# Synthesis of Naphthopyrans and Spironaphthoxazines Annulated to Crown Ether Fragments through a Macrocyclization Strategy

Sergey V. Paramonov,[a,b] Vladimir Lokshin,[b] Olga A. Fedorova*[a]

[a] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilova st., 119991 Moscow, Russian Federation
Fax +7(499)1355085; E-mail: fedorova@ineos.ac.ru

[b] Aix-Marseille Université, CNRS, CINaM UMR 7325, 13288 Marseille, France
E-mail: lokshin@cinam.univ-mrs.fr

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**Abstract:** A practical and convenient procedure for the synthesis of naphthopyrans and spironaphthoxazines annulated to crown ether fragments has been developed. This innovative and general strategy based on a macrocyclization is a flexible and variable synthetic approach for other similar types of compounds.

**Key words:** chromenes, spironaphthoxazine, crown ether, synthesis, macrocyclization

Photochromic compounds represent a large class of compounds able to participate in light-induced reversible transformations. Among photochromes undergoing a cyclohexa-1,3-diene–hexa-1,3,5-triene-type phototransformation, of the greatest interest are spiropyrans, spirooxazines, and chromenes.[1–3] Photochromism of these compounds is due to photochemical conversion of the initial, the so-called 'closed' or spiro (SP) form into the isomeric merocyanine (MC), or 'open', form. In the cases of chromenes, spiropyrans, and spirooxazines the reverse process is both thermal and photochemical. Such transformations are accompanied by color change as closed and open forms usually absorb in the UV and visible region, respectively.

A number of publications and reviews are devoted to the development of synthetic approaches and investigation of this group of photochromes.[4,5] During the last years, the interest to such compounds was caused by a possibility of creation of molecular systems, which may be reversibly changed by light irradiation. The development of such compounds is of importance for the preparation of novel materials for information processing and storage.[6] The photochromic principle is the basis of photoswitches and optical sensors elaborated for environmentally safe technologies used in many branches of modern industry.[6–12]

The exploration of the complex formation process in crown ether systems led to a novel approach for the modification of photochromic behavior.[13] Thus, the binding of metal ions with crown ether moieties of photochromic molecules can change their spectral and photochromic properties. Otherwise, the important feature of the systems is a reversible change in the capacity of a photochromic host molecule for association with guests upon irradiation. Such type of photochromic systems can be regarded as being promising for traditional applications (photochromic ophthalmic lenses or camera filters, reversible holographic systems, and cosmetics) and for molecular electronics, biomimetic chemistry, and optical information storage.[14]

In the structure of the majority of crown-containing naphthopyrans or spiroxazines known in the literature, no macrocyclic fragment is included into the chromophore system of the photochrome, but is bound to it via a bridge.[8] In this case, the formation of coordination bond between metal ions in crown ether moiety and carbonyl group of open merocyanine form can have remarkable influence on the stability of photomerocyanine. In the photochromes annulated to crown ether fragment, the macrocyclic part is the strong donor substituent. The formation of complex reduces the donor character of macrocycle, which can influence on the photochromic characteristics of molecule. Thus, the crown ether participation in the electron density redistribution upon photochromic transformations seems to be of the highest efficacy. Therefore, in this work, we chose chromenes and spironaphthoxazines containing annulated crown ether fragment as the target compounds.

Previously, we have described the synthetic route to the chromene systems annulated with oxacrown ether fragment (Scheme 1, route 1) by introduction of photochromic function into a substrate already containing a crown ether fragment.[15] In the route 2 developed in this paper, a crown ether fragment is introduced into a photochromic molecule.

The detailed scheme of synthesis by route 1 is presented in Scheme 2. The high or good yields of the crown-containing substrates by this route seem to be promising for preparing oxacrown ether containing derivatives of benzo- and naphthopyrans. But this synthetic strategy has got some disadvantages. The accessibility of crown annulated substrates limits significantly the use of the first approach. Mostly, oxacrown ether containing derivatives of benzene or naphthalene used as initial reagents are commercially

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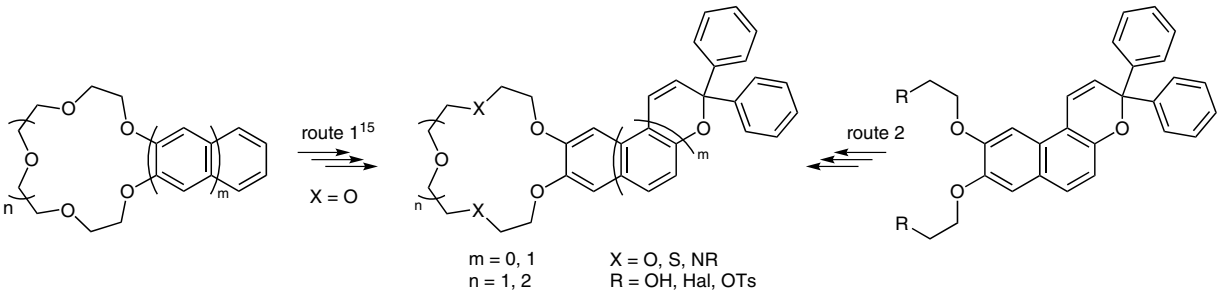


