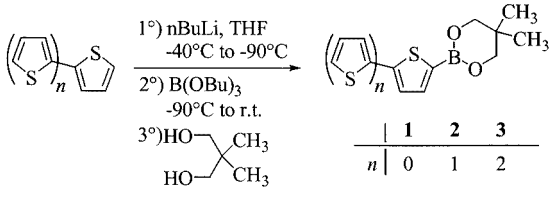


Scheme 3. General synthesis of 3*H*-naphtho[2,1-*b*]pyranic structures

In a previous work,[16] we have shown that the PTSA (*p*-toluenesulfonic acid) originally used, can be advantageously replaced by PPTS[17] (pyridinium *p*-toluenesulfonate), in order to avoid subsequent degradation of the highly acid-sensitive product, and to limit the formation of by-products. Although longer reaction times are required, varying from one to a few days, the yield increases by an average of 20%.

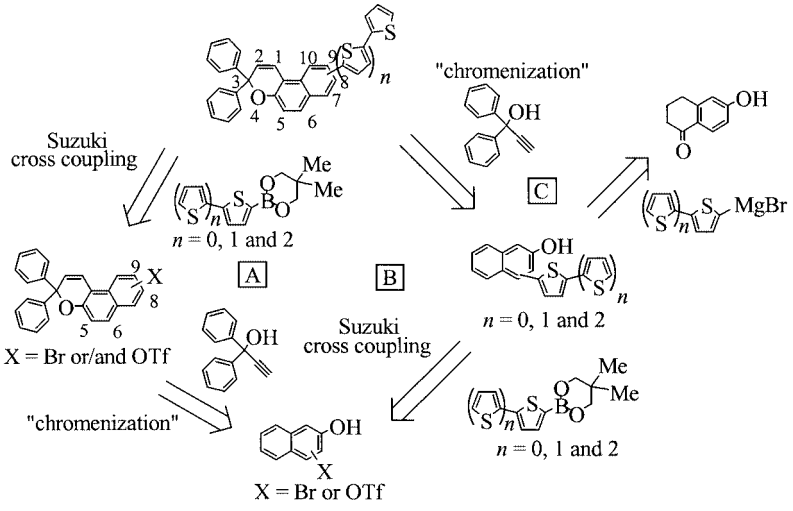
In order to introduce directly the thiophene moiety on positions 5 to 9 of the naphthopyran, three different synthetic approaches (retrosyntheses A, B, and C) have been developed, which are based on a convergent route, as outlined in Scheme 4. Substitution on the 10-position has not been targeted. Indeed, it has been proved that substituents on this position lead to colored forms having very low half-life times due to steric hindrance.[18]

Linkage of the thiophene entity, performed via a Suzuki cross-coupling reaction, can occur after (pathway A) or before (pathway B) the formation of the chromenic structure.



	1	2	3
n	0	1	2

Scheme 5. Synthesis of the thiophene boronates **1**, **2**, and **3**



Scheme 4. Retrosynthetic analysis and strategies for the total synthesis of the target molecules **VI** to **XVII**

A comparison of these two synthetic approaches allowing the linkage of thiophene units on positions 5, 6, 8, and 9 has been performed. Both synthetic routes involve thiophene boronic esters **1**−**3** (Scheme 5) and suitable prefunctionalized naphth-2-ols (**5**, **8**, **9**, **10**, and **11**) as common target building blocks.

Synthesis of thiophenic boronic esters **2** and **3**, requires the preliminary preparation of 2,2′-bithiophen[19] and 2,2′:5′,2′′-terthiophen,[19,20] which are obtained according to literature methods.

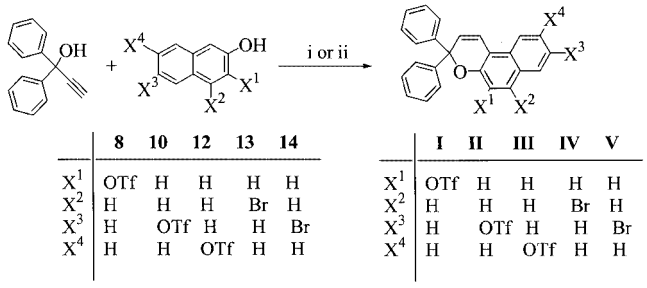
The α-metallation reaction[21] of mono-, bi-, and terthiophene with *n*BuLi, in THF at −40 °C for 1 h, followed by quenching with an excess of tributylborate at −90 °C, resulted in the formation of the crude corresponding boronic esters, not isolated.

Transesterification of these crude intermediates into their cyclic homologues was achieved using an excess of the commercially available 2,2-dimethylpropane-1,3-diol. This reaction proceeds rapidly (15 min) and smoothly at room temperature, in a very simple procedure. Furthermore, it is noteworthy that acidic conditions are never used.

The thiophene boronic esters **1**, **2**, and **3** were conveniently obtained with 92, 86, and 64% yield, respectively. The second key-intermediates needed in both A and B strategies are naphth-2-ols functionalized by a bromine atom or a triflate group. This latest substitution allows the introduction of the thiophene moiety via the Suzuki method, efficient for Csp^2-Csp^2 bond formation.[22,23] Bromonaphth-2-ols are not commercially available, except for 6-bromonaphth-2-ol. The preparation of these bifunctional key intermediates is generally non-univocal. The purification of crude product is often tricky and the isolated yields are generally moderate to low and fickle. In this context, the chemistry of aryl triflates, which has been extensively explored and applied to a variety of chemical transformations of aromatic compounds,[24] constitutes an alternative solution. Moreover, 2,3-dihydroxynaphthalene (**4**), 2,6-dihydroxynaphthalene (**5**), and 2,7-dihydroxynaphthalene (**6**) are commercially available. Triflation of **4**, **5**, and **6** with triflic anhydride, carried out at 0 °C in pyridine,[25] afforded the required monotriflated naphth-2-ols, together with the corresponding ditriflates (Scheme 6).

The mixture of these two products was easily purified via column chromatography on silica gel. The triflated naphthols were obtained in variable yield ranging from 24 to 48%. Attempts to optimize the yield of triflated naphth-2-ol by modifying the reaction temperature and the concentrations were unsuccessful. Independently of the selected synthetic pathway (A or B), the triflated naphth-2-ols **8**, **10**, and **12** allow the introduction of the thiophene entity on positions 5, 8, and 9 of the chromenic structure, respectively.

As for the 6-position, the preparation of 4-bromonaphth-2-ol or its triflated homologue was essential, so 4-bromonaphth-2-ol was prepared from 1-naphthylamine in three steps[26] and 49% overall yield, according to a literature procedure. The previous triflated and brominated naphth-2-ols were subsequently involved in the standard chromenization procedures as outlined in Scheme 7.



	8	10	12	13	14
X^1	OTf	H	H	H	H
X^2	H	H	H	Br	H
X^3	H	OTf	H	H	Br
X^4	H	H	OTf	H	H

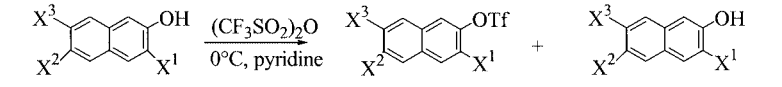
	I	II	III	IV	V
X^1	OTf	H	H	H	H
X^2	H	H	H	Br	H
X^3	H	OTf	H	H	Br
X^4	H	H	OTf	H	H

(i) PPTS, CH_2Cl_2, Δ or (ii) PTSA, CH_2Cl_2, r.t.

Scheme 7. Preparation of the chromeric key intermediates **I** to **V**

The photochromic compounds **I**−**V** were obtained in satisfactory yields, varying between 66 and 80%, from condensation of triflated or brominated naphth-2-ol with the commercially available 1,1-diphenyl-2-yn-1-ol. The reaction was monitored by TLC and was stopped when one of the starting materials had been consumed. For monotriflated naphthols (**8**, **10**, and **12**), the reaction proceeds in refluxing dichloromethane, in the presence of a catalytic amount of PTSA, for five days. For both brominated naphthols (**13** and **14**), the condensation takes place at room temperature. The use of PTSA instead of PPTS, brings down the reaction time to 2 h. After successfully accomplishing the synthesis of key intermediates **1**−**3** and **I**−**V**, our attention turned towards the Suzuki cross-coupling reaction, which constitutes the ultimate step of synthetic path A (Scheme 8).

The palladium-catalyzed cross-coupling reaction of triflated and brominated intermediates with thiophene boronic ester, under classic Suzuki conditions,[22b] was investigated by using tetrakis(triphenylphosphane)palladium (5 mol %) and anhydrous K_3PO_4 as base. The reaction was



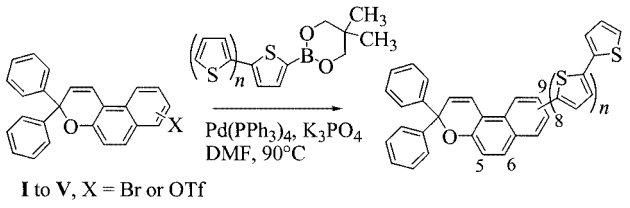
	4	5	6
X^1	OH	H	H
X^2	H	OH	H
X^3	H	H	OH

	7	9	11
X^1	OTf	H	H
X^2	H	OTf	H
X^3	H	H	OTf

	8	10	12
X^1	OTf	H	H
X^2	H	OTf	H
X^3	H	H	OTf

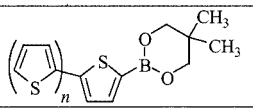
Scheme 6. Preparation of the monotriflated naphthols **8**, **10**, and **12**

performed in DMF at 90 °C for 15 h. The results are summarized in Table 1.



Scheme 8. Suzuki cross-coupling reaction of prefunctionalized 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans (**I** to **V**) with thiophene boronates

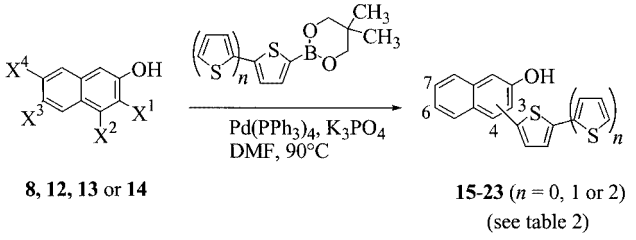
Table 1. Yields in the synthesis of 3*H*-naphtho[2,1-*b*]pyrans **VI** to **XVII**

Entry	Starting materials		Product and Yield[a] [%]
1	**I** (5-OTf)	**1** (n = 0)	**VI** (87)
2	**I** (5-OTf)	**2** (n = 1)	**XI** (82)
3	**IV** (6-Br)	**1** (n = 0)	**VII** (38)
4	**IV** (6-Br)	**2** (n = 1)	**XII** (42)
5	**II** (8-OTf)	**1** (n = 0)	**IX** (94)
6	**II** (8-OTf)	**2** (n = 1)	**XIV** (88)
7	**II** (8-OTf)	**3** (n = 2)	**XVI** (64)
8	**V** (8-Br)	**1** (n = 0)	**IX** (89)
9	**V** (8-Br)	**2** (n = 1)	**XIV** (86)
10	**V** (8-Br)	**3** (n = 2)	**XVI** (54)
11	**III** (9-OTf)	**1** (n = 0)	**X** (81)
12	**III** (9-OTf)	**2** (n = 1)	**XV** (83)
13	**III** (9-OTf)	**3** (n = 2)	**XVII** (65)

[a] All the yields are for pure, isolated products.

According to data reported in this table, except for the 6-position (entries 3 and 4), the linkage of the thiophene and bithiophene moiety to the prefunctionalized 3*H*-naphtho[2,1-*b*]pyrans, was accomplished efficiently, the yield varying from 81 to 94%. Although the reactivity of electrophiles towards organoboron compounds decreases in the order R−Br > R−OTf,[24b] the obtained yields in coupling products (entries 5, 6, 8, and 9) did not vary in a significant way. By comparison with their thiophene and bithiophene homologues, the terthiophene-substituted 3*H*-naphtho[2,1-*b*]pyrans **XVI** and **XVII** are obtained in moderate yields. This high decrease in yield is attributed to the low solubility of the formed products. We note that compounds **XVI** and **XVII** do not exhibit photochromic properties. The introduction of a terthiophene moiety onto the right side, which brings about a too-large extension of the π-system, inhibits the photoreactivity of the naphthopyran unit (C−O bond breaking) and favors the luminescence: fluorescence is qualitatively observed. A similar result had been already observed, when a terthiophene entity is introduced onto the 8-position of the naphthalenic nucleus via an acetylenic junction.[27] Thus, the introduction of an oligothiophene attached to the naphthalenic nucleus must be restricted to a bithiophen if the photochromic properties have to be retained.

Naphthopyran-linked thiophene or oligothiophenes on positions 5, 6, 8, and 9 have, for comparison, also been synthesized via retrosynthesis B (Scheme 4). This convergent synthetic strategy involves the grafting of the thiophene moiety onto the prefunctionalized naphthols **8**, **12**, **13**, and **14** previously synthesized (Scheme 9), just before the final step of chromenization.

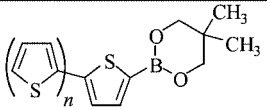


Scheme 9. Synthesis of thiophenic naphth-2-ols via the Suzuki cross-coupling reaction

The results are collected in Table 2.

