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Chiroptical molecular switches

de Lange, Ben

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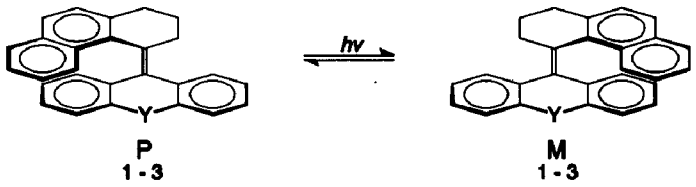
CHAPTER 3

CHIROPTICAL MOLECULAR SWITCHES: STRUCTURAL VARIATIONS

3.1 Introduction

The principles and requirements for a molecular optical data storage system based on photochemical switching between two chiral isomers **P** and **M** of sterically overcrowded alkenes have been explained in Chapter 2, including a description of the basic structure of these molecules (Scheme 3.1, Y = O, S, -). An excellent synthetic route for this class of compounds has been presented based on a diazo-thioketone cycloaddition between the upper and lower halves of the molecules.



Scheme 3.1. P and M isomers of alkenes 1 - 3.

From the various criteria, enumerated in Section 2.3.3, which have to be fulfilled by these ethylenes to be suitable for application as chiroptical molecular switches, the prerequisite is thermal stability of both isomers **P** and **M**; i.e. both forms should be able to exist as stable enantiomers without the occurrence of isomerization at normal temperatures (approximately -20 – 50 °C). In principle, isomerization can occur by two mechanisms: rotation around the double bond or by movement of the naphthalene moiety in the upper half of the molecule along the aromatic groups in the lower part.[1] Steric interactions as well as π-electron (de)stabilization are responsible for the energy barriers of these processes, which therefore largely depend on the conformation of these molecules and the substitution patterns present.[1]
Based upon these considerations and the successful separation of the enantiomers of alkenes **1** - **3** (see Section 3.2.4), we decided to synthesize a variety of sterically overcrowded alkenes in order to elucidate the influence of several structural features on the isomerization barriers. Furthermore, X-ray analyses are essential, as they can provide a detailed insight into the molecular structure of these helically shaped molecules. These investigations can indicate which types of inherently dissymmetric alkenes possess sufficient thermal stability required for application in reversible optical data storage.
So far, the diazo-thioketone reaction has been applied for the synthesis of alkenes **1** - **3** with structural variations in the bridging group in the lower part of the molecule (Y = O, S, -, Scheme 3.1). The next section will deal with the extension of the synthetic

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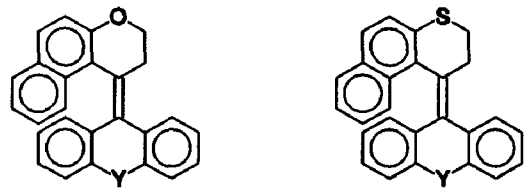
[1] The mechanisms of these isomerization pathways, which have been proposed for sterically overcrowded bistricyclic ethylenes, are discussed in Chapter 4.

methodology developed in the previous chapter and will describe the synthesis of alkenes functionalized with oxygen (**4** - **6**) and sulfur (**7** - **9**) atoms in the upper part of the molecule, i.e. "oxo"- and "thio"-phenanthrene analogues of the "all carbon" compounds described in Chapter 2, whereby the lower part will be a xanthene, thioxanthene or fluorene tricyclic unit (Y = O, S, -, respectively, Figure 3.1).



4 - 6 **7 - 9**

Figure 3.1. "Oxo and "thio" phenanthrene based alkenes 4 - 9.

3.2 "Oxo" and "Thio" Phenanthrene Based Alkenes

3.2.1 Synthesis of 2,3-Dihydronaphtho(thio)pyranones

The presence of a 2-naphthol or 2-thionaphthol[2] derived structural moiety in the upper part of **4** - **9** can be recognized. These commercially available compounds can be used as starting materials for the synthesis of 2,3-dihydronaphtho(thio)-pyranones (**12**) and (**16**), shown in Scheme 3.2, following essentially the procedures described by Bachman and Levine.[3]

The Michael addition of 2-naphthol (**10**) to acrylonitrile was performed by refluxing both compounds in the presence of benzyltrimethylammonium hydroxide (Triton B) as a base and afforded adduct **11**, which was converted to the cyclic ketone **12** by stirring in 85% aqueous H_2SO_4 in 61% overall yield.

In the case of 2-thionaphthol, the Michael addition step was performed more carefully at lower temperatures (-5 – 65 °C), due to the enhanced reactivity of the thiol group in **14** compared with the less nucleophilic oxygen atom in 2-naphthol (**10**). Lower reaction temperatures also suppressed the formation of large amounts of polymeric material. Thiols are known to give radicals easily, which can initiate the polymerization of acrylonitrile. Some polymeric material could be removed from the adduct **15** by the addition of ether to the reaction mixture which caused the precipitation of polyacrylonitrile. The use of polyphosphoric acid instead of 85% aqueous H_2SO_4 for the intramolecular ring closure of the Michael adduct **15** to the ketone **16** increased the chemical yield for this step from 42%[3] to 98%. The low yield obtained when H_2SO_4 is used to effect the ring closure might be ascribed to easy sulfonation of the naphthalene ring, which is activated by the presence of the thiol group. These two steps furnished the ketone **16** in an overall yield of 96%.

Hydrazones **13** and **17** were prepared by refluxing the ketones in ethanol with an excess of hydrazine hydrate according to the general method described in Chapter 2.7.

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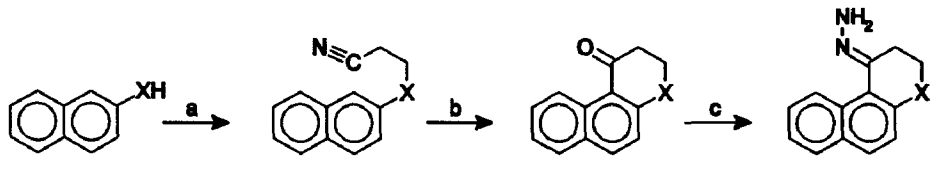
[2] The use of 2-naphthylamine (X = N-H) has not been considered, due to the known strongly carcinogenic character of amino-functionalized naphthalenes. See e.g. Vogel, A. *Textbook of Practical Organic Chemistry 4th ed.* Longman Inc.: New York, 1978, p 21, 667.

[3] Bachman, G.B.; Levine, A.H. *J. Am. Chem. Soc.* **1947**, *69*, 2311.



10 X = O
14 X = S

11 X = O
15 X = S

12 X = O
16 X = S

13 X = O
17 X = S

Scheme 3.2. Synthesis of hydrazones 13 and 17. Reagents, conditions and yields: X = O: a) acrylonitrile, Triton B, Δ, 18h, 67%; b) 85% aqueous H_2SO_4, RT, 2h, 91%; c) $NH_2.NH_2.H_2O$, ethanol, Δ, 2h, 83%. X = S: a) acrylonitrile, Triton B, -5 - 65 °C, 1h, 94%; b) polyphosphoric acid, 110 °C, 3h, 98%; c) $NH_2.NH_2.H_2O$, ethanol, Δ, 2h, 79%.

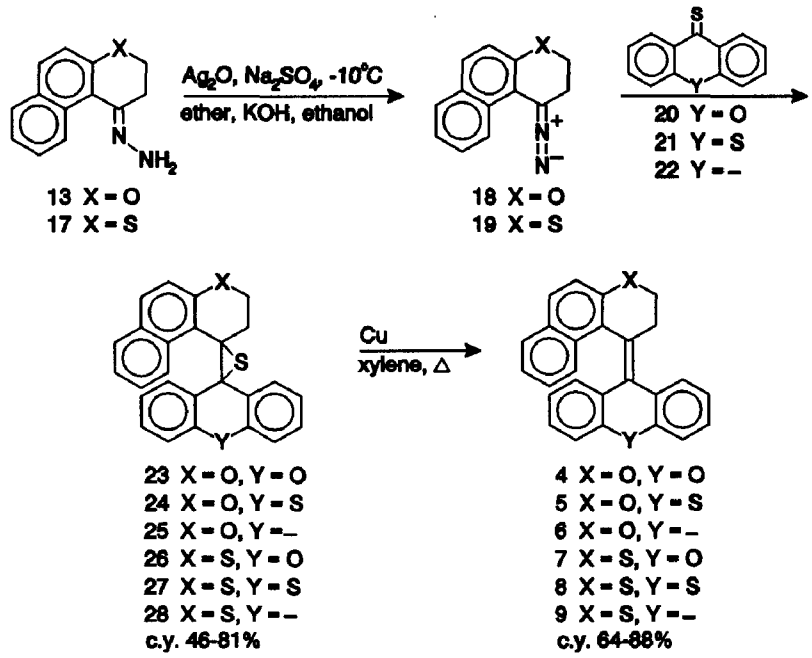
This three step procedure to obtain 2,3-dihydronaphtho(thio)pyran functionalized diazo precursors for the upper part of the ethylenes has some important advantages compared with the synthesis of the "all carbon" tetrahydrophenanthrene precursor described in the previous chapter:

- The tetrahydrophenanthrenone used in Chapter 2 required a lengthy 7 steps synthesis, which will be a limiting factor for further functionalization studies.
- The reactions described here can be performed on a large scale using relatively cheap starting materials in high overall yields.
- Functionalization should be possible by using substituted 2-naphthol or 2-thionaphthol derivatives.
- The presence of an electron donating group (the ether or sulfide group) in the naphthopyran moiety, which may be important for directing the electronic properties of the molecules (see Section 2.3.4).
- The possibility to obtain an electron accepting group via oxidation of the sulfide to a sulfone functionality, as will be illustrated in Section 3.2.3.

3.2.2 Synthesis of 2,3-Dihydronaphtho(thio)pyran Based Alkenes

The diazo-thioketone reaction has been performed in an identical way as described in Chapter 2 and is depicted in Scheme 3.3. Hydrazones **13** and **17** were oxidized with silver(I)oxide to the corresponding red diazo compounds, which afforded, after addition of 9H-xanthene-9-thione (**20**), 9H-thioxanthene-9-thione (**21**) or 9H-fluorene-9-thione (**22**), thiiranes **23** - **28**. The episulfides were converted to the ethylenes **4** - **9** following the general method with copper powder in boiling xylene. Crystallization from ethanol furnished the alkenes as analytically pure solids. The overall yields for the two steps are 30 and 32% for the fluorene functionalized alkenes **6** and **9**, respectively, and vary between 60 and 69% for the (thio)xanthene derivatives. The rather low yields for **6** and **9** can be explained by the difficulties described in Section 2.5.3 to synthesize the unstable 9H-fluorene-9-thione (**22**).
As indicated in Chapter 2, the oxidation step seemed to be dependent on the quality of the silver(I)oxide used, which was observed in particular during the oxidation of the naphthothiopyran hydrazone **17**. In some cases, the oxidation of 4 mmol of **17** was completed within seconds, whereby even a small increase in temperature could be noticed. However during other experiments, using silver(I)oxide from other batches or

even the same batch (!?), the reaction proceeded very slowly and after 3 hours only a slightly red colour was observed. The reason for this strange behaviour is still unclear.



Scheme 3.3. Synthetic scheme for "oxo and "thio" phenanthrene based alkenes 4 - 9.

The aliphatic protons at C-2 and C-3[4] in the upper part of the naphthopyran based alkenes **4** - **6** were observed as four well separated absorptions in the ^{1}H NMR spectrum, indicating the chiral conformation of these structures. The ^{1}H NMR and ^{13}C NMR absorptions of the primary and secondary groups (CH and CH_2) of **4** have been assigned completely by using combined NOESY, COSY and HETCOR 2D NMR techniques and the results are given in the Experimental Section.

3.2.3 Oxidation of the Sulfide to a Sulfone Group

An important aspect for the application of these sterically overcrowded ethylenes as chiroptical molecular switches is the ability to control the electronic properties via the introduction of electron donating and accepting groups, as has been discussed in Section 2.3.4. A facile and convenient method can be the oxidation of the sulfur atom to an electron accepting sulfone group, whereby the ether group can function as the donor moiety. The use of ether and sulfone groups as electron donor- and acceptor-groups, respectively, is also considered as an excellent substituent combination for future applications of these organic molecules in non-linear optics.[5]

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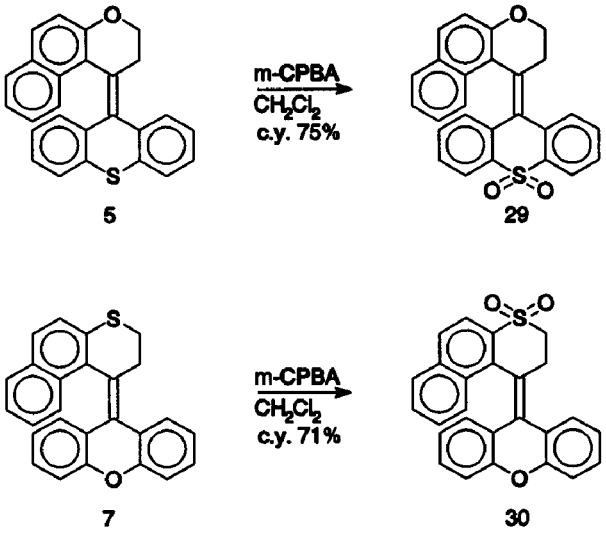
4 See numbering scheme in Experimental Section (Figure 3.6).

5 Nijhuis, S.; Rikken, G.L.J.A.; Havinga, E.E.; Meijer, E.W.; ten Hoeve, W.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1990**, 1093. For an introduction in non-linear optics see e.g. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D.S.; Zyss, J. Eds.; Academic Press: Orlando, 1987.

This aim was achieved by the oxidation of the sulfide group in alkenes **5** and **7** with 3 equivalents of *m*-CPBA in CH_2Cl_2, which furnished **29** and **30**, as yellow solids in chemical yields of 75 and 71%, respectively (Scheme 3.4). Apart from the downfield shifts observed in the ^1H NMR spectra for the protons next to the electron withdrawing sulfone group (see Experimental Section), the presence of this group was confirmed by characteristic IR absorptions at approximately 1330 and 1150 cm^{-1}. Although the procedure described here was not performed for the other alkenes in Scheme 3.3 containing sulfide groups, no problems are to be expected for similar conversions.



Scheme 3.4. Oxidation of the sulfide groups of 5 and 7.

3.2.4 Resolution and Thermal Isomerization Barriers[6]

In order to determine the thermal isomerization barriers of the individual molecules, resolution is essential.[7,8] Resolution has been investigated using HPLC columns equipped with two types of chiral stationary phases coated on silica:

- (+)-TAPA, 2-[(2,4,5,7-tetranitro-9-fluorenylidene)aminooxy]-propionic acid. The resolution of (hetero)helicenes using TAPA is well established[9,10,11]

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6 This part of the research has been performed by Wolter Jager and some of the results will be described here briefly; for an extensive discussion of the different aspects, the reader is referred to: Jager, W.F. forthcoming Ph.D. Thesis, Groningen, 1993.

7 The fact that no resolution can be realized does not necessarily imply that thermally stable isomers do not exist; see Chapter 4, Section 4.8 for a discussion on this subject.

8 The determination of isomerization barriers of several -thermally unstable- ethylenes ($\Delta G^{\ddagger} <$ 24 $kcal.mol^{-1}$) could also be performed without prior resolution using dynamic NMR techniques; see Chapter 4, Section 4.9.

9 Newman, M.S.; Lednicer, D. *J. Am. Chem. Soc.* **1956**, *78*, 4765.

10 (a) Wynberg, H.; Helder, R.; Numan, H. *Recl. Trav. Chim., Pays-Bas* **1976**, *95*, 211. (b) Gil-Av, E.; Boshart, G.; Mikes, F. *J. Chromatogr.*, **1976**, *122*, 205. (c) Wynberg, H.; Lammertsma, K. *J. Am. Chem. Soc.* **1973**, *95*, 7913.

and is based on the principle of diastereomeric charge transfer interactions between helicenes and the chiral π-acceptor TAPA.
- (+)-poly(triphenylmethyl)methacrylate, a helical polymer containing triphenylmethyl groups for π-π interactions.[12]

These methods were successful for the separation of every alkene **1 - 9** synthesized so far (!) (X = CH_2, O, S; Y = O, S, -, Scheme 3.5).[13]

P
1 - 9

M
1 - 9

Scheme 3.5. P and M isomer of alkenes 1 - 9.

Thermal isomerization barriers of **1 - 9** were determined by heating the enantiomerically pure compounds in p-xylene and following the decrease in rotation by polarimetry.[14] The most notable results from these studies are:[6]

- The highest thermal isomerization barriers were found for the fluorene functionalized ethylenes, irrespective of the atom X ($\Delta G^{\ddagger}$ > 30 kcal.mol^{-1}, Y = -). This means that even after prolonged heating at 90 °C in p-xylene no isomerization had occurred.
- The obtained values for the (thio)xanthene based alkenes (Y = O, S) were largely influenced by the atom X in the molecule, whereby the highest isomerization barriers were found for the thiopyran functionalized alkenes (X = S, $\Delta G^{\ddagger}$ > 28 kcal.mol^{-1});[15] e.g. the thermal stability of **8** (X = S, Y = S) increased from 21.7 to 28.9 kcal.mol^{-1} when replacing the oxygen (in **5**) by a sulfur atom in the upper part of the molecule.[16]

These measurements indicated that, apart from the alkenes with a fluorene unit in the lower part of the molecule, thiopyran functionalized ethylenes are especially suitable for application as chiroptical molecular switches, whereby sufficient thermal stability is needed (see Section 2.3.3). A drawback in the synthesis of fluorene based alkenes is the difficult accessibility of the unstable 9H-fluorene-9-thione[17] which leads to a rather low overall yield in the diazo-thioketone reaction (≈ 30 - 40%).
Therefore, we decided to concentrate on thiopyran functionalized alkenes and investigate whether a large variety of atoms Y is allowed in the bridging moiety

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11 Kawazura, H.; Nakagawa, K.; Yamada, K. *J. Chem. Soc., Chem. Commun.* **1989**, 1378.

12 (a) Okamoto, Y.; Hatada, H. *J. Liq. Chromatogr.* **1986**, *9*, 369. (b) Okamoto, Y.; Honda, S.; Okamoto, I.; Murata, S.; Noyori R.; Takaya, H.; Yuki, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971.

13 Due to the very low solubility of **29** and **30**, resolution via HPLC was not achieved so far.

14 The temperature range from 10 - 90 °C allows determination of isomerization barriers between 20 and 30 kcal.mol^{-1} via this method.

15 This means that the half-life $t_{½}$ (the time required for half of the quantity of the enantiomerically pure alkene to undergo isomerization) is more than 200 days at 30 °C.

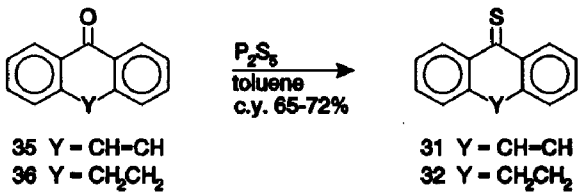
16 See Chapter 4 for an extensive discussion about the influence of the bridging moiety in the lower part of the molecules on the isomerization barriers.

17 See Section 2.5.3 for a discussion on the instability of 9H-fluorene-9-thione.

without significantly lowering the isomerization barriers. In the next section, the synthesis of seven-membered (Y = CH=CH, CH_2CH_2) and six-membered (Y = $C(CH_3)_2$, C=O) "all carbon" containing rings as the central part of the lower linear tricyclic unit will be described. These target molecules **48** - **51** are displayed in Scheme 3.9, but before the synthesis can be realized, the preparation of the thioketones **31** - **34** is required.