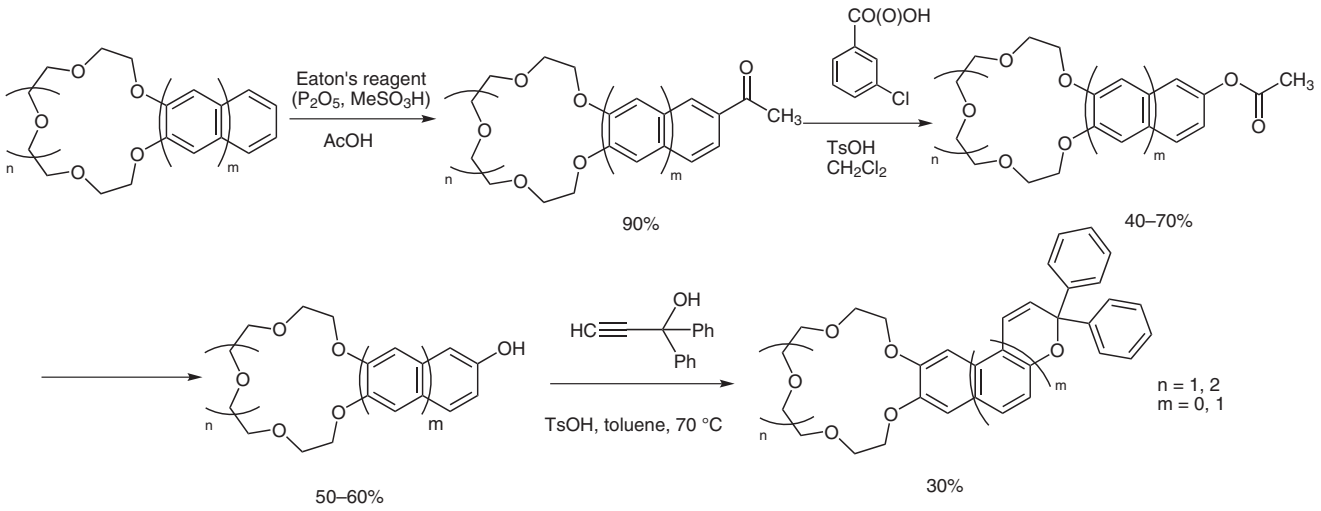

**Scheme 1** Approaches to synthesis of the target benzo- and naphthopyrans

available. Note also that the price of reagents may be rather high in this case. Moreover, a certain type of substitution on the target chromene may require preliminary synthesis of the crown ether. Significant limitation of the approach is the impossibility to use non-oxacrown ether derivatives, because acylation and oxidation conditions applied in the method seem to be rather destructive for aza- or thiacrown ethers. This makes the preparation of the corresponding chromenes impossible by the first approach.

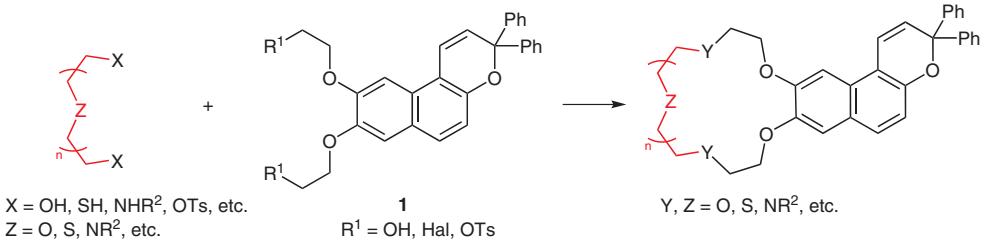
In this paper, we used an alternative synthetic route, which concluded in the crown ether fragment construction after the formation of the photochromic molecule (Scheme 1). Though the second approach involved greater number of stages, it afforded naphthopyrans containing the crown ether fragments of different size and heteroatomic composition.

For the preparation of naphthopyrans annulated to the crown ether fragments of different size and heteroatomic composition, chromenes **1**, containing various terminal groups in the aliphatic fragments, were suggested as the precursors (Scheme 3). Derivatives with the hydroxy, chlorine, and iodine groups are necessary for the synthesis of oxa-, thia-, and azacrown ethers, respectively. Tosylate substituents are rather universal and may be used for preparation of macrocycles of any heteroatomic composition.

The key compounds for the synthesis of chromenes **1** are the appropriate naphthols **2**. Such compounds have not been described. Therefore, synthetic techniques for the preparation of similar molecules and the methods used for




