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Synthesis of Carboxy-Functionalized Polycyclic Arenes by Oxidative Cyclizations of 2,3-Diarylacrylates

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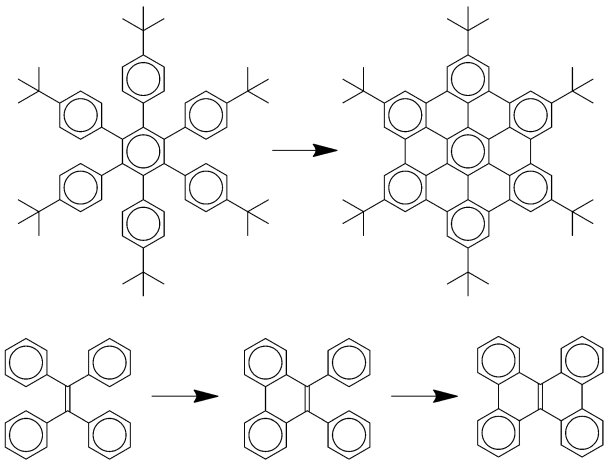
Abstract: The cyclization of esters of Perkin condensation products by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in the presence of $MeSO_3H$ is examined as a three-step approach from arylacetic acids and aromatic aldehydes to functionalized condensed arenes. The method is limited to systems in which one or both of the two aryl moieties are more reactive than a phenyl group, such as 1-naphthyl or, especially, 3-thienyl. Alkoxycarbonyl derivatives of picene, benzo[c]chrysene, three isomeric phenanthrothiophenes, a naphthothiophene, and a benzodithiophene were obtained. The extension of this approach to multiple cyclizations and, thus, to extended partially condensed systems with multiple alkoxycarbonyl substituents appears promising with highly active precursors derived from 3-thienylacetic acid. In this case, conjugated polymers made of short ribbon fragments linked by thiophene–thiophene single bonds appear conceivable. A bifunctional chrysenodithiophene was obtained from 1,5-diformylnaphthalene, together with a highly unusual asymmetric dimer that contains a cyclohepta[de]naphthalene (pleiadiene) moiety.

Keywords: cyclization · dehydrogenation · dimerization · fused-ring systems · oxidation

Introduction

Oxidative dehydrocyclizations are versatile approaches to condensed polycyclic arenes. Biaryl couplings with $AlCl_3$ were first reported by Scholl et al. one century ago,[1,2] but their extensive use for intramolecular cyclizations has been pioneered by Müllen and co-workers only in the last two decades. A particularly efficient implementation of this reaction is the oxidation of branched oligophenyl networks with $FeCl_3$, which leads to a variety of extended graphene fragments in high yields by multiple simultaneous ring closures.[3,4] Similar results have also been obtained with other oxidants, such as phenyliodine(III) bis(trifluoroacetate) (PIFA) or $MoCl_5$.[5] Very recently, Rathore and co-workers proposed an alternative oxidation system based on the combination of a quinone oxidant, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), with methanesulfonic acid in dichloromethane.[6] Quinone oxidants, such as DDQ or chloranil, are proficient tools to aromatize saturated or partially saturated cyclic compounds, such as those obtained by Diels–Alder reactions at high temperature,[7–10] and are tolerant to substituents, such as ester, imide, or anhydride groups, but are inefficient for inducing Scholl-type cyclizations. The combination with an acid, such anhydrous methanesulfonic acid, renders DDQ surprisingly active for such cyclizations even at room temperature or below. It finds its limit at an oxidation potential of approximately $E_{ox} = 1.7$ V versus a saturated calomel electrode, such that hexa(4-*tert*-butylphenyl)benzene with $E_{ox} = 1.6$ V can be efficiently hexacyclized to the corresponding hexa-*tert*-butylhexabenzocoronene, whereas unsubstituted hexaphenylbenzene, with a slightly higher E_{ox} of 1.8 V, does not react (Scheme 1).[6] Similarly, tetraphenylethylene ($E_{ox} = 1.36$ V) reacts twice via the less reactive 9-10-diphenylphenanthrene ($E_{ox} = 1.59$ V) to slowly give the corresponding dibenzochrysene, whereas the reaction of tetra-(4-bromophenyl)-ethylene ($E_{ox} = 1.51$ V) does not go beyond the bis(bromophenyl)phenanthrene ($E_{ox} = 1.80$ V).[11] In these examples,



Scheme 1. Reported ring closures with $DDQ/MeSO_3H$.[6,11]

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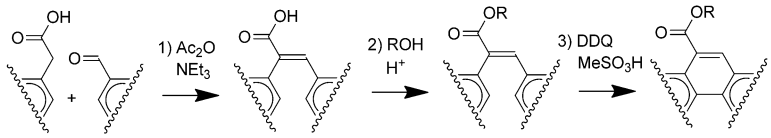
the lower oxidation potentials and higher reactivities of oligoaryl-substituted ethylenes compared with oligoaryl-substituted benzenes points to stilbenes as better substrates than *o*-terphenyls.

Stilbene-type precursors, including ester-substituted ones, can also be transformed into phenanthrene-type arenes by oxidative photocyclization, but photocyclizations of stilbenes often suffer from competing photochemical [2+2] cycloadditions either between two stilbenes or between the phenanthrene product and the stilbene substrate, and are thus generally conducted in high dilution.[12] A particularly versatile access route to cyclizable, carboxy-substituted precursors to polycyclic arenes is the Perkin reaction of an aromatic aldehyde with an arylacetic acid, which gives α-aryl-*trans*-cinnamic acids (=alkoxycarbonyl-*cis*-stilbenes)[13–15] with the two aryl moieties in the appropriate *cis*-configuration for oxidative cyclization to 9-carboxy-phenanthrene-type arenes.

As our group has a long-standing interest in carboxy-substituted polycyclic arenes and their esters and imides, because carboxylic substitution is an efficient lever for the tuning of electronic properties and often leads to liquid crystalline self-assembly,[10,16–22] we wondered whether the use of DDQ/H^+ would allow Scholl-type oxidative cyclizations to be conducted in the presence of carboxylic ester substituents on stilbene-type substrates (Scheme 2). Oxidative ring closures of stilbenecarboxylic esters with $FeCl_3$ or VOF_3 as the oxidant have only been reported for systems in which the aromatic residues are activated by several electron-donating alkoxy substituents,[23,24] except for the lone substituent-free case of VOF_3-induced cyclization of methyl *trans*-2,3-bis-(1-naphthyl)acrylate to methyl picene-14-carboxylate in 47% yield.[25]



Scheme 2. Three-step access to phenanthrene-type arenecarboxylates by 1) Perkin condensation of an arylacetic acid with an arenealdehyde, 2) esterification, and 3) oxidative cyclization.