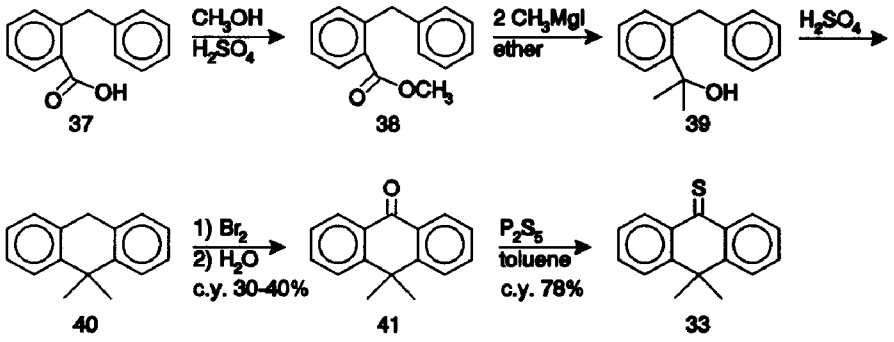
3.2.5 Structural Variations in the Lower Part of 2,3-Dihydrothiopyran Based Alkenes

The synthesis of 5H-dibenzo[a,d]cycloheptene-5-thione (**31**) and the 10,11-dihydro analogue (**32**) could be accomplished by refluxing ketones **35** and **36** in toluene with 2 equivalents of P_2S_5 (Scheme 3.6) according to the general procedure for the synthesis of thioketones described in the previous chapter. These compounds were isolated as a green solid (**31**) or a dark blue oil (**32**) in 65 and 72% yield, respectively.[18]



Scheme 3.6. Preparation of thioketones 31 and 32.

Thioketones **31** and **32** proved to be unstable and slow conversion to undefined (yellow) products was observed. Consequently, **31** and **32** had to be used fairly rapidly and stored at -18 °C to suppress this decomposition to some extent.[17]
For the synthesis of the 10,10-dimethyl substituted anthracene-9-thione (**33**), the first aim was to obtain ketone **41**. This compound was prepared in 4 steps starting from 2-benzylbenzoic acid (**37**) following the method described by Taylor *et al.*, which is outlined in Scheme 3.7.[19]



Scheme 3.7. Synthetic scheme for the preparation of 10,10-dimethyl-9(10H)-anthracene-9-thione (33).

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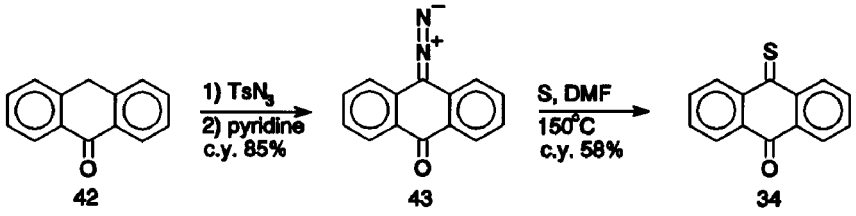
[18] Another procedure to obtain these thioketones is via the reaction of dichlorides derived from the ketones with potassium xanthogenate: Schönberg, A.; Frese E. *Chem. Ber.* **1967**, *101*, 701.

[19] Falshaw, C.P.; Hashi, N.A.; Taylor, G.A. *J. Chem. Soc., Perkin Trans. I* **1985**, 1837.

After esterification of **37**, reaction of **38** with an excess of the Grignard reagent prepared from methyl iodide afforded alcohol **39**. This alcohol underwent a Friedel-Crafts-like intramolecular cyclization by stirring in 70% aqueous H_2SO_4 to furnish **40**. Subsequently, the benzylic protons were brominated with Br_2 in CCl_4 upon irradiation to afford, after hydrolysis of the dibromo intermediate with H_2O, 10,10-dimethyl-9(10H)-anthracene-9-one (**41**) in 30-40% overall yield. This synthetic route will also allow the introduction of other substituents instead of the two methyl groups by using miscellaneous Grignard reagents, e.g. more sterically demanding propyl or (functionalized) phenyl groups.[20]
Ketone **41** was converted into thioketone **33** using P_2S_5 in toluene, which furnished **33** as beautiful blue-purple sparkling crystals[21] in 78% yield (Scheme 3.7). This thioketone proved to be stable and no decomposition was observed even after storage for six months at room temperature.
Finally, the synthesis of (mono)-thioanthraquinone **34** was needed. Direct (mono)-thionation of anthraquinone cannot be used, because this would lead to the formation of oligomers or polymers, as has been reported by Cava *et al.*[22] Thioketone **34** could be conveniently obtained by the method described by Raasch.[23] This route is depicted in Scheme 3.8 using anthrone as the starting material.
The first step involved the reaction of anthrone (**42**) with in situ prepared p-toluenesulfonyl azide, which afforded after treatment with base diazoanthrone **43** as dark brown needles in 85% yield.[24] The reaction of elemental sulfur with **43** in DMF provided thioketone **34** as a stable green solid in 58% yield. The second step is rather curious because immediate reaction between the diazo compound and the thioketone, which is formed while the reaction in progress, would be expected. Although the reaction of sulfur with diazofluorene to form episulfides has been reported as a synthetically useful method,[25] no thiiranes were found following this procedure.[24]



Scheme 3.8. Synthesis of (mono)-thioanthraquinone 34.

Thioketones **31** - **34** were used for the formation of ethylenes **48** - **51**, following the general diazo-thioketone coupling method (Scheme 3.9). The alkenes were obtained in overall yields between 57 and 70%.

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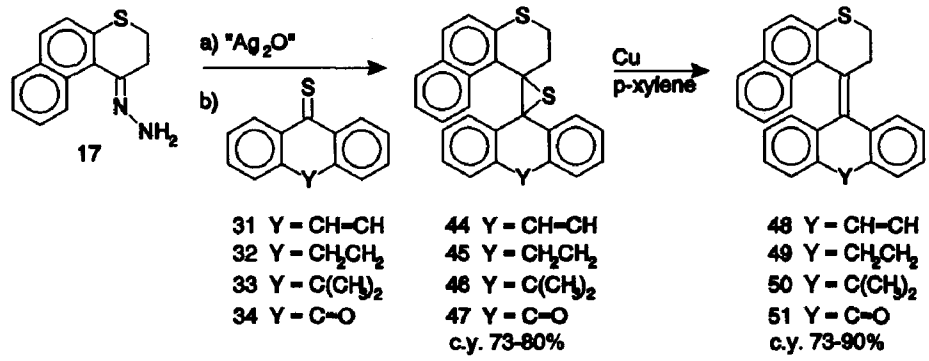
20 The size of the substituents at position 10 has an important influence on the racemization barriers of sterically overcrowded bistricyclic ethylenes, as will be shown in Chapter 4.
21 In Chapter 5 an X-ray investigation of this thioketone will be presented.
22 Cava, M.P.; Lakshmikantham, M.V.; Levinson, M.; Menachery, M. *J. Org. Chem.* **1986**, *51*, 411.
23 Raasch, M.A. *J. Org. Chem.* **1979**, *44*, 632.
24 See for the formation of diazoanthrone via this method: Regitz, M. *Chem. Ber.* **1964**, *97*, 2742.
25 Schönberg, A.; Frese, E *Chem. Ber.* **1962**, *95*, 2810.



Scheme 3.9. Diazo-thioketone coupling.

Ethylenes **48**, **49** and **50** could be resolved as described in Section 3.2.4. For these compounds, isomerization barriers between 28.8 and 30.0 kcal.mol^{-1} were found,[6] which indicate that a large variety of bridging groups Y in the lower part of the thiopyran based alkenes is tolerated, without significantly changing the isomerization barriers. Surprisingly, **51** with a carbonyl group in the lower tricyclic unit could not be resolved. No explanation for this unexpected result can be given at the moment.

3.2.6 X-ray Analyses

In order to gain insight into the molecular structure of the ethylenes synthesized so far and because of our interest to search for a relation between the conformation and isomerization barriers and other properties of these sterically overcrowded alkenes in further studies, X-ray crystallographic investigations are highly needed. X-ray analyses can provide information with respect to the amount of torsion in the central double bond, the presence of distortions from planarity in other parts of the molecules and the helical shape of these compounds. Until now, one X-ray structure of an inherently dissymmetric alkene which could also be resolved into optical isomers has been reported; a C-2 symmetrical trans octahydrobiphenanthrylidene.[26]
In this section, the X-ray structures of racemic 2,3-dihydro-1-(9'H-fluorene-9'-ylidene)-1H-naphtho[2,1-b]pyran (**6**) and 2,3-dihydro-1-(9'H-xanthene-9'-ylidene)-1H-naphtho-[2,1-b]pyran (**7**) will be presented.
Suitable crystals of **6** were grown from n-hexane by slow evaporation of the solvent. Alkene **6** crystallized as small yellow crystals in the P1 space group with four molecules per unit cell and two molecules of **6** (P and M) were found to be independent.[27]

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[26] Feringa, B.L; Duisenberg, A.J.M.; Spek, A.L.; Wynberg, H *Recl. Trav. Chim., Pays-Bas* **1979**, *98*, 1.

[27] The triclinic cell parameters and volume are:[30] a = 8.446(1) Å, b = 12.423(3) Å, c = 17.254 (7) Å, α = 87.29(3)°, β = 85.91(2)°, γ = 80.51(2)° and V = 1779.9 Å^3. The molecular crystal structure of **6** was solved to a final R index of 0.047.

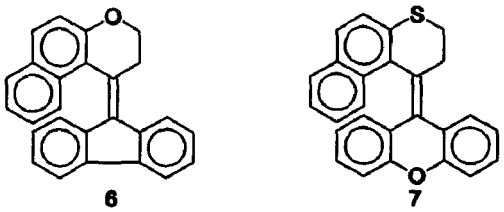

Figure 3.2. Structures of alkenes 6 and 7.

Crystallization from ethanol afforded **7** as small slightly yellow needles suitable for X-ray analysis. This compound crystallized in the C2/c space group, whereby each unit cell contained eight molecules of **7** and one molecule was found to be independent.[28] The structures of **6** and **7** including the adopted numbering schemes are pictured in Figure 3.3 and 3.4 respectively. In order to allow an easy comparison between both alkenes selected bond distances, bond angles and torsional angles of **6** (left column) and **7** (right column) are listed together in Tables 3.1, 3.2 and 3.3.[29]

Table 3.1. Selected bond distances for 6 and 7 in Ångströms.[30,31]

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C(1)	C(2)	1.467(6)	C(1)	C(2)	1.488(6)
C(1)	C(14)	1.514(6)	C(1)	C(14)	1.523(5)
C(1)	C(15)	1.367(6)	C(1)	C(15)	1.339(5)
C(2)	C(3)	1.436(6)	C(2)	C(3)	1.437(6)
C(2)	C(11)	1.398(7)	C(2)	C(11)	1.393(6)
C(3)	C(4)	1.427(7)	C(3)	C(4)	1.422(6)
C(3)	C(8)	1.427(6)	C(3)	C(8)	1.429(6)
C(11)	O(12)	1.363(6)	C(11)	S(12)	1.761(5)
O(12)	C(13)	1.445(5)	S(12)	C(13)	1.821(5)
C(13)	C(14)	1.524(7)	C(13)	C(14)	1.524(6)
C(15)	C(16)	1.503(6)	C(15)	C(16)	1.482(6)
C(15)	C(27)	1.483(6)	C(15)	C(28)	1.483(5)
C(16)	C(17)	1.390(6)	C(16)	C(17)	1.402(6)
C(16)	C(21)	1.408(6)	C(16)	C(21)	1.403(5)
C(21)	C(22)	1.456(6)	O(22)	C(21)	1.386(5)
			O(22)	C(23)	1.390(5)

[28] The unit cell dimensions are:[30] a = 34.825(2) Å, b = 6.755(1) Å, c = 16.211(2) Å, ß = 106.48(1)° and V = 3656.9 Å^3. The molecular structure of **7** was solved to a final R index of 0.043.

[29] The tables of least-squares planes, thermal vibrations, thermal and positional parameters including the complete data of bond distances, bond angles and torsional angles are available on request.

[30] Numbers in parentheses are estimated deviations in the least significant digits.

[31] Bond distances for **6** in left column and for **7** in right column.

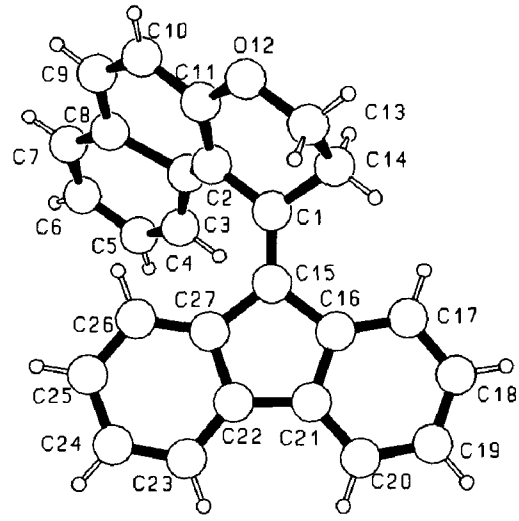

Figure 3.3. Molecular structure of 6.

Table 3.2. Selected bond angles for 6 (left column) and 7 (right column) in degrees.[30]

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(2)	C(1)	C(14)	110.6(4)	C(2)	C(1)	C(14)	110.4(3)
C(2)	C(1)	C(15)	126.0(4)	C(2)	C(1)	C(15)	125.6(3)
C(14)	C(1)	C(15)	123.0(4)	C(14)	C(1)	C(15)	124.1(4)
C(1)	C(15)	C(16)	126.6(4)	C(1)	C(15)	C(16)	124.4(3)
C(1)	C(15)	C(27)	127.7(4)	C(1)	C(15)	C(28)	124.4(4)
C(16)	C(15)	C(27)	105.3(3)	C(16)	C(15)	C(28)	111.0(3)
C(1)	C(2)	C(3)	124.5(4)	C(1)	C(2)	C(3)	124.0(3)
C(1)	C(2)	C(11)	118.2(4)	C(1)	C(2)	C(11)	117.6(4)
C(3)	C(2)	C(11)	117.0(4)	C(3)	C(2)	C(11)	118.2(4)
C(1)	C(14)	C(13)	106.0(4)	C(1)	C(14)	C(13)	110.7(3)
O(12)	C(13)	C(14)	112.8(4)	S(12)	C(13)	C(14)	113.5(3)
C(11)	O(12)	C(13)	117.8(4)	C(11)	S(12)	C(13)	104.3(2)
C(16)	C(21)	C(20)	121.0(4)	C(16)	C(21)	C(20)	122.7(4)
C(16)	C(21)	C(22)	109.2(4)	C(16)	C(21)	O(22)	120.7(4)
C(20)	C(21)	C(22)	129.8(4)	C(20)	C(21)	O(22)	116.5(3)
				C(21)	O(22)	C(23)	115.2(3)

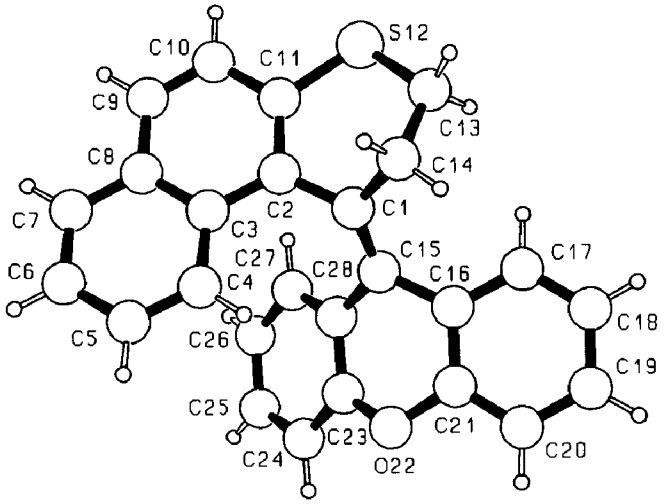

Figure 3.4. Molecular structure of 7.

Table 3.3. Selected torsional angles for 6 (left column) and 7 (right column) in degrees.

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C(14)	C(1)	C(15)	C(16)	-19.4	C(14)	C(1)	C(15)	C(16)	3.81
C(14)	C(1)	C(15)	C(27)	152.5	C(14)	C(1)	C(15)	C(28)	178.64
C(2)	C(1)	C(15)	C(16)	168.9	C(2)	C(1)	C(15)	C(16)	-178.52
C(2)	C(1)	C(15)	C(27)	-19.2	C(2)	C(1)	C(15)	C(28)	-3.69
C(1)	C(15)	C(27)	C(22)	-171.0	C(1)	C(15)	C(28)	C(23)	-140.09
C(1)	C(15)	C(27)	C(26)	1.3	C(1)	C(15)	C(28)	C(27)	39.40
C(15)	C(1)	C(2)	C(3)	-45.6	C(15)	C(1)	C(2)	C(3)	55.55
C(15)	C(1)	C(2)	C(11)	140.5	C(15)	C(1)	C(2)	C(11)	-129.77
C(1)	C(2)	C(3)	C(4)	-5.2	C(1)	C(2)	C(3)	C(4)	3.39
C(1)	C(2)	C(3)	C(8)	177.5	C(1)	C(2)	C(3)	C(8)	-177.98
C(1)	C(2)	C(11)	C(10)	-177.4	C(1)	C(2)	C(11)	C(10)	179.39
C(1)	C(2)	C(11)	O(12)	1.6	C(1)	C(2)	C(11)	S(12)	1.86
C(21)	C(22)	C(27)	C(15)	-2.2	O(22)	C(23)	C(28)	C(15)	-2.93
C(23)	C(22)	C(27)	C(15)	175.9	C(24)	C(23)	C(28)	C(15)	176.07
C(25)	C(26)	C(27)	C(15)	-174.7	C(26)	C(27)	C(28)	C(15)	-177.35
C(15)	C(16)	C(17)	C(18)	-178.1	C(15)	C(16)	C(17)	C(18)	178.43
C(16)	C(21)	C(22)	C(23)	-176.7	C(23)	O(22)	C(21)	C(16)	30.44
C(20)	C(21)	C(22)	C(23)	3.7	C(23)	O(22)	C(21)	C(20)	-148.91

The molecular structures of **6** and **7** clearly show the helical shape, responsible for the chirality of these overcrowded ethylenes. The most striking difference between **6** and **7** is the conformation of the "lower" linear tricyclic aromatic unit. Important structural characteristics of **6** and **7** are:

- Due to the presence of a more *flexible six*-membered central ring in the xanthene part of **7** compared with the *rigid five*-membered central ring in the fluorene moiety of **6**, the "lower" aromatic unit in **7** can adopt a folded structure. This can be clearly seen from the bending of the two phenyl groups next to the central twisted-boat shaped cyclohexane ring: the least-squares planes through these phenyl rings are positioned at an angle of 36°. In contrast, the fluorene functionalized ethylene **6** cannot adopt this folded conformation and forms a nearly planar structure with an angle of only 0.2° between the two phenyl rings annulated to the central non-flexible cyclopentene ring.[29]
- Large differences are observed for the central double bond structure of **6** and **7**. Only small double bond torsion and deviation from planarity is present in alkene **7**, which can release most of the steric strain between the phenanthrene and xanthene moieties through folding of the latter group. Because such a folded structure cannot occur in the case of **6**, the steric strain for this compound is merely released through large deviations of the -normally planar sp^2 hybridized- central olefinic double bond. Due to the planar structure of the fluorene unit, the carbon atoms around the double bond adopt a twisted conformation. In Figure 3.5, the Newman projections of **6** and **7** seen along the C(1)-C(15) bond are pictured together with the torsion angles.[32]

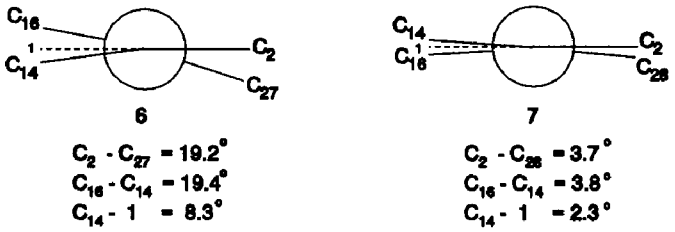

Figure 3.5. Newman projections of 6 and 7.