**Scheme 2** Synthesis of benzo- and naphthopyrans by route 1



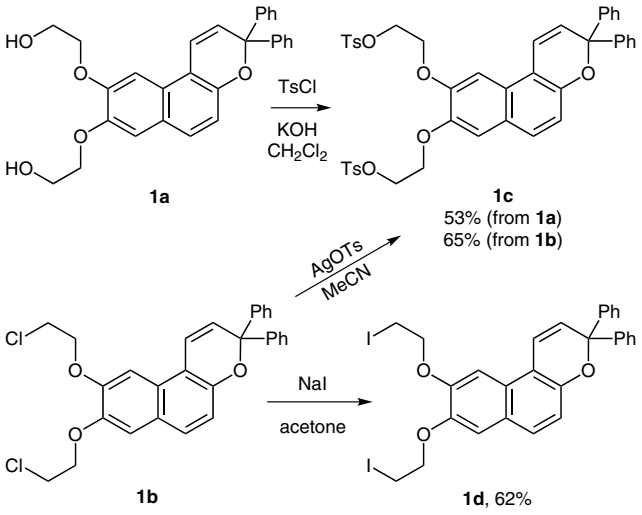

**Scheme 3** The concept of crown ether fragment importation into chromene molecule



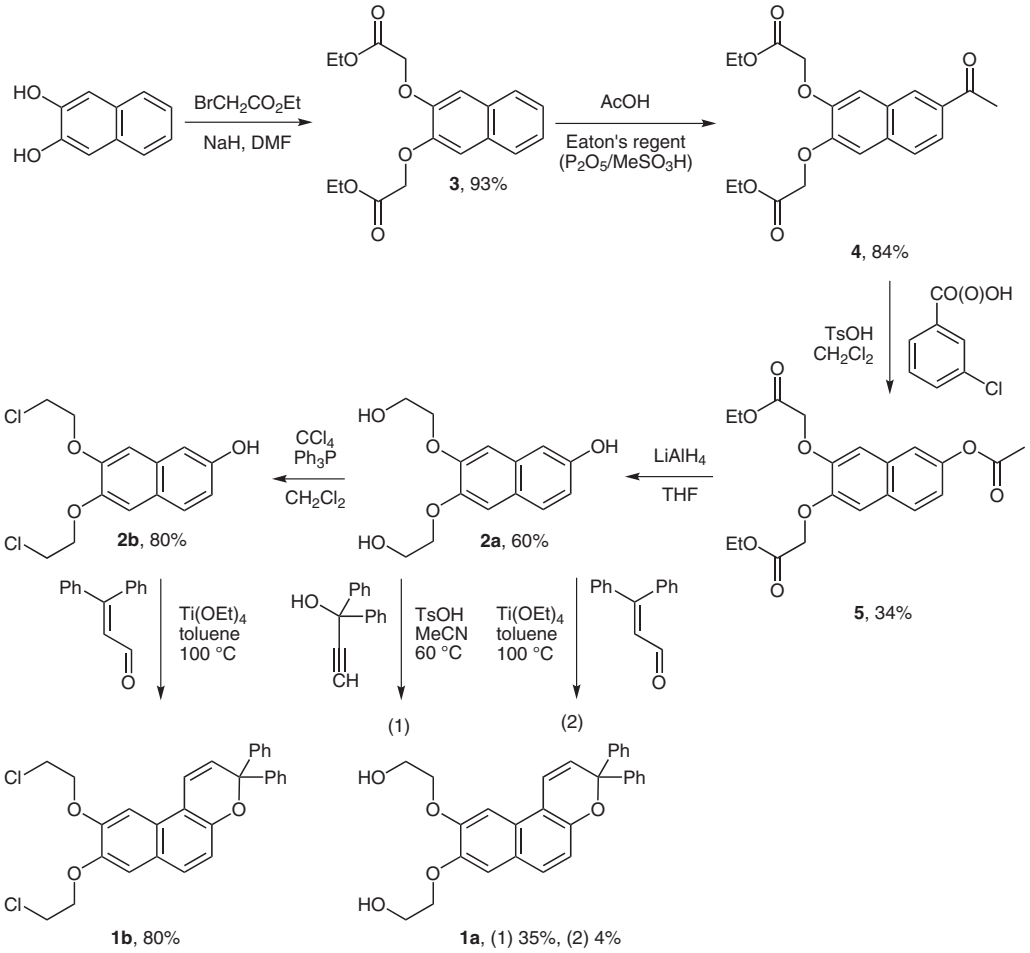
obtaining crown-containing phenols were adapted from the literature.[16–19] As a result, we used a route for the synthesis of naphthols **2** from dihydroxynaphthalene by its successive O-alkylation, acylation, Baeyer–Villiger oxidation, and $LiAlH_4$ reduction (Scheme 4; experimental details are presented in the Supporting Information). The most complicated stage was the oxidation of ketone **4** to ester **5**, which afforded only 34% yield. Other stages gave high or moderate yields. Naphthol **2a** was also successfully converted into chloro-substituted derivative **2b** (80%).

The next stage was the synthesis of chromenes from naphthols **2** (Scheme 4). Due to high polarity, the compound **2a** was insoluble in toluene, which was usually used as a solvent in the reaction with β-phenylcinnamaldehyde. This led to extremely low reaction yield (4%). Accordingly, photochromic derivative **1a** was synthesized using the method with propargyl alcohol. Acetonitrile, in which the solubility of compound **2a** was much higher than in toluene, was used as a solvent. In this case, the yield was found to be satisfactory (35%). Chromene **1b** was obtained in high yield (80%) by the second method from naphthol **2b**. Terminal substituents in compounds **1a** and **1b** were replaced by tosylate groups and iodine (Scheme 5). Direct tosylation of compound **1a** with TsCl in the presence of a base gave chromene **1c** in 53% yield. Also,




**Scheme 5** Replacement of terminal groups in chromenes **1a** and **1b**

**1c** was obtained from compound **1b** by reaction with AgOTs in acetonitrile. In this case, reflux of the reaction for four days gave a mixture of the initial chromene and substitution products with predominant content of monosubstituted component (mixed terminal groups). The exposure of the reaction mixture to 140 °C during 20 hours




**Scheme 4** Synthesis of chromene-precursors **1a** and **1b**

increased the conversion of compound **1b** and produced compound **1c** in 65% yield (see the Supporting Information). Diiodo derivative **1d** was synthesized from **1b** according to the standard technique (see the Supporting Information).

For obtaining the target crown-containing chromenes, the precursors were reacted with oligoethylene glycols containing various end groups. Compounds **1a** and **1c** were used for obtaining oxacrown derivative **6**; compounds **1b** and **1d** were employed for the synthesis of dithia- **7** and diazacrown **8** derivatives, respectively (Scheme 6). It should be noted that the obtained yields correspond to the average yields in crown ether syntheses. Nevertheless, the yield of naphthopyran **6** differs from analogous thia and aza derivatives by 2–4 times, which is probably associated with lower nucleophilic character of oxygen atoms of OH groups in chromene **1a** or diethylene glycol in the reaction with chromene **1c**. Structure of compound **7b** was proved by X-ray crystal structure analysis (Figure 1). In the synthesis of compound **7a**, a nonphotochromic product **9**, resulting from the addition of water molecule to the double bond of the pyran ring, was detected. The suggestion about its structure was made on the basis of 1D and 2D $^1$H NMR spectra in $CDCl_3$ (Figure 2, and Figure S1 in the Supporting Information).