Results and Discussion

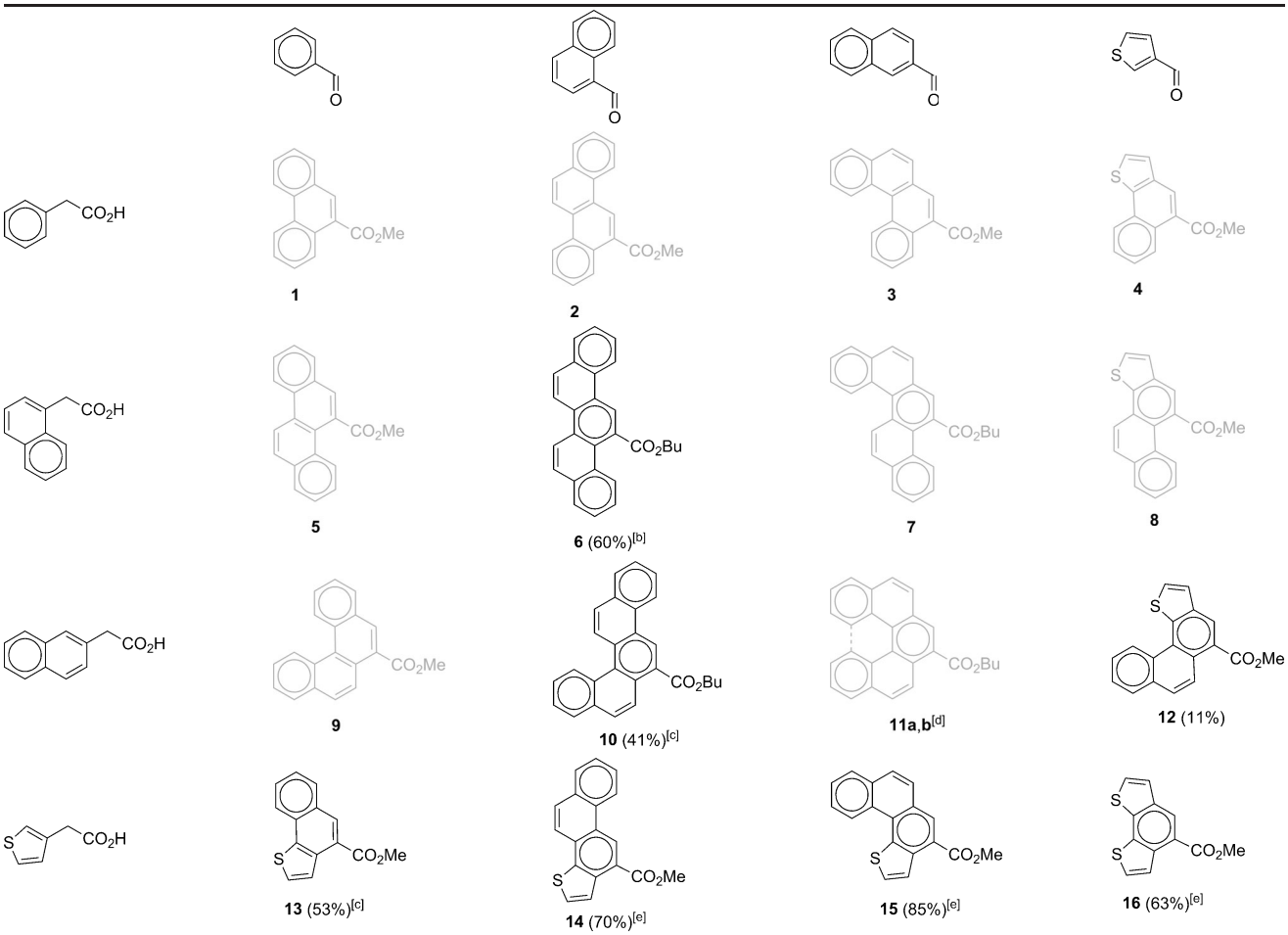
To investigate the potential of the DDQ/H^+ oxidation on esterified Perkin products with no activating substituents, we chose, as set of aryl groups with varying reactivities, the four moieties phenyl, 1-naphthyl, 2-naphthyl, and 3-thienyl, and prepared the sixteen corresponding methyl or butyl *trans*-2,3-diarylacrylates to test their ability to cyclize to the corresponding kata-annellated arenecarboxylic esters **1**–**16** (Table 1). The four dinaphtyl acrylates that supposedly yield the least soluble cyclization products were made as butyl esters, whereas the methyl esters of the twelve other acrylic acids were made to optimize crystallinity.

Perkin condensations are usually conducted in acetic anhydride at reflux (b.p. 140 °C), which acts simultaneously as a solvent and activator of the arylacetic acid by mixed anhydride formation. At this high reaction temperature, side products form that include decarboxylated stilbene, 1,3-diaryl-2-propanone from a Claisen condensation, and the Perkin condensation product of the aromatic aldehyde with acetic anhydride itself, that is, the α-unsubstituted *trans*-cinnamic acid.[26] Buckles and Cooper showed that the reaction proceeds with good yield and that side product formation can be largely suppressed if the reaction is carried out at 65 °C with an arenecarboxaldehyde starting material, benzaldehyde in their case, as a solvent. We found that the Perkin condensation can conveniently be conducted under mild conditions with isolated yields of around 45% (including the subsequent esterification of the crude condensation product) while avoiding the use of excess starting material, if THF at reflux (b.p. 66 °C) is chosen as the solvent.

The 2,3-diarylacrylates obtained were treated with DDQ/$MeSO_3H$ in dichloromethane at room temperature for up to three days. No cyclizations to **1**–**4** could be achieved with any of the four acrylates derived from phenylacetic acid (with, as counterparts, benzaldehyde, 1- and 2-naphthaldehyde, and 3-formylthiophene), and the starting material was largely recovered. Three of the four acrylates derived from 3-thienylacetic acid gave the desired cyclization products **14**–**16** in yields between 63 and 85% and the reaction was completed after 16 h. The exception was the least reactive case based on 3-thienylacetic acid and benzaldehyde, where the reaction proceeded slowly to reach a yield of 53% of **13** after 64 h. The latter case is the only benzaldehyde-based system among the four tested that reacted (**1**, **5**, **9**, and **13**).

Interestingly, the reactivity depends strongly on the location of the alkoxycarbonyl moiety with respect to the two aryl residues on the acrylate starting material. Reversing the substitution pattern from 2-thienyl-3-phenyl/naphthyl- to 2-phenyl/naphthyl-3-thienyl decreased the reactivity considerably. No reaction occurred with the systems based on 3-formylthiophene and either phenyl- or 1-naphthyl-acetic acid (**4** and **8**), and only an 11% yield of **12** was obtained after three days alongside recovered starting ester in the case of 3-formylthiophene with 2-naphthylacetic acid. A striking difference in reactivity was also found between 1-naphthaldehyde- and 2-naphthaldehyde-based cases when comparing the four 2,3-dinaphthylacrylates. Both systems based on 1-naphthaldehyde, that is, butyl 2-(2-naphthyl)-3-(1-naphthyl)acrylate and butyl 2,3-bis(1-naphthyl)acrylate, cyclize to **6** and **10**, respectively, albeit slowly. However, the two systems based on 2-naphthaldehyde, that is, butyl 2-(1-

Table 1. Targets of oxidative cyclizations of Perkin condensation products[a]



[a] Conditions: Ester of Perkin condensation product (3 mmol) with DDQ (3.6 mmol, 1.2 equiv.) and $MeSO_3H$ (30 mmol) in dichloromethane; [b] At 0 °C for 64 h; [c] At 20 °C for 64 h; [d] with DDQ (7.2 mmol) and $MeSO_3H$ (60 mmol); [e] At 20 °C for 16 h. Black: Perkin starting materials and obtained products (yield). Gray: Not formed after 64 h at 20 °C.

naphthyl)-3-(2-naphthyl)acrylate and butyl 2,3-bis(2-naphthyl)acrylate, do not cyclize to **7** or **11**, respectively, within 64 h even though in the latter case, where a further DDQ-induced oxidative ring closure of the primarily formed [5]helicene **11a** to the benzo[g,h,i]perylene **11b** is to be expected, we doubled the amount of oxidant used.

When we conducted the oxidative cyclization of butyl 2,3-bis-(1-napthyl)acrylate at room temperature, cyclization took place accompanied by loss of the alkyl group to give a sparingly soluble product. The ^{1}H NMR spectrum of this product has one aromatic hydrogen less than expected (three instead of four triplets as well as one downfield singlet and eight doublets). This spectrum is compatible with either a ketone formed by intramolecular Friedel–Crafts acylation or a lactone formed by a further oxidative cyclodehydrogenation. Both of these overreactions are plausible with regard to the known reactions of chrysene-6-carboxylic acid, which gives the corresponding pentagonal ketone upon dehydration in liquid HF and the corresponding intramolecular lactone upon irradiation in the presence of air and iodine.[27] The mass spectrum, with a dominant peak at 320.0836 Da that corresponds to $[C_{23}H_{12}O_2]^+$, is in agreement with the lactone structure **17**. As shown in Figure 1, the ^{1}H NMR spectrum of **17** has a singlet very far downfield at $\delta = 9.92$ ppm (compared with $\delta = 9.02$ ppm in the ester) because of the rigidly coplanar carbonyl (which is free to rotate in the butyl ester), and a doublet at $\delta =$ 7.58 ppm, which is upfield of the triplets and is indicative of a proton next to a phenolic oxygen.