- Both heterocyclic rings in **7** adopt twisted-boat conformations relieving the steric interactions present in this molecule. The atoms S(12) and C(1) are located slightly below the mean plane of the six-membered ring (0.18 and 0.41 Å, respectively) and the atoms O(22) and C(15) above the mean plane found for the cyclohexane ring in the lower part of the molecule (0.33 and 0.44 Å, respectively). A half-chair conformation is found for the cyclohexane ring in **6**.
- Large dihedral angles between the least-squares planes through the naphthalene group and the double bond moiety were observed for **7** (50.9°)

[32] The carbon atom C(2) is used arbitrarily to define the mean plane through the central double bond and the dotted line 1 in Figure 3.4 is drawn to show the deviations from planarity observed for the C(1)-C(14) and C(15)-C(16) bonds.

and **6** (120.5°, between the naphthalene group and the five-membered ring in the lower part of the molecule). This means that through-bond conjugation between e.g. donor groups in the "upper" phenanthrene part and acceptor groups in the "lower" part of these compounds, will be reduced to a large extent!

- The bond length obtained for the central double bond in **7** (1.339 Å, C_1 - C_{15}) is a characteristic value for a simple non-conjugated double bond (1.337 Å).[33] The bond length found for **6** is elongated to 1.367 Å. An explanation for this increase in bond distance between carbon atoms C(1) and C(15) might be the observed large twist in this double bond (19°), leading to a decrease in π-electron overlap and therefore to some single bond character.[34,35]
- For both compounds only small distortions from planarity are found in the naphthalene moieties. The deviations from the least-squares planes through the naphthalene units never exceed 0.069 Å for **6** and 0.080 Å for **7**.

Based upon these X-ray structure determinations, the ethylenes **1** - **9** can be divided into two distinctive sets: (i) the fluorene functionalized alkenes **3**, **6** and **9** with a nearly planar fluorene unit, whereby the steric hindrance in the molecules is released through twisting and torsion of the central double bond and, (ii) the thio(xanthene) functionalized alkenes,[36] which adopt a folded conformation in order to diminish the steric strain around the double bond.

3.3 The Reverse Diazo-Thioketone Reaction: Benzannulated and Naphthopyran Based Alkenes.

A characteristic feature of the alkenes described so far is the presence of a phenanthrene type unit with two or three aliphatic CH_2 groups in the upper part of the molecule. In this section we will describe two approaches to introduce substituents next to the heterocyclic six-membered ring, namely via annulation of an additional aromatic ring (**52**, X = O, S, benzannulated alkenes, Section 3.3.1) or via introduction of a double bond next to the heteroatom, which allows further functionalization with conjugated aromatic rings (**53**, X = O, naphthopyran alkenes, Section 3.3.2).
Apart from our interest in the influence of these structural variations on the isomerization barriers, the synthesis of these types of alkenes is stimulated by the ability to introduce various substituents R_1 or R_2 in the additional aromatic rings following similar routes as will be described in Section 3.3.1 and 3.3.2.

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33 *Handbook of Chemistry and Physics*; Astle, M.J.; Weast, R.C. Eds.; CRC Press, Boca Raton, Florida, 1980, F-218.

34 See e.g. a) Lenoir, D.; Lemmen, P. *Chem. Ber.* **1980**, *113*, 3112. (b) Ammon, H.L.; Wheeler, G.L. *J. Am. Chem. Soc.* **1975**, *97*, 2326.

35 The large twist (40°) and the C=C bond length (1.39 Å) found in bifluorenylidenes have been cited as evidence for diradical character of this double bond. Bailey, N.A.; Hull, S.E. *J. Chem. Soc., Chem. Commun.* **1971**, 960.

36 The thioxanthene units in the lower part of ethylenes **2**, **5** and **8** will also adopt a folded conformation similarly as has been found for the xanthene moiety in **7**; see the molecular structure of 9-(2'-methyl-9'H-thioxanthene-9'-ylidene)-9H-xanthene (**15**) in Section 4.7.

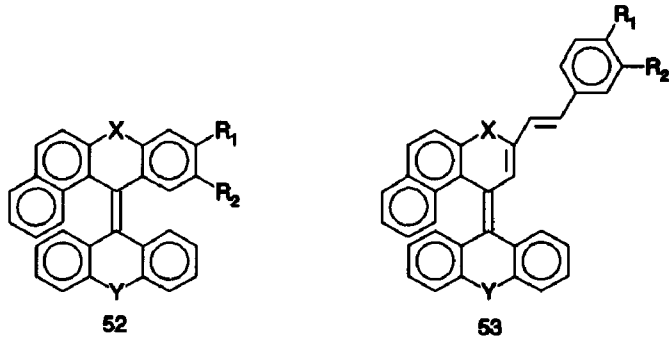
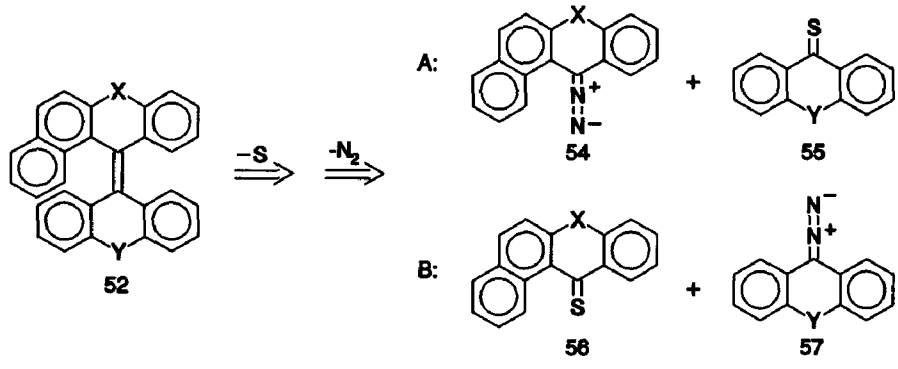


Figure 3.6. Structures of benzannulated alkenes 52 and naphthopyran based alkenes 53.

3.3.1 Benzannulated Alkenes

In contrast to the diazo-thioketone coupling procedures described so far, two possible synthetic routes, A and B, can be followed for the benzannulated alkenes **52** (Scheme 3.10). The absence of α-hydrogen atoms next to the thiocarbonyl functionality allows the synthesis of stable thioketones necessary for the "upper" part **56** as well as for the "lower" part **55** of the ethylenes.[37] In this case, we decided to use the approach B depicted in Scheme 3.10 and therefore, thioketones **56** (X = O, S) and the hydrazone precursors for diazo compounds **57** (Y = O, S) had to be prepared.



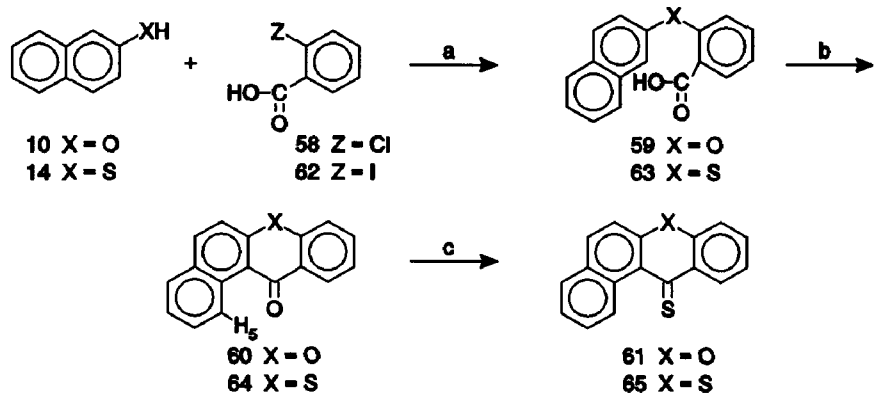
Scheme 3.10. Retrosynthetic scheme for the preparation of alkenes 52.

3.3.1.2 Synthesis of 12H-Benzo[a](thio)xanthene-12-thione

12H-Benzo[a]xanthene-9-thione (**61**) was prepared in a three step synthesis starting from 2-naphthol (**10**) and 2-chlorobenzoic acid (**58**) (Scheme 3.11). The synthesis of

[37] See Chapter 2, Section 2.5.1 for a discussion on this subject.

12H-benzo[a]xanthene-12-one (**60**) has been described in the literature,[38] where the first step involved an Ullmann coupling between the metal salts (e.g. sodium or potassium) of 2-naphthol (**10**) and acid **58** in the melt at 180 - 225 °C. However, following this classical method **59** was obtained in a rather low yield (35%, 10 mmol scale) and problems can be expected when performing this reaction on a larger scale.[39] A more convenient procedure to reach the high temperatures needed for this type of reactions is to use a high boiling solvent like nitrobenzene[40] or 1-pentanol.[41]



Scheme 3.11. Synthesis of thioketones 61 and 65. Reagents, conditions and yields: X = O: a) K_2CO_3, Cu, 1-pentanol, Δ, 48h, 71%; b) $SOCl_2$, benzene, then $AlCl_3$, Δ, 1h, 87%; c) P_2S_5, toluene, Δ, 3h, 73%. X = S: a) KOH, Cu, H_2O, Δ, 20h, 95%; b) polyphosphoric acid, 110 °C, 3h, 73%; c) P_2S_5, toluene, Δ, 62%.

By refluxing a mixture of 2-naphthol (**10**) and 2-chlorobenzoic acid (**58**) in 1-pentanol with an excess of K_2CO_3 in the presence of copper-bronze powder for 40 h, acid **59** was obtained in 71% yield on a 0.5 mol scale without difficulty. Subsequently, this acid underwent a Friedel-Crafts ring closure using $AlCl_3$ via the acid chloride to furnish the ketone **60** in 87% yield, similarly as described by Ullmann.[38c]
Ketone **60** could be easily characterized by the presence of a double doublet at 10.04 ppm in the ^1H NMR spectrum, which can be ascribed to the proton at position 5 (see Scheme 3.11). Due to the proximity of the electron withdrawing carbonyl functionality, this absorption is shifted downfield compared with the other aromatic absorptions which are found between 7.4 and 8.4 ppm.
The conversion to the thioketone was accomplished by refluxing **60** with P_2S_5 in toluene according to the general procedures described in Chapter 2. Thioketone **61** was obtained as small dark green needles in 73% yield.[42] The characteristic ^1H NMR absorption for H-5 was found at 10.48 ppm.

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38 (a) Ullmann, F. *Ber.* **1903**, *36*, 2382. (b) Ullmann, F.; Wagner, C. *Annalen* **1904**, *355*, 359. (c) Ullmann, F.; Zlokasoff, M. *Ber.* **1905**, *38*, 2111.

39 The presence of small amounts of methanol, which have to be evaporated from the metal salts before the temperature is raised, can easily lead to inflammation of the mixture.

40 Goldberg, A.A.; Walker, H.A. *J. Chem. Soc.* **1953**, 1348.

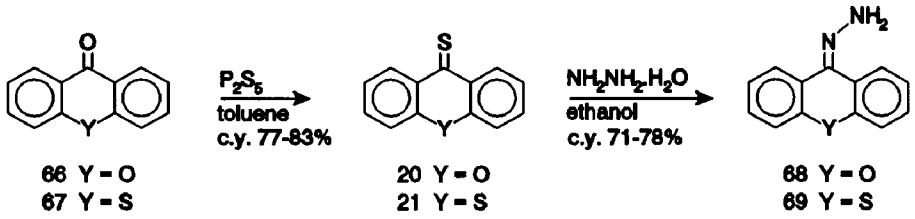
41 Davies, J.S.H.; Lamb, F.; Suschitzky, H. *J. Chem. Soc.* **1958**, 1790.

42 Mustafa and Hilmy prepared this thioketone in two steps starting from ketone **60** using oxalylchloride and thiolacetic acid: Mustafa, A.; Hilmy, M.K. *J. Chem. Soc.* **1952**, 1343.

12H-Benzo[a]thioxanthene-12-one (**65**) has been prepared following a similar reaction sequence, although somewhat different reaction conditions have been used (Scheme 3.11). The coupling between 2-thionaphthol (**14**) and 2-iodobenzoic acid (**62**) was performed in H_2O with KOH as a base in the presence of a small amount of copper powder according to a literature procedure,[43] which furnished the acid **63** in 95% yield.[44] The reason for the relatively mild reaction conditions which can be used and the high yield obtained via this procedure is the enhanced nucleophilicity of thiol group compared with the hydroxy group in 2-naphthol and the improved leaving ability of the iodium atom replacing the chlorine atom in **58**.
By heating **63** in polyphosphoric acid at 110 °C, it was cyclized to ketone **64** in 73% yield, following the same method as described for nitrile **15** in Scheme 3.2. Finally, this ketone was converted to thioketone **65** with P_2S_5 in toluene in 62% yield. An additional chromatographic purification was needed to remove some phosphorus salts, which still contaminated **65** after two crystallizations from xylene.

3.3.1.3 Synthesis of 9H-(Thio)Xanthene-9-one hydrazone

Surprisingly, we have been unsuccessful to accomplish the direct conversion of the carbonyl groups of ketones **66** and **67** (Scheme 3.12) into hydrazones by refluxing these compounds with hydrazine hydrate in ethanol in an identical manner as performed for the various hydrazones prepared so far.



66 Y = O
67 Y = S

20 Y = O
21 Y = S

68 Y = O
69 Y = S

Scheme 3.12. Synthesis of hydrazones 68 and 69.

This problem was solved by using the more reactive thioketones **20** and **21** instead of the ketones as starting materials, following the procedure described by Schönberg and Stolpp.[45] This method involved the slow addition of hydrazine hydrate to a boiling solution of the thioketone in ethanol. During this reaction evolution of H_2S was observed accompanied by a colour change of the solution from green to yellow. After cooling of the solvent, the hydrazones **68** and **69** separated from the solution as slightly yellow solids in 71-78% yield.

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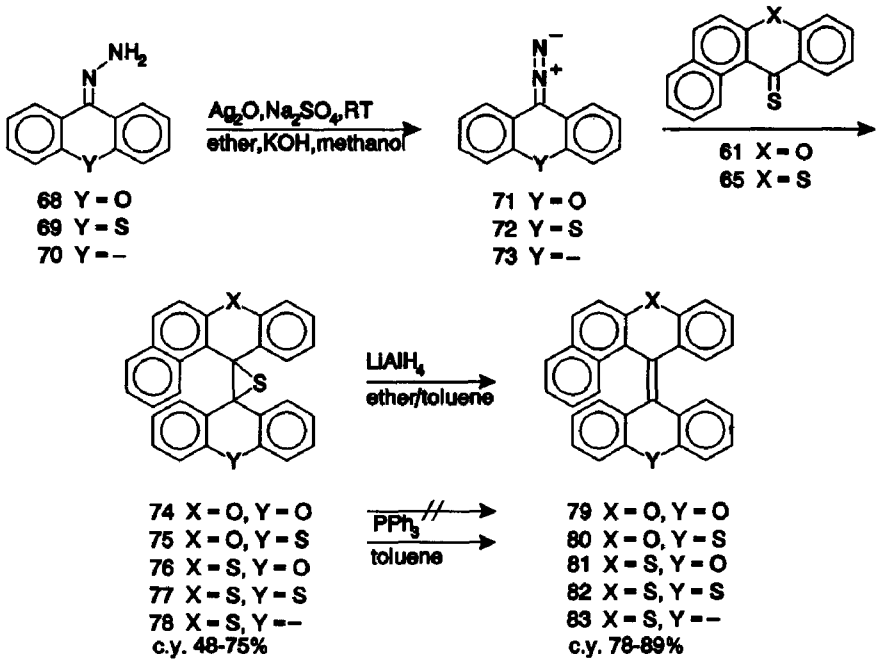
[43] (a) Protiva, M.; Kopicova, Z.; Svatek, E. *Coll. Czech., Chem. Commun* **1975**, *40*, 1960. (b) see also: Protiva, M.; Pelz, K. *Coll. Czech., Chem. Commun* **1967**, *32*, 2161.

[44] This compound can also be prepared using the classical Ullmann procedure (the reported yield is 60%): Goldberg, I. *Ber.* **1904**, *37*, 4526.

[45] Schönberg, A.; Stolpp, T. *Ber.* **1930**, *63*, 3102.

3.3.1.4 The Diazo-Thioketone Reaction: Benzannulated Alkenes

The reaction between diazo compounds **71** - **73** and thioketones **61** and **65** afforded episulfides **74** - **78** following essentially the same procedure as has been used for the various episulfides synthesized so far (Scheme 3.13).[46] In this case, the oxidation of the hydrazones could be performed at room temperature due to the presence of two aromatic rings next to the diazo functionality, which increase the stability of the diazo group compared to the rather unstable aliphatic diazo derivatives used in our previous studies.[47]



Scheme 3.13. Synthesis of benzannulated alkenes via the diazo-thioketone coupling method.

Despite several attempts, we did not succeed in desulfurizing any of these episulfides with copper in boiling xylene! Upon heating of the episulfides in xylene in the presence of copper powder, the colour of the mixture rapidly turned brown. After work up, ^{1}H NMR analysis of the obtained dark brown oil indicated at least 50% starting episulfide contaminated with unidentified impurities. Even refluxing of **74** (X = O, Y = O) during 40 hours with a large excess of copper powder did not desulfurize this compound completely. In contrast with these results, Latif *et al.* reported the desulfurization of the episulfides **74** and **75** to be complete in 1 hour via this method, followed by crystallization of the alkenes from the solution in nearly

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[46] The reaction between diazofluorene (**73**) and 12H-benzo[a]xanthene-12-thione (**61**) has not been performed. Apart from the observed difficulties to desulfurize this type of compounds (vide infra), the most important reason is that alkene **83** (X = S, Y = -) could not be resolved into the enantiomers. Because this negative result is also expected for the benzoxanthone functionalized alkene (X = O, Y = -), the synthesis of this compound has been omitted.

[47] *Diazoalkane, Eigenschaften und Synthesen;* Regitz, M.; Thieme Verlag: Stuttgart, 1977, p 30.

quantitative yield!?[48,49] Considering the large experience in running this type of reaction during our own studies and the lack of success in repeating the results of Latif *et al.* in several attempts, we consider the validity of the reported investigations rather doubtful. In other studies Latif and Fathy claimed that episulfides **74** and **75** could be reduced with $LiAlH_4$ in ether to the corresponding alkenes.[49b] However, when we followed exactly their conditions described for episulfides **74** and **75**, a mixture of the alkene (≈ 30%), episulfide (≈ 40%) and some unknown impurities was obtained. Longer reaction times or excess of $LiAlH_4$ led to the formation of considerable amounts of alkane (i.e. reduction of the central double bond).
Surprisingly, this reduction method could be successfully applied for the desulfurization of episulfides **76** - **78** to provide alkenes **81** - **83** in 78-90% yield (Scheme 3.13). The reason for the difference in reactivity of episulfides **76** - **78** containing a sulfur atom in the "upper" part of the compound compared with episulfides **74** and **75** with an oxygen atom is unclear.
Finally, we were able to desulfurize **75** using PPh_3 in boiling toluene.[50] This very convenient procedure afforded alkene **80** in 87% yield as a slightly yellow crystalline solid. For unknown reasons, this method failed for episulfide **74**, which could therefore not be desulfurized so far. In this case, the starting material was recovered (≈ 50%) together with undefined dark red side-products.