The NMR spectra possess a triplet signal of aliphatic proton (6.12 ppm and 6.57 ppm in $CDCl_3$ and DMSO-$d_6$ solutions, respectively) shifted downfield. This testifies about closely located electron-withdrawing group. In addition, the aliphatic part of the spectrum demonstrates a doublet proton signal (see expanded spectrum fragments in Figure 2). The coupling constants of the signals coincide and are equal to 7.2 Hz. The COSY spectrum proves mutual coupling of the signals (Figure S1 in the Supporting Information). An indirect proof of OH group presence is a singlet proton signal (8.85 ppm) in the $^1$H NMR spectrum in DMSO-$d_6$ (Figure 2, b). The values of integral intensities also prove the occurrence of three additional protons. The position of 1-H at about 6 ppm would suggest a benzylic-type proton over the alternative;[19] thus, the most probable structure is designated as **9b**.

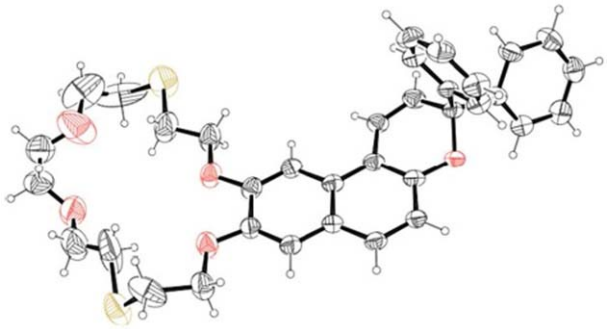
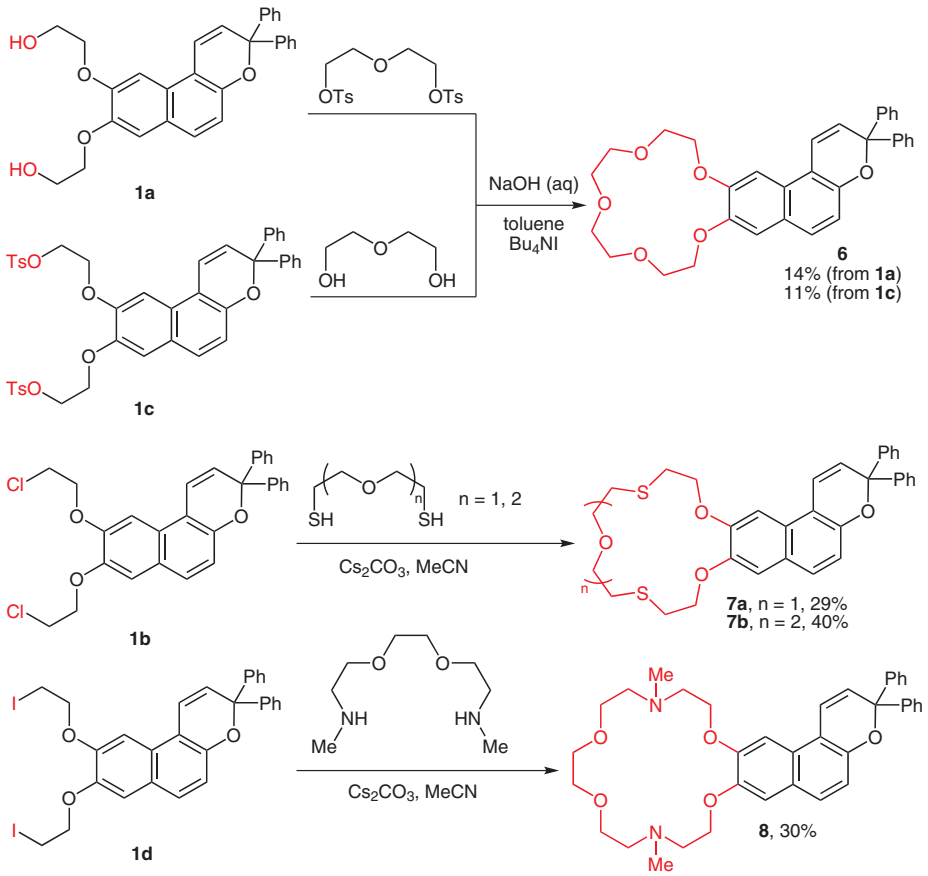