To explain the variations in reactivity between the different alkyl 2,3-diarylacrylates, we consider that in the strongly acidic reaction medium, protonation at the ester carbonyl creates a positive charge localized in the terminal (aldehyde-derived) aryl substituent of the diarylacrylate, and leads to electrophilic attack by the positively charged aldehyde-derived aryl group on the intermediate (arylacetic-acid-derived) aryl group (Scheme 3). Stabilization of the positive charge on the central aryl group is mesomerically forbidden. Reactivity is thus controlled by the ease of electrophilic attack on the intermediate aryl group, and the ex-

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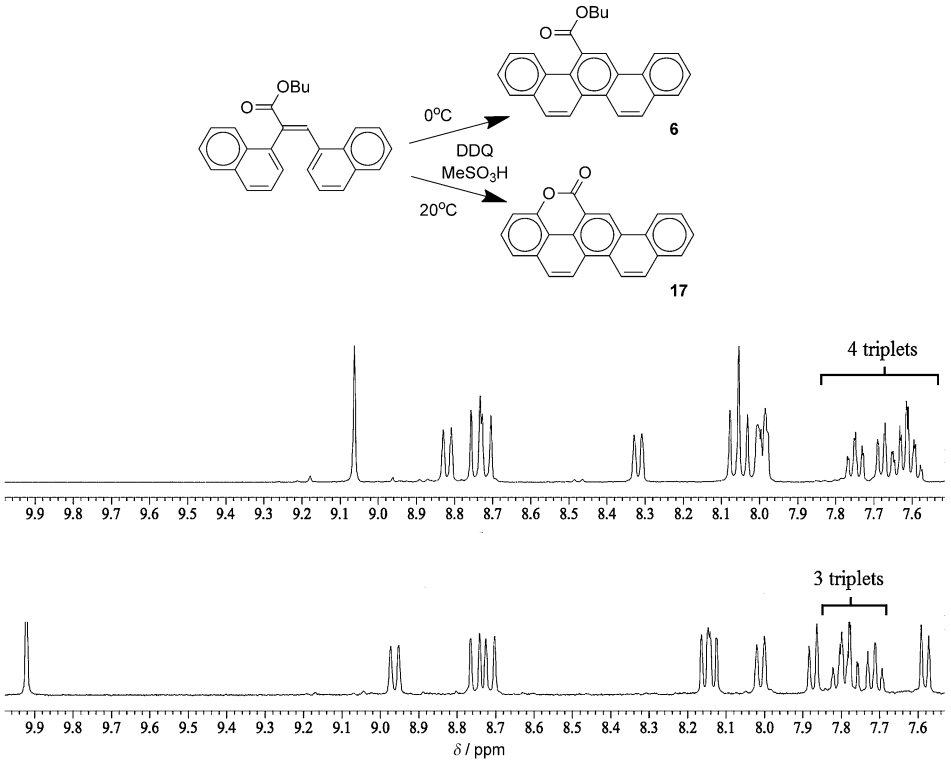
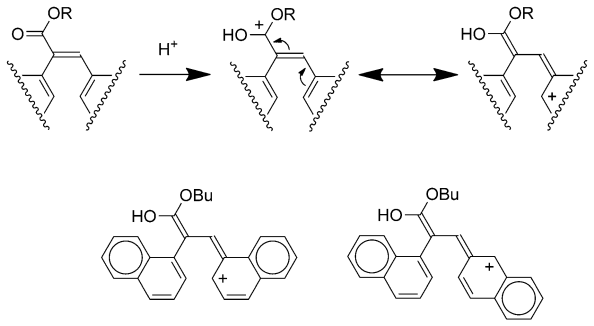


Figure 1. Top: oxidative cyclodehydrogenation of butyl 2,3-bis-(1-naphthyl)acrylate to butyl picene-9-carboxylate (**6**, at 0 °C) and to the corresponding intramolecular lactone **17** (at 20 °C). Bottom: aromatic region of the ^{1}H NMR spectra of the ester (top spectrum) and the lactone (bottom spectrum) in $CDCl_3$.



Scheme 3. Top: Protonation-induced creation of a positively charged reaction site on the terminal aryl substituent. Bottom: Maximally conjugated and sterically least crowded conformations of protonated *trans*-2-(1-naphthyl)-3-(1-/2-naphthyl)acrylates.

pected order of reactivity should be 3-thienyl (attacked in the very reactive 2-position) ≫ 2-naphthyl (attacked in the more reactive 1-position) > 1-naphthyl (attacked in the less reactive 2-position) ≫ phenyl, which concords with our results. To tentatively explain the reactivity differences between substrates on the same intermediate aryl group and different terminal aryl group, especially between the four dinaphthylacrylates, steric effects may be considered. Whereas in 1-naphthyl and 2-naphthyl substituents, charge localization in the substituted ring of the naphthalene unit is favored, as the aromatic sextet can only be maintained if localized on the unsubstituted ring of the naphthalene, a suitable orientation of the charged position close to the intermediate aryl substituent is sterically favored in a 1-naphthyl substituent but disfavored in a 2-naphthyl group (Scheme 3).

We thus find that the Scholl-analogous oxidative cyclization of dialkyl 2,3-diarylacrylates with DDQ/$MeSO_3H$ in dichloromethane is feasible largely independently of the nature of the terminal aryl substituent if the intermediate aryl substituent is 3-thienyl, and also if the terminal substituent is 1-naphthyl and the intermediate substituent is either 1- or 2-naphthyl.

Butyl benzo[c]chrysene-6-carboxylate **10**, the condensation product obtained from butyl 2-(2-naphthyl)-3-(1-naphthyl)acrylate, is the most sterically crowded cyclization product obtained and contains a [4]helicene fragment. We obtained single crystals that were good enough for X-ray diffraction analysis, which allowed us to quantify the deviation from planarity in this arene system. Compound **10** crystallizes in racemic crystals with two molecules of opposite helix sense in the unit cell (Figure 2). The torsion angle between the a priori parallel "bay shore" C–C bonds of the first and fourth

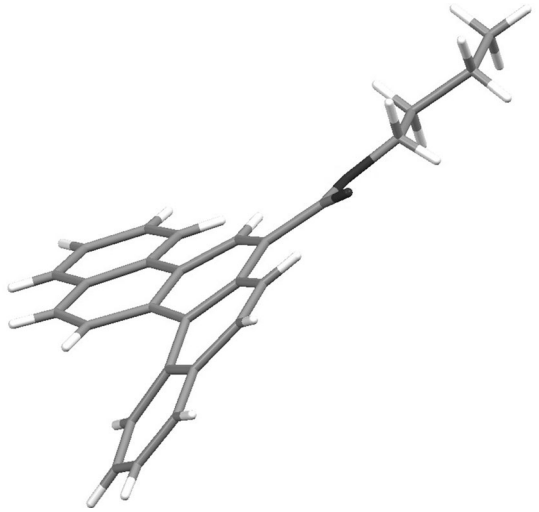


Figure 2. Structure of crystallized butyl benzo[c]chrysene-6-carboxylate **10**. The disorder on the butyl group is omitted for clarity.

helical rings is 37.1° and the distance between the two hydrogen-bearing carbons on opposite sides of the bay is 2.97 Å, which is very slightly smaller than in unsubstituted [4]helicene (3.00 Å).[28]

We obtained a crystal structure from methyl phenanthro-[1,2-b]thiophene-9-carboxylate **14**, which is the cyclization product of methyl 2-(3-thienyl)-3-(1-naphthyl)acrylate (Figure 3). This molecule is planar, with the carbonyl group

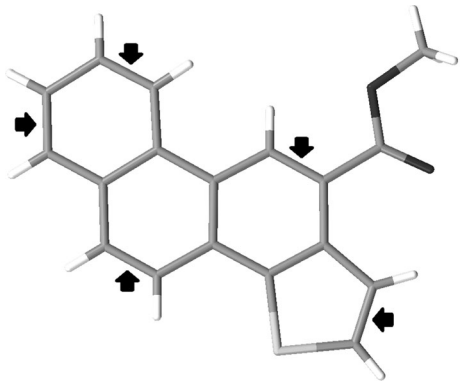


Figure 3. Structure of crystallized methyl phenanthro[1,2-b]thiophene-9-carboxylate **14**. Arrows indicate C–C bonds of less than 1.38 Å length; all others are longer than 1.40 Å.

aligned in the plane of the aromatic moiety and pointing towards the thiophene side. The carbonyl group is thus, as in the [4]helicene structure, in the same orientation towards the hydrogen atom on the closest neighboring ring instead of towards the hydrogen atom on the same ring, even though in the case of thiophene the hydrogen atom on the next ring is further away than the hydrogen atom on the same ring, whereas in the case of [4]helicene it is closer than the hydrogen atom on the same ring. In both molecules, the shortest C–C bonds (that is, the bonds with the strongest double-bond character) are those in the *meta* position to the ring-fusing bonds. It appears, thus, that the orientation of the carbonyl double bond is not dominated by steric effects but by a tendency towards *transoid* alignment with the most double-bond-like conjugated aromatic C–C bond. Conformational considerations of this type are important for the prediction of space-filling preferences and, thus, the propensity of liquid crystalline self-assembly to occur in arenes with several ester substituents.

Methyl phenanthro[4,3-b]thiophene-5-methylcarboxylate **12**, the cyclization product of methyl 2-(2-naphthyl)-3-(3-thienyl)-2-acrylate, also crystallized well enough for us to obtain an X-ray crystal structure (Figure 4). It is an analogue of [4]helicene, in which one of the terminal benzene rings is replaced by a thiophene ring with an inward-pointing sulfur atom. As a result of the comparatively smaller steric hindrance, the torsion angle is reduced to 8.6°. And as in the [4]helicene **10** and in isomeric **14**, the carbonyl oxygen atom is pointing towards the hydrogen atom on the closest neighboring ring, not towards the hydrogen atom on the same ring.