3.3.1.5 Resolution of Benzannulated Alkenes[6]

Resolution of alkenes **80** - **83** has been attempted using HPLC, similarly as has been described in Section 3.2.4 and the results are summarized in Table 3.4. The benzannulated alkenes **80** - **82** could be separated into their enantiomers, whereby the highest thermal racemization barrier is observed for alkene **82** with a sulfur atom in both parts of the molecule.[16] Unfortunately, the fluorene functionalized alkene **83** in this series could not be resolved with HPLC.

Table 3.4. Thermal Isomerization Barriers of Benzannulated Ethylenes 80 - 83.

Compound	X	Y	yield[a] (%)	isomerization barriers[b] (kcal.mol^{-1})
80	O	S	42	26.7
81	S	O	55	25.9
82	S	S	67	28.4
83	S	-	57	c

a) Isolated yields based on the amount of added thioketones.
b) ± 0.2 - 0.3 kcal.mol^{-1}.
c) This alkene could not be separated into the enantiomers.

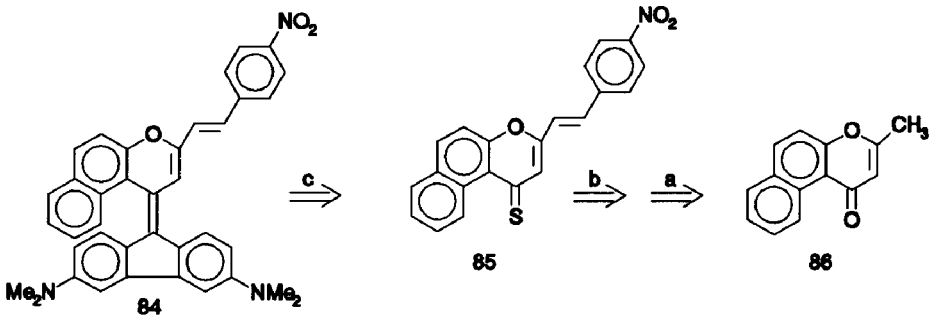
[48] Although the synthesis of some alkenes in this series has been described[49] (X = O, Y = S,O) following this route, their preparation seemed interesting in order to study their chiroptical properties.

[49] (a) Latif, N.; Mishriky, N.; Zeid, I. *J. Prak. Chem.* **1970**, *312*, 421. (b) Latif, N.; Fathy, I. *Can. J. Chem.* **1966**, *44*, 1075.

[50] See for an example of this procedure: Seitz, G.; Hoffmann, H. *Synthesis* **1977**, 201.

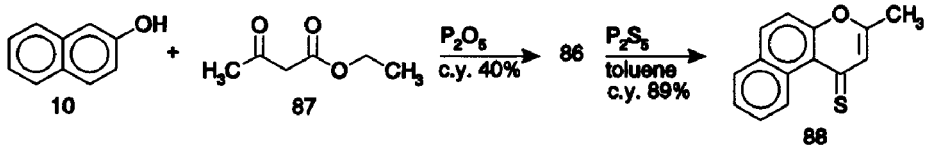
3.3.2 (Attempted) Synthesis of Naphthopyran Alkenes

The introduction of donor and acceptor groups in the sterically overcrowded alkenes might be essential to direct the electronic properties of the molecules. In this section an approach will be described based on ketone **86** (Scheme 3.14). The methyl group in ketone **86**, which is activated by the carbonyl functionality, can be deprotonated with base followed by a Knoevenagel condensation with aldehydes, whereby an additional aromatic ring is connected to the naphthopyran via a double bond.[51] The next steps would involve the synthesis of thioketone **85** which might be used in the diazo-thioketone cycloaddition. This approach is exemplified in the retrosynthetical Scheme 3.14. A target molecule can be the nitro-substituted alkene **84**, which might also have interesting properties for applications in non-linear optics.[5,52]



Scheme 3.14. Retrosynthetic scheme for the preparation of naphthopyran based alkenes. Reagents: a) O_2N-Ar-CH=O, KOH, ethanol; b) P_2S_5, toluene; c) diazo-thioketone reaction.

The synthesis of ketone **86** is shown in Scheme 3.15 and starts from 2-naphthol (**10**) and ethylacetoacetate (**87**), which forms ketone **86** in 40% yield upon addition of P_2O_5.[53] This ketone was converted in the red thioketone **88** by refluxing with P_2S_5 in toluene.[54]



Scheme 3.15. Synthesis of thioketone 88.

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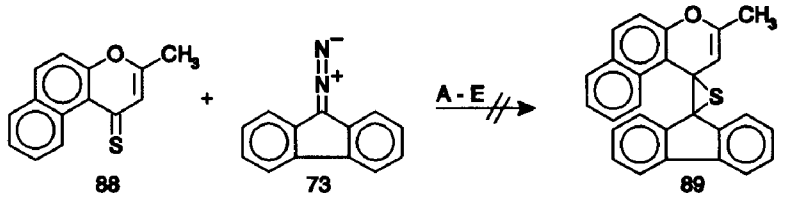
51 See e.g. (a) Schönberg, A.; Fateen, A.E.K.; Sammour, A.E.M.A. *J. Am. Chem. Soc.* **1956**, *78*, 4689. (b) Elkaschef, M.A.F.; Nosseir, M.H.; Kader, A.A. *J. Chem. Soc* **1963**, 440.

52 Staring, E.G.J. *Recl. Trav. Chim., Pays-Bas* **1991**, *110*, 492.

53 See for a similar approach starting from 2-anthrol: Sethna, S.; Shah, N.H. *J. Org. Chem.* **1959**, *24*, 1783.

54 Sammour, A.; Kamel, S.; Zimaity, T. *J. Prak. Chem.* **1972**, *314*, 271.

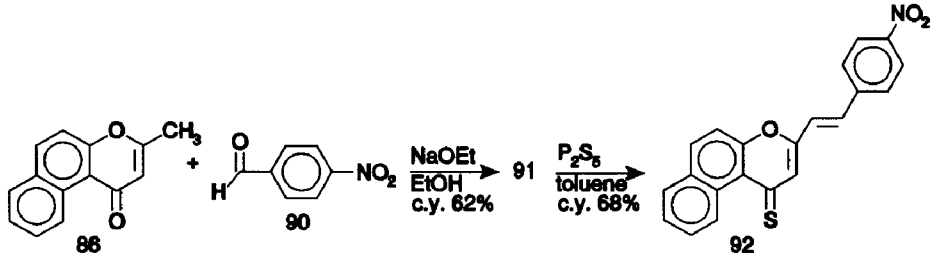
In order to explore the reactivity of this type of thioketones, we tried to achieve the diazo-thioketone cycloaddition between **88** and diazofluorene **73**. However, following the normal procedure by stirring these two compounds at room temperature in ether, no reaction could be accomplished and only starting materials were isolated (reaction conditions A). Upon prolonged stirring at room temperature, only decomposition of the diazo compound had occurred (B). Despite several attempts based on increasing the solvent polarity (C) and temperature (D, E), no reaction between diazo compound **73** and thioketone **88** was observed.



Scheme 3.16. Attempted synthesis of naphthopyran based alkene 89. Reaction conditions: (A) RT, ether, 4h; (B) RT, ether, 4d; (C) RT, DMF, 4d; (D) Δ, ether, 4h; (E) Δ, p-xylene, 4h.

This failure to obtain the desired episulfide might be due to insufficient reactivity of the thioketone and/or diazo compound or perhaps to very large steric hindrance during the cycloaddition of the planar non-flexible fluorene moiety preventing this reaction to occur.[55] Perhaps, the use of more flexible (thio)xanthene functionalized diazo compounds **71** and **72**, might lead to the formation of the corresponding episulfides.

Despite the lack of success to synthesize an episulfide based on **88**, we also decided to investigate the nitro substituted thioketone **92** in the diazo-thioketone method (Scheme 3.17). The presence of an additional electron withdrawing group in conjugation with the thiocarbonyl functionality might influence the reactivity of **92** compared with **88**. The synthesis of thioketone **92** is shown in Scheme 3.17 and involved a condensation of **86** with 4-nitrobenzaldehyde[54] followed by reaction with P_2S_5 in toluene to afford thioketone **92** as a dark green powder.



Scheme 3.17. Synthesis of thioketone 92.

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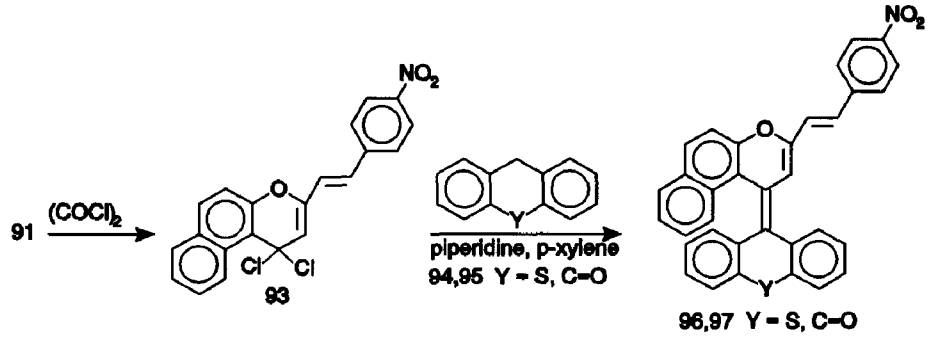
[55] The reverse diazo-thioketone coupling method (i.e. approach A in Scheme 3.10) cannot be used, because attempts to obtain the required hydrazone derived from the naphthopyran unit led to the formation of pyrazoles; see Sammour *et al.*[54]

However, reaction of this thioketone and diazofluorene under similar conditions as described for **88** in Scheme 3.16, failed to give the desired episulfide.
Although the results in the synthesis of naphthopyran based alkenes are somewhat disappointing so far, these compounds may be accessible using an alternative method,[56] which is illustrated in Scheme 3.18. This approach involves the synthesis of the *gem*-dichloro-derivative **93**, followed by reaction with e.g. thioxanthene **94** or anthrone **95** using piperidine as a base in p-xylene. Two-fold elimination of HCl might lead to the alkenes **96** or **97**.



Scheme 3.18. Proposed reaction scheme for the synthesis of alkenes 96 and 97.

3.4 Conclusions

In this chapter, we have shown that the diazo-thioketone methodology can be applied successfully for the preparation of various 2,3-dihydronaphtho(thio)pyran functionalized alkenes and benzannulated analogues. Despite several attempts, the synthesis of naphthopyran based alkenes has failed so far. The introduction of an acceptor group has been realized via oxidation of the sulfur atom in **5** and **7** to a sulfone.
X-ray analyses have revealed the molecular structure of two types of alkenes, whereby large differences in conformation were observed for the *twisted* fluorene based alkene **6** compared with the *folded* xanthene derivative **7**.
Resolution of most of the inherently dissymmetric ethylenes described in this chapter was achieved by HPLC, which allowed the determination of thermal isomerization barriers. The fluorene functionalized alkenes **3**, **6** and **9** possessed the highest thermal stabilities, whereby no isomerization was observed after heating the enantiomerically pure compounds for several hours in p-xylene at 90 °C. The thermal stabilities of the thio(xanthene) based alkenes were strongly dependent on the nature of the (hetero)atom in the *upper* part of the molecule, whereby the highest values for the racemization barriers have been found for ethylenes with a sulfur atom present. The effect of the bridging moiety Y on the isomerization barriers of these 2,3-dihydrothiopyran functionalized ethylenes proved to be very small. In the next chapter, the influence of the (hetero)atoms and ring size c.q. rigidity present in the

[56] See for the synthesis of sterically hindered alkenes via this method e.g. (a) Kortüm, G.; Zoller, W. *Chem. Ber.* **1970**, *103*, 2062. (b) Föhlisch, B.; Krockenberger, D. *Chem. Ber.* **1968**, *101*, 3990. (c) Schönberg, A.; Ismail, A.F.A.; Asker, W. *J. Chem. Soc.* **1946**, 442.

lower linear tricyclic unit on the isomerization barriers of symmetrically sterically overcrowded alkenes will be discussed.
Since sufficient thermal stability is essential for application of these compounds as chiroptical molecular switches, we can conclude that thiopyran (X = S) and the - synthetically difficult accessible - fluorene functionalized alkenes (Y = -) are well suited for this purpose.

3.5 Experimental Section

For general remarks, see Section 2.7. 5H-Dibenzo[a,d]cycloheptene-5-thione (**31**) and 10,11-dihydro-5H-dibenzo[a,d]cycloheptene-5-thione (**32**) were prepared according the general method for the synthesis of thioketones described in Section 2.7 and proved to be identical with the compounds prepared by Schönberg and Frese.[18] Anthraquinone-9-thione (**34**) was prepared following the method described by Raasch.[23] 10,10-Dimethyl-9(10H)-anthracene-9-one (**41**) was prepared according to the procedure described by Taylor *et al.*[19] 3-(4-Nitrostyryl)-1H-naphtho[2.1-b]pyran-1-thione (**92**) was prepared following the method given by Sammour *et al.*[54]

3-(2-Naphthyloxy)-propiononitrile (11)
To a stirred mixture of 2-naphthol (**10**, 222.0 g, 1.54 mol) and acrylonitrile (500 mL, 400 g, 7.70 mol) was carefully added Triton B (25 mL, 40% solution in methanol). After stirring and refluxing for 18 h, the dark brown solution was cooled to 0 °C and the crystallized solid isolated by filtration. The brown solid was washed with 5% aqueous NaOH (500 mL), H_2O (250 mL) and dried to afford **11** as a light brown powder (205.0 g, 1.05 mol, 67.6%). This compound was shown to be >95% pure by ^1H NMR analysis and was used without further purification in the next step: mp 103.2-105.6 °C (lit:[3] mp 105-106 °C); ^1H NMR (60 MHz) δ 2.59 (t, J = 6.6 Hz, 2H), 4.08 (t, J = 6.6 Hz, 2H), 6.90-7.84 (m, 7H).

2,3-Dihydro-1H-naphtho[2,1-b]pyran-1-one (12)[4]
Nitrile **11** (39.4 g, 0.20 mol) was added to a stirred mixture of concentrated H_2SO_4 (340 mL) and H_2O (60 mL) in 15 min at room temperature. The solid slowly dissolved and after stirring for 2 h, the brown solution was poured onto ice (1.5 kg). The precipitated ketone was isolated by filtration, washed with saturated aqueous $NaHCO_3$ (300 mL), H_2O (250 mL) and dried to yield **12** as a light brown solid (36.2 g, 0.18 mol, 91.4%): mp 48.1-49.6 °C (lit:[3] 50-51 °C); ^1H NMR (300 MHz) δ 2.85 (t, J = 6.6 Hz, 2H, H-2), 4.55 (t, J = 6.6 Hz, 2H, H-3), 7.04 (d, J = 8.7 Hz, 1H, H-5), 7.39 (ddd, J = 7.8, 7.2, 1.1 Hz, 1H, H-8), 7.59 (ddd, J = 8.7, 7.2, 1.5 Hz, 1H, H-9), 7.69 (d, J = 7.8 Hz, 1H, H-7), 7.84 (d, J = 8.7 Hz, 1H, H-6), 9.45 (d, J = 8.7 Hz, 1H, H-10); ^{13}C NMR δ 38.67 (t), 66.76 (t), 112.64 (s), 118.49 (d), 124.55 (d), 125.70 (d), 128.13 (d), 128.88 (s), 129.35 (d), 131.35 (s), 137.13 (d), 163.64 (s), 192.56 (s, C=O).

2,3-Dihydro-1H-naphtho[2,1-b]pyran-1-one hydrazone (13)
This compound was prepared similarly as described for 1,2,3,4-tetrahydrophenanthrene-4-one hydrazone (**26**) in Section 2.7. Starting from **12** (19.8 g, 100 mmol), **13** was obtained as a light yellow crystalline solid (17.8 g, 84 mmol, 83.9%) after cooling of the ethanol solution to -18 °C: mp 98.9-100.1 °C; ^1H NMR (300 MHz) δ 2.87 (t, J = 6.4 Hz, 2H, H-2), 4.33 (t, J = 6.4 Hz, 2H, H-3), 5.39 (br s, 2H, NH_2), 7.08 (d, J = 8.8 Hz, 1H, H-5), 7.37 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H, H-8), 7.53 (ddd, J = 8.5, 6.8, 1.5

Hz, 1H, H-9), 7.68 (d, J = 8.8 Hz, 1H, H-6), 7.75 (dd, J = 8.0, 1.5 Hz, 1H, H-7), 9.37 (dd, J = 8.5, 1.2 Hz, 1H, H-10); ^{13}C NMR δ 25.33 (t), 64.55 (t), 114.15 (s), 118.48 (d), 123.73 (d), 127.03 (d), 127.026 (d), 128.09 (d), 130.05 (s), 130.41 (d), 130.75 (s), 143.75 (s), 156.02 (s); HRMS Calcd for $C_{13}H_{12}N_2O$ 212.095, found 212.095; Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.69; N, 13.19. Found C, 74.02; H, 5.82; N, 13.23.

3-(2-Naphthylthio)-propiononitrile (15)
Triton B (1 ml, 40% solution in methanol) was carefully added to magnetically stirred acrylonitrile (54.0 mL, 43.5 g, 0.82 mol) cooled to -5 °C. To this solution 2-thionaphthol (**14**, 34.0 g, 0.21 mol) was added portionwise in 1 h, whereupon the colour of the mixture changed to yellow and then slowly to light green. The solution was heated to 65 °C and stirred for 1 h at this temperature. After cooling of the now dark green mixture to room temperature, Et_2O (500 mL) was added and the Triton B cautiously neutralized with acetic acid (7 mL). The yellow solution was filtered to remove some precipitated polymer, washed with saturated aqueous $NaHCO_3$ (2 x 200 mL), brine (1 x 100 mL) and dried (Na_2SO_4). Removal of the solvent under reduced pressure yielded **15** as a brown oil (42.6 g, 0.20 mol, 94.6%): ^{1}H NMR (60 MHz) δ 2.50 (t, J = 8.0 Hz, 2H), 3.12 (t, J = 8.0 Hz, 2H), 7.17-7.85 (m, 7H).

2,3-Dihydro-1H-naphtho[2,1-b]thiopyran-1-one (16)
To mechanically stirred polyphosphoric acid (500 mL) heated at 60 °C was added **15** (41.4 g, 0.195 mol) in 1 h, whereupon the colour of the viscous mixture changed to brown-red. After the addition was complete, the temperature was raised to 110 °C and stirring continued at this temperature for 3 h. The dark brown mixture was cooled to 70 °C and poured onto crushed ice (2 kg). After standing overnight, the yellow precipitate was isolated by filtration, washed with water (1 L) and dried to afford the ketone **16** as a yellow powder (41.2 g, 0.193 mol, 98.7%). ^{1}H NMR analysis showed it to be >95% pure: mp 62.6-64.7 °C (lit:[3] 68-69 °C); ^{1}H NMR (300 MHz) δ 3.02-3.07 (m, 2H), 3.19-3.23 (m, 2H), 7.21 (d, J = 8.8 Hz, 1H), 7.41 (ddd, J = 8.8, 8.1, 1.2 Hz, 1H), 7.58 (ddd, J = 8.8, 7.1, 1.5 Hz, 1H), 7.67-7.69 (m, 2H), 9.17 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 26.00 (t), 40.96 (t), 125.07 (d), 125.25 (s), 125.33 (d), 125.81 (d), 128.16 (d), 128.83 (d), 131.42 (s), 132.17 (s), 133.27 (d), 144.88 (s), 195.79 (s, C=O).