Except for brominated naphth-2-ol **13** (entries 3 and 4), the coupling products were obtained in excellent yields, ranging from 78 to 89%. Surprisingly, product **21** (entry 7), bearing a terthiophene entity was isolated in a yield of 81%. For compound **13** (entries 3 and 4), the coupling products are obtained in moderate yields of 54 and 49%, respectively. This decrease in yield is similar to the one observed during the coupling reaction of prefunctionalized 3*H*-naphtho[2,1-

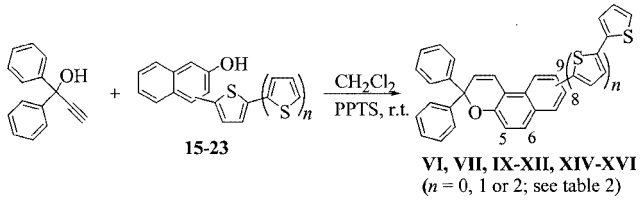
Table 2. Yields in the synthesis of the thiophene naphthols and of the 3*H*-naphtho[2,1-*b*]pyrans

Entry	Starting triflated or brominated naphthol		Product and cross-coupling yield [a][%]	Product and chromenization yield [a][%]
1	**8**	**1** (n = 0)	**15** (89)	**VI** (62)
2	**8**	**2** (n = 1)	**16** (84)	**XI** (47)
3	**13**	**1** (n = 0)	**17** (54)	**VII** (58)
4	**13**	**2** (n = 1)	**18** (49)	**XII** (51)
5	**14**	**1** (n = 0)	**19** (88)	**IX** (62)
6	**14**	**2** (n = 1)	**20** (78)	**XIV** (22)
7	**14**	**3** (n = 2)	**21** (81)	**XVI** (9)
8	**12**	**1** (n = 0)	**22** (86)	**X** (59)
9	**12**	**2** (n = 1)	**23** (82)	**XV** (54)

[a] All the yields are for pure, isolated products.

b]pyrans (Table 1, entries 3 and 4). These results suggest that the α-position of the naphthalenic nucleus is less reactive than the β- position, the oxidative addition step being more difficult. The Suzuki cross-coupling reaction is an efficient method for Csp^2-Csp^2 bond formation, perfectly compatible with the presence of a free hydroxyl group.

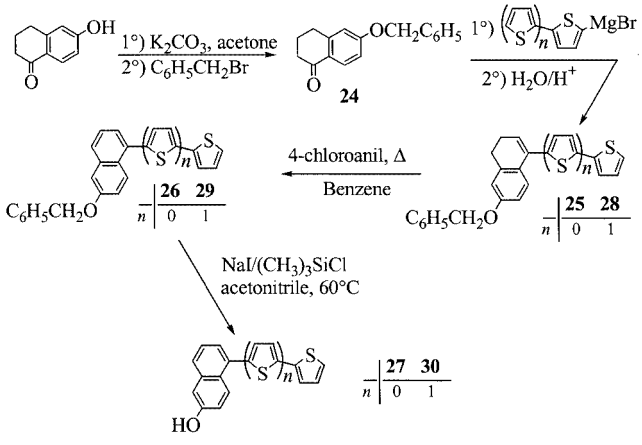
The key intermediates **15**−**23** were condensed with commercially available 1,1-diphenyl-2-yn-1-ol. PTSA cannot be used as catalyst: in these experimental conditions, the expected products are formed, but they were gradually degraded. When the starting materials had been totally consumed, only decomposition products were obtained. In contrast, the reaction works using the less-acidic pyridinium salt of PTSA (Scheme 10).



Scheme 10. Chromenization of thiophenic naphth-2-ols with 1,1-diphenyl-2-yn-1-ol

As can be seen from Table 2, the photochromic compounds bearing a mono- or bithiophene were isolated in low to moderate yield, varying from 22 to 62%. The terthiophene compound **XVI** was obtained in very low yield (9%). This result is attributed to the poor solubility of the starting naphthol.

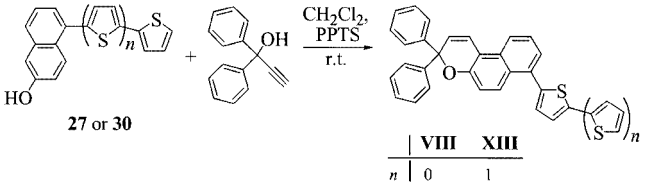
The attachment of a mono or bithiophene moiety to the 7-position of the photochromic structure, has been performed via retrosynthetic pathway C (Scheme 4). This convergent synthetic strategy, required the preparation of two key intermediates **27** and **30** (Scheme 11).



Scheme 11. Synthesis of the thiophene naphth-2-ols **27** and **30**

The synthesis of **27** and **30** from commercially available 6-hydroxy-1-tetralone, were carried out in four steps with overall yields of 56 and 58%, respectively. Conversion of 6-hydroxy-1-tetralone to its benzyl ether was efficiently accomplished in 92% yield, by treatment with benzyl bromide and K_2CO_3 in refluxing acetone.[28] The reaction of (thiophen-2-yl)magnesium bromide[19d] and of (2,2′-bithien-5-yl)magnesium bromide[20a] with **24**, followed by acid hydrolysis[29] afforded **25** and **28** in over 80% yield. Subsequent oxidation of **25** and **28** with an excess of 4-chloroanil,[30] in refluxing benzene, gave **26** and **29** in high yields. The benzyl group was removed by treatment with $(CH_3)_3SiCl/NaI$ in acetonitrile[31] at 60 °C, to lead to the key derivatives **27** and **30** in yields of 82 and 88% respectively.

The target molecules **VIII** and **XIII** were synthesized (in yields over 60%) respectively by condensation of **27** or **30** with 3,3-diphenylprop-1-yn-3-ol in dry CH_2Cl_2, at room temperature, in the presence of a catalytic amount of PPTS (Scheme 12).



Scheme 12. Synthesis of the target molecules **VIII** and **XIII**

Conclusion

We have described different synthetic approaches, via coupling reactions to naphtho[2,1-*b*]pyrans bearing one, two, or three thiophene units on different positions of the naphthalenic ring. Access to naphthopyrans substituted on the 5, 6, 8, or 9 positions has been achieved using Suzuki cross-coupling reactions. Of the two different ways investigated, pathway A (the chromenization reaction before the coupling reaction) showed undoubtedly better results than pathway B (the coupling reaction before the chromenization reaction). For substitution on the 7-position of the naphthopyran, the final cyclization to a pyran ring is "essential", but in this case the thiophene-linked naphthol was obtained through a Grignard reaction.

Most of the prepared compounds show photochromic behavior under UV irradiation as well in solutions as in a polymeric matrix. In recent papers we described the spectroscopic properties (absorption, emission)[32] and the photochromic characteristics[33] of compounds **IX**, **XIV**, **XVI**, and **XVII**. It has been demonstrated that the photochromic properties strongly depend on the number and position of the thienyl units. For instance, the switching wavelengths (from closed to open forms) range from 346 nm to 397 nm, the absorption of the colored forms ranges from 470 nm to 520 nm and an important observation concerns the lack of photochromism when a terthienyl group is linked either on the 8 or on the 9-position. In these last cases (**XVI** and **XVII**), the fluorescence of the oligothiophenic substituent totally inhibits the photochromic process.

The set of described compounds including one or two thiophene units, are good candidates for the design of molecular optical switches devoted to photomodulation of the electric properties of conducting materials.

Experimental Section

General Remarks: Melting points were determined in capillary tubes on a Buchi 510 apparatus and are uncorrected. Glassware used in the reactions described below was dried for a minimum of 12 h in an oven at 120 °C. All reactions were performed in standard glassware under an inert atmosphere of Ar. A positive pressure of Ar was essential to the success of all Pd-catalyzed reactions. Degassing of solvents was accomplished by vigorously bubbling Ar through the solution for at least 40 min. Fourier transform IR spectra were recorded on a Matson Polaris spectrophotometer from samples as KBr pellets or as solutions in CCl_4. The frequencies of band positions are given in cm^{-1} ($\tilde{\nu}$). Nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded on either a Bruker AC250 (250 and 62.5 MHz, respectively), or a Bruker AMX400 (400 and 100 MHz, respectively) spectrometer. Chemical shifts are reported in parts per million (δ) relative to the nondeuterated solvent peak. Coupling constants (*J* values) are expressed in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), br. s (broad singlet). Elemental analyses were performed on an LECO-932-CNS analyzer.

Column chromatography was carried out using silica gel 60 230−400 mesh (Merck & Co.). Silica TLC was conducted on precoated aluminum sheets (60 F_{254}) with a 0.2 mm thickness (Aldrich Chemical Co.).

Chemicals: THF and Et_2O were distilled prior to use from sodium benzophenone ketyl under argon, while dichloromethane (CH_2Cl_2) was distilled from calcium hydride, and stored over 3-Å molecular sieves. Benzene, acetonitrile, pyridine, and DMF were purchased from S.D.S. Chemicals Co. and used as supplied. 2,2′-bithiophen[19] and 2,2′:5′,2′′-terthiophen[19,20] were synthesized according to the literature procedure. 4-bromonaphth-2-ol was prepared by standard methods[26] from 1-naphthylamine (three steps, 49% overall yield).

Commercial [$Pd(PPh_3)_4$] was purchased from Strem and used as received.

General Procedure (1) for the Synthesis of Thiopheneboroxines 1, 2, and 3: A stirred solution of thiophenic compound (30 mmol) in anhydrous THF (120 mL) under an Ar atmosphere was cooled to −40 °C. A 2.5 M solution of *n*BuLi in hexane (13.25 mL, 31.5 mmol) was added dropwise, and the solution was stirred at −40 °C for 1 h. The solution was cooled to −90 °C, and tributylborate (20 mL, 90 mmol) was added rapidly via syringe. The resulting solution was maintained at −90 °C for 1 h, and then allowed to warm to room temperature. 2,2-dimethylpropane-1,3-diol (15.62 g, 150 mmol) was then added, and the resulting mixture stirred for a further 15 min. The reaction was quenched with water (100 mL), and extracted with benzene (4 × 50 mL). The combined organic layers were washed well with brine (3 × 100 mL), dried ($MgSO_4$), and the solvents were evaporated. Details for purification and data of the individual compounds are given below.

As a consequence of incomplete decoupling of the B−C spin-spin coupling by ^{11}B (or ^{10}B) quadrupolar relaxation,[34] the signal of carbon bonded to the boron atom, which should be very broad, was not observed.

General Procedure (2) for the Preparation of Monotriflated Naphthols 8, 10 and 12: Trifluoromethanesulfonic anhydride (2.1 mL, 12 mmol) was added dropwise over a 10 min period to a stirred solution of dihydroxynaphthalene (2 g, 12 mmol) in dry pyridine (20 mL) at 0 °C under Ar. The purple mixture was then warmed to room temperature, and stirring was continued for 16 h. The reaction mixture was poured onto ice-cooled water (30 mL), and extracted with diethyl ether (3 × 20 mL). The organic layers were combined, washed with 1 N aqueous HCl (2 × 25 mL), water (3 × 20 mL), and brine (3 × 20 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (SiO_2; Et_2O/cyclohexane gradient 100:0 to 60:40 furnished, by order of elution, the bitriflated naphthol followed by the monotriflated naphthol.

General Procedure (3) for the Synthesis of Triflated Naphthopyrans I, II, and III: A round-bottomed flask, equipped with a magnetic stirrer and a reflux condenser, was charged with triflic naphthol (1.50 g, 5.1 mmol), 3,3-diphenylprop-1-yn-3-ol (1.17 g, 5.6 mmol), a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS), and dry dichloromethane (15 mL), purged with Ar and stirred for five days in an oil bath at 70 °C. The progress of the reaction was monitored by TLC (pentane/diethyl ether, 1:1). The reaction mixture was allowed to come to ambient temperature. The solvent was removed under reduced pressure and the solution concentrated to dryness. The crude material was purified by column chromatography and recrystallization to afford the product. Details for purification and data of the individual compounds are given below.

For compounds **I**, **II**, and **III**, the signal of the quaternary carbon bonded to fluorine atoms does not appear under registration conditions.

General Procedure (4) for the Synthesis of Brominated Naphthopyrans IV and V: A 50-mL round-bottomed flask was charged with 3,3-diphenylprop-1-yn-3-ol (2.46 g, 11 mmol), the appropriate bromonaphthol (2.08 g, 10 mmol) (4-bromonaphth-2-ol or 6-bromonaphth-2-ol), a catalytic amount of *p*-toluenesulfonic acid (PTSA), and anhydrous dichloromethane (20 mL), purged with Ar and stirred at room temperature. The reaction was monitored by TLC (pentane/Et_2O, 1:1) and was judged complete after 12 h. The reaction mixture was washed with 5% w/v aqueous $NaHCO_3$ solution (2 × 20 mL) and brine (2 × 20 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated to dryness under reduced pressure. The crude material was purified by column chromatography and recrystallization to afford the product. Details for purification and data of the individual compounds are given below.

General Procedure (5) for the Suzuki Cross-coupling Reaction, Synthesis of VI to XVII: A 15-mL round-bottomed flask, equipped with a reflux condenser, a septum inlet and a magnetic stirrer bar, was charged with triflated or brominated naphthopyran (1 mmol), the glycol ester of the appropriate boronic acid (1.2 mmol), $Pd(PPh_3)_4$ (58 mg, 5×10^{-2} mmol), K_3PO_4 (318 mg, 1.5 mmol), and dry degassed DMF (6−8 mL), and purged with Ar. The reaction mixture was heated at 110 °C in an oil bath for 15 h, cooled to ambient temperature, and then quenched by addition of saturated aqueous NH_4Cl (8 mL). The resulting mixture was filtered through a Celite pad, the filter cake being thoroughly rinsed with benzene (2 × 10 mL). The organic layer was separated, and the aqueous layer was extracted with benzene (2 × 10 mL). The organic layers were combined, washed with brine (4 × 15 mL), and dried with $MgSO_4$. The solvent was removed under reduced pressure to give

a crude solid residue, which was subjected to column chromatography. Details for purification by column chromatography and recrystallization, together with the data for the individual compounds, are given below.