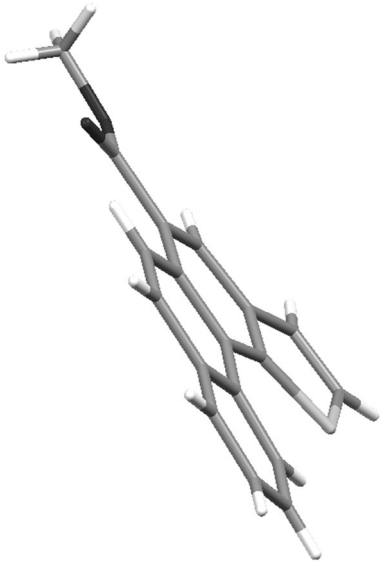
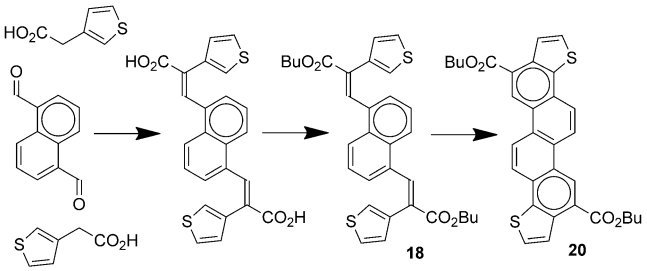


Figure 4. Structure of crystallized phenanthro[4,3-b]thiophene-5-methylcarboxylate **12**.

The good reactivity of diarylacrylates derived from 3-thienylacetic acid opens the possibility of using this method for obtaining carboxy-functionalized arenodithiophenes that result from the combination of sufficiently reactive diformylarenes with 3-thienylacetic acid (Scheme 4). Such



Scheme 4. Approach to ester-functionalized arenodithiophene polymerization precursors, exemplified by 1,5-diformylnaphthalene.

arenodithiophenes would be suitable monomers for obtaining rigidified poly(alkoxycarbonylthiophene) analogues[29] with enhanced planarity in the conjugated backbone and possibly enhanced semiconducting properties that are exploitable in organic electronics. In this case, the presence of ester side chains allows both the tuning of physical properties by adjusting the size and form of the alkyl substituents, and the generation of conjugated polyelectrolytes by saponification.

We thus synthesized 1,5-diformylnaphthalene from commercially available 1,5-dimethylnaphthalene as reported, by radical bromination and subsequent oxidation with *N*-methylmorpholine-*N*-oxide,[30] then condensed it in a double Perkin reaction with 3-thienylacetic acid. After esterification to the dibutyl ester **18**, we attempted a double cycliza-

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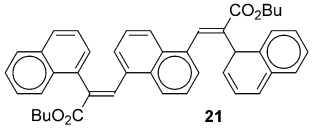
tion with DDQ/$MeSO_3H$ in dichloromethane. To our chagrin, the reaction yielded product **19**, the mass of which (1078.2 Da) corresponds to double the desired dicyclized product minus two hydrogen atoms. The ^1H NMR spectrum has the right ratio between aliphatic and aromatic protons for a dimer of the expected chrysenodithiophene **20**. Compound **19** was obtained at 20 and at 0 °C in reasonable yield (ca. 50 %) within 16 h. Such a dimer could have been formed by oxidative dimerization at the reactive thiophene position, but four different sets of butyl chain signals and twice the expected number of different signals in the aromatic region testify to an asymmetric dimeric structure. The ^1H NMR spectrum of the symmetric dimer obtained from coupling in the activated position adjacent to a sulfur atom should have six aromatic doublets and three aromatic singlets, whereas the spectrum of the product obtained has 12 doublets, five singlets, and one triplet. The presence of a triplet, necessarily located on naphthalene, implies that one of the four oxidative thiophene-to-naphthalene cyclizations did not take place in the desired way, and also suggests that the corresponding thiophene unit has reacted otherwise. We finally succeeded in obtaining crystals that were suitable for X-ray diffraction analysis. The structure reveals that after the double cyclization, the active position adjacent to the sulfur atom attacks at the naphthalene moiety of a molecule of the starting material or a monocyclized intermediate, whereupon one thienyl unit of the attacked molecule strangely couples with the carbon atom next to the attacked position to form a 7-membered ring, which is part of a pleiadiene (cyclohepta[d,e]naphthalene) unit (Figure 5). This scenario implies that with more dilute reaction conditions, this unexpected dimerization should be avoidable. We were indeed able to suppress the dimerization by using an increased amount of solvent together with slow addition of the methanesulfonic acid, to successfully isolate the desired doubly cyclized monomer **20** in 50 % yield.

Having 1,5-diformylnaphthalene in hand, we also treated it with naphthyl-1-acetic acid, but the resulting diester **21** (Scheme 5) did not even monocyclize with DDQ/$MeSO_3H$,



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Scheme 5. Potential precursor to [8]phenacene dicarboxylate, synthesized from 1,5-diformylnaphthalene, that proved to be inert towards DDQ/$MeSO_3H$.

neither at 20 °C for 64 h, nor even at reflux for 16 h. Apparently a distant second ester substituent is decisively deactivating in this case.

As the successful cyclization of methyl 2,3-bis(3-thienyl)-acrylate easily gave benzodithiophene monoester **16** with two thiophene extremities for potential polymerization, we wondered whether the introduction of a second ester group

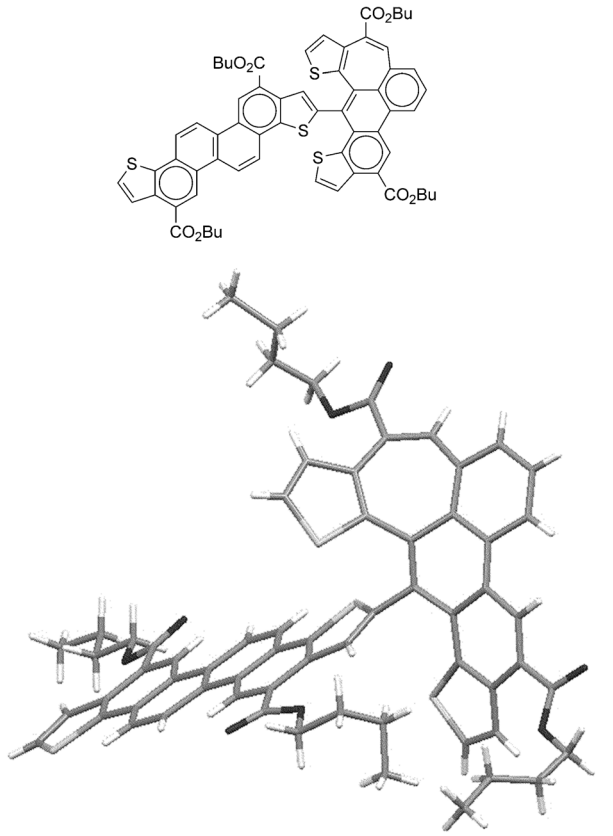

Figure 5. Structure of crystallized unexpected dimer **19** formed by oxidation of **18**.

would still allow the reaction to occur. This would offer the potential for more varied substitution, for example, by replacement of the ester groups by an imide function after successful cyclization. Perkin reactions have also been reported with a phenylglyoxylic acid in place of the aromatic aldehyde to give diarylmaleic anhydrides,[31,32] which may be esterified prior to cyclization attempts. As 3-thienylglyoxylic acid is not commercially available but 2-thienylglyoxylic acid is, we condensed the latter with 3-thienylacetic acid to obtain, after esterification, dimethyl 2-(2-thienyl)-3-(3-thienyl)maleate **22**. The reaction proceeded slowly and gave the expected product **23** in only moderate yield (34 %) after 64 h, accompanied by substantial amounts of side products. One relatively polar side product that could be separated in 10 % yield by column chromatography has no methyl signals in the ^1H NMR spectrum, and HRMS revealed its formula to be $C_{12}H_6O_3S_2$. This composition and the ^1H and ^{13}C NMR spectra (four aromatic doublets and one aromatic singlet in the proton spectrum, strong downfield shift of one of the two carbonyl ^{13}C signals) point to the formation of a thiopyranone heterocycle by insertion of one of the two ester carbonyl groups into the adjacent thiophene, to give thieno[3,2-*g*]-1*H*-2-benzothiopyran-1-one-10-carboxylic acid **24** (Figure 6).