2,3-Dihydro-1H-naphtho[2,1-b]thiopyran-1-one hydrazone (17)
This compound was prepared in an identical way as described for the preparation of 1,2,3,4-tetrahydrophenanthrene-4-one hydrazone (**26**) in Section 2.7. Starting from ketone **16** (21.4 g, 0.10 mol), **17** was obtained as slightly orange crystals (18.1 g, 0.08 mol, 79.4%): mp 129.7-130.9 °C; ^{1}H NMR (300 MHz) δ 2.87 (s, 4H), 5.43 (bs, 2H), 7.31 (d, J = 8.4 Hz, 1H), 7.37 (ddd, J = 8.1, 7.0, 1.1 Hz), 7.46 (ddd, J = 8.8, 7.0, 1.5 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.72 (dd, J = 8.1, 1.5 Hz, 1H), 8.65 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 27.27 (t), 30.31 (t), 124.93 (d), 126.37 (d), 126.46 (d), 126.66 (d), 127.59 (d), 127.85 (d), 129.60 (s) 131.39 (s), 132.94 (s), 135.94 (s), 145.23 (s); HRMS Calcd for $C_{13}H_{12}N_2S$: 228.072, found 228.073; Anal. Calcd for $C_{13}H_{12}N_2S$: C, 68.39; H, 5.30; N, 12.27; S, 14.04. Found C, 68.40; H, 5.39; N, 12.29; S, 13.90.

Episulfides 23-28 were prepared according to the general procedures described for 35 and 37 in Section 2.7.

Dispiro[2,3-dihydro-1H-naphtho[2,1-b]pyran-1, 2'-thiirane-3', 9"-(9"H)-xanthene] (23)
Hydrazone **13** (424 mg, 2.00 mmol) was oxidized to the deep red diazo compound **18**, whereupon 9H-xanthene-9-thione (**20**, 338 mg, 1.59 mmol) was added. After

crystallization from ethanol (150 mL), **23** was obtained as a slightly yellow solid (510 mg, 1.29 mmol, 80.9%, based on the thioketone): mp 152.2-152.8 °C; ^{1}H NMR (300 MHz) δ 2.26 (ddd, J = 12.9, 8.1, 2.2 Hz, 1H), 2.68 (ddd, J = 12.9, 10.0, 9.0 Hz, 1H), 3.38 (ddd, J = 10.3, 10.0, 8.1 Hz, 1H), 3.87 (ddd, J = 10.3, 9.0, 2.2 Hz, 1H), 6.25 (ddd, J = 7.8, 7.3, 1.5 Hz, 1H), 6.79 (d, J = 8.8 Hz, 1H), 6.82 (ddd, J = 8.8, 8.1, 1.5 Hz, 1H), 6.89 (dd, J = 8.1, 1.5 Hz, 1H), 6.92 (dd, J = 8.1, 1.2 Hz, 1H), 7.19 (ddd, J = 8.8, 7.8, 1.5 Hz, 1H), 7.25 (dd, J = 8.1, 1.2 Hz, 1H), 7.28-7.39 (m, 2H), 7.42 (d, J = 8.3 Hz, 1H), 7.53 (ddd, J = 8.3, 6.6, 1.2 Hz, 1H), 7.62 (dd, J = 8.1, 0.5 Hz, 1H), 7.78 (dd, J = 7.8, 1.5 Hz, 1H), 9.18 (dd, J = 8.8 Hz, 1H); ^{13}C NMR δ 35.77 (t), 51.80 (s, C-S), 52.68 (s, C-S), 65.86 (t), 115.21 (d), 116.22 (d), 118.02 (d), 118.45 (s), 121.29 (s), 121.72 (d), 122.45 (d), 122.60 (d), 122.94 (d), 125.44 (d), 126.31 (s), 127.45 (d), 127.82 (d), 128.31 (d), 128.49 (d), 128.86 (d), 129.04 (d), 129.41 (s), 132.76 (s), 153.80 (s), 155.29 (s), 155.31 (s); HRMS Calcd for $C_{26}H_{18}O_2S$: 394.103, found 394.102; Anal. Calcd for $C_{26}H_{18}O_2S$: C, 79.19; H, 4.57; S, 8.12. Found C, 79.00; H, 4.61; S, 8.24.

Dispiro[2,3-dihydro-1H-naphtho[2,1-b]pyran-1, 2'-thiirane-3', 9"-(9"H)-thioxanthene] (24)

Starting from **13** (636 mg, 3.00 mmol) and 9H-thioxanthene-9-thione (**21**, 500 mg, 2.19 mmol), crystallization from ethanol (300 mL) yielded **24** as a light yellow solid (670 mg, 1.63 mmol, 74.6%, based on the thioketone): mp 167.2-168.8 °C; ^{1}H NMR (300 MHz) δ 1.67 (ddd, J = 13.7, 4.6, 1.2 Hz, 1H), 2.74 (ddd, J = 13.7, 13.4, 6.7 Hz, 1H), 3.90 (ddd, J = 13.4, 10.7, 4.6 Hz, 1H), 4.05 (ddd, J = 10.7, 6.7, 1.2 Hz, 1H), 6.63 (ddd, J= 7.7, 7.4, 1.5 Hz, 1H), 6.73 (ddd, J = 7.6, 7.4, 1.5 Hz, 1H), 6.84 (d, J = 8.9 Hz, 1H), 7.03 (dd, J = 7.6, 1.2 Hz, 1H), 7.13 (ddd, J = 7.6, 7.0, 1.2 Hz, 1H), 7.25-7.43 (m, 5H), 7.48 (dd, J = 7.0, 1.5 Hz, 1H), 7.66 (dd, J = 7.6, 1.5 Hz, 1H), 7.80 (dd, J = 7.6, 1.5 Hz, 1H), 9.60 (d, J = 9.1 Hz, 1H); ^{13}C NMR δ 35.23 (t), 52.96 (s, C-S), 61.53 (s, C-S), 64.83 (t), 110.70 (s), 118.46 (d), 122.21 (d), 123.98 (d), 124.47 (d), 125.17 (d), 126.09 (d), 126.27 (d), 126.61 (d), 126.62 (d), 127.34 (d), 127.61 (d), 128.53 (s), 128.54 (s), 129.63 (d), 129.69 (d), 130.60 (d), 133.08 (s), 134.33 (s), 134.60 (s), 137.26 (s), 155.45 (s); HRMS Calcd for $C_{26}H_{18}OS_2$: 410.080, found 410.079; Anal. Calcd for $C_{26}H_{18}OS_2$: C, 76.09; H, 4.39; S, 15.61. Found C, 75.79; H, 4.56; S, 15.30.

Dispiro[2,3-dihydro-1H-naphtho[2,1-b]pyran-1, 2'-thiirane-3', 9"-(9"H)-fluorene] (25)

To diazo compound **18** (prepared from **13**, 424 mg, 2.00 mmol) in Et_2O was added a freshly prepared solution of 9H-fluorene-9-thione (**22**, 720 mg, 4.00 mmol) in toluene. The brown residue obtained after evaporation of the solvents was stirred in ethanol (50 mL) to afford an orange solid (600 mg), which could be crystallized from ethanol to afford **25** as a yellow-orange solid (350 mg, 0.93 mmol, 46.3%, based on the hydrazone): mp 151.2-153.1 °C; ^{1}H NMR (300 MHz) δ 2.84-2.92 (m, 2H), 3.42-3.51 (m, 1H), 4.00-4.06 (m, 1H), 6.14 (dd, J = 8.8, 1.5 Hz, 1H), 6.50 (ddd, J = 7.8, 7.3, 1.0 Hz, 1H), 6.77 (d, J = 8.8 Hz, 1H), 7.06 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 7.27-7.31 (m, 1H), 7.37-7.44 (m, 2H), 7.51-7.60 (m, 4H), 7.71-7.76 (m, 1H), 7.80 (d, J = 8.8 Hz, 1H), 9.32 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 36.65 (t), 47.73 (s, C-S), 54.54 (s, C-S), 66.14 (t), 118.69 (d), 119.34 (d), 119.88 (s), 120.46 (d), 122.51 (d), 123.18 (d), 123.33 (d), 123.64 (d), 125.90 (d), 126.14 (d), 126.48 (d), 127.48 (d), 128.28 (d), 128.77 (d), 129.22 (s), 129.50 (d), 132.52 (s), 140.03 (s), 141.65 (s), 143.05 (s), 143.26 (s), 154.98 (s); HRMS Calcd for $C_{26}H_{18}OS$: 378.108, found 378.106; Anal. Calcd for $C_{26}H_{18}OS$: C, 82.51; H, 4.79, S, 8.47. Found C, 82.81, H, 4.92, S, 8.32.

Dispiro[2,3-dihydro-1H-naphtho[2,1-b]thiopyran-1, 2'-thiirane-3', 9"-(9"H)-xanthene] (26)

Starting from **17** (912 mg, 4.00 mmol) and 9H-xanthene-9-thione (**20**, 460 mg, 2.17 mmol), the episulfide was isolated by filtration to provide **26** as a white solid (648 mg, 1.58 mmol, 72.8%, based on the thioketone): mp 153.1-154.0 °C; ^{1}H NMR (300 MHz) δ 2.06 (ddd, J = 13.9, 10.9, 5.9 Hz, 1H), 2.63 (ddd, J = 12.8, 9.9, 5.9 Hz, 1H), 2.72 (ddd, J = 13.9, 9.9, 4.0 Hz, 1H), 2.89 (ddd, J = 12.8, 10.9, 4.0 Hz, 1H), 6.19 (ddd, J = 8.4, 8.1, 1.5 Hz, 1H), 6.36 (dd, J = 8.1, 1.1 Hz, 1H), 6.90 (ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 6.96 (dd, J = 7.7, 1.1 Hz, 1H), 7.00 (dd, J = 8.1, 1.1 Hz, 1H), 7.16-7.26 (m, 2H), 7.36-7.48 (m, 3H), 7.59 (ddd, J = 8.4, 7.0, 1.1 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.88 (dd, J = 8.1, 1.5 Hz, 1H), 8.88 (d, J = 8.4 Hz, 1H); ^{13}C NMR δ 27.70 (t), 36.38 (t), 52.11 (s, C-S), 57.62 (s, C-S), 115.20 (d), 116.31 (d), 119.96 (s), 121.18 (d), 121.38 (s), 122.06 (d), 122.63 (d), 124.51 (d), 125.36 (d), 126.31 (d), 127.04 (d), 127.27 (d), 127.54 (d), 128.41 (d), 128.63 (d), 128.85 (d), 132.33 (s), 132.52 (s), 132.56 (s), 137.95 (s), 153.44 (s), 154.32 (s); HRMS Calcd for $C_{26}H_{18}OS_2$ 410.080, found 410.079; Anal. Calcd for $C_{26}H_{18}OS_2$: C, 76.07; H, 4.42; S, 15.62. Found C, 75.22; H, 4.61; S, 15.36 (due to slow decomposition of this episulfide (the colour of **26** changed to pink) in the solid state, a slightly incorrect elemental analysis was obtained.

Dispiro[2,3-dihydro-1H-naphtho[2,1-b]thiopyran-1, 2'-thiirane-3', 9"-(9"H)-thioxanthene] (27)

Starting from hydrazone **17** (1.14 g, 5.00 mmol) and 9H-thioxanthene-9-thione (**21**, 0.99 g, 4.5 mmol), **27** was obtained as a light yellow solid (1.52 g, 3.57 mmol, 71.3%, based on the thioketone) after crystallization from ethanol (± 400 mL): mp 189.9-190.8 °C; ^{1}H NMR (300 MHz) δ 2.24-2.34 (m, 1H), 2.46-2.65 (m, 3H), 6.27 (dd, J = 8.0, 0.7 Hz, 1H), 6.95-7.02 (m, 3H), 7.25-7.33 (m, 5H), 7.39-7.49 (m, 2H), 7.54 (d, J = 8.0 Hz, 1H), 8.02-8.05 (m, 1H), 9.05 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 26.90 (t), 36.52 (t), 58.32 (s, C-S), 60.14 (s, C-S), 123.19 (d), 123,93 (d), 124.43 (d), 124.95 (d), 125.07 (d), 125.54 (d), 125.66 (d), 126.06 (d), 126.31 (d), 127.05 (d), 127.33 (d), 128.08 (d), 128.26 (s), 129.49 (d), 130.93 (s), 131.02 (d), 131.86 (s), 131.87 (s), 133.20 (s), 133.69 (s), 136.06 (s), 138.04 (s); HRMS Calcd for $C_{26}H_{18}S_3$: 426.057, found 426.056; Anal. Calcd for $C_{26}H_{18}S_3$: C, 73.20; H, 4.25; S, 22.55. Found: C, 72.79; H, 4.29; S, 22.41.

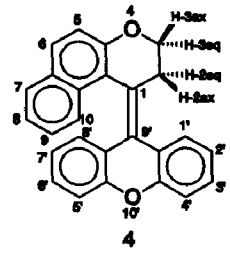
Dispiro[2,3-dihydro-1H-naphtho[2,1-b]thiopyran-1, 2'-thiirane-3', 9"-(9"H)-fluorene] (28)

To diazo compound **19** (prepared from **17**, 456 mg, 2.00 mmol) in Et_2O was added a freshly prepared solution of 9H-fluorene-9-thione (**22**, 720 mg, 4.00 mmol) using the column chromatography method as described for the synthesis of **37** in Section 2.7. The orange brown residue obtained after evaporation of the solvents was stirred in ethanol (50 mL) to afford a yellow solid (580 mg). Crystallization from ethanol (80 mL) furnished **28** as a white solid (395 mg, 1.00 mmol, 50.1%, based on the hydrazone): mp 164.3-166.1 °C; ^{1}H NMR (300 MHz) δ 2.45 (ddd, J = 12.5, 8.6, 4.2 Hz, 1H), 2.76 (m, 2H), 3.32-3.39 (m, 1H), 5.57 (dd, J = 7.8, 0.5 Hz, 1H), 6.51 (ddd, J = 8.5, 7.8, 1.2 Hz, 1H), 7.07 (d, J = 8.3 Hz, 1H), 7.11 (ddd, J = 8.1, 7.6, 1.0 Hz, 1H), 7.30 (ddd, J = 8.8, 7.6, 1.2 Hz, 1H), 7.43 (ddd, J = 8.1, 7.3, 1.0 Hz, 1H), 7.48-7.53 (m, 1H), 7.58 (m, 3H), 7.66 (d, J = 7.7 Hz, 1H), 7.78 (dd, J = 7.1, 0.7 Hz, 1H), 7.86 (dd, J = 8.6, 0.7 Hz, 1H), 8.93 (d, J = 8.5 Hz, 1H); 13C NMR δ 27.32 (t), 37.90 (t), 52.78 (s, C-S), 52.79 (s, C-S), 118.97 (d), 120.37 (d), 122.92 (d), 122.98 (d), 123.78 (d), 125.00 (d), 125.65 (d), 125.66 (d), 126.56 (d), 127.18 (d), 127.26 (d), 127.65 (d), 127.94 (d), 128.72 (d), 131.45 (s), 132.37 (s), 135.34 (s), 137.22 (s), 140.98 (s), 141.92 (s), 142.97 (s), 144.88 (s); HRMS Calcd for C26$H_{18}S_2$ 394.085, found 394.086; Anal. Calcd for

$C_{26}H_{18}S_2$: C, 79.15; H, 4.60; S, 16.25. Found: C, 79.02; H, 4.70; S, 16.41.

Alkenes 4-9 were prepared using the general desulfurization procedure described for 38 in Section 2.7.

9-(2',3'-Dihydro-1'H-naphtho[2,1-b]pyran-1'-ylidene)-9H-xanthene (4)
Starting from **23** (394 mg, 1.00 mmol), alkene **4** was obtained as a white crystalline solid (310 mg, 0.86 mmol, 85.6%) after crystallization from ethanol (120 mL): mp 182.7-184.9 °C; ^{1}H NMR (300 MHz, assignment based on HETCOR, NOESY and COSY 2D NMR, for numbering scheme see Figure 3.7) δ 2.56 (ddd, J = 13.9, 13.2, 5.9 Hz, 1H, H-2_{ax}), 3.69 (ddd, J = 13.2, 4.4, 0.7 Hz, 1H, H-2_{eq}), 4.62 (ddd, J = 13.9, 10.3, 4.4 Hz, 1H, H-3_{ax}), 4.85 (ddd, J = 10.3, 5.9, 0.7 Hz, 1H, H-3_{eq}), 6.23 (ddd, J = 8.0, 7.2, 1.1 Hz, 1H, H-7'), 6.47 (dd, J = 8.0, 1.5 Hz, 1H, H-8'), 6.82 (ddd, J = 8.4, 7.3, 1.1 Hz, 1H, H-9), 6.85 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H, H-6'), 6.98 (ddd, J = 8.0, 7.3, 1.1 Hz, 1H, H-8), 7.06 (d, J = 8.8 Hz, 1H, H-5), 7.09 (dd, J = 8.8, 1.1 Hz, 1H, H-5'), 7.13 (m, 1H, H-10), 7.16 (m, 1H, H-2'), 7.24 (m, 1H, H-4'), 7.26 (m, 1H, H-3'), 7.41 (d, J = 7.3 Hz, 1H, H-1'), 7.52 (d, J = 8.0 Hz, 1H, H-7), 7.59 (d, J = 8.8 Hz, 1H, H-6); ^{13}C NMR δ 29.27 (t, C-3), 69.40 (t, C-2), 116.22 (d, C-5'), 116.74 (d, C-4'), 118.33 (d, C-10), 118.91 (s), 122.23 (s), 122.33 (d, C-7'), 122.63 (d, C-7), 122.78 (d, C-2'), 124.43 (d, C-5), 125.19 (d, C-6), 125.47 (s), 125.62 (s), 126.14 (s), 126.72 (d, C-1'), 127.45 (d, C-8), 127.51 (d, C-6'), 127.97 (d, C-3'), 127.98 (d, C-8'), 128.09 (s), 128.64 (s), 129.68 (d, C-9), 153.34 (s), 153.92 (s), 154.68 (s); HRMS Calcd for $C_{26}H_{18}O_2$: 362.131, found 362.131; Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.19; H, 4.97. Found C, 86.31; H, 5.03.



4

Figure 3.7. Adopted numbering scheme for 4.