General Procedure (6) for the Synthesis of Thiophenic Naphthols 15 to 24: Triflic or brominated naphthol (1 mmol), the glycol ester of the appropriate boronic acid (1.2 mmol), $Pd(PPh_3)_4$ (58 mg, $5\cdot10^{-2}$ mmol), and K_3PO_4 (318 mg, 1.5 mmol) were placed in a 20-mL round-bottomed flask fitted with a condenser. The system was flushed with Ar and dry degassed DMF (15 mL) was added via syringe to the flask. This heterogeneous mixture was stirred at 100 °C, under an Ar atmosphere for 20 h. After cooling, the crude reaction was filtered through a plug of Celite, the filter cake being thoroughly rinsed with benzene (2 × 15 mL), and washed with saturated NaCl solution. The organic layer was dried with $MgSO_4$ and the solvent was removed in vacuo. The resulting residue was subjected to column chromatography to yield the cross-coupling product as a powdery colored solid.

Details for purification, together with the data for the individual compounds, are given below.

General Procedure (7) of "Chromenization" from Thiophene Naphthol: A 50-mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser, was charged with the thiophenic naphthol (10 mmol), 3,3-diphenylprop-1-yn-3-ol (2.30 g, 11 mmol), a catalytic amount of pyridinium toluene-*p*-sulfonate (PPTS), and dry dichloromethane (20 mL), purged with Ar and refluxed for 3−6 days. The progress of the reaction was monitored by TLC (pentane/Et_2O, 1:1). After complete disappearance of the thiophenic naphthol, the reaction mixture was cooled to ambient temperature and the solvent was removed under reduced pressure. The crude material was purified by column chromatography and recrystallization to yield the product. Details for purification and data of the individual compounds are given below.

5,5-Dimethyl-2-thien-2-yl[1,3,2]dioxoborinane (1): This compound was prepared by General Procedure (1), starting from thiophene (2.52 g, 30 mmol). Purification by column chromatography of the concentrate (SiO_2; eluent: pentane/dichloromethane, 4:1) yielded the pure compound **1** (5.40 g, 27.56 mmol, 92%) as a white powder; m.p. 96 °C. IR (KBr): ṽ = 3110, 2970, 2959, 2873, 1517, 1480, 1422, 1378, 1365, 1345, 1283, 1254, 1107, 1043, 918, 850, 812, 738, 696, 660 cm^{-1}. ^1H NMR (250 MHz, [D$_6$]benzene): δ = 0.65 (s, 6 H), 3.46 (s, 4 H), 7.01 (dd, *J* = 3.4, 4.7 Hz, 1 H), 7.36 (dd, *J* = 0.9, 4.7 Hz, 1 H), 8.05 (dd, *J* = 0.9, 3.4 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]benzene): δ = 21.8 (2 × CH_3−), 31.9 (C), 72.3 (2 × −OCH_2−), 128.0 (−CH=), 131.2 (−CH=), 135.5 (−CH=) ppm. $C_9H_{13}BO_2S$: C 55.13, H 6.68, S 16.3; found C 55.14, H 6.62, S 16.1.

5,5-Dimethyl-2-(2,2′-bithien-5-yl)[1,3,2]dioxoborinane (2): This compound was prepared by General Procedure (1), starting from 2,2′-bithiophene (4.98 g, 30 mmol). Purification by column chromatography of the concentrate (SiO_2; pentane/dichloromethane, 4:1) yielded the pure compound **2** (7.17 g, 25.8 mmol, 86%) as a pale-greenish powder, m.p. 80−81 °C. IR (KBr): ṽ = 3074, 2959, 2933, 2901, 2873, 1537, 1511, 1480, 1457, 1419, 1375, 1369, 1333, 1317, 1298, 1254, 1242, 1109, 1075, 1047, 901, 843, 828, 809 cm^{-1}. ^1H NMR (250 MHz, [D$_6$]benzene): δ = 0.71 (s, 6 H), 3.49 (s, 4 H), 6.77 (dd, *J* = 3.6, 5.1 Hz, 1 H), 6.85 (dd, *J* = 1.1, 5.1 Hz, 1 H), 7.23 (dd, *J* = 1.1, 3.6 Hz, 1 H), 7.30 (d, *J* = 3.5 Hz, 1 H), 7.93 (d, *J* = 3.5 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]benzene): δ = 21.9 (2 × CH_3−), 32.1 (C), 72.4 (2 × −OCH_2−), 124.1 (−CH=), 124.7 (−CH=), 124.9 (−CH=), 127.9 (−CH=), 136.4 (−CH=), 137.6 (C), 143.1 (C) ppm. $C_{13}H_{15}BO_2S_2$: C 56.12, H 5.43, S 23.0; found C 56.13, H 5.47, S 22.9.

5,5-Dimethyl-2-(2,2′:5′,2"-terthien-5-yl)[1,3,2]dioxoborinane (3): This compound was prepared by General Procedure (1), starting from 2,2′:5′,2′′-terthiophene (7.44 g, 30 mmol). Purification by column chromatography (SiO_2; pentane/dichloromethane, 4:1) yielded the pure compound **3** (6.91 g, 19.2 mmol, 64%) as a pale-greenish powder, m.p. 174 °C. IR (KBr): ṽ = 3106, 3072, 3061, 2957, 2938, 2899, 2872, 1531, 1504, 1479, 1463, 1445, 1416, 1374, 1365, 1337, 1301, 1274, 1255, 1240, 1106, 1065, 1047, 867, 837, 828, 802 cm^{-1}. ^1H NMR (250 MHz, [D$_6$]benzene): δ = 0.82 (s, 6 H), 3.55 (s, 4 H), 6.80 (dd, *J* = 3.7, 5.1 Hz, 1 H), 6.86 (d, *J* = 3.8 Hz, 1 H), 6.91 (d, *J* = 3.8 Hz, 1 H), 6.96 (dd, *J* = 3.7, 1.0 Hz, 1 H), 6.97−7.02 (m, 2 H), 7.24 (d, *J* = 3.6 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]benzene): δ = 21.9 (2 × CH_3−), 32.1 (C), 72.4 (2 × −OCH_2−), 123.8 (−CH=), 124.4 (−CH=), 124.5 (−CH=), 124.7 (−CH=), 124.8 (−CH=), 127.9 (−CH=), 136.4 (C), 136.5 (−CH=), 136.6 (C), 137.1 (C), 142.7 (C) ppm. $C_{17}H_{17}BO_2S_3$: C 56.66, H 4.75, S 26.7; found C 56.55, H 4.74, S 26.7.

Naphthalene-2,3-diyl Bis(trifluoromethanesulfonate) (7): This compound was obtained by General Procedure of triflation (2), as a by-product in the synthesis of **8**, in 31% yield (1.57 g, 3.70 mmol) as white spangles, m.p. 83.5 °C. IR (KBr): ṽ = 3072, 1601, 1513, 1466, 1434, 1253, 1231, 1212, 1140, 1130, 1054, 905, 900, 884, 827, 757, 686, 610 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 6.3 Hz, 1 H), 7.49 (d, *J* = 6.3 Hz, 1 H), 7.70−7.76 (m, 4 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 118.9 (q, $J_{C,F}$ = 320.9 Hz, 2 × C), 122.4 (2 × −CH=), 128.3 (2 × −CH=), 129.0 (2 × −CH=), 132.0 (2 × C), 138.2 (2 × C) ppm. $C_{12}H_6F_6O_6S_2$: C 33.97, H 1.42, S 15.1; found C 33.95, H 1.51, S 15.2.

3-(Trifluoromethylsulfonyl)naphth-2-ol (8): This compound was obtained by General Procedure of triflation (2), from 2,3-dihydroxynaphthalene in 24% yield (840 mg, 2.87 mmol) as a pale-pink powder, m.p. 64−65 °C. IR (KBr): ṽ = 3499, 3063, 3034, 1633, 1605, 1524, 1480, 1414, 1397, 1221, 1211, 1164, 1137, 1074, 924, 880, 803, 752, 619 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 5.64 (br. s, 1 H), 7.47 (s, 1 H), 7.50−7.66 (m, 2 H), 7.82 (d, *J* = 8.5 Hz, 1 H), 7.85 (s, 1 H), 7.89 (d, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 113.4 (−CH=), 119.0 (q, $J_{C,F}$ = 320.6 Hz, C), 121.0 (−CH=), 125.5 (−CH=), 126.6 (−CH=), 127.9 (−CH=), 128.1 (−CH=), 128.4 (C), 133.5 (C), 138.4 (C), 145.5 (C) ppm. $C_{11}H_7F_3O_4S$: C 45.21, H 2.41, S 11.0; found C 45.09, H 2.51, S 10.9.

Naphthalene-2,6-diyl Bis(trifluoromethanesulfonate) (9): This compound was obtained by General Procedure of triflation (2), as a by-product in the synthesis of **10**, in 24% yield (1.22 g, 2.87 mmol) as white spangles, m.p. 83 °C. IR (KBr): ṽ = 3077, 1603, 1513, 1425, 1223, 1200, 1139, 1110, 940, 899, 850 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.40 (dd, *J* = 2.4, 9.0 Hz, 2 H),7.73 (d, *J* = 2.4 Hz, 2 H), 7.88 (d, *J* = 9.0 Hz, 2 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 118.9 (q, $J_{C,F}$ = 320.9 Hz, 2 × C), 119.6 (2 × −CH=), 121.6 (2 × −CH=), 131.0 (2 × −CH=), 132.5 (2 × C), 148.0 (2 × C) ppm. $C_{12}H_6F_6O_6S_2$: C 33.97, H 1.42, S 15.1; found C 33.94, H 1.46, S 14.8.

6-(Trifluoromethylsulfonyl)naphth-2-ol (10): This compound was obtained by General Procedure of triflation (2), from 2,6-dihydroxynaphthalene in 48% yield (1.68 g, 5.74 mmol) as a pale-pink powder, m.p. 80 °C. IR (KBr): ṽ = 3600−3200, 1603, 1527, 1429, 1393, 1254, 1206, 1131, 1108, 938, 893, 805 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 5.48 (s, 1 H), 7.00−7.10 (m, 2 H), 7.18 (dd, *J* = 2.6, 8.9 Hz, 1 H), 7.50−7.58 (m, 2 H), 7.60 (d, *J* = 8.6 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 109.7 (−CH=),

118.8 (q, $J_{C,F}$ = 320.8 Hz, C), 119.2 (−CH=), 119.5 (−CH=), 120.1 (−CH=), 128.5 (C), 128.8 (−CH=), 129.9 (−CH=), 133.7 (C), 145.5 (C), 154.4 (C) ppm. $C_{11}H_7F_3O_4S$: C 45.21, H 2.41, S 11.0; found C 45.12, H 2.44, S 11.2.

Naphthalene-2,7-diyl Bis(trifluoromethanesulfonate) (11): This compound was obtained by General Procedure of triflation (2), as a by-product in the synthesis of **12**, in 27% yield (1.38 g, 3.25 mmol) as white spangles, m.p. 59.5 °C. IR (KBr): $\tilde{\nu}$ = 3093, 1634, 1582, 1513, 1415, 1251, 1216, 1143, 1113, 970, 959, 898, 885, 852, 841 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.40 (dd, *J* = 2.4, 9.1 Hz, 2 H), 7.73 (d, *J* = 2.4 Hz, 2 H), 7.92 (d, *J* = 9.1 Hz, 2 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 119.0 (q, $J_{C,F}$ = 320.8 Hz, 2 × C), 119.7 (2 × −CH=), 121.3 (2 × −CH=), 131.0 (2 × −CH=), 131.5 (C), 133.8 (C), 148.4 (2 × C) ppm. $C_{12}H_6F_6O_6S_2$: C 33.97, H 1.42, S 15.1; found C 33.98, H 1.43, S 15.2.

7-(Trifluoromethylsulfonyl)naphth-2-ol (12): This compound was obtained by General Procedure of triflation (2), from 2,7-dihydroxynaphthalene in 39% yield (1.37 g, 4.68 mmol) as a pale-orange powder, m.p. 55.5−60 °C. IR (KBr): $\tilde{\nu}$ = 3650−3100, 1637, 1584, 1515, 1450, 1421, 1244, 1213, 1140, 1109, 972, 957, 889, 874, 835 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 5.89 (br. s, 1 H), 7.10−7.25 (m, 3 H), 7.53 (d, *J* = 2.4 Hz, 1 H), 7.74 (d, *J* = 8.9 Hz, 1 H), 7.79 (d, *J* = 8.9 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 110.0 (−CH=), 117.2 (−CH=), 117.9 (−CH=), 119.1 (q, $J_{C,F}$ = 320.7, C), 119.3 (−CH=), 128.0 (C), 130.2 (−CH=), 130.7 (−CH=), 135.0 (C); 148.0 (C), 154.8 (C) ppm. $C_{11}H_7F_3O_4S$: C 45.21, H 2.41, S 11.0; found C 45.15, H 2.39, S 10.7.

3-(Thien-2-yl)naphth-2-ol (15): This compound was prepared by General Procedure (6) from **1** (235 mg, 1.20 mmol) and **8** (292 mg, 1.00 mmol). Purification by column chromatography (SiO_2; cyclohexane/Et_2O, 90:10) afforded the pure compound **15** (145 mg, 0.64 mmol, 64%) as a beige solid after recrystallization (cyclohexane/EtOH), m.p. 103 °C. IR (KBr): $\tilde{\nu}$ = 3550−3200, 3100, 1628, 1600, 1510, 1449, 1436, 1398, 1366, 1321, 1260, 1208, 1165, 1122, 1077, 1058, 953, 905, 877, 867, 849, 743, 711 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 5.52 (br. s, 1 H), 7.11 (dd, *J* = 3.6, 5.1 Hz, 1 H), 7.22−7.28 (m, 2 H), 7.31 (dd, *J* = 1.5, 8.5 Hz, 1 H), 7.34−7.41 (m, 2 H), 7.62 (d, *J* = 8.0 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.85 (br. s, 1 H) ppm. ^{13} C NMR (250 MHz, $CDCl_3$): δ = 110.49 (−CH=), 110.50 (−CH=), 123.1 (C), 124.1 (−CH=), 126.1 (−CH=), 126.7 (−CH=), 126.8 (−CH=), 127.8 (−CH=), 128.0 (−CH=), 128.8 (C), 129.4 (−CH=), 134.2 (C), 138.5 (C), 150.5 (C) ppm. $C_{14}H_{10}OS$: C 74.31, H 4.45, S 14.2; found C 74.29, H 4.40, S 14.1.