We also obtained a crystallographic structure of the expected product **23** (Figure 6), which allowed us to quantify

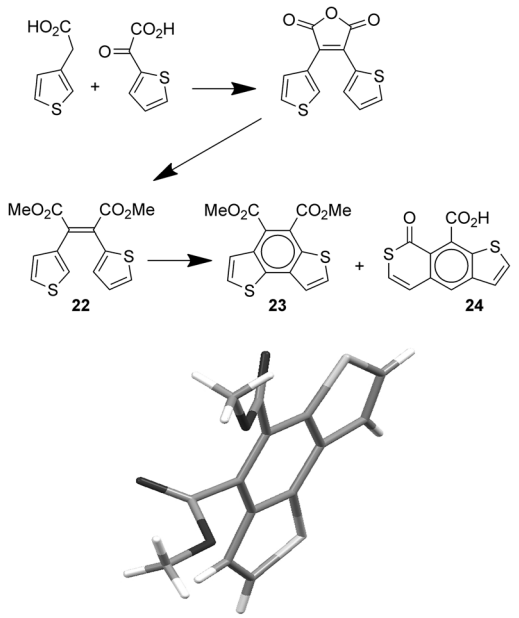

Figure 6. Synthesis of unsymmetrical dimethyl benzodithiophene dicarboxylate **23** together with its structure in the crystal.

the sterically imposed out-of-plane orientation of the two carbonyl groups. The carbonyl groups make angles of approximately 60° and 30° with the aromatic plane (values differ slightly between the two molecules in the crystallographic unit cell) and are surprisingly oriented towards the same side of the plane. The aromatic moiety is perfectly planar, and because of the compensating positions of the pentagon-deforming sulfur atoms in the two thiophene rings, the two C–H bonds next to the sulfur atoms on opposite sides of the molecule make an angle of 120° with each other.

Conclusions

In summary, oxidative ring closure of esterified Perkin products with the DDQ/$MeSO_3H$ system allows convenient access to a variety of polycyclic carboxy-substituted systems if the 2-aryl substituent of the Perkin ester, that is, the aryl moiety introduced by the arylacetic acid, has a high electron density on the ring-closing carbon atom. This is especially the case for substrates derived from 3-thienylacetic acid, which allows the synthesis dicarboxylic derivatives of arenodithiophenes, exemplified here by a substituted chrysenodithiophene obtained from 3-thienylacetic acid and 1,5-diformylnaphthalene. Such arenodithiophenes that contain two solubilizing substituents may allow the elaboration of rigidified and, thus, particularly well-conjugated polythiophene analogues. Ring closures in unexpected positions, favoring heptagon formation over benzannelation, are possible with this oxidation system, and indicate that this chemistry may hold further surprises that are comparable to the formation of an annelated pleiadiene obtained here.

Experimental Section

Crystal Structure Determinations and Refinements

X-ray crystallographic data were collected on a Bruker APEX II CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda =$ 0.71073 Å). The single crystal was coated with Paratone N-oil and mounted on a fiber loop and the data were collected at 100(2) K for compounds **14** and **23** or at 120(2) K for **10**, **12**, and **19**. The program SAINT was used to integrate the data while the absorption correction was based on multiple and symmetry-equivalent reflections in the data set by using the SADABS program.[33] The structure was solved by direct methods and refined by full-matrix least squares on F^2 by using SHELXL-97.[34] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed by using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. For compound **10**, the end of the butyl group was found to be disordered over two positions with relative occupancies of 0.5/0.5. Because of the presence of only light atoms in the crystal structure, the absolute structure of this compound cannot be determined unequivocally. Therefore, the Flack parameter was removed from the .cif file. Further refinement details and crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications. CCDC 890959, 890960, 890961, 890962, and 890963 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via href="http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi"www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for Single Perkin Condensations

Aldehyde (30 mmol) and THF (50 mL) were added to a mixture of arylacetic acid (30 mmol), triethylamine (5.05 g, 50 mmol) and acetic anhydride (10.2 g, 100 mmol). The mixture, which turned into a homogeneous solution upon heating, was stirred at reflux under exclusion of moisture for 16 h. Water (50 mL) was added and the reflux continued for 1 h. The mixture was concentrated under reduced pressure. The residue was dissolved in 20% aqueous potassium hydroxide (200 mL) and the crude product was precipitated by acidification with concentrated hydrochloric acid. The precipitate was filtered, dried in air and esterified without further purification.

General Procedure for Acidic Esterifications to Methyl Esters with Sulfuric Acid

A solution of concentrated sulfuric acid in methanol (2 mL in 10 mL, caution during preparation!) was added dropwise to a solution of the crude product of the Perkin condensation in methanol (300 mL) through a reflux condenser. The reaction mixture was heated to reflux for 5 h under exclusion of moisture and then concentrated at reduced pressure to a volume of 100 mL. It was kept overnight in the freezer and the ensuing precipitate was filtered and recrystallized from methanol. All methyl esters except **pre16** were obtained by this procedure.

General Procedure for Basic Esterifications to Methyl or Butyl Esters with DBU

DBU (9.1 g, 60 mmol) and iodomethane (14.2 g, 100 mmol) or 1-bromobutane (13.7 g, 100 mmol) were added to a solution of the crude product of the Perkin condensation in methanol (300 mL, for methyl ester) or *n*-butanol (300 mL, for butyl esters). The solution was stirred at 60 °C for four hours under exclusion of moisture, then concentrated under reduced pressure and purified by chromatography on a silica gel column with chloroform as eluent. The product was recrystallized from methanol (methyl ester) or *n*-butanol (butyl esters). All butyl esters and the methyl ester **pre16** were obtained by this procedure.

The ester substrates for the successful or failed oxidative cyclizations to the cyclized esters **1**–**16** (Table 1) are designated as **pre1** to **pre16**. The 7 methyl *trans*-2,3-diarylacrylates **pre1**[35] (yield of Perkin condensation plus esterification: 3.4 g (48%)), **pre2**[36] (3.4 g (39%)), **pre3**[35] (4.3 g

(49%)), **pre4**[12] (3.6 g (49%)), **pre5**[37] (3.5 g (40%)), **pre9**[35] (4.2 g (48%)) and **pre16**[38] (3.0 g (40%)) are known substances.

*Butyl trans-2,3-di-(1-naphthyl)-acrylate (**pre6**)*

Yield from naphthyl-1-acetic acid and naphthalene-1-carbaldehyde after basic esterification: 5.2 g (46%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (s, 1H), 8.23 (d, 1H, J = 8.2 Hz), 7.84 (d, 2H, J = 8.7 Hz), 7.78 (d, 1H, J = 8.2 Hz), 7.75 (d, 1H, J = 8.0 Hz), 7.60 (m, 2H), 7.51 (d, 1H, J = 6.9 Hz), 7.41 (m, 2H), 7.28 (d, 1H, J = 7.3 Hz), 7.14 (d, 1H, J = 6.0 Hz), 6.92 (t, 1H, J = 7.8 Hz), 6.81 (d, 1H, J = 7.3 Hz), 4.18 (m, 2H), 1.56 (m, 2H), 1.13 (m, 2H), 0.78 ppm (t, 3H, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 139.8, 134.0, 133.9, 133.5, 133.4, 132.7, 132.1, 131.9, 129.1, 128.8, 128.6, 128.2, 127.7, 127.3, 126.7, 126.3, 126.1, 125.9, 125.6, 125.3, 125.1, 124.1, 65.2, 30.6, 19.1, 13.7 ppm. Elemental analysis calcd (%) for $C_{27}H_{24}O_2$: C 85.23, H 6.36; found: C 85.19, H 6.46.

*Butyl trans-2-(1-naphthyl)-3-(2-naphthyl)acrylate (**pre7**)*

Yield from naphthyl-1-acetic acid and naphthalene-2-carbaldehyde after basic esterification: 5.0 g (44%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.91 (dd, 2H, J = 2.8 Hz, 7.79 Hz), 7.82 (d, 1H, J = 8.2 Hz), 7.62 (m, 2H), 7.57 (d, 1H, J = 7.8 Hz), 7.47 (m, 2H), 7.36 (m, 5H), 6.81 (d, 1H, J = 8.7 Hz), 4.16 (m, 2H), 1.50 (m, 2H), 1.15 (m, 2H), 0.79 ppm (t, 3H, J = 7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 141.8, 134.3, 133.8, 133.4, 133.0, 132.2, 131.9, 131.4, 128.6 (2×), 128.5, 128.4, 127.8, 127.5, 127.4, 127.1, 126.6, 126.4, 126.3, 126.1, 125.9, 125.3, 65.1, 30.6, 19.1, 13.7 ppm. Elemental analysis calcd (%) for $C_{27}H_{24}O_2$: C 85.23, H 6.36; found: C 85.28, H 6.45.