2,3-Dihydro-1-(9'H-thioxanthene-9'-ylidene)-1H-naphtho[2,1-b]pyran (5)
Starting from **24** (410 mg, 1.00 mmol), **5** was obtained as a slightly yellow crystalline solid (308 mg, 0.81 mmol, 81.5%) after crystallization from ethanol (200 mL): mp 195.2-196.2 °C; ^{1}H NMR (300 MHz) δ 2.60 (ddd, J = 13.9, 13.2, 5.9 Hz, 1H), 3.59 (ddd, J = 13.2, 4.4, 0.7 Hz, 1H), 4.76 (ddd, J = 13.9, 10.3, 4.4 Hz, 1H), 4.95 (ddd, J = 10.3, 5.9, 0.7 Hz, 1H), 6.48 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 6.67 (dd, J = 8.8 Hz, 1H), 6.82 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 6.88 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 7.02 (ddd, J = 8.1, 6.6, 1.5 Hz, 1H), 7.10 (d, J = 8.8 Hz, 1H), 7.24-7.29 (m, 2H), 7.34 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 7.42-7.43 (m ,1H), 7.43 (d, J = 8.1 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 28.88 (t), 69.56 (t), 117.69 (s), 117.97 (d), 122.45 (d), 124.26 (d), 125.14 (d), 125.48 (d), 125.84 (d), 126.06 (d), 126.45 (d), 126.76 (d), 127.12 (d), 127.28 (d), 127.37 (s), 127.49 (d), 127.58 (s), 127.70 (s), 128.89 (d), 129.72 (d), 130.73 (s), 134.27 (s), 135.79 (s), 136.19 (s),

138.36 (s), 153.89 (s); HRMS Calcd for $C_{26}H_{18}OS$ 378.108, found 378.107; Anal. Calcd for $C_{26}H_{18}OS$: C, 82.53; H, 4.76; S, 8.47. Found C, 82.68; H, 4.85; S, 8.59.

2,3-Dihydro-1-(9'H-fluorene-9'-ylidene)-1H-naphtho[2,1-b]pyran (6)
Starting from episulfide **25** (189 mg, 0.50 mmol), crystallization from ethanol (50 mL) furnished **6** as a yellow crystalline solid (111 mg, 0.32 mmol, 64.4%): mp 151.2-153.2 °C; ^{1}H NMR (300 MHz) δ 3.17 (ddd, J = 12.7, 12.5, 5.9, 1H), 4.07 (ddd, J = 12.5, 3.7, 2.4 Hz, 1H), 4.35 (ddd, J = 12.7, 11.0, 3.7 Hz, 1H), 4.68 (ddd, J = 11.0, 5.9, 2.4 Hz, 1H), 6.51 (d, J = 8.1 Hz, 1H), 6.71 (ddd, J = 8.3, 8.1, 1.0 Hz, 1H), 7.11-7.18 (m, 2H), 7.25-7.29 (m, 2H), 7.34-7.40 (m, 2H), 7.68 (d, J = 7.6 Hz, 1H), 7.77-7.85 (m, 4H), 8.02 (dd, J = 8.3, 1.5 Hz, 1H); ^{13}C NMR δ 30.67 (t), 66.87 (t), 116.65 (s), 118.39 (d), 118.79 (d), 119.70 (d), 123.46 (d), 124.86 (d), 124.98 (d), 125.10 (d), 126.42 (d), 126.60 (d), 126.93 (d), 127.03 (d), 127.24 (d), 128.16 (d), 128.77 (s), 130.69 (s), 131.51 (d), 133.16 (s), 133.47 (s), 137.77 (s), 138.44 (s), 139.30 (s), 140.64 (s), 153.98 (s); HRMS Calcd for $C_{26}H_{18}O$: 346.136, found 346.134; Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found C, 90.35; H, 5.31.

9-(2',3'-Dihydro-1'H-naphtho[2,1-b]thiopyran-1'-ylidene)-9H-xanthene (7)
Starting from episulfide **26** (600 mg, 1.46 mmol), crystallization from ethanol (± 100 mL), afforded **7** as small white needles (459 mg, 1.21 mmol, 83.0%): mp 206.6-208.2 °C; ^{1}H NMR δ (300 MHz) 2.20 (ddd, J = 12.8, 12.7, 7.7 Hz, 1H), 3.49-3.57 (m, 2H), 3.81 (ddd, J = 12.8, 6.3, 2.5 Hz, 1H), 6.24 (ddd, J = 8.1, 7.7, 0.7 Hz, 1H), 6.33 (dd, J = 7.7, 1.5 Hz, 1H), 6.85 (ddd, J = 8.8, 8.1, 1.5 Hz, 1H), 6.96 (ddd, J = 8.4, 8.1, 1.1 Hz, 1H), 7.08 (dd, J = 8.8, 1.5 Hz, 1H), 7.09-7.13 (m, 1H), 7.19-7.24 (m, 1H), 7.30-7.35 (m, 3H), 7.39 (d, J = 8.8 Hz, 1H), 7.54 (dd, J = 8.8, 1.5 Hz, 1H), 7.59 (dd, J = 8.8, 1.1 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 29.03 (t), 29.91 (t), 115.75 (d), 116.63 (d), 122.11 (d), 122.83 (d), 123.88 (d), 124.22 (d), 124.46 (s), 124.57 (s), 125.51 (s), 125.56 (d), 125.76 (d), 126.40 (d), 127.54 (d), 127.55 (d), 127.62 (d), 127.79 (s), 128.11 (d), 128.18 (d), 130.07 (s), 131.23 (s), 134.04 (s), 135.08 (s) 152.93 (s), 154.25 (s); HRMS Calcd for $C_{26}H_{18}OS$: 378.108, found 378.108; Anal. Calcd for $C_{26}H_{18}OS$: C, 82.51; H, 4.79; S, 8.47. Found C, 82.26; H, 4.75; S, 8.55.

9-(2',3'-Dihydro-1'H-naphtho[2,1-b]thiopyran-1'-ylidene)-9H-thioxanthene (8)
Starting from **27** (852 mg, 2.00 mmol), alkene **8** was obtained as small white shining needles (690 mg, 1.75 mmol, 87.5%) after crystallization from ethanol (200 mL): mp 179.9-181.0 °C; ^{1}H NMR (300 MHz) δ 2.16-2.27 (m, 1H), 3.51-3.66 (m, 3H), 6.44 (ddd, J = 8.4, 7.7, 1.1 Hz, 1H), 6.52 (dd, J = 7.7, 1.5 Hz, 1H), 6.76 (ddd, J = 8.8, 7.7, 1.5 Hz, 1H), 7.02 (ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 7.11 (ddd, J = 8.0, 7.0, 1.5 Hz, 1H), 7.24-7.38 (m, 3H), 7.37 (d, J = 8.8 Hz, 1H), 7.53-7.62 (m, 5H); ^{13}C NMR δ 29.12 (t), 30.06 (t), 124.20 (d), 124.28 (d), 125.33 (d), 125.59 (d), 125.65 (d), 126.00 (d), 126.20 (d), 126.21 (d), 126.73 (d), 127.16 (d), 127.33 (d), 127.45 (d), 127.66 (d), 128.34 (s), 129.10 (d), 131.20 (s), 132.21 (s), 133.62 (s), 133.78 (s), 134.12 (s), 134.64 (s), 135.46 (s), 135.68 (s), 137.83 (s); HRMS Calcd for $C_{28}H_{18}S_2$: 394.085, found 394.084; Anal. Calcd for $C_{28}H_{18}S_2$: C, 79.15; H, 4.60; S, 16.25. Found C, 78.95; H, 4.59; S, 16.24.

2,3-Dihydro-1-(9'H-fluorene-9'-ylidene)-1H-naphtho[2,1-b]thiopyran (9)
Desulfurization of **28** (394 mg, 1.00 mmol) yielded an orange solid, which proved to be **9** contaminated with some impurities. Column chromatography (Al_2O_3, hexane/Et_2O 90:10, R_f alkene = 0.41) afforded analytically pure **9** as a yellow solid (230 mg, 0.64 mmol, 63.5%): mp 189.0-190.2 °C; ^{1}H NMR (300 MHz) δ 2.87-2.97 (m, 1H), 3.10-3.19 (m, 2H), 4.21-4.32 (m, 1H), 5.87 (d, J = 8.1 Hz, 1H), 6.51 (ddd, J = 8.8, 8.1,

1.5 Hz, 1H), 7.00 (ddd, *J* = 8.8, 8.1, 1.5 Hz, 1H), 7.14 (ddd, *J* = 8.8, 8.1, 1.5 Hz, 1H), 7.24-7.38 (m, 3H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.55 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.69-7.79 (m, 3H), 7.86 (d, *J* = 8.1 Hz, 1H), 8.02 (dd, *J* = 8.8, 1.5 Hz, 1H); ^{13}C NMR δ 29.37 (t), 34.98 (t), 118.76 (d), 119.64 (d), 124.83 (d), 124.99 (d), 125.23 (d), 125.36 (d), 126.51 (d), 126.86 (d), 126.99 (d), 127.12 (d), 127.36 (d), 127.79 (d), 128.08 (d), 128.30 (d), 131.82 (s), 131.83 (s), 135.19 (s), 135.46 (s), 136.34 (s), 136.79 (s), 137.49 (s), 138.23 (s), 139.57 (s), 141.12 (s); HRMS Calcd for $C_{26}H_{18}S$: 362.113, found 362.113; Anal. Calcd for $C_{26}H_{18}S$: C, 86.15; H, 5.01; S, 8.84. Found: C, 85.96; H, 5.23; S, 8.82.

2,3-Dihydro-1-(10'10,-dioxo-9'H-thioxanthene-9'-ylidene)-1H-naphtho[2,1-b]pyran (29)
To a solution of **5** (189 mg, 0.50 mmol) in CH_2Cl_2 (20 mL) was added *m*-CPBA (258 mg, 1.50 mmol, 3 equiv.). After stirring for 16 h at room temperature, precipitation of 3-chlorobenzoic acid had occurred. Subsequently, CH_2Cl_2 (25 mL) and 5% aqueous NaOH were added. The organic layer was separated, washed with 5% aqueous NaOH (2 x 25 mL), brine (1 x 50 mL), dried (Na_2SO_4) and evaporated under reduced pressure to afford **29** as a yellow solid (154 mg, 0.38 mmol, 75.1%): mp > 300 °C; IR (KBr) cm^{-1} 1328, 1157 (SO_2); ^{1}H NMR δ (300 MHz) 2.84 (ddd, *J* = 14.2, 13.2, 6.8 Hz, 1H), 3.65 (ddd, *J* = 13.2, 4.4, 0.7 Hz, 1H), 4.76 (ddd, *J* = 14.2, 10.2, 4.4 Hz, 1H), 4.99 (ddd, *J* = 10.2, 6.8, 0.7 Hz, 1H), 6.67-6.76 (m, 2H), 6.99-7.14 (m, 4H), 7.51-7.63 (m, 4H), 7.70 (d, *J* = 9.3 Hz, 1H), 7.75 (dd, *J* = 6.8, 1.0 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.5 Hz, 1H); due to the very low solubility of this compound no ^{13}C NMR could be obtained; HRMS Calcd for $C_{26}H_{18}O_3S$ 410.098, found 410.098.

9-(2',3'-Dihydro-4',4'-dioxo-1'H-naphtho[2,1-b]thiopyran-1'-ylidene)-9H-xanthene (30)
This compound was prepared identically as described for **29**. Starting from **7** (189 mg, 0.5 mmol), alkene **30** was obtained as a slightly white solid (146 mg, 0.36 mmol, 71.3%): mp 288.7-290.4 °C; IR (KBr) cm^{-1} 1323, 1169 (SO_2); ^{1}H NMR (300 MHz) δ 2.74-2.81 (m, 1H), 3.82-4.05 (m, 3H), 6.25-6.30 (m, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 6.92 (ddd, *J* = 8.8, 7.3, 1.5 Hz, 1H), 7.11-7.47 (m, 7H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 8.06 (dd, *J* = 8.8, 1.5 Hz, 1H); HRMS Calcd for $C_{26}H_{18}O_3S$ 410.098, found 410.097.

10,10-Dimethyl-9(10H)-anthracene-9-thione (33)
This compound was prepared following the general procedure for the synthesis of thioketones in Section 2.7. Starting from **41** (2.22 g, 10.0 mmol) and P_2S_5 (4.44 g, 20.0 mmol), crystallization from n-hexane (40 mL) afforded **33** as deep blue purple shining crystals (1.85 g, 7.8 mmol, 77.8%): mp 112.2-114.3 °C; ^{1}H NMR (300 MHz) δ 1.68 (s, 6H), 7.29-7.34 (m, 2H), 7.56-7.63 (m, 4H), 8.63 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR δ 32.04 (q), 38.82 (s), 125.50 (d), 126.57 (d), 130.26 (d), 132.79 (d), 137.89 (s), 144.24 (s), 220.63 (s, C=S). HRMS Calcd for $C_{16}H_{14}S$: 238.082, found 238.082.

Episulfides 44-47 were prepared according to the general procedures described for 35 in Section 2.7

Dispiro[5H-dibenzo[a,d]cycloheptene]-5, 2'-thiirane-3', 1"-(2",3"-dihydro-1"H-naphtho [2,1-b]pyran)] (44)
Starting from hydrazone **17** (456 mg, 2.00 mmol) and 5H-dibenzo[a,d]cycloheptene-5-thione (**31**, 355 mg, 1.60 mmol), **44** was obtained as a slightly yellow solid (540 mg, 1.29 mmol, 80.4%, based on the thioketone) after crystallization from ethanol (400 mL): mp 163.1-164.6 °C; ^{1}H NMR (200 MHz) δ 1.93-1.97 (m, 1H), 2.55-2.63 (m, 1H),

2.76-3.07 (m, 2H), 6.55 (d, J = 11.7 Hz, 1H), 6.70-6.72 (m, 1H), 6.73 (d, J = 11.7 Hz, 1H), 6.92 (ddd, J = 8.5, 7.6, 1.4 Hz, 1H), 7.03-7.16 (m, 4H), 7.34-7.49 (m, 5H), 7.73 (d, J = 7.4 Hz, 1H), 7.86 (d, J = 7.7 Hz, 1H), 9.47-9.52 (m, 1H); ^{13}C NMR δ 24.76 (t), 38.14 (t), 56.24 (s, C-S), 66.96 (s, C-S), 123.32 (d), 124.37 (d), 124.94 (d), 125.58 (d), 126.21 (d), 126.33 (d), 127.41 (d), 127.48 (d), 127.58 (d), 127.60 (d), 128.02 (d), 128.46 (d), 129.79 (d), 130.81 (d), 131.18 (d), 131.86 (d), 133.73 (s), 135.09 (s), 135.10 (s), 135.33 (s), 135.34 (s), 136.12 (s), 136.99 (s), 137.00 (s); HRMS Calcd for $C_{28}H_{20}S_2$: 420.101, found 420.101; Anal. Calcd for $C_{28}H_{20}S_2$: C, 79.96; H, 4.79; S, 15.25. Found: C, 79.70; H, 4.84; S, 15.19.

Dispiro[2,3-dihydro-1H-naphtho[2,1-b]pyran-1, 2'-thiirane-3', 5"-(5"H)-dibenzo[a,d] cycloheptene] (45)
Starting from hydrazone **17** (456 mg, 2.00 mmol) and 10,11-dihydro-5H-dibenzo[a,d] cycloheptene-5-thione (**32**, 336 mg, 1.50 mmol), episulfide **45** was obtained as a slightly yellow solid (488 mg, 1.16 mmol, 77.1%, based on the thioketone) after crystallization from ethanol (350 mL): mp 172.3-173.7 °C (dec); ^{1}H NMR (200 MHz) δ 2.28-2.43 (m, 2H), 2.63-2.74 (m, 1H), 2.81-3.10 (m, 3H), 3.45-3.68 (m, 2H), 6.67 (dd, J = 7.3, 1.4 Hz, 1H), 6.86 (ddd, J = 8.8, 7.3, 1.4 Hz, 1H), 6.95-7.28 (m, 7H), 7.43-7.51 (m, 2H), 7.75 (dd, J = 7.6, 1.5 Hz, 1H), 7.92-7.96 (m, 1H), 9.49 (dd, J = 8.6, 1.0 Hz, 1H); ^{13}C NMR δ 24.47 (t), 29.55 (t), 34.06 (t), 39.35 (t), 57.47 (s, C-S), 68.42 (s, C-S), 123.66 (d), 124.45 (d), 125.03 (s), 125.13 (d), 125.81 (d), 125.82 (d), 126.56 (d), 127.32 (d), 127.89 (d), 127.98 (d), 128.05 (d), 128.97 (d), 130.84 (d), 131.32 (d), 131.52 (d), 134.01 (s), 134.87 (s), 136.56 (s), 138.49 (s), 138.94 (s), 138.95 (s), 139.83 (s); HRMS Calcd for $C_{28}H_{22}S_2$: 422.117, found 422.116; Anal. Calcd for $C_{28}H_{22}S_2$: C, 79.58; H, 5.25; S, 15.17. Found: C, 79.27; H, 5.34; S, 15.14.

Dispiro[2,3-dihydro-1H-naphtho[2,1-b]thiopyran-1, 2'-thiirane-3', 9"-(10",10"-dimethyl)-9"(10"H)-anthracene] (46)
Starting from hydrazone **17** (456 mg, 2.00 mmol) and thioketone **33** (328 mg, 1.38 mmol), **46** separated as a white solid from the Et_2O solution (470 mg, 1.08 mmol, 78.1%, based on the thioketone): mp 173.1-174.9 °C; ^{1}H NMR (300 MHz) δ 1.48 (s, 3H), 1.58-1.67 (m, 1H), 2.12 (s, 3H), 2.36-2.47 (m, 1H), 2.55-2.62 (m, 1H), 2.97-3.03 (m, 1H), 6.10 (ddd, J = 8.8, 8.1, 1.5 Hz, 1H), 6.58 (dd, J = 8.8, 1.5 Hz, 1H), 6.84-6.86 (m, 1H), 6.87 (dd, J = 8.1, 1.5 Hz, 1H), 7.20-7.25 (m, 2H), 7.33-7.42 (m, 3H), 7.51-7.58 (m, 2H), 7.69 (dd, J = 8.8, 1.5 Hz, 1H), 8.10 (dd, J = 8.1, 1.5 Hz, 1H), 8.95 (d, J = 8.8 Hz, 1H); 13C NMR δ 25.90 (t), 32.47 (q), 35.57 (t), 38.39 (q), 38.50 (s), 54.66 (s, C-S), 58.16 (s, C-S), 122.34 (d), 123.25 (d), 124.51 (d), 124.72 (d), 125.55 (d), 125.81 (d), 126.40 (d), 126.48 (d), 127.18 (d), 127.36 (d), 127.58 (d), 127.56 (d), 128.54 (d), 128.81 (d), 129.90 (s), 131.96 (s), 132.20 (s), 133.05 (s), 133.37 (s), 135.54 (s), 145.82 (s), 147.42 (s); HRMS Calcd for C29$H_{24}S_2$ 436.132, found 436.133; Anal. Calcd for $C_{29}H_{24}S_2$: C, 79.77; H, 5.54; S, 14.69. Found C, 79.41; H, 5.59; S, 14.65.

Dispiro[2,3-dihydro-1H-naphtho[2,1-b]thiopyran-1, 2'-thiirane-3', 9"-10"-oxo-9" (10"H)-anthracene] (47)
Starting from hydrazone **17** (456 mg, 2.00 mmol) and thioketone **34** (380 mg, 1.70 mmol), **47** separated from the Et_2O solution as a white solid (520 mg, 1.23 mmol, 72.5%, based on **34**): mp 197.6-199.2 °C; ^{1}H NMR (200 MHz) δ 1.67-1.81 (m, 1H), 2.49-2.66 (m, 3H), 6.63 (ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 7.06 (ddd, J = 8.8, 7.4, 1.4 Hz, 1H), 7.35 (d, J = 8.5 Hz, 1H), 7.45 (ddd, J = 9.2, 8.1, 1.2 Hz, 1H), 7.52-7.67 (m, 3H), 7.71 (d, J = 8.1 Hz, 1H), 7.98-8.13 (m, 2H), 8.35-8.39 (m, 1H), 8.82 (d, J = 8.7 Hz, 1H); ^{13}C NMR δ 27.57 (t), 36.90

(t), 54.27 (s, C-S), 58.61 (s, C-S), 122.43 (d), 124.98 (d), 125.89 (d), 126.05 (d), 126.59 (d), 126.98 (d), 127.07 (d), 127.62 (d), 127.79 (d), 128.20 (d), 128.52 (d), 128.71 (d), 130.40 (d), 131.41 (d), 132.16 (s), 132.24 (s), 133.79 (s), 134.30 (s), 135.35 (s), 137.00 (s), 139.00 (s), 140.65 (s), 184.53 (s, C=O); HRMS Calcd for $C_{27}H_{18}OS_2$ 422.080, found 422.080; Anal. Calcd for $C_{27}H_{18}OS_2$: C, 76.75; H, 4.29; S, 15.12. Found C, 76.55; H, 4.28; S, 15.09.