**Figure 1** X-ray crystal structure of naphthopyran **7b**




**Scheme 6** Synthesis of target chromenes from precursors **1**

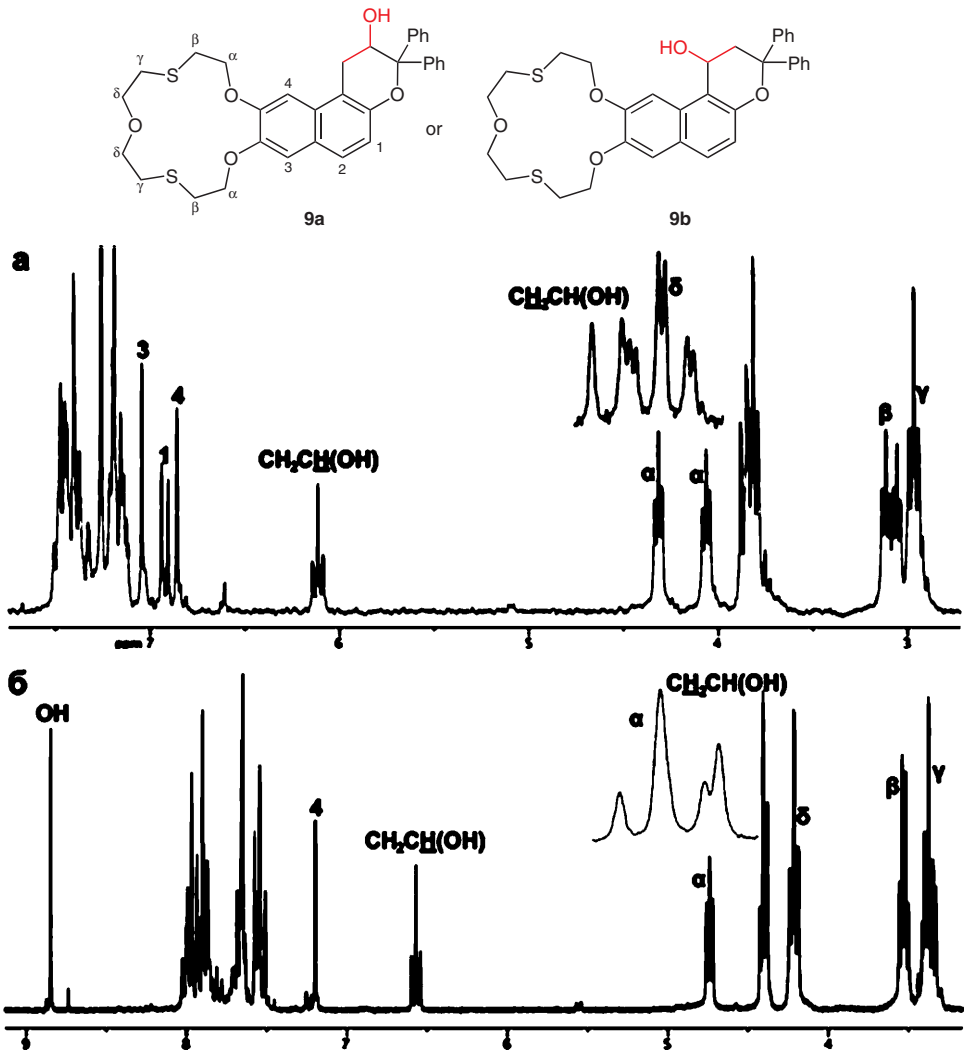



**Figure 2** $^1$H NMR spectra of compound **9** in (a) $CDCl_3$ and (b) DMSO-$d_6$. Inserts correspond to the expanded regions 3.76–3.90 ppm (trace a) and 4.36–4.44 ppm (trace b).

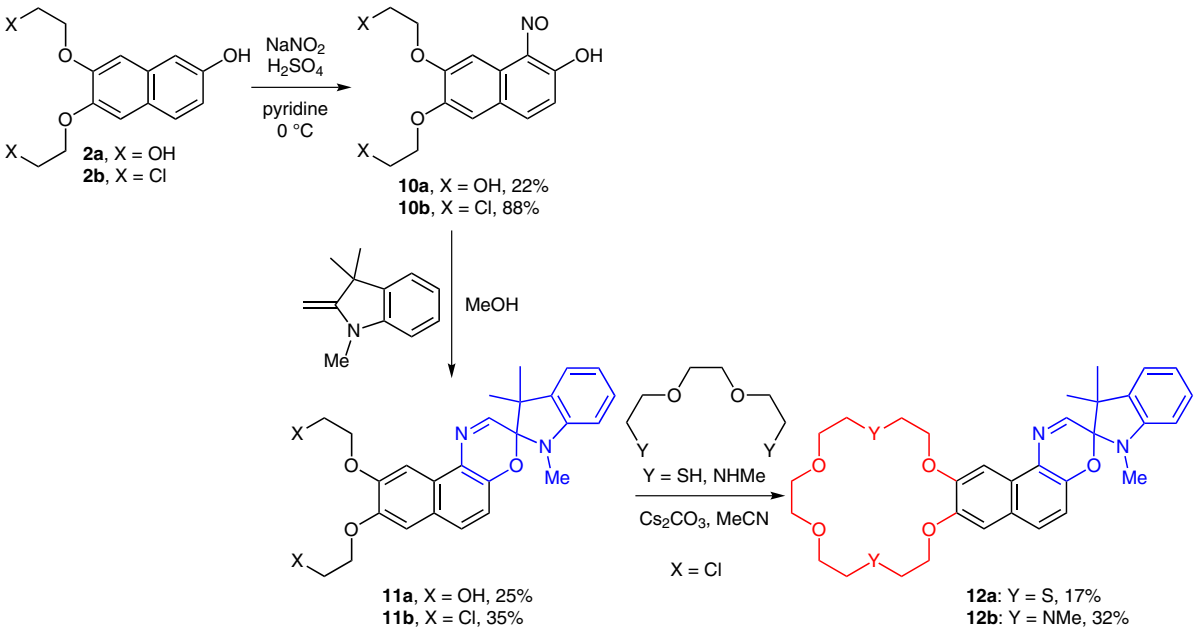
This approach to synthesis of target compounds is rather flexible and allows obtaining different photochromic systems. Hence, using phenols **2**, spironaphthoxazines **11a** and **11b** were synthesized (Scheme 7).[4,12] The key compounds in spironaphthoxazine synthesis are nitrosonaphthols **10a**,**b** obtained by nitrosation of corresponding naphthols. The lower yield of compound **10a** compared with chloro-substituted analogue is due to its good solubility in water and poor solubility in organic solvents that significantly hindered its separation from the reaction mixture.