*Methyl trans-2-(1-naphthyl)-3-(3-thienyl)acrylate (**pre8**)*

Yield from naphthyl-1-acetic acid and thiophene-3-carbaldehyde after acidic esterification: 3.7 g (43%) of pale yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 1H), 7.91 (m, 2H), 7.75 (d, 1H, J = 8.2 Hz), 7.50 (m, 2H), 7.40 (t, 1H, J = 7.8 Hz), 7.35 (d, 1H, 6.9 Hz), 6.98 (s, 1H), 6.96 (m, 1H), 6.23 (d, 1H, J = 5.0 Hz), 3.70 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 136.7, 136.0, 134.2, 133.8, 131.9, 130.0, 128.7, 128.64, 128.55, 128.3, 127.3, 126.6, 126.3, 126.0, 125.6, 125.1, 52.5 ppm. Elemental analysis calcd (%) for $C_{18}H_{14}O_2S$: C 73.44, H 4.79; found: C 73.68, H 4.93.

*Butyl trans-2-(2-naphthyl)-3-(1-naphthyl)acrylate (**pre10**)*

Yield from naphthyl-2-acetic acid and naphthalene-1-carbaldehyde after basic esterification: 5.4 g (47%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 8.22 (d, 1H, J = 11.0 Hz), 7.85 (d, 1H, J = 10.5 Hz), 7.78 (d, 1H, J = 7.8 Hz), 7.73 (s, 1H), 7.67 (m, 3H), 7.61 (pseudo t, 1H, J = 6.9 Hz, 8.2 Hz), 7.54 (pseudo t, 1H, J = 4.1 Hz, 9.6 Hz), 7.43 (m, 2H), 7.25 (d, 1H, J = 6.0 Hz), 7.04 (m, 2H), 4.34 (t, 2H, J = 6.9 Hz), 1.73 (m, 2H), 1.46 (m, 2H), 0.98 ppm (t, 3H, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 138.7, 135.1, 133.5, 133.3, 133.1, 132.8, 132.3, 132.2, 129.6, 129.0, 128.8, 128.4 (2×), 128.2, 127.7, 127.6, 126.7, 126.20, 126.17, 126.0, 125.3, 124.3, 65.4, 30.9, 19.4, 13.9 ppm. Elemental analysis calcd (%) for $C_{27}H_{24}O_2$: C 85.23, H 6.36; found: C 85.11, H 6.47.

*Butyl trans-2,3-di-(1-naphthyl)acrylate (**pre11**)*

Yield from naphthyl-2-acetic acid and naphthalene-2-carbaldehyde after basic esterification: 5.8 g (51%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.86 (pseudo t, 2H, J = 10.5 Hz, 9.2 Hz), 7.73 (m, 3H), 7.64 (d, 1H, J = 7.3 Hz), 7.61 (d, 1H, J = 7.8 Hz), 7.41 (m, 6H), 6.96 (d, 1H, J = 8.7 Hz), 4.23 (t, 2H, J = 6.9 Hz), 1.64 (m, 2H), 1.35 (m, 2H), 0.90 ppm (t, 3H, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 140.6, 133.53, 133.51, 133.4, 133.1, 132.9, 132.8, 132.4, 131.8, 129.2, 128.5, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.1, 126.8, 126.34, 126.27, 126.1, 65.3, 30.7, 19.3, 13.8 ppm. Elemental analysis calcd (%) for $C_{27}H_{24}O_2$: C 85.23, H 6.36; found: C 85.22, H 6.36.

*Methyl trans-2-(2-naphthyl)-3-(3-thienyl)acrylate (**pre12**)*

Yield from naphthyl-2-acetic acid and thiophene-3-carbaldehyde after acidic esterification: 4.3 g (49%) of gray powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 1H), 7.89 (m, 2H), 7.80 (d, 1H, J = 9.2 Hz), 7.75 (s, 1H), 7.49 (m, 2H), 7.33 (d, 1H, J = 8.2 Hz), 7.12 (s, 1H), 6.97 (dd, 1H, J = 5.0 Hz, 3.2 Hz), 6.45 (d, 1H, J = 5.0 Hz), 3.77 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 136.8, 134.8, 133.9, 133.6, 133.0, 130.5, 130.0, 128.8, 128.6, 128.4, 128.3, 127.9, 127.7, 126.4, 126.3, 125.7, 52.5 ppm. Elemental analysis calcd (%) for $C_{18}H_{14}O_2S$: C 73.44, H 4.79; found: C 73.79, H 4.84.

*Methyl trans-2-(3-thienyl)-3-phenylacrylate (**pre13**)*

Yield from thienyl-3-acetic acid and benzaldehyde after acidic esterification: 3.2 g (44%) of brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (s, 1H), 7.31 (dd, 1H, J = 2.8 Hz, 5.0 Hz), 7.21 (m, 4H), 7.10 (m, 2H), 6.93 (dd, 1H, J = 1.4 Hz, 5.0 Hz), 3.81 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 141.2, 135.2, 134.9, 130.3 (2×), 129.2, 129.1, 128.4 (2×), 127.4, 125.5, 125.0, 52.5 ppm. Elemental analysis calcd (%) for $C_{14}H_{12}O_2S$: C 68.83, H 4.95; found: C 68.51, H 5.07.

*Methyl trans-2-(3-thienyl)-3-(1-naphthyl)acrylate (**pre14**)*

Yield from thienyl-3-acetic acid and naphthalene-1-carbaldehyde after acidic esterification: 3.6 g (41%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 8.06 (d, 1H, J = 6.9 Hz), 7.85 (d, 1H, J = 8.2 Hz), 7.75 (d, 1H, J = 8.2 Hz), 7.52 (m, 2H), 7.26 (t, 1H, 8.2 Hz), 7.1 (m, 3H), 6.76 (d, 1H, J = 4.6 Hz), 3.90 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 138.8, 134.8, 134.0, 132.8, 131.8, 129.7, 129.3, 129.0, 128.7, 127.5, 126.6, 126.2, 125.8, 125.3, 124.6, 124.3, 52.6 ppm. Elemental analysis calcd (%) for $C_{18}H_{14}O_2S$: C 73.44, H 4.79; found: C 73.84, H 4.99.

*Methyl trans-2-(3-thienyl)-3-(2-naphthyl)acrylate (**pre15**)*

Yield from thienyl-3-acetic acid and naphthalene-2-carbaldehyde after acidic esterification: 4.1 g (46%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 1H), 7.72 (d, 1H, J = 8.7 Hz), 7.67 (m, 2H), 7.58 (d, 1H, J = 8.7 Hz), 7.43 (m, 2H), 7.32 (dd, 1H, J = 2.7 Hz, 4.58 Hz), 7.19 (dd, 1H, J = 2.7 Hz, 1.4 Hz), 7.05 (dd, 1H, J = 1.4 Hz, 8.7 Hz), 6.95 (dd, 1H, J = 0.9 Hz, 5.0 Hz), 3.82 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 141.3, 135.3, 133.5, 133.1, 132.5, 131.3, 129.2, 128.6, 127.7, 127.6, 127.4, 127.1, 126.7, 126.4, 125.6, 125.3, 52.6 ppm. Elemental analysis calcd (%) for $C_{18}H_{14}O_2S$: C 73.44, H 4.79; found: C 73.17, H 4.84. HRMS: m/z: calcd for $C_{18}H_{14}O_2S$: 294.0714 $[M]^+$; found: 294.0700.

*trans,trans-1,5-Bis-(2-(3-thienyl)-2-(butoxycarbonyl)-vinyl)naphthalene (**18**)*

Naphthalene-1,5-di-carbaldehyde (5.53 g, 30 mmol) and THF (100 mL) were added to a mixture of thienyl-3-acetic acid (8.52 g, 60 mmol), triethylamine (10.1 g, 100 mmol), and acetic anhydride (20.4 g, 200 mmol). The mixture, which turned into a homogeneous solution upon heating, was stirred at reflux under exclusion of moisture for 16 h. The Perkin condensation product precipitated upon cooling to room temperature and was filtered off after 5 h, washed with water, dried on air, and dissolved in butanol (500 mL). DBU (9.1 g, 60 mmol) and 1-bromobutane (13.7 g, 100 mmol) were added and the solution was stirred at 60 °C for 4 hours under exclusion of moisture. The solution was then concentrated under reduced pressure and purified by chromatography on a silica gel column with chloroform as eluent. The product was recrystallized from butanol. Yield: 9.0 g (55%) of pale yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 7.95 (d, 1H, J = 8.3 Hz), 7.29 (t, 1H, J = 7.3 Hz), 7.12 (m, 3H), 6.73 (d, 1H, J = 4.6 Hz), 4.30 (t, 2H, J = 6.9 Hz), 1.73 (m, 2H), 1.44 (m, 2H), 0.97 ppm (t, 3H, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 138.3, 134.6, 133.6, 131.7, 130.4, 129.2, 127.6, 125.8 (2×), 125.1, 124.4, 65.4, 34.8, 19.3, 13.9 ppm. HRMS: m/z: calcd for $C_{32}H_{32}O_4S_2$: 544.1742 $[M]^+$; found: 544.1760.