Alkenes 48-51 were prepared using the general method described for 38 in Section 2.7.

1-(5'H-Dibenzo[a,d]cycloheptene-5'-ylidene)-2,3-dihydro-1H-naphtho[2,1-b]thiopyran (48)
Starting from **44** (420 mg, 1.00 mmol), crystallization from ethanol/p-xylene (80:20, 300 mL) yielded alkene **48** as a white solid (317 mg, 0.82 mmol, 81.7%): mp 160.3-162.1 °C; ^{1}H NMR (300 MHz) δ 2.08 (ddd, J = 12.8, 9.9, 8.8 Hz, 1H), 3.16 (ddd, J = 12.8, 11.0, 3.3 Hz, 1H), 3.31-3.44 (m, 2H), 6.55 (dd, J = 7.7, 1.5 Hz, 1H), 6.61 (ddd, J = 8.8, 7.7, 1.1 Hz, 1H), 6.76 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 7.00-7.06 (m, 2H), 7.08-7.13 (m, 3H), 7.31 (ddd, J = 7.8, 7.3, 1.5 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.37-7.57 (m, 5H), 7.57 (dd, J = 8.4, 0.7 Hz, 1H); ^{13}C NMR δ 29.13 (t), 30.27 (t), 124.51 (d), 125.06 (d), 125.34 (d), 126.14 (d), 126.28 (d), 126.97 (d), 127.00 (d), 127.26 (d), 127.54 (d), 127.74 (d), 128.13 (d), 128.21 (d), 128.33 (d), 128.53 (d), 128.90 (s), 131.38 (s), 131.47 (d), 131.86 (d), 133.48 (s), 134.09 (s), 134.36 (s), 135.28 (s), 135.70 (s), 137.69 (s), 138.46 (s), 140.84 (s); HRMS Calcd for $C_{28}H_{20}S$: 388.128, found 388.129; Anal. Calcd for $C_{28}H_{20}S$: C, 86.56; H, 5.19; S, 8.25. Found: C, 86.01; H, 5.17; S, 8.29.

1-(10',11'-Dihydro-5'H-dibenzo[a,d]cycloheptene-5'-ylidene)-2,3-dihydro-1H-naphtho[2,1-b]thiopyran (49)
Starting from **45** (422 mg, 1.00 mmol), crystallization from ethanol/p-xylene (70:30, 300 mL) afforded **49** as small white shining needles (352 mg, 0.90 mmol, 90.3%): mp 185.0-186.2 °C; ^{1}H NMR (300 MHz) δ 2.17 (ddd, J = 12.8, 10.6, 8.1 Hz, 1H), 2.91-2.99 (m, 1H), 3.07-3.19 (m, 2H), 3.26-3.41 (m, 2H), 3.50-3.58 (m, 1H), 3.93-4.03 (ddd, J = 13.9, 13.5, 4.8 Hz, 1H), 6.32-6.38 (m, 2H), 6.66 (ddd, J= 8.4, 6.6, 1.8 Hz, 1H), 6.80 (d, J = 7.7 Hz, 1H), 7.12 (d, J = 6.6 Hz, 1H), 7.13 (d, J = 6.2 Hz, 1H), 7.20-7.36 (m, 5H), 7.53-7.57 (m, 2H), 8.01-8.04 (m, 1H); ^{13}C NMR δ 29.69 (t), 30.25 (t), 32.08 (t), 33.58 (t), 124.33 (d), 124.62 (d), 124.68 (d), 125.10 (d), 126.18 (d), 126.69 (d), 127.48 (d), 127.67 (d), 127.69 (d), 127.86 (d), 127.89 (d), 128.02 (d), 129.16 (s), 129.71 (d), 130.30 (d), 131.57 (s), 131.92 (s), 134.46 (s), 135.18 (s), 135.85 (s), 138.57 (s), 138.71 (s), 140.23 (s), 143.09 (s); HRMS Calcd for $C_{28}H_{22}S$: 390.144, found 390.144; Anal. Calcd for $C_{28}H_{22}S$: C, 86.11; H, 5.68; S, 8.21. Found: C, 85.37; H, 5.74; S, 8.18.

2,3-Dihydro-1-(10',10'-dimethyl-9'(10'H)-anthracene-9'-ylidene)-1H-naphtho[2,1-b]thiopyran (50)
Starting from episulfide **46** (218 mg, 0.50 mmol), alkene **50** was obtained as white small block shaped crystals (148 mg, 0.37 mmol, 73.3%) after crystallization from ethanol (± 100 mL): mp 238.4-239.9 °C; ^{1}H NMR (300 MHz) δ 1.83 (s, 3H), 1.92 (s, 3H), 2.31 (ddd, J = 12.5, 10.5, 9.9 Hz, 1H), 3.53-3.58 (m, 2H), 3.82-3.88 (m, 1H), 6.30-6.36 (m, 2H), 6.81-6.86 (m, 1H), 6.91-6.96 (m, 1H), 7.15 (ddd, J = 7.7, 7.0, 0.7 Hz, 1H), 7.30-7.35 (m, 2H), 7.39 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.60-7.67 (m, 4H); ^{13}C NMR δ 25.27 (q), 29.96 (t), 30.68 (t), 32.28 (q), 40.02 (s), 123.03 (d), 123.43 (d), 124.34 (d), 124.43 (d), 124.80 (d), 124.95 (d), 125.23

(d), 126.25 (d), 126.83 (d), 127.00 (d), 127.10 (d), 127.48 (d), 127.61 (d), 127.62 (d), 128.88 (s), 130.09 (s), 131.71 (s), 133.59 (s), 134.27 (s), 136.79 (s), 137.08 (s), 137.33 (s), 144.07 (s), 147.03 (s); HRMS Calcd for $C_{29}H_{24}S$: 404.160, found 404.160; Anal. Calcd for $C_{29}H_{24}S$: C, 86.10; H, 5.98; S, 7.92. Found: C, 85.84; H, 6.09; S, 7.92.

2,3-Dihydro-1-(10'-oxo-9'(10'H)-anthracene-9'-ylidene)-1H-naphtho[2,1-b]thiopyran (51)

Starting from episulfide **47** (211 mg, 0.50 mmol), alkene **51** was obtained as yellow small crystals (172 mg, 0.44 mmol, 88.2%) after crystallization from ethanol (200 mL): mp 248.6-250.1 °C; ^{1}H NMR (300 MHz) δ 2.28 (ddd, J = 12.7, 12.5, 8.1 Hz, 1H), 3.52-3.68 (m, 2H), 3.89 (ddd, J = 12.7, 6.8, 1.7 Hz, 1H), 6.57-6.65 (m, 2H), 6.94 (ddd, J = 8.5, 7.8, 1.2 Hz, 1H), 6.97-7.15 (m, 3H), 7.43 (d, J = 8.5 Hz, 1H), 7.54 (ddd, J = 8.3, 8.1, 0.9 Hz, 1H), 7.57-7.69 (m, 3H), 7.75 (d, J = 7.3 Hz, 1H), 7.98 (dd, J = 8.1, 0.7 Hz, 1H), 8.30 (dd, J = 7.6, 1.2 Hz, 1H); ^{13}C NMR δ 29.35 (t), 30.58 (t), 123.75 (d), 124.53 (d), 126.03 (d), 126.04 (d), 126.38 (d), 126.99 (d), 127.30 (d), 127.61 (d), 127.69 (d), 128.09 (s), 128.37 (d), 128.39 (d), 128.66 (d), 129.21 (s), 130.30 (d), 131.20 (d), 131.45 (s), 132.24 (s), 133.65 (s), 134.03 (s), 135.91 (s), 137.03 (s), 138.86 (s), 140.26 (s), 185.81 (s, C=O); HRMS Calcd for $C_{27}H_{18}OS$: 390.108, found 390.108; Anal. Calcd for $C_{27}H_{18}OS$: C, 83.05; H, 4.65; S, 8.21. Found: C, 82.85; H, 4.61; S, 8.27.

2-(2-Naphthyloxy)-benzoic acid (59)

To a stirred solution of 2-naphthol (**10**, 72.0 g, 0.50 mol) and 2-chlorobenzoic acid (**58**, 78.3 g, 0.50 mol) in 1-pentanol (600 mL) was slowly added K_2CO_3 (172.8 g, 1.25 mol) and Cu powder (1.5 g). After refluxing for 48 h, the grey coloured mixture was cooled to room temperature, 20% aqueous HCl (400 mL) was added very carefully until pH = 1 was reached followed by steam-distillation to remove the 1-pentanol. The brown oil, which separated upon cooling, was isolated by extraction with CH_2Cl_2 (2 x 200 mL). The combined organic layers were washed with H_2O (1 x 100 mL), brine (1 x 100 mL), dried on Na_2SO_4 and evaporated under reduced pressure to afford **59** as a light brown oil (93.5 g, 0.35 mol, 70.8%) which slowly solidified upon standing. This compound proved to be > 90% pure by ^{1}H NMR analysis and was used in the following step without further purification. A small sample was crystallized from toluene (5.0 g/100 mL) to give a white solid: mp 123.5-125.1 °C (lit:[38c] mp 125 °C); ^{1}H NMR (300 MHz) δ 6.93 (d, J = 8.3 Hz, 1H), 7.24 (ddd, J = 8.3, 6.8, 1.0 Hz, 1H), 7.29 (dd, J = 9.3, 2.4 Hz, 1H), 7.43-7.54 (m, 4H), 7.75 (dd, J = 9.3, 2.0 Hz, 1H), 7.86 (dd, J = 7.8, 2.0 Hz, 1H), 7.90 (d, J = 9.3 Hz, 1H), 8.21 (dd, J = 7.8, 1.5 Hz, 1H), 11.28 (bs, 1H); ^{13}C NMR δ 114.88 (d), 119.27 (d), 119.64 (d), 120.59 (s), 123.36 (d), 125.01 (d), 126.54 (d), 127.03 (d), 127.58 (d), 130.02 (d), 130.35 (s), 132.89 (d), 133.92 (s), 134.53 (d), 153.55 (s), 157.06 (s), 168.96 (s, C=O).

12H-Benzo[a]xanthene-12-one (60)

A solution of acid **59** (5.2 g, 20 mmol) and $SOCl_2$ (11.9 g, 100 mmol) in benzene (50 mL) was refluxed for 30 min. After cooling to room temperature, benzene and excess $SOCl_2$ were removed in vacuo and the residue stripped with benzene (1 x 50 mL). The yellow semi-solid was dissolved in benzene (50 mL), cooled to 5 °C and subsequently powdered $AlCl_3$ (8.0 g, 60 mmol) was added. The mixture was refluxed for 60 min and after cooling to 0 °C 10% aqueous HCl was added until pH 1 was reached followed by extraction with Et_2O (3 x 100 mL). The combined Et_2O layers were washed with saturated aqueous $NaHCO_3$ (2 x 100 mL) and brine (1 x 100 mL), dried (Na_2SO_4) and after evaporation of the solvent in vacuo a slightly yellow solid (5.1 g) was obtained. This compound was crystallized from ethanol (± 125 mL) to

afford **60** as a white solid (4.2 g, 17 mmol, 86.5%): mp 139.0-140.9 °C (lit:[38c] mp 140 °C); ^{1}H NMR (300 MHz) δ 7.37 (m,1H), 7.44 (d, J = 8.1 Hz, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.53 (m, 1H), 7.66 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 7.72 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 8.37 (dd, J = 8.1, 1.5 Hz, 1H), 10.04 (dd, J = 8.8, 1.1 Hz, 1H); ^{13}C NMR δ 114.24 (s), 117.23 (d), 117.75 (d), 123.27 (s), 124.00 (d), 125.80 (d), 126.35 (d), 126.66 (d), 128.06 (d), 129.22 (d), 129.80 (s), 130.84 (s), 133.59 (d), 136.33 (d), 154.31 (s), 157.24 (s), 178.12 (s, C=O).

12H-Benzo[a]xanthene-12-thione (61)
Compound **61** was prepared according to the procedures described for the synthesis of thioketones described in Section 2.7. After 3 h TLC analysis (SiO_2, hexane/Et_2O 90:10, starting material R_f = 0.29, product R_f = 0.43), indicated the total conversion of **60** (2.46 g, 10.0 mmol) to thioketone **61**. Crystallization from xylene (40 mL) yielded **61** as small dark green crystals (1.90 g, 7.3 mmol, 73.0%): mp 144.3-146.1 (lit:[44] mp 147 °C); ^{1}H NMR (300 MHz) δ 7.38 (m, 1H), 7.46 (d, J = 8.1 Hz, 1H), 7.48 (d, J = 8.8 Hz, 1H), 7.56 (m, 1H), 7.63 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 7.74 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 8.65 (dd, J = 8.1, 1.5 Hz, 1H), 10.48 (dd, J = 8.8, 1.1 Hz, 1H); ^{13}C NMR δ 117.02 (d), 117.60 (d), 123.88 (s), 124.89 (d), 126.36 (d), 126.37 (d), 128.37 (d), 128.86 (d), 129.87 (d), 130.78 (s), 131.03 (s), 132.25 (s), 133.10 (d), 136.49 (d), 147.87 (s), 151.11 (s), 204.61 (s, C=S); HRMS Calcd for $C_{17}H_{10}OS$: 262.045, found 262.044.

2-(2-Naphthylthio)-benzoic acid (63)
2-Thionaphthol (**14**, 16.0 g, 100 mmol) was added to a solution of KOH (19.0 g, 333 mmol in H_2O (250 mL). This mixture was stirred for 5 min and then Cu powder (0.6 g) and 2-iodobenzoic acid (**62**, 24.8 g, 100 mmol) were added successively. After refluxing for 20 h, the cooled mixture was filtered and slowly poured into 10% aqueous HCl (400 mL). The precipitated solid was isolated by filtration and dried to afford **63** as a white powder (26.7 g, 95 mmol, 95%): mp 195.4-198.2 °C (lit:[43] mp 199-200 °C). This compound was used in the next step without further purification.

12H-Benzo[a]thioxanthene-12-one (64)
This compound was prepared identically as described for **15**. Starting from **63** (26.0 g, 93 mmol), crystallization from ethanol (700 mL) afforded **64** as a gold coloured solid (17.8 g, 68 mmol, 73%): mp 130.3-132.1 °C (lit:[57] mp 128-130 °C); ^{1}H NMR (200 MHz) δ 7.37 (d, J = 8.7 Hz, 1H), 7.41-7.56 (m, 4H), 7.69 (ddd, J = 8.6, 7.0, 1.5 Hz, 1H), 7.77 (dd, J = 8.8, 1.1 Hz, 1H), 7.80 (d, J = 8.6 Hz, 1H), 8.58 (dd, J = 8.8, 1.1 Hz, 1H), 9.85 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 123.45 (d), 123.64 (s), 124.90 (d), 126.33 (d), 126.42 (d), 126.60 (d), 128.30 (d), 128.85 (d), 129.50 (d), 131.08 (d), 131.75 (s), 132.05 (s), 132.45 (s), 133.18 (d), 134.71 (s), 139.65 (s), 181.71 (s, C=O).

12H-Benzo[a]thioxanthene-12-thione (65)
To a stirred solution of **64** (5.0 g, 19 mmol) in dry toluene (200 mL) was added P_2S_5 (10.0 g, 45 mmol). After refluxing for 20 h, TLC analysis (SiO_2, hexane/Et_2O 90:10, starting material R_f = 0.23, product R_f = 0.39), showed no starting material left (In some cases the conversion was not complete, then more P_2S_5 (5.0 g, 22 mmol) was added and refluxing continued for another 20 h). The dark green mixture was cooled,

[57] Young, T.E.; Ohnmacht, C.J. *J. Org. Chem.* **1967**, *32*, 444.

filtered and the smelly residue washed with hot toluene (200 mL) and CH_2Cl_2 until the washings were only slightly green. The solvents were removed under reduced pressure and the brown-green mass dissolved in CH_2Cl_2 (400 mL). This solution was filtered over a short path of silica gel and the column eluted with CH_2Cl_2 until the colour of the efluens was light green. After evaporation of the solvent, the solid was crystallized from xylene (150 mL) to afford **65** as dark green small needles (3.3 g, 12 mmol, 62%, in two fractions): mp 187.6-188.7 °C; ^{1}H NMR (300 MHz) δ 7.40-7.45 (m, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.48-7.57 (m, 4H), 7.78 (dd, J = 8.4, 1.1 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 8.48 (dd, J = 8.1, 1.1 Hz, 1H), 9.38 (dd, J = 8.4, 1.1 Hz, 1H); ^{13}C NMR δ 122.52 (s), 122.55 (d), 124.05 (s), 124.06 (d), 125.74 (d), 126.74 (d), 126.96 (d), 127.35 (d), 127.93 (d), 130.36 (d), 130.90 (s), 131.07 (d), 131.58 (d), 132.24 (s), 133.04 (s), 135.89 (s), 216.39 (s, C=S); HRMS Calcd for $C_{17}H_{10}S_2$: 278.022, found 278.021.

9H-Xanthene-9-one hydrazone (68)
Partly dissolved 9H-xanthene-9-thione (**20**, 4.2 g, 20.0 mmol) was stirred and refluxed in absolute ethanol (50 mL). To this clear green solution was added in small portions $NH_2NH_2.H_2O$ (≈ 5.8 mL, 5.0 g, 100.0 mmol) until the dark-green colour had changed to yellow. After the addition was completed the mixture was refluxed for 1 h and filtered while hot. Upon cooling to -18 °C, **68** separated from the solution as light-yellow crystals (3.0 g, 14.2 mmol, 71.0%, in two fractions): mp 121.3-123.0 °C (lit:[45] mp 128-130 °C); ^{1}H NMR (200 MHz) δ 5.83 (bs, 2H), 7.13-7.46 (m, 6H), 7.93 (dd, J = 8.3, 1.5 Hz, 1H), 8.31 (dd, J = 7.9, 1.5 Hz, 1H); ^{13}C NMR 116.45 (d), 117.48 (s), 117.49 (s), 118.08 (d), 122.50 (d), 123.27 (s), 123.86 (d), 124.06 (d), 127.32 (d), 129.29 (d), 130.71 (d), 135.66 (s), 153.85 (s).

9H-Thioxanthene-9-one hydrazone (69)
This compound was prepared identically as described for **68**. Starting from 9H-thioxanthene-9-thione (**21**, 2.28 g, 10.0 mmol), crystallization from ethanol afforded **69** as a yellow solid (1.76 g, 7.8 mmol, 78.1%): mp 115.9-117.0 °C (lit:[45] mp 115 °C); ^{1}H NMR (200 MHz) δ 5.91 (bs, 2H), 7.27-7.58 (m, 6H), 7.77-7.80 (m, 1H), 8.02-8.08 (m, 1H); ^{13}C NMR δ 125.44 (d), 125.63 (d), 126.11 (d), 126.53 (s), 126.84 (d), 127.67 (d), 127.90 (d), 127.91 (d), 128.81 (d), 131.63 (s), 134.96 (s), 135.70 (s), 141.50 (s).