On the contrary, derivative **10b** is insoluble in water that considerably favored the workup. Spironaphthoxazines **11a**,**b** were synthesized from nitrosonaphthols by interaction with 2-methylenetrimethylindolenine in methanol in typical yields (25% and 35% for OH and Cl derivative, respectively). Similar to the previously described procedures for chromene preparation, dithia- or diaza-18-crown-6 ether derivatives **12a**,**b** were synthesized from precursor **11b** (Scheme 7).

Thus, for the first time, an approach to the synthesis of crown-annulated chromenes and spironaphthoxazines from the available starting materials through macrocyclic strategy was developed. By varying substituents of terminal alkyl fragments in precursors, several chromenes with oxa, dithia, and diazacrown ethers as well as spironaphthoxazine with dithiacrown ether were synthesized.

In the approach used in the present work, the crown ether is formed at the final stage of the synthesis. Therefore, various macrocyclic derivatives with different heteroatomic composition and size may be synthesized. The advantage of the synthetic way is its flexibility and variability that also allows using the synthetic approach for other photochromic compounds, such as spironaphthoxazines whose synthesis by the first method[15] is rather difficult (especially at the nitrosation stage).

Note that the synthesis presented herein constitutes a rare example of undertaking the macrocyclization post chromene/oxazine ring formation. The macrocyclization occurs with yields slightly lower than those in the case of




**Scheme 7** Spironaphthoxazine synthesis

more simple benzene or naphthalene derivatives.[15] This opens the way for introducing macrocyclic fragments into other similarly structured molecules.

NMR spectra were recorded on a Bruker Avance 250 and 400 MHz instruments for solutions in $CDCl_3$ and DMSO-$d_6$ unless otherwise stated; δ values are given in ppm, coupling constants are quoted in Hz. Melting points are not corrected. All chemicals were purchased from Aldrich, Acros, or AlfaAesar and used without additional purification.

Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution in $CH_2Cl_2$. X-ray diffraction experiments were carried out with a Bruker APEX II CCD area detector, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans). Reflection intensities were integrated using SAINT software and absorption correction was applied semiempirically using SADABS program. The structures were solved by direct method and refined by the full-matrix least-squares against $F^2$ in anisotropic approximation for non-hydrogen atoms. Crystal data and structure refinement parameters for **7b** are given in Tables S1 and S2 in the Supporting Information. All calculations were performed using the SHELXTL software.[20]

For complete experimental procedures, analytical data, and NMR spectra see the Supporting Information.

**Crown-Annulated Chromenes; Oxacrown Derivatives 6; General Procedure**

The procedure was adopted from the literature.[21] A solution of the appropriate alcohol (0.2 mmol) and $Bu_4NI$ (TBAI, 0.1 mmol) in toluene (5 mL) was heated to 50 °C and 50% aq NaOH (0.4 mL) was added. The mixture was stirred for 30 min, followed by the addition of toluene (5 mL) solution of ditosylate derivative (0.2 mmol). The reaction mixture was refluxed for 16 h, then cooled, and washed with $H_2O$ (50 mL). The organic layer was separated and the solvent was removed. The residue was purified by column chromatography ($CH_2Cl_2$–MeOH, 100:1 → to 20:1).

**Dithia- and Diazacrown Derivatives 7a,b,8,12a,b; General Procedure**

The procedure was adopted from the literature.[22] To a suspension of $Cs_2CO_3$ (2.5 mmol) in anhydrous MeCN (100 mL) was added dropwise simultaneously two 25 mL solutions in MeCN, each containing the appropriate chromene (0.5 mmol) and thiol or amine (1.05 mmol). The mixture was refluxed for 16 h. Upon cooling, the precipitate was filtered off and washed with MeCN (20 mL). The combined organic fractions were evaporated and the residue was dissolved in $CH_2Cl_2$ (50 mL). The resulting solution was washed with $H_2O$ (50 mL) and evaporated in the presence of a small amount of benzene. The residue was purified by column chromatography.

**3,3-Diphenyl-9,10,12,13,15,16,18,19-octahydro-3*H*-[1,4,7,10,13]pentaoxacyclopentadeca[2′,3′:4,5]benzo[*f*]chromene (6)**

According to the general procedure for the preparation of oxacrown derivatives, chromene **1a** (0.45 g, 1 mmol), diethylene glycol ditosylate (0.40 g, 1 mmol), TBAI (0.20 g, 0.5 mmol), and 50% aq NaOH (2 mL) afforded chromene **6** as a viscous oil;[15] yield: 0.08 g (14%).

According to the general procedure for the preparation of oxacrown derivatives, chromene **1c** (0.50 g, 0.655 mmol), diethylene glycol (0.07 g, 0.655 mmol), TBAI (0.12 g, 0.3275 mmol), and 50% aq NaOH (1.5 mL) afforded chromene **6** as a viscous oil;[15] yield: 0.04 g (11%).

**3,3-Diphenyl-9,10,12,13,15,16,18,19-octahydro-3*H*-[1,4,10]trioxa[7,13]dithiacyclopentadeca[2′,3′:4,5]benzo[*f*]chromene (7a)**

According to the general procedure for the preparation of dithia- and diazacrown derivatives, chromene **1b** (0.25 g, 0.5 mmol), 2,2′-oxydi(ethanethiol) (0.15 g, 1.05 mmol), and $Cs_2CO_3$ (0.81 g, 2.5 mmol) gave, after chromatographic purification (eluent: EtOAc–cyclohexane, 1:5), chromene **7a** as an orange solid; yield: 0.08 g (29%); mp 138–141 °C (pentane).