3-(2,2′-Bithien-5-yl)naphth-2-ol (16): This compound was prepared by General Procedure (6), from **2** (333 mg, 1.20 mmol) and **8** (292 mg, 1.00 mmol). Purification by column chromatography (SiO_2; CH_2Cl_2) afforded the pure compound **16** (259 mg, 0.84 mmol, 84%) as a beige solid after recrystallization (heptane/THF), m.p. 172 °C. IR (KBr): $\tilde{\nu}$ = 3556−3300, 1621, 1598, 1516, 1497, 1468, 1443, 1423, 1384, 1359, 1338, 1315, 1261, 1181, 1155, 1116, 1066, 869, 841, 800, 746, 695 cm^{-1}. ^1H NMR (250 MHz, [D_6]DMSO): δ = 7.16 (dd, *J* = 3.8, 4.8 Hz, 1 H), 7.32−7.48 (m, 5 H), 7.56 (br. d, *J* = 5.0 Hz, 1 H), 7.76 (br. d, *J* = 8.1 Hz, 1 H), 7.82 (d, *J* = 3.9 Hz, 1 H), 7.92 (br. d, *J* = 8.0 Hz, 1 H), 8.32 (br. s, 1 H), 10.79 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, [D_6]DMSO): δ = 109.6 (−CH=), 122.9 (C), 123.3 (−CH=), 123.6 (−CH=), 123.7 (−CH=), 125.1 (−CH=), 125.4 (−CH=), 126.1 (−CH=), 126.2 (−CH=), 126.6 (−CH=), 127.6 (−CH=), 127.7 (−CH=), 128.3 (−CH=), 133.4 (C), 136.5 (C), 136.6 (C), 137.9 (C), 151.8 (C) ppm. $C_{18}H_{12}OS_2$: C 70.10, H 3.92, S 20.8; found C 70.14, H 3.90, S 20.8.

4-(Thien-2-yl)naphth-2-ol (17): This compound was prepared by General Procedure (6), from **1** (235 mg, 1.20 mmol) and **13** (199 mg, 1.00 mmol). Purification by column chromatography (SiO_2; *n*-pentane/EtOAc, 95:5) afforded the pure compound **17** (122 mg, 0.54 mmol, 54%) as a white solid after recrystallization (heptane/Et_2O), m.p. 69 °C. IR (KBr): $\tilde{\nu}$ = 3450−3100, 3061, 1630, 1606, 1564, 1506, 1435, 1374, 1348, 1278, 1228, 1171, 1123, 983, 915, 840, 823, 760, 739 cm^{-1}. ^1H NMR (250 MHz, [D_6]DMSO): δ = 7.31 (dd, *J* = 3.8, 5.0 Hz, 1 H), 7.52−7.75 (m, 7 H), 8.08 (br. s, 1 H), 10.61 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, [D_6]DMSO): δ = 109.6 (−CH=), 123.2 (C), 123.5 (−CH=), 123.7 (−CH=), 125.2 (−CH=), 125.5 (−CH=), 126.3 (−CH=), 126.5 (−CH=), 127.6 (−CH=), 128.7 (−CH=), 133.3 (C), 136.6 (C), 138.6 (C), 152.4 (C) ppm. $C_{14}H_{10}OS$: C 74.31, H 4.45, S 14.2; found C 74.21, H 4.38, S 14.1.

4-(2,2′-Bithien-5-yl)naphth-2-ol (18): This compound was prepared by General Procedure (6), from **2** (333 mg, 1.20 mmol) and **13** (199 mg, 1.00 mmol). Purification by column chromatography (SiO_2; *n*-pentane/EtOAc, 95:5) yielded the pure compound **18** (151 mg, 0.49 mmol, 49%) as a beige solid after recrystallization (heptane/THF), m.p. 97 °C. IR (KBr): $\tilde{\nu}$ = 3450−3110, 3100, 3081, 1621, 1596, 1513, 1451, 1428, 1391, 1372, 1344, 1307, 1275, 1224, 1159, 1138, 1079, 1058, 986, 907, 860, 839, 797, 773, 742, 678 cm^{-1}. ^1H NMR (250 MHz, [D_6]DMSO): δ = 7.22 (dd, *J* = 3.8, 4.8 Hz, 1 H), 7.48−7.65 (m, 7 H), 7.80 (d, *J* = 3.9 Hz, 1 H), 8.19 (br. s, 1 H), 9.89 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, [D_6]DMSO): δ = 109.6 (−CH=), 123.1 (C), 123.4 (−CH=), 123.6 (−CH=), 123.8 (−CH=), 125.1 (−CH=), 125.5 (−CH=), 126.2 (−CH=), 126.4 (−CH=), 126.8 (C), 127.6 (−CH=), 128.0 (−CH=), 128.5 (−CH=), 133.4 (C), 136.7 (C), 136.8 (C), 138.9 (C), 152.7 (C) ppm. $C_{18}H_{12}OS_2$: C 70.10, H 3.92, S 20.8; found C 70.28, H 3.84, S 20.8.

6-(Thien-2-yl)naphth-2-ol (19): This compound was prepared by General Procedure (6), from **1** (235 mg, 1.20 mmol) and **14** (199 mg, 1.00 mmol). Purification by column chromatography (SiO_2; CH_2Cl_2) yielded the pure compound **19** (199 mg, 0.88 mmol, 88%) as a white solid after recrystallization (heptane/Et_2O), m.p. 120 °C. IR (KBr): $\tilde{\nu}$ = 3500−3075, 3067, 1632, 1603, 1573, 1507, 1481, 1449, 1427, 1369, 1244, 1207, 1188, 1151, 959, 904, 887, 878, 868, 853, 812 cm^{-1}. ^1H NMR (250 MHz, [D_6]DMSO): δ = 7.24−7.42 (m, 3 H), 7.57 (dd, *J* = 1.1, 5.1 Hz, 1 H), 7.66 (dd, *J* = 1.1, 3.6 Hz, 1 H), 7.96−8.10 (m, 3 H), 8.18 (s, 1 H), 10.74 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, [D_6]DMSO): δ = 109.0 (−CH=), 117.9 (−CH=), 122.8 (−CH=), 123.6 (−CH=), 125.3 (−CH=), 126.2 (−CH=), 126.4 (−CH=), 127.5 (−CH=), 128.7 (C), 129.8 (−CH=), 132.5 (C), 133.9 (C), 142.6 (C), 156.5 (C) ppm. $C_{14}H_{10}OS$: C 74.31, H 4.45, S 14.2; found C 74.29, H 4.47, S 14.1.

6-(2,2′-Bithien-5-yl)naphth-2-ol (20): This compound was prepared by General Procedure (6), from **2** (333 mg, 1.20 mmol) and **14** (199 mg, 1.00 mmol). Purification by column chromatography (SiO_2; CH_2Cl_2) afforded the pure compound **20** (241 mg, 0.78 mmol, 78%) as yellow crystals after recrystallization (heptane/THF), m.p. 241 °C. IR (KBr): $\tilde{\nu}$ = 3500−3120, 3100, 3061, 1624, 1602, 1569, 1501, 1483, 1452, 1427, 1397, 1366, 1352, 1280, 1257, 1218, 1186, 1155, 1125, 1082, 1066, 1046, 960, 904, 881, 860, 838, 810, 795, 694 cm^{-1}. ^1H NMR (250 MHz, [D_6]DMSO): δ = 6.91−7.34 (m, 7 H), 7.56 (br. s, 2 H), 7.65 (d, *J* = 8.5 Hz, 1 H), 7.89 (br. s, 1 H), 9.72 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, [D_6]DMSO): δ = 109.1 (−CH=), 119.7 (−CH=), 123.6 (−CH=), 124.0 (−CH=), 124.1 (−CH=), 124.3 (−CH=), 125.3 (−CH=), 125.5 (−CH=), 127.1 (−CH=), 127.9 (C), 128.0 (C), 128.6 (−CH=), 129.9 (−CH=), 134.3 (C), 135.5 (C), 136.8 (C), 142.9

(C), 156.1 (C) ppm. $C_{18}H_{12}OS_2$: C 70.10, H 3.92, S 20.8; found C 70.08, H 3.87, S 20.7.

6-(2,2′:5′,2′′-Terthien-5-yl)naphth-2-ol (21): This compound was prepared by General Procedure (6), from **3** (432 mg, 1.20 mmol) and **14** (199 mg, 1.00 mmol). Purification by column chromatography (SiO_2; CH_2Cl_2/Et_2O, 80:20) gave the pure compound **21** (317 mg, 0.81 mmol, 81%) as a yellow solid after recrystallization (heptane/benzene), m.p. 271 °C. IR (KBr): $\tilde{\nu}$ = 3560−3100, 3063, 1729, 1623, 1600, 1576, 1498, 1483, 1438, 1426, 1391, 1376, 1353, 1285, 1207, 1183, 1152, 1134, 1072, 1039, 960, 903, 881, 860, 834, 815, 792, 688 cm^{-1}. ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 7.16 (dd, *J* = 3.8, 4.8 Hz, 1 H), 7.32−7.48 (m, 6 H), 7.56 (br. d, *J* = 5.0 Hz, 1 H), 7.76 (br. d, *J* = 8.1 Hz, 1 H), 7.82 (d, *J* = 3.9 Hz, 2 H), 7.92 (br. d, *J* = 8.0 Hz, 1 H), 8.32 (br. s, 1 H), 10.79 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): δ = 109.6 (−CH=), 122.9 (C), 123.3 (−CH=), 123.6 (−CH=), 123.7 (−CH=), 124.1 (−CH=), 125.1 (−CH=), 125.4 (−CH=), 126.1 (−CH=), 126.2 (−CH=), 126.6 (C), 127.6 (−CH=), 127.7 (−CH=), 128.3 (−CH=), 129.4 (C), 133.4 (C), 136.5 (C), 136.6 (C), 137.9 (C), 151.8 (C) ppm. $C_{22}H_{14}OS_3$: C 67.66, H 3.61, S 24.6; found C 67.58, H 3.70, S 24.7.

7-(Thien-2-yl)naphth-2-ol (22): This compound was prepared by General Procedure (6), from **1** (235 mg, 1.20 mmol) and **12** (292 mg, 1.00 mmol). Purification by column chromatography (SiO_2; cyclohexane/Et_2O, 90:10) gave the pure compound **22** (195 mg, 0.86 mmol, 86%) as a white solid after recrystallization (*n*-pentane/EtOH), m.p. 164 °C. IR (KBr): $\tilde{\nu}$ = 3600−3114, 3095, 1627, 1608, 1576, 1529, 1508, 1471, 1438, 1350, 1362, 1256, 1247, 1223, 1180, 1070, 1050, 963, 886, 847, 829, 809, 750, 703 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 4.95 (s, 1 H), 7.04 (dd, *J* = 2.5, 8.8 Hz, 1 H), 7.09 (dd, *J* = 3.6, 5.1 Hz, 1 H), 7.13 (d, *J* = 2.5 Hz, 1 H), 7.29 (dd, *J* = 1.1, 5.1 Hz, 1 H), 7.40 (dd, *J* = 1.1, 3.6 Hz, 1 H), 7.57 (dd, *J* = 2.0, 8.5 Hz, 1 H), 7.70 (d, *J* = 9.0 Hz, 1 H), 7.74 (d, *J* = 8.8 Hz, 1 H), 7.86 (br ppm. s, 1 H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 108.29 (−CH=), 108.31 (−CH=), 116.4 (−CH=), 121.0 (−CH=), 121.4 (−CH=), 122.2 (−CH=), 123.7 (−CH=), 126.8 (C), 126.9 (C), 127.1 (−CH=), 128.3 (−CH=), 131.1 (C), 133.5 (C), 152.6 (C) ppm. $C_{14}H_{10}OS$: C 74.31, H 4.45, S 14.2; found C 74.22, H 4.37, S 14.0.

7-(2,2′-Bithien-5-yl)naphth-2-ol (23): This compound was prepared by General Procedure (6), from **2** (333 mg, 1.20 mmol) and **12** (292 mg, 1.00 mmol). Purification by column chromatography (SiO_2; heptane/EtOAc, 95:5) yielded the pure compound **23** (253 mg, 0.82 mmol, 82%) as a yellow solid after recrystallization (heptane/Et_2O), m.p. 232 °C. IR (KBr): $\tilde{\nu}$ = 3523, 3105, 3061, 1621, 1600, 1521, 1506, 1451, 1430, 1387, 1367, 1317, 1277, 1249, 1228, 1194, 1177, 1150, 1128, 1065, 1045, 884, 840, 806, 792, 697 cm^{-1}. ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 7.23−7.44 (m, 5 H), 7.61 (d, *J* = 5.0 Hz, 1 H), 7.68−7.78 (m, 2 H), 7.86 (d, *J* = 9.1 Hz, 1 H), 7.91 (d, *J* = 8.8 Hz, 1 H), 8.10 (br. s, 1 H), 10.00 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): δ = 108.8 (−CH=), 118.8 (C), 120.2 (−CH=), 121.6 (−CH=), 123.9 (−CH=), 124.8 (−CH=), 125.0 (−CH=), 125.3 (−CH=), 127.0 (−CH=), 128.2 (−CH=), 128.4 (−CH=), 129.1 (−CH=), 130.8 (C), 134.8 (C), 135.8 (C), 136.3 (C), 142.4 (C), 155.9 (C) ppm. $C_{18}H_{12}OS_2$: C 70.10, H 3.92, S 20.8; found C 70.24, H 3.85, S 20.0.