*trans,trans-1,5-Bis-(2-(1-naphthyl)-2-(butoxycarbonyl)-vinyl)naphthalene (**21**)*

Compound **21** was synthesized by following the procedure for **18** with naphthyl-1-acetic acid (11.17 g, 60 mmol) instead of thienyl-3-acetic acid. Yield: 9.3 g (58%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (s, 1H), 8.00 (d, 1H, J = 8.2 Hz), 7.84 (d, 1H, J = 8.2 Hz), 7.80 (d, 1H, J = 8.2 Hz), 7.76 (d, 1H, J = 8.2 Hz), 7.47 (d, 1H, J = 6.9 Hz), 7.40 (broad s, 1H), 7.27 (broad s, 1H), 7.05 (broad s, 1H), 7.01 (d, 1H, J = 7.8 Hz), 6.87 (d, 1H, J = 7.3 Hz), 4.15 (m, 2H), 1.47 (m, 2H), 1.10 (m, 2H), 0.75 ppm (t, 3H, J = 7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 139.8 (2×), 133.7, 133.5, 132.7, 132.6, 132.9, 128.6, 128.2, 127.7, 127.4, 126.3, 125.9, 125.7, 125.5, 125.2, 125.0, 65.2, 30.6, 19.1, 13.8 ppm. HRMS: m/z: calcd for $C_{44}H_{40}O_4$: 632.2926 $[M]^+$; found: 632.2904.

*Dimethyl 2-(2-Thienyl)-3-(3-thienyl)maleate (**22**)*

Thienyl-2-glyoxylic acid (4.70 g, 30 mmol) and THF (50 mL) were added to a mixture of thienyl-3-acetic acid (4.26 g, 30 mmol), triethylamine (5.05 g, 50 mmol), and acetic anhydride (10.2 g, 100 mmol). The mixture, which turned into a homogeneous solution upon heating, was stirred at reflux under exclusion of moisture for 2 h. Water (50 mL) was added and the reflux was continued for 1 h. The mixture was concentrated under reduced pressure. The residue was dissolved in 20% aqueous potassium hydroxide (200 mL) and the crude product was precipitated by acidification with concentrated hydrochloric acid. The precipitate was filtered, dried in air, and dissolved in methanol. DBU (13.7 g, 90 mmol) and methyl iodide (15.6 g, 120 mmol) was added. The solution was stirred at room temperature for three days, concentrated at reduced pressure and purified by chromatography on a silica gel column with chloroform as eluent. The product was recrystallized from methanol. Yield: 5.6 g (61%) of yellow needles. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (dd, 1H, J = 3.2 Hz, 5.0 Hz), 7.31 (d, 1H, J = 5.0 Hz), 7.25 (d, 1H, J = 3.2 Hz), 7.03 (d, 1H, J = 5.0 Hz), 6.93 (dd, 1H, J = 3.7 Hz, 5.0 Hz), 6.85 (d, 1H, J = 5.0 Hz), 3.93 (s, 3H), 3.76 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 168.2, 167.1, 136.3, 136.2, 133.8, 131.5, 130.6, 128.5, 127.0 (2×), 126.7, 126.4, 125.6, 52.9, 52.7 ppm. Elemental analysis calcd (%) for $C_{14}H_{12}O_4S_2$: C 54.53, H 3.92; found: C 54.18, H 3.86.

General Procedure for Oxidative Ring Closures

Except when stated otherwise, all cyclodehydrogenation reactions with DDQ were performed in an argon atmosphere in septum-sealed 50 mL round bottom flasks. Methanesulfonic acid (3 mL, ca. 10 equiv.) and anhydrous dichloromethane (30 mL) were added to a mixture of the ester substrate (3 mmol) and DDQ (820 mg, 3.6 mmol, 1.2 equivalents) at 0 °C with stirring. The dark green solution was stirred at room temperature (0 °C for **6**). The progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was quenched with 10% $NaHCO_3$ solution (100 mL). The dichloromethane layer was separated, washed with water and brine solution, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure and the crude product was purified by chromatography on a silica gel column with dichloromethane as eluent and recrystallized from methanol (methyl esters) or butanol (butyl esters).

*Butyl Picene-13-carboxylate (**6**)*

Reaction time: 64 h at 0 °C. Yield: 680 mg (60%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.06 (s, 1H), 8.82 (d, 1H, J = 8.7 Hz), 8.75 (d, 1H, J = 9.6 Hz), 8.72 (d, 1H, J = 9.2 Hz), 8.32 (d, 1H, J = 8.2 Hz), 8.07 (t, 2H, J = 9.2 Hz), 7.99 (m, 2H), 7.75 (m, 1H), 7.63 (m, 3H), 4.47 (t, 2H, J = 6.9 Hz), 1.69 (m, 2H), 1.31 (m, 2H), 0.89 ppm (t, 3H, J = 7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.6, 132.7, 132.1, 130.5, 129.9 (2×), 129.5, 129.4, 129.2, 128.6 (2×), 128.4, 127.5, 127.3, 127.1, 127.0, 126.7, 126.0, 125.9, 124.0, 123.3, 121.3 (2×), 65.9, 30.5, 19.2, 13.7 ppm. Elemental analysis calcd (%) for $C_{27}H_{22}O_2$: C 85.69, H 5.86; found: C 85.49, H 6.12. MS m/z (%): 378.2 (100) $[M]^+$, 379.2 (30) $[M+H]^+$, 380.2 (5) $[M+2H]^+$, HRMS: m/z: calcd for $C_{27}H_{22}O_2Na^+$: 401.1512 $[M+Na]^+$; found: 401.1521.

Reaction at 20 °C for 64 h gives lactone **17**. Yield: 410 mg (43%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.92 (s, 1H), 8.96 (d, 1H, J = 8.2 Hz), 8.75 (d, 1H, J = 9.2 Hz), 8.71 (d, 1H, J = 9.2 Hz), 8.15 (dd, 2H, J = 7.3 Hz, 9.2 Hz), 8.01 (d, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 8.2 Hz), 7.80 (m, 2H), 7.71 (Pseudo t, 1H, J = 7.8 Hz, 7.3 Hz), 7.58 ppm (d, 1H, J = 7.8 Hz). HRMS: m/z: calcd for $C_{23}H_{12}O_2$: 320.0837 $[M]^+$; found: 320.0836.

The corresponding methyl ester has previously been obtained in 47% yield by oxidative cyclization with VOF_3.[25]

*Butyl Benzo[c]chrysene-6-carboxylate (**10**)*

Reaction time: 64 h at 20 °C. Yield: 465 mg (41%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.44 (s, 1H), 8.95 (d, 1H, J = 9.6 Hz), 8.93 (d, 1H, J = 9.2 Hz), 8.85 (d, 1H, J = 9.2 Hz), 8.84 (d, 1H, J = 8.2 Hz), 8.03 (m, 3H), 7.96 (d, 1H, J = 9.2 Hz), 7.77 (t, 1H, J = 8.2 Hz), 7.70 (d, 1H, J = 6.9 Hz), 7.66 (d, 1H, J = 9.6 Hz), 7.65 (dd, 1H, J = 1.4 Hz, 3.2 Hz), 4.54 (t, 2H, J = 6.9 Hz), 1.92 (m, 2H), 1.61 (m, 2H), 1.07 ppm (t, 3H, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 168.4, 133.3, 131.7, 130.7, 130.6, 129.9, 129.2, 129.0, 128.7, 128.4, 128.33, 128.26 (2×), 128.2, 127.3, 127.1, 126.64 (2×), 126.60, 125.9, 125.7, 123.6, 123.3, 65.5, 31.0, 19.6, 14.0 ppm. Elemental analysis calcd (%) for $C_{27}H_{22}O_2$: C 85.69, H 5.86 found: C 85.71, H 5.83. Crystals suitable for X-ray crystallography were obtained by slow diffusion of methanol into a solution in chloroform. Crystallographic data: $C_{27}H_{22}O_2$; monoclinic, space group Pc, a = 10.093(3), b = 12.737(4), c = 7.613(2) Å, β = 90.795(11)°, V = 2659.3(16) Å^3, T = 120 K, Z = 2, 17013 reflections measured, 2899 unique (R_{int} = 0.0438), $Goof$ = 1.051, final R_1 and wR_2 (all reflections) were 0.0431 and 0.1156.