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 2.88–2.92 (m, 4 H, 2 × $SCH_2$), 3.04–3.09 (m, 4 H, 2 × $SCH_2$), 3.70–3.73 (m, 4 H, $CH_2OCH_2$), 4.23–4.25 and 4.33–4.38 (m, 4 H, 2 × $OCH_2$), 6.56 (d, $J$ = 9.9 Hz, 1 H, H-2), 7.12 (d, $J$ = 8.7 Hz, 1 H, H-5), 7.25–7.27 (m, 3 H), 7.32–7.36 (m, 4 H), 7.41 (s, 1 H, H-7), 7.49–7.51 (m, 5 H), 7.59 (d, $J$ = 8.7 Hz, 1 H, H-6).



$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 30.80, 31.26, 71.06, 71.09, 71.13, 71.21, 81.74, 102.89, 109.15, 113.97, 116.24, 120.57, 125.02, 125.75, 127.78, 126.76, 127.83, 128.38, 128.61, 145.38, 147.26, 149.52, 149.98.

HRMS: *m*/*z* calcd for $C_{33}H_{32}O_4S_2$ + Na : 579.1639; found: 579.1628.

Anal. Calcd for $C_{33}H_{32}O_4S_2$: C, 71.19; H, 5.79. Found: C, 72.95; H, 5.92.

**3,3-Diphenyl-9,10,12,13,15,16,18,19,21,22-decahydro-3*H*-[1,4,10,13]tetraoxa[7,16]dithiacyclooctadeca[2′,3′:4,5]benzo[*f*]chromene (7b)**

According to the general procedure for the preparation of dithia- and diazacrown derivatives, chromene **1b** (0.25 g, 0.5 mmol), 2,2′-(ethane-1,2-dioxy)di(ethanethiol) (0.19 g, 1.05 mmol), and $Cs_2CO_3$ (0.81 g, 2.5 mmol) gave, after chromatographic purification (eluent: EtOAc–cyclohexane, 1:5), chromene **7b** as a yellow solid; yield: 0.12 g (40%); mp 189–192 °C (*n*-heptane–benzene).

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 2.92–2.96 (m, 4 H, 2 × $SCH_2$), 3.10–3.17 (m, 4 H, 2 × $SCH_2$), 3.58 (s, 4 H, 2 × $OCH_2$), 3.69–3.73 (m, 4 H, $OCH_2CH_2O$), 4.21–4.24 (m, 2 H, $OCH_2$), 4.30–4.33 (m, 2 H, $OCH_2$), 6.39 (d, *J* = 9.9 Hz, 1 H), 7.04–7.08 (m, 2 H, H-5, H-2), 7.13–7.37 (m, 8 H), 7.50–7.53 (m, 5 H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 30.35, 30,67, 31.41, 69.67, 70.07, 72.16, 77.69, 77.90, 78.12, 101.59, 101.71, 108.10, 115.94, 120.19, 120.25, 124.85, 125.48, 126.71, 127.19, 127.51, 128.05, 128.14, 128.22, 145.06, 146.97, 149.37, 149.59.

HRMS: *m*/*z* calcd for $C_{35}H_{36}O_5S_2$ + Na: 623.1901; found: 623.1890.

Anal. Calcd for $C_{35}H_{36}O_5S_2$: C, 69.97; H, 6.04. Found: C, 68.23; H, 5.97.

**11,20-Dimethyl-3,3-diphenyl-9,10,12,13,15,16,18,19,21,22-decahydro-3*H*-[1,4,10,13]tetraoxa[7,16]diazacyclooctadeca[2′,3′:4,5]benzo[*f*]chromene (8)**

According to the general procedure for the preparation of dithia- and diazacrown derivatives, chromene **1d** (0.50 g, 0.74 mmol), *N*,*N*′-dimethyl-2,2′-(ethane-1,2-dioxy)di(ethylamine) (0.15 g, 0.815 mmol), and of $Cs_2CO_3$ (1.1 g (3.34 mmol) gave, after chromatographic purification (eluent: EtOAc–MeOH, 100:1 → 0:1), chromene **8** as a yellow oil; yield: 0.15 g (30%).

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 2.31 (s, 3 H, $NCH_3$), 2.33 (s, 3 H, $NCH_3$), 2.76, 2.95 (m, 8 H, 4 × $NCH_2$), 3.50 (m, 4 H, $OCH_2CH_2O$), 3.56–3.58 (m, 4 H, 2 × $OCH_2$), 4.11, 4.22 (m, 4 H, 2 × $OCH_2$), 6.56 (d, *J* = 9.9 Hz, 1 H, H-2), 7.10 (d, *J* = 8.7 Hz, 1 H, H-5), 7.24–7.27 (m, 3 H), 7.33–7.36 (m, 4 H), 7.40 (s, 1 H, H-7), 7.49–7.53 (m, 5 H), 7.56 (d, *J* = 8.7 Hz, 1 H, H-6).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 29.70, 31.17, 42.51, 42.89, 52.22, 55.60, 57.00, 66.90,68.91, 70.13, 81.71, 102.14, 103.17, 109.04, 113.94, 116.06, 118.56, 120.05, 124.97, 125.67, 126.76, 127.82, 128.00, 143.40, 147.17, 149.24, 150.04.

HRMS: *m*/*z* calcd for $C_{37}H_{43}N_2O_5$: 595.3171; found: 595.3159.

Anal. Calcd for $C_{37}H_{42}N_2O_5$: C, 74.72; H, 7.12. Found: C, 75.08; H, 7.32.