5-(Thien-2-yl)naphth-2-ol (27): This compound was prepared in four steps (56.5% overall yield) from 6-hydroxy-1-tetralone as follows:

(a) 6-Benzyloxy-1-tetralone (24): A solution of 6-hydroxy-1-tetralone (5 g, 30.8 mmol) and K_2CO_3 (8.29 g, 61.20 mmol) in anhydrous acetone (100 mL) was refluxed for 2 h, benzyl bromide (4.30 mL, 36 mmol) was added via syringe, and the resulting mixture stirred at reflux for a further 3 h. After cooling to room temperature, inorganic salts were filtered off, the filtrate was concentrated and the residue was recrystallized from dichloromethane/heptane to afford **24** (7.78 g, 92%) as pale-yellow crystals, m.p. 98 °C. IR (KBr): $\tilde{\nu}$ = 3072, 3042, 2938, 2870, 1656, 1623, 1599, 1498, 1452, 1432, 1392, 1353, 1323, 1287, 1250, 1189, 1160, 1113, 1067, 998, 927, 896, 872, 826, 764, 724, 708, 698 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.90 (q, *J* = 6.1 Hz, 2 H), 2.40 (t, *J* = 6.1 Hz, 2 H), 2.71 (t, *J* = 6.1 Hz, 2 H), 4.90 (s, 2 H), 6.58 (d, *J* = 2.3 Hz, 1 H), 6.69 (dd, *J* = 2.3, 8.5 Hz, 1 H), 7.12−7.24 (m, 5 H), 7.84 (d, *J* = 8.5 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.6 (−CH_2−), 30.4 (−CH_2−), 39.1 (−CH_2−), 70.3 (−OCH_2−), 113.8 (−CH=), 113.9 (−CH=), 126.8 (C), 127.7 (2 × −CH=), 128.4 (−CH=), 128.9 (2 × −CH=), 129.9 (−CH=), 136.5 (C), 147.2 (C), 162.9 (C), 197.3 (C=O) ppm. $C_{17}H_{16}O_2$: C 80.93, H 6.39; found C 80.91, H 6.39.

(b) 4-(Thien-2-yl)-7-benzyloxy-1,2-dihydronaphthalene (25): Mg turnings (0.46 g, 18.73 mmol) and dry Et_2O (7 mL) were introduced successively to a flask equipped with a magnetic stirrer and a reflux condenser under Ar flow. A solution of 2-bromothiophene (2.9 g, 17.84 mmol) in dry Et_2O (25 mL) was added dropwise. The rate of addition was adjusted so as to maintain the reflux of the reaction mixture. Once the addition was complete, stirring was continued at room temperature for 30 min, the Grignard solution was transferred to the pressure-equalizing dropping funnel of a second apparatus via a cannula, and added dropwise over a period of 30 min to an ice-cooled solution of **24** (3 g, 11.90 mmol) in dry Et_2O (70 mL) while the reaction flask temperature was maintained below 5 °C. After completion of the addition, the ice bath was removed. The resulting mixture was allowed to warm to room temperature with stirring and refluxed for 3 h under argon. After cooling (ice-bath), the reaction was quenched with 1 N aqueous HCl (100 mL). The separated aqueous layer was extracted with Et_2O (3 × 50 mL), and the combined organic solutions were washed with water (2 × 50 mL), brine (2 × 50 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The oily residue obtained was purified by column chromatography (dichloromethane) yielding **25** (3.34 g, 88%) as a pale-yellow oil. IR (film): $\tilde{\nu}$ = 3104, 3069, 3027, 2998, 2936, 2883, 2830, 1606, 1567, 1496, 1454, 1432, 1361, 1303, 1279, 1219, 1166, 1152, 1109, 1022, 943, 922, 868, 853, 825, 798, 748, 739, 698 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.26 (m, 2 H), 2.68 (t, *J* = 7.7 Hz, 2 H), 4.94 (s, 2 H), 6.10 (t, *J* = 4.8 Hz, 1 H), 6.65 (dd, *J* = 2.6, 8.5 Hz, 1 H), 6.74 (br. d, *J* = 8.5 Hz, 1 H), 7.09−7.33 (m, 9 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.6 (−CH_2−), 28.7 (−CH_2−), 70.0 (−OCH_2−), 111.9 (−CH=), 114.9 (−CH=), 124.1 (−CH=), 125.6 (−CH=), 126.7 (−CH=), 126.8 (−CH=), 127.2 (−CH=), 127.6 (2 × −CH=), 127.9 (C), 128.1 (−CH=), 128.7 (2 × −CH=), 132.6 (C), 137.2 (C), 138.8 (C), 143.0 (C), 158.2 (C) ppm. $C_{21}H_{18}OS$: C 79.21, H 5.70, S 10.1; found C 79.15, H 5.73, S 10.1.

(c) 2-Benzyloxy-5-(thien-2-yl)naphthalene (26): A heterogeneous mixture of **25** (2.80 g, 8.80 mmol) and 4-chloroanil (6.49 g, 26.4 mmol) in dry benzene (70 mL) was heated to reflux under argon for 5 h. After being cooled to room temperature, the resulting brown solution was filtered through a bed of Celite, washed with saturated aqueous sodium bicarbonate solution (2 × 20 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by column chromatography (dichloromethane) yielding the desired compound **26** (2.38 g, 85%) as a white crystalline solid, m.p. 77 °C. IR (KBr): $\tilde{\nu}$ = 3103, 3069,

3050, 2956, 2933, 2905, 2885, 2834, 1623, 1594, 1526, 1507, 1445, 1434, 1376, 1349, 1334, 1257, 1229, 1169, 1100, 1055, 1027, 951, 906, 848, 829, 754, 699, 646 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 5.08 (s, 2 H), 7.06 (dd, *J* = 3.5, 5.1 Hz, 1 H), 7.15−7.68 (m, 12 H), 8.05 (d, *J* = 9.0 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 70.3 (−OCH_2−), 107.9 (−CH=), 119.7 (−CH=), 125.9 (−CH=), 126.2 (−CH=), 126.4 (−CH=), 127.6 (−CH=), 127.7 (−CH=), 127.8 (2 × −CH= and C), 127.9 (2 × −CH=), 128.4 (−CH=), 128.9 (2 × −CH=), 132.7 (C), 135.4 (C), 137.1 (C), 142.2 (C), 157.1 (C) ppm. $C_{21}H_{16}OS$: C 79.71, H 5.10, S 10.1; found C 79.65, H 5.15, S 10.1.

(d) 5-(Thien-2-yl)naphth-2-ol (27): Distilled trimethylsilyl chloride (1.70 g, 15.80 mmol) was added via syringe to a solution of NaI (2.36 g, 15.80 mmol) in dry acetonitrile (20 mL) at 25 °C. The resulting mixture was purged with Ar and stirred at the same temperature for 20 min before **26** (2 g, 7.90 mmol) dissolved in dry acetonitrile (70 mL) was added dropwise over 15 min. The resulting mixture was heated at 60 °C. The disappearance of the benzyl ether was monitored by TLC (pentane/diethyl ether, 1:1), and the reaction was judged complete after 3 h. After cooling to ambient temperature, water (30 mL) was added, and stirring was continued for 30 min. The separated aqueous layer was extracted with Et_2O (3 × 30 mL), and the combined organic layers were washed with aqueous saturated sodium sulfite, filtered, and the solvents were removed under reduced pressure. The crude residue was purified by column chromatography (dichloromethane) to yield **27** (1.17 g, 82%) as a white crystalline solid, m.p. 75 °C. IR (KBr): ν̃ = 3622, 3444−3249, 3102, 2924, 1627, 1511, 1465, 1435, 1393, 1293, 1261, 1227, 1162, 1098, 1074, 1036, 958, 908, 854, 837, 789, 756, 703 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 5.14 (br. s, 1 H), 7.05 (dd, *J* = 2.6, 9.2 Hz, 1 H), 7.10−7.20 (m, 4 H), 7.30−7.41 (m, 2 H), 7.63 (dd, *J* = 2.6, 6.8 Hz, 1 H), 8.08 (d, *J* = 9.1 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 110.4 (−CH=), 118.4 (−CH=), 125.9 (−CH=), 126.3 (−CH= and C), 126.4 (−CH=), 127.2 (−CH=), 127.6 (2 × −CH=), 128.3 (−CH=), 132.7 (C), 135.4 (C), 142.1 (C), 153.4 (C) ppm. $C_{14}H_{10}OS$: C 74.31, H 4.45, S 14.2; found C 74.25, H 4.40, S 14.3.

5-(2,2′-Bithien-5-yl)naphth-2-ol (30): This compound was prepared in four steps (58.5% overall yield) from 6-hydroxy-1-tetralone.

(a) 7-Benzyloxy-4-(2,2′-bithien-5-yl)-1,2-dihydronaphthalene (28): A stirred solution of 2,2′-bithiophene (3.95 g, 23.78 mmol) in anhydrous Et_2O (70 mL), under an Ar atmosphere was cooled to 0 °C and treated dropwise over a period of 10 min with *n*BuLi (10.46 mL of 2.5 M solution in hexane, 26.15 mmol). The reaction mixture was stirred at the same temperature for an additional 1 h, before further portions of $MgBr_2$. Et_2O (7.68 g, 29.7 mmol) were added from a tip tube over 30 min. After completion of the addition, the reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. The Grignard solution was transferred to the pressure-equalizing dropping funnel of a second apparatus via a cannula, and added dropwise over a period of 35 min, maintaining the reaction temperature below 5 °C, to an ice-cooled solution of **24** (3 g, 11.90 mmol) in dry Et_2O (70 mL). Subsequently, the reaction mixture was allowed to warm to ambient temperature and heated to reflux for 3 h, under argon. Upon cooling (ice-bath), the reaction was quenched by addition of 1 N aqueous HCl (100 mL). The separated aqueous layer was extracted with Et_2O (3 × 50 mL), and the combined organic solutions were washed with water (2 × 60 mL), brine (2 × 50 mL), dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure, and the remaining residue was purified by column chromatography (dichloromethane) yielding the desired compound (3.90 g, 82%) as a powdery pale-yellow solid, after recrystallization from ethanol/heptane, m.p. 101 °C. IR (KBr): ν̃ = 3096, 3067, 3035, 2928, 2888, 2827, 1606, 1564, 1490, 1453, 1423, 1382, 1282, 1246, 1149, 1112, 1035, 1023, 938, 910, 868, 839, 797, 742, 729, 699 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.27 (m, 2 H), 2.69 (t, *J* = 7.6 Hz, 2 H), 4.97 (s, 2 H), 6.08 (t, *J* = 4.8 Hz, 1 H), 6.68 (dd, *J* = 2.6, 8.5 Hz, 1 H), 6.76 (d, *J* = 2.5 Hz, 1 H), 6.85 (d, *J* = 3.7 Hz, 1 H), 6.91 (dd, *J* = 3.6, 5.1 Hz, 1 H), 7.01 (d, *J* = 3.7 Hz, 1 H), 7.06 (dd, *J* = 1.1, 3.6 Hz, 1 H), 7.09 (dd, *J* = 1.1, 5.1 Hz, 1 H), 7.24−7.35 (m, 6 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5 (−CH_2−), 28.6 (−CH_2−), 70.1 (−OCH_2−), 111.8 (−CH=), 114.9 (−CH=), 123.6 (−CH=), 123.8 (−CH=), 124.2 (−CH=), 126.2 (−CH=), 126.6 (−CH=), 126.8 (C), 127.5 (C), 127.6 (2 × −CH=), 127.9 (−CH=), 128.1 (−CH=), 128.7 (2 × −CH=), 132.4 (C), 135.8 (C), 137.1 (−CH=), 137.7 (C), 138.8 (C), 142.1 (C), 158.2 (C) ppm. $C_{25}H_{20}OS_2$: C 74.31, H 5.03, S 16.0; found C 75.01, H 4.95, S 15.8.

(b) 2-Benzyloxy-5-(2,2′-bithien-5-yl)naphthalene (29): Under an atmosphere of Ar, a 150-mL round-bottomed flask equipped with a condenser, was charged with **28** (3 g, 7.48 mmol), 4-chloroanil (6.49 g, 26.4 mmol) and dry benzene (70 mL). The heterogeneous reaction mixture was refluxed for 6 h, cooled to ambient temperature, and filtered through a plug of Celite, which was then thoroughly rinsed with benzene (3 × 10 mL). The resulting solution was washed with saturated aqueous sodium bicarbonate solution (2 × 40 mL), dried with anhydrous Na_2SO_4, and concentrated in vacuo. The oily crude residue was subjected to column chromatography (dichloromethane) to afford **29** (2.63 g, 88%) as a highly viscous pale-yellow oil that solidified upon storage, m.p. 115 °C. IR (KBr): ν̃ = 3106, 3082, 3064, 3019, 2924, 2883, 2866, 2828, 1625, 1598, 1527, 1475, 1439, 1382, 1349, 1326, 1299, 1246, 1209, 1209, 1168, 1145, 1120, 1085, 1037, 863, 841, 818, 795, 760, 753, 701 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 5.10 (s, 2 H), 7.08 (dd, *J* = 3.6, 5.1 Hz, 1 H), 7.15−7.68 (m, 14 H), 8.12 (d, *J* = 9.0 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 70.4 (−OCH_2−), 108.2 (−CH=), 119.8 (−CH=), 124.1 (−CH=), 124.4 (−CH=), 124.8 (−CH=), 126.3 (−CH=), 127.5 (C), 127.78 (−CH=), 127.85 (−CH=), 128.0 (3 × −CH=), 128.3 (−CH=), 128.4 (−CH=), 129.0 (3 × −CH=), 132.3 (C), 135.7 (C), 137.2 (C), 137.7 (C), 137.9 (C), 141.3 (C), 157.2 (C) ppm. $C_{25}H_{18}OS_2$: C 75.34, H 4.55, S 16.1; found C 75.48, H 4.50, S 15.9.