General procedure for the syntheses of benzannulated episulfides 74 - 78

Dispiro[12H-benzo[a]xanthene-12, 2'-thiirane-3', 9"-(9"H)-xanthene] (74)
9H-Xanthene-9-one hydrazone (**68**, 840 mg, 4.00 mmol) was partly dissolved in dry Et_2O (40 mL) by magnetically stirring. To this suspension was added, successively, Na_2SO_4 (≈ 2.0 g), Ag_2O (1854 mg, 8.00 mmol) and 5 drops of saturated KOH in methanol, whereupon the mixture rapidly turned dark green. After stirring for 30 min, the solution of the diazo compound **71** was filtered and the remaining residue washed with Et_2O (15 mL). To the clear dark green solution was added **61** in small portions. Only very slow evolution of nitrogen was observed. The thioketone was added until the evolution of nitrogen had ceased and the colour of the solution had become light brown. A total amount of 340 mg (1.30 mmol, 0.33 equiv.) was necessary. After stirring for 4 h, the precipitated episulfide **74** was isolated by filtration (430 mg). Crystallization from ethanol (350 mL) furnished **74** as small white needles (380 mg, 0.86 mmol, 66.2%, based on **61**): mp 186.7-188.2 °C; ^{1}H NMR (300 MHz) δ 6.20 (ddd, J = 8.0, 6.3, 1.8 Hz, 1H), 6.70 (ddd, J = 7.7, 7.0, 1.1 Hz, 1H), 6.77-7.01 (m, 8H), 7.08 (d, J = 8.8 Hz, 1H), 7.19 (dd, J = 7.7, 1.5 Hz, 1H), 7.31-7.35 (m, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.54 (ddd, J = 8.4, 7.0, 1.1 Hz, 1H), 7.58-7.62 (m, 2H), 9.20 (d, J = 8.8 Hz,

1H); ^{13}C NMR δ 54.20 (s, C-S), 55.08 (s, C-S), 114.65 (s), 114.75 (d), 115.14 (d), 115.24 (d), 116.41 (d), 120.45 (s), 120.68 (s), 121.43 (d), 121.79 (d), 122.65 (d), 122.99 (d), 123.68 (d), 125.63 (d), 125.91 (s), 127.67 (d), 127.98 (d), 128.04 (d), 128.05 (d), 128.11 (d), 128.24 (d), 128.53 (d), 128.58 (d), 130.57 (s), 132.49 (s), 154.04 (s), 154.37 (s), 154.97 (s), 155.61 (s); HRMS Calcd for $C_{30}H_{18}O_2S$: 442.103, found 442.103.

Dispiro[12H-benzo[a]xanthene-12, 2'-thiirane-3', 9"-(9"H)-thioxanthene] (75)
After oxidation of thioxanthene-9-one, hydrazone (**69**, 340 mg, 1.50 mmol) to the blue-violet diazo compound **72** and addition of thioketone **61** (300 mg, 1.15 mmol), **75** precipitated from the Et_2O solution and was isolated by filtration as a white powder (300 mg). Crystallization from ethanol (400 mL) yielded **75** as a white solid (256 mg, 0.56 mmol, 48.7%, based on the thioketone): mp 203.1-204.8 °C; ^{1}H NMR (300 MHz) δ 6.50 (ddd, J = 7.7, 7.3, 1.1 Hz, 1H), 6.70 (ddd, J = 7.7, 7.3, 1.1 Hz, 1H), 6.87 (ddd, J = 7.7, 6.9, 1.1 Hz, 1H), 6.93-7.05 (m, 5H), 7.14 (dd, J = 7.3, 1.1 Hz, 1H), 7.19 (dd, J = 8.8, 1.5 Hz, 1H), 7.23-7.58 (m, 7H), 9.51 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 55.35 (s, C-S), 63.61 (s, C-S), 111.74 (s), 114.73 (d), 116.79 (d), 122.19 (d), 122.94 (s), 123.29 (d), 123.75 (d), 124.54 (d), 124.92 (d), 125.07 (d), 125.21 (d), 125.70 (d), 126.32 (d), 126.54 (d), 127.67 (d), 127.87 (d), 128.66 (d), 128.96 (d), 129.74 (d), 129.99 (d), 130.35 (s), 132.15 (s), 132.32 (s), 132.98 (s), 135.40 (s), 135.77 (s), 154.10 (s), 154.39 (s); HRMS Calcd for $C_{30}H_{18}S_2O$: 458.080, found 458.081.

Dispiro[9H-xanthene-9, 2'-thiirane-3', 12"-(12"H)-benzo[a]thioxanthene] (76)
Starting from 9H-xanthene-9-one hydrazone **68** (420 mg, 2.00 mmol) and thioketone **65** (361 mg, 1.30 mmol), **76** was obtained as a slightly yellow solid (420 mg, 0.92 mmol, 70.6%, based on the thioketone): mp 228.0-229.5 °C (dec); ^{1}H NMR (300 MHz) δ 6.16 (ddd, J = 8.1, 7.3, 1.5 Hz, 1H), 6.44-6.52 (m, 2H), 6.83-6.92 (m, 2H), 6.94-7.03 (m, 3H), 7.10 (dd, J = 8.4, 1.1 Hz, 1H), 7.14 (dd, J = 8.1, 1.5 Hz, 1H), 7.18-7.28 (m, 2H), 7.38 (d, J = 8.4 Hz, 1H), 7.43 (ddd, J = 8.1, 7.3, 1.5 Hz, 1H), 7.58 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.93 (dd, J = 7.3, 1.5 Hz, 1H), 8.91 (dd, J = 8.8, 0.7 Hz, 1H); ^{13}C NMR δ 53.09 (s, C-S), 62.25 (s, C-S), 115.48 (d), 116.97 (d), 119.88 (s), 120.07 (s), 121.03 (d), 121.19 (d), 122.29 (d), 122.89 (d), 124.37 (d), 124.79 (s), 124.85 (d), 125.76 (d), 125.87 (d), 126.70 (d), 127.71 (d), 128.00 (d), 128.06 (d), 128.22 (d), 128.35 (d), 128.75 (d), 129.71 (d), 132.60 (s), 132.76 (s), 137.19 (s), 137.35 (s), 137.78 (s), 153.22 (s), 153.57 (s); HRMS Calcd for $C_{30}H_{18}S_2O$: 458.080, found 458.079.

Dispiro[12H-benzo[a]thioxanthene-12, 2'-thiirane-3', 9"-(9"H)-thioxanthene] (77)
Starting from 9H-thioxanthene-9-one hydrazone (**69**, 452 mg, 2.00 mmol) and thioketone **65** (334 mg, 1.20 mmol), **77** was obtained as a slightly yellow solid (425 mg, 0.90 mmol, 74.7%, based on the thioketone): mp 217.4-218.1 °C (dec); ^{1}H NMR (200 MHz) δ 6.24 (ddd, J = 8.4, 7.0, 1.3 Hz, 1H), 6.68-6.79 (m, 2H), 6.85-7.08 (m, 5H), 7.13-7.18 (m, 3H), 7.31 (d, J = 8.5 Hz, 1H), 7.38 (dd, J = 8.0, 1.2 Hz, 1H), 7.47 (dd, J = 8.0, 1.4 Hz, 1H), 7.53 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.61 (dd, J = 7.7, 1.4 Hz, 1H), 7.88 (dd, J = 7.7, 1.4 Hz, 1H), 8.95 (dd, J = 8.6, 0.9 Hz, 1H); ^{13}C NMR δ 60.00 (s, C-S), 61.85 (s, C-S), 122.95 (d), 124.06 (d), 124.40 (d), 124.51 (d), 124.52 (d), 124.89 (d), 125.13 (d), 125.22 (d), 125.44 (d), 125.45 (d), 126.11 (d), 126.55 (d), 126.63 (d), 126.64 (d), 128.12 (d), 128.96 (s), 129.42 (s), 129.88 (d), 129.98 (d), 130.94 (d), 132.53 (s), 132.54 (s), 132.76 (s), 133.22 (s), 133.62 (s), 135.29 (s), 136.82 (s), 137.03 (s); HRMS Calcd for $C_{30}H_{18}S_3$: 474.057, found 474.055.

Dispiro[12H-benzo[a]thioxanthene-12, 2'-thiirane-3', 9"-(9"H)-fluorene] (78)
Starting from 9H-fluorene-9-one hydrazone (**70**, 388 mg, 2.00 mmol) and thioketone **65** (318 mg, 1.14 mmol), **78** was obtained as a white powder (320 mg, 0.72 mmol, 63.5%, based on **65**): mp 231.7-233.8 °C; ^{1}H NMR (200 MHz) δ 5.78 (d, J = 7.7 Hz, 1H), 6.21 (d, J = 7.7 Hz, 1H), 6.59 (ddd, J = 8.7, 7.7, 1.1 Hz, 1H), 6.80 (ddd, J = 8.7, 7.7, 1.1 Hz, 1H), 7.05-7.35 (m, 5H), 7.42-7.72 (m, 6H), 7.90 (dd, J = 8.1, 1.1 Hz, 1H), 8.17 (dd, J = 8.7, 1.1 Hz, 1H), 9.09 (d, J = 8.7 Hz, 1H); ^{13}C NMR δ 56.49 (s, C-S), 57.26 (s, C-S), 119.61 (d), 119.73 (d), 123.16 (d), 123.28 (d), 125.43 (d), 125.55 (d), 126.02 (d), 126.05 (d), 126.11 (d), 126.19 (d), 126.40 (d), 126.52 (d), 126.99 (d), 127.07 (d), 127.60 (d), 127.67 (d), 128.77 (d), 128.84 (d), 130.96 (s), 132.05 (s), 132.55 (s), 138.13 (s), 138.83 (s), 139.75 (s), 140.77 (s), 141.15 (s), 143.34 (s), 143.44 (s); HRMS Calcd for $C_{30}H_{18}S_2$: 442.085, found 442.084.

12-(9'H-Thioxanthene-9'-ylidene)-12H-benzo[a]xanthene (80)
To a solution of episulfide **75** (735 mg, 1.60 mmol) in dry toluene (25 mL) was added PPh_3 (425 mg, 1.62 mmol). This clear solution was refluxed for 4 h, cooled to room temperature and the solvent evaporated in vacuo. The yellow residue was crystallized from ethanol to afford **80** as a slightly yellow solid (592 mg, 1.39 mmol, 86.6%): mp 232.1-233.8 °C; ^{1}H NMR (200 MHz) δ 6.36-6.47 (m, 2H), 6.81-7.49 (m, 12H), 7.50 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H); ^{13}C NMR δ 116.21 (d), 116.73 (d), 117.71 (s), 122.31 (s), 122.56 (d), 123.50 (d), 124.91 (d), 125.06 (d), 125.18 (d), 125.30 (s), 125.46 (d), 125.98 (d), 126.34 (d), 126.98 (d), 126.99 (d), 127.32 (d), 127.53 (d), 127.75 (d), 128.39 (d), 128.97 (d), 129.06 (d), 130.16 (s), 130.17 (s), 134.95 (s), 135.71 (s), 136.17 (s), 136.18 (s), 137.70 (s), 153.57 (s), 154.33 (s); HRMS Calcd for $C_{30}H_{18}SO$: 426.108, found 426.108.

9-(12'H-Benzo[a]thioxanthene-12'-ylidene)-9H-xanthene (81)
To a solution of **76** (229 mg, 0.50 mmol) in toluene/Et_2O (30 mL, 50:50) was added $LiAlH_4$ (38 mg, 1.00 mmol). After stirring and refluxing for 5 h, the mixture was cooled to 0 °C and the excess of $LiAlH_4$ was quenched by careful addition of methanol (3 mL) and 10% aqueous HCl (30 mL). The water layer was extracted with Et_2O (2 x 30 mL). The combined organic layers were washed with 10% aqueous HCl (1 x 50 mL), saturated aqueous $NaHCO_3$ (1 x 50 mL), brine (1 x 50 mL) and dried (Na_2SO_4). After removal of the solvents under reduced pressure a yellow solid was obtained (200 mg). Crystallization from ethanol (250 mL) yielded **81** as a slightly yellow solid (165 mg, 0.39 mmol, 77.5%): mp 238.9-240.1 °C; ^{1}H NMR (300 MHz) δ 6.17-6.24 (m, 2H), 6.71 (m, 1H), 6.74 (ddd, J = 8.4, 8.1, 1.5 Hz, 1H), 6.86-6.92 (m, 1H), 7.01 (ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 7.06 (ddd, J = 8.8, 7.0, 1.5 Hz, 1H), 7.13 (d, J = 8.1 Hz, 1H), 7.14-7.27 (m, 5H), 7.61 (d, J = 8.4 Hz, 1H), 7.64-7.69 (m, 4H); ^{13}C NMR δ 116.15 (d), 116.49 (d), 121.95 (d), 122.18 (d), 123.68 (d), 124.33 (s), 124.49 (s), 125.06 (d), 125.29 (d), 125.89 (d), 126.27 (d), 126.38 (d), 126.97 (d), 127.34 (d), 127.59 (s), 127.70 (d), 127.80 (s), 127.85 (s), 128.01 (d), 128.29 (d), 128.60 (d), 128.76 (d), 129.15 (d), 132.33 (s), 132.44 (s), 135.23 (s), 136.87 (s), 137.44 (s), 153.54 (s), 154.48 (s); HRMS Calcd for $C_{30}H_{18}SO$: 426.108, found 426.108.

12-(9'H-Thioxanthene-9'-ylidene)-12H-benzo[a]thioxanthene (82)
This compound was prepared following the procedure described for **81**. Starting from **77** (237 mg, 0.50 mmol), crystallization from ethanol (300 mL) yielded **82** as yellow solid (198 mg, 0.45 mmol, 89.6%): mp 240.1-242.3 °C; ^{1}H NMR (300 MHz) δ 6.39-6.41 (m, 2H), 6.75-6.83 (m, 2H), 6.91 (ddd, J = 8.0, 7.3, 1.2 Hz, 1H), 6.98-7.19 (m, 6H), 7.39 (d, J = 7.6 Hz, 1H), 7.57 (dd, J = 7.3, 1.2 Hz, 1H), 7.61-6.65 (m, 4H), 7.72

(d, J = 8.0 Hz, 1H); ^{13}C NMR δ 124.70 (d), 124.86 (d), 124.93 (d), 125.16 (d), 125.53 (d), 125.88 (d), 126.03 (d), 126.35 (d), 126.38 (d), 126.60 (d), 126.61 (d), 126.73 (d), 126.84 (d), 127.13 (d), 127.43 (d), 128.34 (d), 128.96 (d), 129.11 (s), 129.95 (d), 131.43 (s), 131.52 (s), 132.17 (s), 132.18 (s), 134.45 (s), 134.48 (s), 135.20 (s), 135.77 (s), 136.01 (s), 136.51 (s), 136.99 (s); HRMS Calcd for $C_{30}H_{18}S_2$: 442.085, found 442.084.

12-(9'H-Fluorene-9'-ylidene)-12H-benzo[a]thioxanthene (83)
This compound was synthesized following the procedure described for **81**. Starting from **78** (200 mg, 0.45 mmol), crystallization from ethanol (150 mL) afforded **83** as yellow small needles (165 mg, 0.40 mmol, 89.4%): mp 232.7-234.1 °C; ^{1}H NMR (200 MHz) δ 6.18 (d, J = 8.0 Hz, 1H), 6.61 (ddd, J = 8.0, 7.4, 1.2 Hz, 1H), 7.06 (ddd, J = 8.7, 6.6, 1.2 Hz, 1H), 7.15-7.50 (m, 7H), 7.65 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 7.3 Hz, 1H), 7.76-7.99 (m, 5H), 8.16 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ 118.95 (d), 119.35 (d), 125.38 (d), 125.54 (d), 125.83 (d), 126.26 (d), 126.27 (d), 126.28 (d), 126.44 (d), 126.45 (d), 126.97 (d), 127.12 (d), 127.24 (d), 128.11 (d), 128.37 (d), 128.38 (d), 128.47 (d), 128.48 (d), 130.24 (s), 132.01 (s), 132.77 (s), 133.56 (s), 133.57 (s), 134.91 (s), 136.84 (s), 137.19 (s), 137.57 (s), 137.88 (s), 140.74 (s), 141.18 (s); HRMS Calcd for $C_{30}H_{18}S$: 410.113, found 410.112.

3-Methyl-1H-naphtho[2,1-b]pyran-1-one (86)
To mechanically stirred ethylacetoacetate (**87**) (65.0 g, 0.50 mol) was added 2-naphthol (**10**, 72.0 g, 0.5 mol). After heating of this dark grey mixture to 110 °C, P_2O_5 (total amount ≈ 170 g, 0.84 mol) was added very carefully (foaming!) over a period of 2 h. The now dark brown very viscous mixture was stirred for 3 h at 110 °C. After cooling to 10 °C, ice was added very slowly (1.5 kg) taking care to keep the inner temperature below 30 °C, followed by extraction with Et_2O (4 x 400 mL). The combined ether layers were washed with 5% aqueous NaOH (4 x 250 mL), brine (1 x 200 mL) and dried (Na_2SO_4). The ether was removed in vacuo to afford an orange brown viscous oil, which slowly solidified upon standing (52.0 g). This semi-solid was purified by crystallization from ethanol to furnish **86** as small slightly yellow crystals (42.5 g, 0.20 mol, 40.5%): mp 164.2-165.9 °C (lit:[58] mp 168 °C); ^{1}H NMR (300 MHz) δ 2.33 (s, 3H), 6.24 (s, 1H), 7.36 (d, J = 9.5 Hz, 1H), 7.51-7.56 (m, 1H), 7.68 (ddd, J = 8.8, 6.6, 1.5 Hz, 1H), 7.80 (d, J = 7.3 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 9.98 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 19.62 (q), 113.26 (d), 116.44 (s), 117.23 (d), 126.14 (d), 126.84 (d), 127.82 (d), 128.77 (d), 130.20 (s), 130.21 (s), 134.78 (d), 157.30 (s), 162.98 (s), 179.83 (s, C=O); HRMS Calcd for $C_{14}H_{10}O_2$: 210.068, found 210.068.

3-Methyl-1H-naphtho[2,1-b]pyran-1-thione (88)
This compound was prepared following the procedure described for 9H-xanthene-9-thione (**30**) in Section 2.7. Starting from **86** (2.10 g, 10.0 mmol) and Lawesson's reagent (2.80 g, 7.0 mmol), chromatography (SiO_2, Et_2O, starting material R_f = 0.34, product R_f = 0.45) followed by crystallization from ethanol (80 mL), afforded **88** as small dark red crystals (2.00 g, 8.8 mmol, 88.5%): mp 147.3-149.2 °C (lit:[54] mp 150 °C); ^{1}H NMR (300 MHz) δ 2.20 (s, 3H), 7.12 (s, 1H), 7.24 (d, J = 8.8 Hz, 1H), 7.52-7.58 (m, 1H), 7.64 (ddd, J = 8.8, 8.1, 1.5 Hz, 1H), 7.78 (dd, J = 8.8, 1.5 Hz, 1H), 7.92 (d, 1H), 10.98 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 18.63 (q), 117.34 (d), 123.48 (s), 126.35 (d), 126.59 (d), 127.81 (d), 128.24 (d), 128.82 (d), 130.56 (s), 130.80 (s), 135.72

[58] Osbourne A.G. *Monatshefte für Chemie* **1984**, *115*, 613.

(d), 152.05 (s), 153.24 (s), 202.65 (s, C=S); HRMS Calcd for $C_{14}H_{10}OS$: 226.045, found 226.044.