**Spironaphthoxazines**

**9′,10′,12′,13′,15′,16′,18′,19′,21′,22′-Decahydro-1,3,3-trimethylspiro[indoline-2,3′-[3*H*][1,4,10,13]tetraoxa[7,13]dithiacyclooctadeca[2′,3′:6,7]naphtho[2,1-*b*][1,4]oxazine] (12a)**

According to the general procedure for the preparation of dithia- and diazacrown derivatives, spironaphthoxazine **11b** (0.50 g, 1.03 mmol), 2,2′-(ethane-1,2-dioxy)di(ethanethiol) (0.40 g, 2.165 mmol), and $Cs_2CO_3$ (1.70 g, 5.15 mmol) gave, after chromatographic purification (eluent: $CH_2Cl_2$–cyclohexane, 1:1 → 1:0), spironaphthoxazine **12a** as a beige solid; yield: 0.10 g (17%); mp 184–186 °C (MeCN).

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 1.25 and 1.28 (2 s, 6 H, 2 × $CH_3$), 2.69 (s, 3 H, $NCH_3$), 2.93–2.97 (m, 4 H, 2 × $SCH_2$), 3.11–3.15 (m, 4 H, 2 × $SCH_2$), 3.54 (s, 4 H, $OCH_2CH_2O$), 3.64–3.67 (m, 4 H, $CH_2OCH_2CH_2OCH_2$), 4.21 (t, *J* = 6.7 Hz, 2 H, $OCH_2$), 4.29 (t, *J* = 6.7 Hz, 2 H, $OCH_2$), 6.65 (d, *J* = 7.8 Hz, 1 H, H-4), 6.89 (ddd, *J* = 7.4, 7.4, 1.0 Hz, 1 H, H-5), 6.90 (d, *J* = 8.9 Hz, 1 H, H-6′), 7.13–7.18 (m, 2 H, H-6, H-7), 7.30 (s, 1 H, H-7′), 7.61 (d, *J* = 8.8 Hz, 1 H, H-5′), 7.77 (s, 1 H, H-24′), 7.83 (s, 1 H, H-2′).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 20.92, 25,62, 29.75, 43.34, 51.91, 55.80, 57.10, 67.09, 69.26, 69.50, 98.60, 103.04, 107.58, 110.76, 115.01, 120.01, 121.98, 122.37, 125.02, 126.91, 128.31, 136.60, 143.31, 146.99, 147.81, 149.76, 151.87.

HRMS: *m*/*z* calcd for $C_{32}H_{38}N_2O_5S_2$ + Na: 617.2119; found: 617.2107.

Anal. Calcd for $C_{32}H_{38}N_2O_5S_2$: C, 64.62; H, 6.44. Found: C, 64.96; H, 6.51.

**11′,20′-Dimethyl-9′,10′,12′,13′,15′,16′,18′,19′,21′,22′-Decahydro-1,3,3-trimethylspiro[indoline-2,3′-[3*H*][1,4,10,13]tetraoxa[7,13]diazacyclooctadeca[2′,3′:6,7]naphtho[2,1-*b*][1,4]oxazine] (12b)**

According to the general procedure for the preparation of dithia- and diazacrown derivatives, spironaphthoxazine **11b** (0.50 g, 1.03 mmol), *N*,*N*′-dimethyl-2,2′-(ethane-1,2-dioxy)di(ethylamine) (0.20 g, 1.1 mmol) and $Cs_2CO_3$ (1.55 g, 4.65 mmol) gave, after chromatographic purification (eluent: $CH_2Cl_2$–cyclohexane, 1:1 → 1:0), spironaphthoxazine **12b** as a yellow oil; yield: 0.10 g (32%).

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 1.25 and 1.27 (2 s, 6 H, 2 × $CH_3$), 2.29 and 2.31 (2 s, 6 H, 2 × $NCH_3$), 2.69 (s, 3 H, $NCH_3$), 2.73–2.78 (m, 4 H, 2 × $NCH_2$), 2.93–2.97 (m, 4 H, 2 × $NCH_2$), 3.50 (s, 4 H, $OCH_2CH_2O$), 3.55–3.57 (m, 4 H, $CH_2OCH_2CH_2OCH_2$), 4.11 (t, *J* = 5.7 Hz, 2 H, $OCH_2$), 4.18 (t, *J* = 5.7 Hz, 2 H, $OCH_2$), 6.64 (d, *J* = 7.8 Hz, 1 H, H-4), 6.83 (ddd, *J* = 7.4, 7.4, 1.0 Hz, 1 H, H-5), 6.88 (d, *J* = 8.9 Hz, 1 H, H-6′), 7.13–7.18 (m, 2 H, H-6, H-7), 7.28 (s, 1 H, H-7′), 7.59 (d, *J* = 8.8 Hz, 1 H, H-5′), 7.78 (s, 1 H, H-24′), 7.82 (s, 1 H, H-2′).

$^{13}$C NMR 100 MHz, DMSO-$d_6$): δ = 20.93, 25,63, 29.76, 43.17, 51.87, 55.80, 57.10, 67.09, 69.34, 70.22, 98.50, 101.31, 101.59, 107.56, 108.53, 114.31, 119.97, 121.97, 122.36, 124.82, 126.58, 128.98, 136.05, 143.02, 147.4, 153.39, 155.65.

HRMS: *m*/*z* calcd for $C_{34}H_{45}N_4O_5$ + $C_{34}H_{44}N_4O_5$ + Na: 589.3389 + 611.3209; found: 589.3374 + 611.3201.

Anal. Calcd for $C_{34}H_{44}N_4O_5$: C, 68.71; H, 7.69. Found: C, 68.76; H, 7.61.

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**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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