(c) 5-(2,2′-Bithien-5-yl)naphth-2-ol (30): Distilled trimethylsilyl chloride (1.35 g, 12.48 mmol) was added via syringe to a solution of NaI (1.87 g, 12.48 mmol) in dry acetonitrile (16 mL) at 25 °C. The resulting mixture was flushed with Ar and stirred at the same temperature for 20 min before **29** (2 g, 5 mmol) dissolved in dry acetonitrile (70 mL) was added dropwise over 15 min. The resulting mixture was heated at 60 °C. The disappearance of the benzyl ether was monitored by TLC (pentane/diethyl ether, 1:1) and the reaction was found to be complete after 2 h. Workup was carried out as given for compound **27**. The crude material was purified by column chromatography (dichloromethane) yielding the title compound (1.17 g, 88%) as a powdery yellow solid, m.p. 139 °C. IR (KBr): ν̃ = 3492, 3106, 3082, 3064, 1621, 1595, 1522, 1460, 1439, 1385, 1347, 1324, 1233, 1209, 1185, 1170, 1098, 1040, 958, 900, 858, 842, 816, 790, 760, 704 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 5.09 (br. s, 1 H), 7.05 (dd, *J* = 3.7, 5.0 Hz, 1 H), 7.11 (d, *J* = 2.7 Hz, 1 H), 7.12−7.30 (m, 5 H), 7.43 (br. s, 1 H), 7.49 (d, *J* = 5.1 Hz, 1 H), 7.64−7.74 (m, 1 H), 8.22 (d, *J* = 9.1 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 110.3 (−CH=), 118.5 (−CH=), 124.0 (−CH=), 124.3 (−CH=), 124.7 (−CH=), 126.2 (−CH=), 126.4 (−CH=), 127.3 (−CH=), 127.4 (C), 128.1 (−CH=), 128.2 (−CH=), 128.3 (−CH=), 132.3 (C), 135.5 (C), 137.6 (C), 137.8

(C), 141.1 (C), 153.7 (C) ppm. $C_{18}H_{12}OS_2$: C 70.10, H 3.92, S 20.8; found C 70.32, H 3.95, S 20.8.

3,3-Diphenyl-5-(trifluoromethylsulfonyl)-3*H*-naphtho[2,1-*b*]pyran (I): This compound was prepared according to General Procedure (3), from **8**. Purification by column chromatography (SiO_2; cyclohexane/Et_2O, gradient 100:0 to 70:30), followed by recrystallization (*n*-pentane/$CHCl_3$) afforded **I** (1.77 g, 3.66 mmol, 72%) as a white solid, m.p. 145 °C. IR (KBr): $\tilde{\nu}$ = 3085, 3064, 3027, 1632, 1513, 1491, 1456, 1447, 1426, 1409, 1267, 1245, 1206, 1143, 1106, 1039, 1024, 1008, 890, 825, 808, 750, 700, 630, 620 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.45 (d, *J* = 10.1 Hz, 1 H), 7.30−7.77 (m, 14 H), 7.82 (d, *J* = 8.1 Hz, 1 H), 8.08 (d, *J* = 8.5 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 84.2 (C), 117.3 (C), 119.1 (−CH=), 120.7 (−CH=), 121.7 (−CH=), 125.4 (−CH=), 126.2 (4 × −CH=), 127.1 (−CH=), 127.8 (2 × −CH=), 128.0 (C), 128.4 (4 × −CH=), 128.5 (C), 128.8 (−CH=), 129.8 (−CH=), 138.1 (C), 144.0 (C), 144.6 (2 × C) ppm. $C_{26}H_{17}F_3O_4S$: C 64.72, H 3.55, S 6.6; found C 64.69, H 3.61, S 6.7.

3,3-Diphenyl-8-(trifluoromethylsulfonyl)-3*H*-naphtho[2,1-*b*]pyran (II): This compound was prepared according to General Procedure (3), from **10**. Purification by column chromatography (SiO_2; cyclohexane/Et_2O, gradient 100:0 to 70:30), followed by recrystallization (*n*-pentane/$CHCl_3$) afforded **II** (1.63 g, 3.37 mmol, 66%) as a white solid, m.p. 107 °C. IR (KBr): $\tilde{\nu}$ = 3057, 3019, 1634, 1614, 1596, 1518, 1493, 1447, 1420, 1239, 1222, 1140, 1097, 1097, 1084, 1013, 939, 884, 857, 833, 813, 766, 701, 625, 601 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.29 (d, *J* = 9.9 Hz, 1 H), 7.15−7.50 (m, 13 H), 7.56 (d, *J* = 2.5 Hz, 1 H), 7.62 (d, *J* = 8.8 Hz, 1 H), 7.96 (d, *J* = 9.3 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 82.9 (C), 114.3 (C), 118.9 (−CH=), 119.8 (−CH=), 120.1 (−CH=), 120.3 (−CH=), 124.0 (−CH=), 127.0 (4 × −CH=), 127.8 (2 × −CH=), 128.2 (4 × −CH=), 128.8 (−CH=), 128.9 (C), 129.2 (C), 129.7 (−CH=), 144.4 (2 × C), 145.6 (C), 151.5 (C) ppm. $C_{26}H_{17}F_3O_4S$: C 64.72, H 3.55, S 6.6; found C 64.69, H 3.54, S 6.6.

3,3-Diphenyl-9-(trifluoromethylsulfonyl)-3*H*-naphtho[2,1-*b*]pyran (III): This compound was prepared according to General Procedure (3), from **12**. Purification by column chromatography (SiO_2; cyclohexane/Et_2O, gradient 100:0 to 70:30), followed by recrystallization (*n*-pentane/$CHCl_3$) afforded **III** (1.82 g, 3.77 mmol, 74%) as a white solid, m.p. 154 °C. IR (KBr): $\tilde{\nu}$ = 3062, 1638, 1623, 1515, 1492, 1453, 1404, 1241, 1231, 1213, 1134, 1123, 960, 890, 865, 839, 765, 734, 700, 642 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.22 (d, *J* = 10.0 Hz, 1 H), 7.00−7.45 (m, 13 H), 7.58 (d, *J* = 8.9 Hz, 1 H), 7.68 (d, *J* = 9.2 Hz, 1 H), 7.70 (d, *J* = 2.8 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 84.0 (C), 117.2 (C), 119.0 (−CH=), 120.6 (−CH=), 121.6 (−CH=), 125.3 (−CH=), 127.0 (4 × −CH=), 127.7 (−CH=), 127.9 (2 × −CH=), 128.2 (C), 128.3 (4 × −CH=), 128.7 (−CH=), 129.7 (−CH=), 130.1 (C), 138.0 (C), 142.5 (C), 143.9 (2 × C) ppm. $C_{26}H_{17}F_3O_4S$: C 64.72, H 3.55, S 6.6; found C 64.70, H 3.58, S 6.6.

6-Bromo-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (IV): This compound was prepared according to General Procedure (4), from **13**. Purification by column chromatography (SiO_2; *n*-pentane/Et_2O, gradient 100:0 to 60:40), followed by recrystallization (cyclohexane/$CHCl_3$) afforded **IV** (2.77 g, 6.70 mmol, 67%) as a white solid, m.p. 167 °C. IR (KBr): $\tilde{\nu}$ = 3092, 3056, 3024, 1637, 1598, 1583, 1500, 1444, 1238, 1210, 1089, 998, 879, 804, 756, 765, 698 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.28 (d, *J* = 10.0 Hz, 1 H), 7.03−7.43 (m, 12 H), 7.46 (dd, *J* = 1.5, 8.2 Hz, 1 H), 7.56 (br. s, 1 H), 7.95 (d, *J* = 8.1 Hz, 1 H), 8.12 (d, *J* = 7.5 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 84.0 (C), 116.3 (C), 117.2 (C), 119.0 (−CH=), 120.6 (−CH=), 121.6 (−CH=), 125.3 (−CH=), 126.9 (4 × −CH=), 127.7 (−CH=), 127.9 (2 × −CH=), 128.2 (C), 128.3 (4 × −CH=), 128.7 (−CH=), 129.7 (−CH=), 130.1 (C), 138.0 (C), 143.9 (2 × C) ppm. $C_{25}H_{17}BrO$: C 72.64, H 4.14; found C 72.50, H 4.10.

8-Bromo-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (V): This compound was prepared according to General Procedure (4), from **14**. Purification by column chromatography (SiO_2; *n*-pentane/Et_2O, gradient 100:0 to 60:40), followed by recrystallization (toluene), yielded **V** (3.30 g, 7.99 mmol, 80%) as a white solid, m.p. 149.5 °C. IR (KBr): $\tilde{\nu}$ = 3084, 3055, 3024, 1634, 1582, 1499, 1446, 1244, 1213, 1092, 1000, 878, 809, 771, 763, 752, 733, 700 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.19 (d, *J* = 10.0 Hz, 1 H), 7.05−7.50 (m, 14 H), 7.71 (d, *J* = 9.1 Hz, 1 H), 7.75 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 82.9 (C), 114.3 (C), 117.5 (C), 119.2 (−CH=), 119.6 (−CH= and C), 123.3 (−CH=), 127.1 (4 × −CH=), 127.8 (2 × −CH=), 128.3 (4 × −CH=), 128.4 (−CH=), 129.0 (−CH=), 129.9 (−CH=), 130.5 (−CH=), 130.6 (C), 144.8 (2 × C), 150.9 (C) ppm. $C_{25}H_{17}BrO$: C 72.64, H 4.14; found C 72.60, H 4.13.

3,3-Diphenyl-5-(thien-2-yl)-3*H*-naphtho[2,1-*b*]pyran (VI): This compound was obtained by General Procedure (5), from **I** (482 mg, 1.00 mmol) and **1** (235 mg, 1.20 mmol). Purification by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 70:30) afforded the pure compound **VI** (362 mg, 0.87 mmol, 87%) as a white solid after recrystallization from EtOH. This compound was also prepared by General Procedure (7), from **15** (2.26 g, 10 mmol). The reaction mixture was stirred under reflux for four days. Purification of the concentrate by column chromatography and recrystallization carried out as mentioned above, yielded **VI** (2.58 g, 6.19 mmol, 62%) as a white solid, m.p. 161 °C. IR (KBr): $\tilde{\nu}$ = 3061, 3021, 1635, 1520, 1488, 1436, 1344, 1290, 1257, 1219, 1207, 1093, 1055, 1004, 947, 899, 882, 851, 825, 765, 735, 698, 689 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ = 6.32 (d, *J* = 9.9 Hz, 1 H), 7.16 (dd, *J* = 3.7, 5.1 Hz, 1 H), 7.21−7.60 (m, 14 H), 7.72 (dd, *J* = 1.1, 3.7 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.98 (d, *J* = 8.4 Hz, 1 H), 8.06 (br ppm. s, 1 H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 83.8 (C), 114.9 (C), 120.0 (−CH=), 121.3 (−CH=), 123.9 (C), 124.2 (−CH=), 126.1 (−CH=); 126.4 (−CH=), 126.6 (−CH=), 127.1 (−CH=), 127.2 (4 × −CH=), 127.6 (2 × −CH=), 127.9 (−CH=), 128.08 (−CH=), 128.12 (4 × −CH=), 128.6 (−CH=), 129.0 (C), 129.1 (C), 138.9 (C), 144.5 (2 × C), 147.2 (C) ppm. $C_{29}H_{20}OS$: C 83.62, H 4.84, S 7.7; found C 83.61, H 4.87, S 7.5.

3,3-Diphenyl-6-(thien-2-yl)-3*H*-naphtho[2,1-*b*]pyran (VII): This compound was obtained by General Procedure (5), from **IV** (413 mg, 1.00 mmol) and **1** (235 mg, 1.20 mmol). Purification by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 70:30) afforded the pure compound **VII** (158 mg, 0.38 mmol, 38%) as a pale-yellow solid after recrystallization (cyclohexane/$CHCl_3$). This compound was also prepared by General Procedure (7), from **17** (2.26 g, 10 mmol). The reaction mixture was stirred under reflux for four days. Purification of the concentrate by column chromatography and recrystallization carried out as mentioned above, yielded **VII** (2.42 g, 5.81 mmol, 58%) as a pale-yellow solid, m.p. 152 °C. IR (KBr): $\tilde{\nu}$ = 3055, 3025, 2853, 2924, 1637, 1567, 1510, 1488, 1445, 1365, 1325, 1263, 1215, 1105, 1057, 1007, 943, 912, 866, 846, 756, 736, 698 cm^{-1}. ^1H NMR (400 MHz, [D_5]pyridine): δ = 6.55 (d, *J* = 10.0 Hz, 1 H), 7.03 (dd, *J* = 3.6, 5.1 Hz, 1 H), 7.28 (m, 2 H), 7.32 (dd, *J* = 1.1, 5.1 Hz, 1 H), 7.40 (m, 4 H), 7.41 (ddd, *J* = 1.1, 6.7, 8.6 Hz, 1 H), 7.47 (dd, *J* = 1.1, 3.6 Hz, 1 H), 7.58 (s, 1 H), 7.58 (d, *J* = 10.0 Hz, 1 H), 7.56 (ddd, *J* = 1.3, 6.9, 8.3 Hz, 1 H), 7.75 (m, 4 H), 8.20 (br. d, *J* = 8.4 Hz,

1 H), 8.28 (br. d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_5$]pyridine): δ = 83.5 (C), 115.3 (C), 120.2 (−CH=), 120.7 (−CH=), 123.0 (−CH=), 124.5 (−CH=), 125.2 (−CH=), 127.0 (−CH=), 127.78 (4 × −CH=), 127.82 (−CH=), 128.0 (−CH=), 128.48 (C), 128.5 (2 × −CH=), 129.2 (4 × −CH=), 129.6 (−CH=), 131.4 (C), 132.8 (−CH=), 134.6 (C), 141.6 (C), 146.0 (2 × C), 150.7 (C) ppm. $C_{29}H_{20}OS$: C 83.62, H 4.84, S 7.7; found C 83.70, H 4.80, S 7.7.

3,3-Diphenyl-7-(thien-2-yl)-3*H*-naphtho[2,1-*b*]pyran (VIII): This compound was obtained by General Procedure (7), from **27** (2.26 g, 10 mmol). The reaction mixture was stirred under reflux for five days. The residue was purified by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 70:30) to afford the pure compound **VIII** (2.84 g, 6.81 mmol, 68%) as a white solid after recrystallization from EtOH, m.p. 82 °C. IR (KBr): ṽ = 3100, 3000, 1629, 1585, 1489, 1446, 1405, 1252, 1216, 1066, 983, 947, 903, 849, 831, 763, 698 cm^{-1}. ^{1}H NMR (400 MHz, [D$_5$]pyridine): δ = 6.55 (d, J = 10.0 Hz, 1 H), 7.21 (dd, J = 3.5, 4.6 Hz, 1 H), 7.22 (dd, J = 1.7, 3.5 Hz, 1 H), 7.27 (m, 2 H), 7.37 (m, 4 H), 7.42 (d, J = 9.3 Hz, 1 H), 7.45 (dd, J = 1.7, 4.6 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 1 H), 7.57 (dd, J = 1.6, 7.6 Hz, 1 H), 7.58 (d, J = 10.0 Hz, 1 H), 7.71 (m, 4 H), 8.13 (dd, J = 1.6, 7.6 Hz, 1 H), 8.14 (d, J = 9.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_5$]pyridine): δ = 83.4 (C), 115.6 (C), 119.6 (−CH=), 120.7 (−CH=), 123.0 (−CH=), 124.9 (−CH=), 126.9 (−CH=), 127.1 (−CH=), 127.8 (4 × −CH=), 128.4 (2 × −CH=), 128.58 (C), 128.64 (−CH=), 129.08 (4 × −CH=), 129.09 (−CH=), 129.4 (−CH=), 131.4 (C), 133.8 (C), 138.0 (−CH=), 142.5 (C), 145.9 (2 × C), 151.5 (C) ppm. $C_{29}H_{20}OS$: C 83.62, H 4.84, S 7.7; found C 83.64, H 4.84, S 7.6.

3,3-Diphenyl-8-(thien-2-yl)-3*H*-naphtho[2,1-*b*]pyran (IX): This compound was obtained by General Procedure (5), from **II** (482 mg, 1.00 mmol) and **1** (235 mg, 1.20 mmol). Purification by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 70:30) afforded the pure compound **IX** (392 mg, 0.94 mmol, 94%) as a white solid after recrystallization from heptane/$CHCl_3$. This compound was also prepared by General Procedure (5), from **V** (413 mg, 1.00 mmol) and **1** (235 mg, 1.20 mmol). Purification by column chromatography and recrystallization carried out as mentioned above, yielded **IX** (371 mg, 0.89 mmol, 89%) as a white solid. This compound was also prepared by General Procedure (7), from **19** (2.26 g, 10 mmol). The reaction mixture was stirred under reflux for four days. Purification of the concentrate by column chromatography and recrystallization carried out as mentioned above, afforded **IX** (2.58 g, 6.19 mmol, 62%) as a white solid, m.p. 216−217 °C. IR (KBr): ṽ = 3102, 3058, 3027, 1630, 1589, 1502, 1491, 1467, 1449, 1427, 1381, 1372, 1244, 1219, 1209, 1183, 1093, 1055, 1009, 961, 882, 849, 817, 778, 762, 744, 726, 702 cm^{-1}. ^{1}H NMR (400 MHz, [D$_5$]pyridine): δ = 6.52 (d, J = 10.0 Hz, 1 H), 7.16 (dd, J = 3.6, 5.1 Hz, 1 H), 7.27 (m, 2 H), 7.37 (m, 4 H), 7.41 (d, J = 8.9 Hz, 1 H), 7.45 (dd, J = 1.1, 5.1 Hz, 1 H), 7.52 (d, J = 10.0 Hz, 1 H), 7.56 (dd, J = 1.1, 3.6 Hz, 1 H), 7.70 (m, 4 H), 7.76 (d, J = 8.9 Hz, 1 H), 7.92 (dd, J = 1.8, 8.9 Hz, 1 H), 8.14 (d, J = 1.9 Hz, 1 H), 8.14 (d, J = 8.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_5$]pyridine): δ = 83.5 (C), 115.2 (C), 119.8 (−CH=), 120.3 (−CH=), 123.3 (−CH=), 124.4 (−CH=), 125.7 (−CH=), 125.9 (−CH=), 126.0 (−CH=), 127.8 (4 × −CH=), 128.4 (2 × −CH=), 129.1 (4 × −CH=), 129.21 (−CH=), 129.24 (−CH=), 130.0 (C), 130.6 (C), 130.8 (C), 130.9 (−CH=), 145.0 (C), 146.0 (2 × C), 151.6 (C) ppm. $C_{29}H_{20}OS$: C 83.62, H 4.84, S 7.7; found C 83.60, H 4.90, S 7.7.

3,3-Diphenyl-9-(thien-2-yl)-3*H*-naphtho[2,1-*b*]pyran (X): This compound was obtained by General Procedure (5), from **III** (482 mg, 1.00 mmol) and **1** (235 mg, 1.20 mmol). Purification by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 60:40) afforded the pure compound **X** (337 mg, 0.81 mmol, 81%) as a white solid after recrystallization from heptane/CH_2Cl_2. This compound was also prepared by General Procedure (7), from **22** (2.26 g, 10 mmol). The reaction mixture was stirred under reflux for four days. Purification of the concentrate by column chromatography and recrystallization carried out as mentioned above, yielded **X** (2.46 g, 5.90 mmol, 59%) as a white solid, m.p. 154 °C. IR (KBr): ṽ = 3067, 3057, 3021, 1634, 1616, 1592, 1506, 1490, 1447, 1379, 1252, 1238, 1220, 1209, 1202, 1094, 1057, 1022, 981, 941, 835, 816, 765, 753, 734, 695, 674 cm^{-1}. ^{1}H NMR (400 MHz, [D$_5$]pyridine): δ = 6.54 (d, J = 10.0 Hz, 1 H), 7.18 (dd, J = 3.6, 5.0 Hz, 1 H), 7.27 (m, 2 H), 7.37 (m, 4 H), 7.38 (d, J = 8.6 Hz, 1 H), 7.50 (dd, J = 1.1, 5.1 Hz, 1 H), 7.63 (d, J = 10.0 Hz, 1 H), 7.65 (dd, J = 1.1, 3.6 Hz, 1 H), 7.71 (m, 4 H), 7.71 (d, J = 8.6 Hz, 1 H), 7.72 (dd, J = 1.7, 8.5 Hz, 1 H), 7.77 (d, J = 8.4 Hz, 1 H), 7.95 (br ppm. s, 1 H). ^{13}C NMR (100 MHz, [D$_5$]pyridine): δ = 83.4 (C), 115.3 (C), 118.9 (−CH=), 119.2 (−CH=), 120.5 (−CH=), 123.2 (−CH=), 125.1 (−CH=), 126.5 (−CH=), 127.8 (4 × −CH=), 128.4 (2 × −CH=), 129.0 (−CH=), 129.1 (4 × −CH=), 129.3 (−CH=), 129.6 (C), 130.2 (−CH=), 130.7 (−CH=), 131.1 (C), 133.7 (C), 145.3 (C), 146.0 (2 × C), 152.0 (C) ppm. $C_{29}H_{20}OS$: C 83.62, H 4.84, S 7.7; found C 83.43, H 4.77, S 7.4.

5-(2,2′-Bithien-5-yl)-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (XI): This compound was obtained by General Procedure (5), from **I** (482 mg, 1.00 mmol) and **2** (333 mg, 1.20 mmol). Purification by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 60:40) afforded the pure compound **XI** (409 mg, 0.82 mmol, 82%) as a yellow solid after recrystallization (heptane/benzene). This compound was also prepared by General Procedure (7), from **16** (3.08 g, 10 mmol). The reaction mixture was stirred under reflux for four days. Purification of the concentrate by column chromatography and recrystallization carried out as mentioned above, yielded **XI** (2.34 g, 4.69 mmol, 47%) as a yellow solid, m.p. 159 °C. IR (KBr): ṽ = 3104, 3059, 3024, 1630, 1490, 1458, 1447, 1433, 1257, 1222, 1155, 1081, 1005, 957, 840, 794, 734, 696 cm^{-1}. ^{1}H NMR (400 MHz, [D$_5$]pyridine): δ = 6.55 (d, J = 10.0 Hz, 1 H), 7.38 (dd, J = 3.6, 5.1 Hz, 1 H), 7.16 (d, J = 3.7 Hz, 1 H), 7.28 (m, 2 H), 7.37 (d, J = 3.7 Hz, 1 H), 7.40 (m, 4 H), 7.40 (dd, J = 1.1, 3.6 Hz, 1 H), 7.41 (ddd, J = 1.1, 3.6, 8.6 Hz, 1 H), 7.43 (dd, J = 1.1, 5.1 Hz, 1 H), 7.58 (s, 1 H), 7.58 (d, J = 10.0 Hz, 1 H), 7.56 (ddd, J = 1.3, 6.9, 8.3 Hz, 1 H), 7.75 (m, 4 H), 8.20 (br. d, J = 8.4 Hz, 1 H), 8.28 (br. d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_5$]pyridine): δ = 83.5 (C), 115.5 (C), 120.2 (−CH=), 120.7 (C), 122.9 (−CH=), 125.00 (−CH=), 125.2 (−CH=), 125.3 (−CH=), 126.0 (−CH=), 127.0 (−CH=), 127.8 (4 × −CH=), 127.9 (−CH=), 128.4 (C), 128.5 (2 × −CH=), 129.1 (5 × −CH=), 129.5 (−CH=), 129.6 (−CH=), 131.4 (C), 134.5 (−CH=), 137.9 (C), 138.7 (C), 140.7 (C), 146.0 (2 × C), 150.6 (C) ppm. $C_{33}H_{22}OS_2$: C 79.48, H 4.45, S 12.8; found C 79.32, H 4.51, S 12.6.

6-(2,2′-Bithien-5-yl)-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (XII): This compound was obtained by General Procedure (5), from **IV** (413 mg, 1.00 mmol) and **2** (333 mg, 1.20 mmol). Purification by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 60:40) afforded the pure compound **XII** (210 mg, 0.42 mmol, 42%) as a pale-orange solid after recrystallization (heptane/benzene). This compound was also prepared by General Procedure (7), from **18** (3.08 g, 10 mmol). The reaction mixture was stirred under reflux for six days. Purification of the concentrate by column chromatography and recrystallization carried out as mentioned above, yielded **XII** (2.54 g, 5.09 mmol, 51%) as a pale-orange solid, m.p. 175 °C. IR (KBr): ṽ = 3062, 3028, 2923, 2854, 1630, 1578, 1561,

1489, 1445, 1341, 1276, 1212, 1195, 1132, 1089, 1051, 1002, 949, 907, 877, 836, 805, 764, 741, 696 cm^{-1}. ^1H NMR (400 MHz, [D$_5$]pyridine): δ = 6.55 (d, *J* = 10.0 Hz, 1 H), 7.10 (dd, *J* = 3.6, 5.1 Hz, 1 H), 7.16 (d, *J* = 3.7 Hz, 1 H), 7.28 (m, 2 H), 7.37 (d, *J* = 3.7 Hz, 1 H), 7.40 (m, 4 H), 7.40 (dd, *J* = 1.1, 3.6 Hz, 1 H), 7.41 (ddd, *J* = 1.1, 6.7, 8.6 Hz, 1 H), 7.43 (dd, *J* = 1.1, 5.1 Hz, 1 H), 7.58 (s, 1 H), 7.58 (d, *J* = 10.0 Hz, 1 H), 7.56 (ddd, *J* = 1.3, 6.9, 8.3 Hz, 1 H), 7.75 (m, 4 H), 8.20 (br. d, *J* = 8.4 Hz, 1 H), 8.28 (br. d, *J* = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_5$]pyridine): δ = 83.5 (C), 115.5 (C), 120.2 (−CH=), 120.7 (−CH=), 122.9 (−CH=), 125.00 (−CH=), 125.2 (−CH=), 125.3 (−CH=), 126.0 (−CH=), 127.0 (−CH=), 127.8 (4 × −CH=), 127.9 (−CH=), 128.4 (C), 128.5 (2 × −CH=), 129.1 (5 × −CH=), 129.5 (−CH=), 129.6 (−CH=), 131.4 (C), 134.5 (C), 137.9 (C), 138.7 (C), 140.7 (C), 146.0 (2 × C), 150.6 (C) ppm. $C_{33}H_{22}OS_2$: C 79.48, H 4.45, S 12.8; found C 79.38, H 4.48, S 13.0.

7-(2,2′-Bithien-5-yl)-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (XIII): This compound was obtained by General Procedure (7), from **30** (3.08 g, 10 mmol). The reaction mixture was stirred under reflux for six days. The residue was purified by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 60:40) to afford the pure compound **XIII** (3.19 mg, 6.39 mmol, 64%) as a pale-yellow solid after recrystallization (heptane/benzene), m.p. 155 °C. IR (KBr): ṽ = 3102, 3063, 3023, 2954, 2923, 2853, 1630, 1602, 1583, 1516, 1491, 1458, 1447, 1409, 1373, 1355, 1321, 1255, 1219, 1202, 1157, 1093, 1071, 1052, 1031, 907, 822, 805, 767, 760, 696 cm^{-1}. ^1H NMR (400 MHz, [D$_5$]pyridine): δ = 6.56 (d, *J* = 10.0 Hz, 1 H), 7.06 (d, *J* = 3.8 Hz, 1 H), 7.10 (dd, *J* = 3.6, 5.1 Hz, 1 H), 7.12 (dd, *J* = 1.7, 3.5 Hz, 1 H), 7.28 (m, 2 H), 7.37 (dd, *J* = 1.1, 3.6 Hz, 1 H), 7.38 (m, 4 H), 7.43 (dd, *J* = 1.1, 5.1 Hz, 1 H), 7.46 (dd, *J* = 2.3, 7.1 Hz, 1 H), 7.48 (d, *J* = 9.3 Hz, 1 H), 7.50 (t, *J* = 7.1 Hz, 1 H), 7.58 (d, *J* = 10.0 Hz, 1 H), 7.72 (m, 4 H), 8.14 (dd, *J* = 2.3, 7.1 Hz, 1 H), 8.21 (d, *J* = 9.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_5$]pyridine): δ = 83.3 (C), 115.5 (C), 119.4 (−CH=), 120.7 (−CH=), 122.8 (−CH=), 125.9 (−CH=), 126.9 (C), 127.07 (−CH=), 127.09 (−CH=), 127.8 (4 × −CH=), 128.38 (−CH=), 128.43 (3 × −CH=), 128.48 (−CH=), 128.50 (C), 128.54 (−CH=), 129.1 (4 × −CH=), 129.3 (−CH=), 129.4 (−CH=), 131.4 (C), 133.2 (C), 138.5 (C), 141.5 (C), 145.9 (2 × C), 151.6 (C) ppm. $C_{33}H_{22}OS_2$: C 79.48, H 4.45, S 12.8; found C 79.55, H 4.43, S 12.7.

8-(2,2′-Bithien-5-yl)-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (XIV): This compound was obtained by General Procedure (5), from **II** (482 mg, 1.00 mmol) and **2** (333 mg, 1.20 mmol). Purification by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 50:50) afforded the pure compound **XIV** (439 mg, 0.88 mmol, 88%) as a yellow solid after recrystallization from heptane/benzene. This compound was also prepared by General Procedure (5), from **V** (413 mg, 1.00 mmol) and **2** (333 mg, 1.20 mmol). Purification by column chromatography and recrystallization carried out as mentioned above, yielded **XIV** (429 mg, 0.86 mmol, 86%) as a yellow solid. This compound was also prepared by General Procedure (7), from **20** (3.08 g, 10 mmol). The reaction mixture was stirred under reflux for six days. Purification of the concentrate by column chromatography and recrystallization carried out as mentioned above, afforded **XIV** (1.10 g, 2.20 mmol, 22%) as a yellow solid, m.p. 244 °C. IR (KBr): ṽ = 3059, 3024, 1628, 1587, 1493, 1447, 1243, 1219, 1094, 1009, 949, 883, 813, 795, 751, 696 cm^{-1}. ^1H NMR (400 MHz, [D$_5$]pyridine): δ = 6.53 (d, *J* = 10.0 Hz, 1 H), 7.09 (dd, *J* = 3.6, 5.1 Hz, 1 H), 7.28 (m, 2 H), 7.32 (d, *J* = 3.8 Hz, 1 H), 7.38 (m, 4 H), 7.39 (dd, *J* = 1.1, 3.6 Hz, 1 H), 7.41 (dd, *J* = 1.1, 5.1 Hz, 1 H), 7.44 (d, *J* = 9.0 Hz, 1 H), 7.48 (d, *J* = 3.7 Hz, 1 H), 7.53 (d, *J* = 10.0 Hz, 1 H), 7.71 (m, 4 H), 7.81 (d, *J* = 9.0 Hz, 1 H), 7.88 (dd, *J* = 2.0, 8.8 Hz, 1 H), 8.11 (d, *J* = 1.8 Hz, 1 H), 8.16 (d, *J* = 8.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_5$]pyridine): δ = 83.3 (C), 115.5 (C), 119.9 (−CH=), 120.3 (−CH=), 123.4 (−CH=), 124.8 (−CH=), 125.2 (−CH=), 125.4 (−CH=), 125.6 (−CH=), 125.8 (−CH=), 125.9 (−CH=), 127.8 (4 × −CH=), 128.4 (2 × −CH=), 129.1 (5 × −CH=), 129.3 (−CH=), 130.1 (C), 130.3 (C), 130.6 (C), 131.0 (−CH=), 137.3 (C), 138.2 (C), 143.8 (C), 146.0 (2 × C), 151.7 (C) ppm. $C_{33}H_{22}OS_2$: C 79.48, H 4.45, S 12.8; found C 79.38, H 4.51, S 12.6.

9-(2,2′-Bithien-5-yl)-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (XV): This compound was obtained by General Procedure (5), from **III** (482 mg, 1.00 mmol) and **2** (333 mg, 1.20 mmol). Purification by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 50:50) afforded the pure compound **XV** (414 mg, 0.83 mmol, 83%) as a yellow solid after recrystallization (heptane/benzene). This compound was also prepared by General Procedure (7), from **23** (3.08 mg, 10 mmol). The reaction mixture was stirred under reflux for six days. Purification of the concentrate by column chromatography and recrystallization carried out as mentioned above, afforded **XV** (2.69 g, 5.39 mmol, 54%) as a yellow solid, m.p. 211 °C. IR (KBr): ṽ = 3076, 3064, 3022, 1630, 1614, 1589, 1504, 1447, 1425, 1375, 1243, 1230, 1201, 1086, 1051, 1020, 975, 952, 838, 801, 729, 700 cm^{-1}. ^1H NMR (400 MHz, [D$_5$]pyridine): δ = 6.58 (d, *J* = 10.0 Hz, 1 H), 7.11 (dd, *J* = 3.7, 5.0 Hz, 1 H), 7.29 (m, 2 H), 7.35 (d, *J* = 3.8 Hz, 1 H), 7.38 (d, *J* = 8.8 Hz, 1 H), 7.39 (m, 4 H), 7.41 (dd, *J* = 1.1, 5.0 Hz, 1 H), 7.43 (dd, *J* = 1.1, 3.7 Hz, 1 H), 7.57 (d, *J* = 3.8 Hz, 1 H), 7.68 (d, *J* = 10.0 Hz, 1 H), 7.70 (d, *J* = 8.8 Hz, 1 H), 7.72 (br. d, *J* = 8.6 Hz, 1 H), 7.73 (m, 4 H), 7.79 (d, *J* = 8.6 Hz, 1 H), 8.43 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_5$]pyridine): δ = 83.4 (C), 115.4 (C), 118.7 (−CH=), 119.3 (−CH=), 120.5 (−CH=), 122.8 (−CH=), 124.9 (−CH=), 125.9 (3 × −CH=), 127.8 (4 × −CH=), 128.4 (2 × −CH=), 129.08 (5 × −CH=), 129.1 (−CH=), 129.7 (C), 130.3 (−CH=), 130.7 (−CH= and C), 133.2 (C), 137.9 (C), 138.1 (C), 144.0 (C), 146.0 (2 × C), 152.1 (C) ppm. $C_{33}H_{22}OS_2$: C 79.48, H 4.45, S 12.8; found C 79.41, H 4.53, S 12.8.

3,3-Diphenyl-8-(2,2′:5′,2′′-terthien-5-yl)-3*H*-naphtho[2,1-*b*]pyran (XVI): This compound was obtained by General Procedure (5), from **II** (482 mg, 1.00 mmol) and **3** (432 mg, 1.20 mmol). Purification by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 50:50) afforded the pure compound **XVI** (372 mg, 0.64 mmol, 64%) as a yellow solid after recrystallization from benzene. This compound was also prepared by General Procedure (5), from **V** (413 mg, 1.00 mmol) and **3** (432 mg, 1.20 mmol). Purification by column chromatography and recrystallization carried out as mentioned above, yielded **XVI** (314 mg, 0.54 mmol, 54%) as a yellow solid. This compound was also prepared by General Procedure (7), from **21** (3.90 g, 10 mmol). The reaction mixture was stirred under reflux for six days. Purification of the concentrate by column chromatography and recrystallization carried out as mentioned above, afforded **XVI** (522 mg, 0.09 mmol, 9%) as a yellow solid, m.p. 262 °C. IR (KBr): ṽ = 3060, 3027, 2925, 2854, 1631, 1588, 1495, 1450, 1378, 1345, 1273, 1244, 1220, 1184, 1094, 1075, 1008, 954, 881, 830, 813, 795, 754, 698 cm^{-1}. ^1H NMR (400 MHz, [D$_5$]pyridine): δ = 6.53 (d, *J* = 10.0 Hz, 1 H), 7.09 (dd, *J* = 3.6, 5.1 Hz, 1 H), 7.24 (d, *J* = 3.9 Hz, 1 H), 7.28 (d, *J* = 3.9 Hz, 1 H), 7.29−7.33 (m, 2 H), 7.33 (d, *J* = 3.8 Hz, 1 H), 7.36 (dd, *J* = 1.1, 3.6 Hz, 1 H), 7.40 (dd, *J* = 1.1, 5.1 Hz, 1 H), 7.41−7.46 (m, 4 H), 7.41 (d, *J* = 8.8 Hz, 1 H), 7.44 (d, *J* = 3.8 Hz, 1 H), 7.49 (d, *J* = 10.0 Hz, 1 H), 7.72−7.76 (m, 4 H), 7.79 (d, *J* = 8.8 Hz, 1 H), 7.86 (dd, *J* = 1.9, 8.8 Hz, 1 H), 8.09 (d, *J* = 1.5 Hz, 1 H), 8.13 (d, *J* = 9.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_5$]pyridine): δ = 83.9

(C), 115.1 (C), 119.8 (−CH=), 120.0 (−CH=), 123.1 (−CH=), 124.9 (−CH=), 125.1 (−CH=), 125.4 (−CH=), 125.6 (−CH=), 125.8 (−CH=), 125.9 (−CH=), 127.8 (4 × −CH=), 128.3 (2 × −CH=), 128.8 (−CH=), 128.9 (4 × −CH=), 129.0 (−CH=), 129.9 (C), 130.4 (C), 130.7 (C), 130.9 (−CH=), 137.1 (C), 137.4 (2 × C), 138.0 (C), 144.6 (C), 146.1 (2 × C), 152.0 (C) ppm. $C_{37}H_{24}OS_3$: C 76.52, H 4.17, S 16.7; found C 76.40, H 4.20, S 16.8.

3,3-Diphenyl-9-(2,2′:5′,2′′-terthien-5-yl)-3*H*-naphtho[2,1-*b*]pyran (XVII): This compound was obtained by General Procedure (5), from **III** (482 mg, 1.00 mmol) and **3** (432 mg, 1.20 mmol). Purification by column chromatography (SiO_2; *n*-pentane/CH_2Cl_2, gradient 100:0 to 50:50) afforded the pure compound **XVII** (378 mg, 0.65 mmol, 65%) as a yellow solid after recrystallization from benzene, m.p. 271 °C. IR (KBr): $\tilde{\nu}$ = 3057, 3020, 1629, 1614, 1593, 1536, 1495, 1445, 1427, 1378, 1319, 1240, 1208, 1180, 1093, 1065, 1024, 989, 949, 909, 868, 834, 791, 756, 729, 697 cm^{-1}. ^1H NMR (400 MHz, [D_5]pyridine): δ = 6.59 (d, *J* = 9.9 Hz, 1 H), 7.09 (dd, *J* = 3.6, 5.1 Hz, 1 H), 7.26 (d, *J* = 3.8 Hz, 1 H), 7.27−7.33 (m, 2 H), 7.32 (d, *J* = 3.8 Hz, 1 H), 7.36 (d, *J* = 3.8 Hz, 1 H), 7.36 (dd, *J* = 1.2, 3.6 Hz, 1 H), 7.38−7.43 (m, 4 H), 7.39 (d, *J* = 8.7 Hz, 1 H), 7.40 (dd, *J* = 1.1, 5.1 Hz, 1 H), 7.56 (d, *J* = 3.8 Hz, 1 H), 7.68 (d, *J* = 9.9 Hz, 1 H), 7.70−7.77 (m, 4 H), 7.72 (dd, *J* = 1.7, 8.6 Hz, 1 H), 7.73 (d, *J* = 8.7 Hz, 1 H),7.80 (d, *J* = 8.5 Hz, 1 H), 8.43 (d, *J* = 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D_5]pyridine): δ = 83.6 (C), 115.3 (C), 118.8 (−CH=), 119.3 (−CH=), 120.4 (−CH=), 122.7 (−CH=), 125.0 (−CH=), 125.6 (−CH=), 125.7 (−CH=), 125.95 (−CH=), 125.96 (−CH=), 125.98 (−CH=), 127.8 (4 × −CH=), 128.4 (2 × −CH=), 129.0 (6 × −CH=), 129.8 (C), 130.3 (−CH=), 130.7 (−CH=), 131.2 (C), 133.2 (C), 137.0 (C), 137.3 (C), 137.5 (C), 137.8 (C), 144.4 (C), 146.0 (2 × C), 152.2 (C) ppm. $C_{37}H_{24}OS_3$: C 76.52, H 4.17, S 16.7; found C 76.42, H 4.21, S 16.9.

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