The corresponding carboxylic acid has previously been obtained in 18% yield by cyclization under loss of HBr of a corresponding brominated precursor.[39]

Methyl Phenanthro[4,3-b]thiophene-5-carboxylate (12)

Reaction time: 64 h at 20 °C. Yield: 100 mg (11%) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 (d, 1H, J = 8.2 Hz), 8.89 (d, 1H, J = 9.2 Hz), 8.64 (s, 1H), 8.01 (d, 1H, J = 7.8 Hz), 7.92 (d, 1H, J = 9.2 Hz), 7.82 (t, 1H, J = 8.7 Hz), 7.69 (m, 2H), 7.59 (d, 1H, J = 5.5 Hz), 4.05 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 168.8, 138.6, 137.8, 132.5, 129.4, 129.0, 128.6, 127.9, 127.1 (2×), 127.0, 126.7, 126,4, 126.1, 125.9, 125.1, 124.6, 52.5 ppm. Elemental analysis calcd (%) for $C_{18}H_{12}O_2S$: C 73.95, H 4.14; found: C 73.91, H 4.11. Crystals suitable for X-ray crystallography were obtained by slow diffusion of methanol into a solution in chloroform. Crystallographic data: $C_{18}H_{12}O_2S$; orthorhombic; space group $Pca2(1)$; a = 21.472(2); b = 3.9116(3); c = 15.4115(15) Å; V = 1294.4(2) Å^3; T = 120 K; Z = 4; 20545 reflections measured; 3302 unique (R_{int} = 0.0514); $Goof$ = 0.981; final R_1 and wR_2 (all reflections) were 0.0376 and 0.3730.

*Methyl Naphtho[1,2-b]thiophene-4-carboxylate (**13**)[40]*

Reaction time: 64 h at 20 °C. Yield: 385 mg (53%) of red powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 8.32 (d, 1H, J = 5.5 Hz), 8.15 (d, 1H, J = 8.2 Hz), 8.00 (d, 1H, J = 7.3 Hz), 7.67 (pseudo t, 1H, J = 8.2 Hz, 6.9 Hz), 7.60 (d, 1H, J = 5.5 Hz), 7.56 (pseudo t, 1H, J = 6.9 Hz, 8.2 Hz), 4.03 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 167.4, 131.1, 130.6, 130.4, 130.3, 129.6, 129.2, 128.6, 126.3, 126.0, 125.9, 123.7, 123.4, 52.3 ppm. Elemental analysis calcd (%) for $C_{14}H_{10}O_2S$: C 69.40, H 4.16; found: C 69.08, H 3.97.

Methyl Phenanthro[1,2-b]thiophene-9-carboxylate (14)

Reaction time: 16 h at 20 °C. Yield: 620 mg (70%) of white needles. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.39 (s, 1H), 8.77 (d, 1H, J = 8.2 Hz), 8.35 (d, 1H, J = 5.5 Hz), 8.03 (d, 1H, J = 8.7 Hz), 7.92 (m, 2H), 7.71 (pseudo t, 1H), 7.64 (d, 1H, J = 5.5 Hz), 7.61 (pseudo t, 1H), 4.07 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 140.2, 136.2, 131.9, 131.1, 130.4, 130.0, 129.1, 127.7, 127.0, 126.8, 125.9, 125.9, 124.5, 123.2, 123.0, 122.6, 52.3 ppm. Elemental analysis calcd (%) for $C_{18}H_{12}O_2S$: C 73.95, H 4.14; found: C 73.59, H 4.30. MS: m/z (%): 291.9 (100) $[M]^+$; 292.9 (60) $[M+H]^+$; 293.9 (20), $[M+2H]^+$. Crystals suitable for X-ray crystallography were obtained by slow diffusion of methanol into a solution in chloroform. Crystallographic data: $C_{18}H_{12}O_2S$; monoclinic; space

group $P21/c$; $a=15.7299(7)$; $b=6.1083(2)$; $c=15.8294(6)$ Å; $\beta=118.368(2)°$; $V=1338.29(9)$ Å^3; $T=100$ K; $Z=4$; 12588 reflections measured; 2271 unique ($R_{int}=0.0445$); $Goof=1.055$; final R_1 and wR_2 (all reflections) were 0.0423 and 0.1211.

*Methyl Phenanthro[4,3-b]thiophene-4-carboxylate (**15**)*

Reaction time: 16 h at 20 °C. Yield: 750 mg (85 %) of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.32$ (d, 1H, $J=8.2$ Hz), 8.68 (s, 1H), 8.57 (d, 1H, $J=5.5$ Hz), 8.03 (d, 1H, $J=8.2$ Hz), 7.94 (d, 1H, $J=8.7$ Hz), 7.84 (m, 3H), 7.73 (t, 1H, $J=6.9$ Hz), 4.07 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=167.3$, 137.5, 136.8, 134.0, 130.8, 129.6, 129.3, 129.2, 129.0, 128.2, 127.5, 127.4 (2×), 127.3, 126.5, 124.9, 123.5, 52.4 ppm. Elemental analysis calcd (%) for $C_{18}H_{12}O_2S$: C 73.95, H 4.14; found: C 74.00, H 4.53.

*Methyl Benzo[2,1-b : 3,4-b']dithiophene-5-carboxylate (**16**)*

Reaction time: 16 h at 20 °C. Yield: 470 mg (63 %) of brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.56$ (s, 1H), 8.31 (d, 1H, $J=5.5$ Hz), 7.53 (d, 1H, $J=5.5$ Hz), 7.48 (d, 1H, $J=5.5$ Hz), 7.44 (d, 1H, $J=5.5$ Hz), 4.01 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=167.5$, 138.2, 136.2, 135.7, 134.9, 125.9, 125.8, 125.4, 125.3, 124.5, 122.1, 52.2 ppm. Elemental analysis calcd (%) for $C_{12}H_8O_2S_2$: C 58.04, H 3.25; found: C 57.78, H 3.59.

*Unexpected Dimeric Cyclization Product **19***

Reaction time: 64 h at 20 °C. Yield (from **18**): 825 mg (51 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.57$ (s, 1H), 9.50 (s, 1H), 9.38 (s, 1H), 9.03 (d, 1H, $J=9.2$ Hz), 8.95 (d, 1H, $J=6.9$ Hz), 8.76 (d, 1H, $J=8.2$ Hz), 8.49 (s, 1H), 8.42 (d, 1H, $J=9.2$ Hz), 8.36 (m, 2H), 8.20 (d, 1H, $J=6.0$ Hz), 7.89 (s, 1H), 7.70 (m, 2H), 7.57 (d, 1H, $J=7.3$ Hz), 7.31 (d, 1H, $J=3.2$ Hz), 7.21 (d, 1H, $J=5.5$ Hz), 7.15 (d, 1H, $J=5.0$ Hz), 4.54 (m, 4H), 4.40 (broad m, 4H), 1.91 (m, 4H), 1.77 (m, 4H), 1.54 (m, 4H), 1.50 (m, 4H), 0.95 ppm (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=172.6$, 138.9, 132.7, 132.1, 132.2, 130.5, 129.93, 129.87, 129.52, 129.46 (2×), 129.2, 128.7, 128.6, 128.4, 127.5, 127.44, 127.35, 127.2, 127.1, 127.0, 126.8, 126.1, 126.0, 125.9, 124.4, 124.0, 123.5, 123.3, 121.4 (2×), 66.1, 66.0, 30.6, 30.5, 19.34, 19.25, 13.83, 13.75 ppm. Elemental analysis calcd (%) for $C_{64}H_{54}O_8S_4$: C 71.22, H 5.04; found: C 70.84, H 5.16. MS: m/z (%): 1078.2 (100) $[M]^+$; 1080.2 (80) $[M+2H]^+$; 1082.2 (20) $[M+4H]^+$. Crystals suitable for X-ray diffraction analysis were obtained by diethyl ether vapor diffusion into a solution in DMF. Crystallographic data: $C_{64}H_{54}O_8S_4$; triclinic; space group $P\bar{1}$; $a=11.146(4)$; $b=13.739(5)$; $c=17.971(6)$ Å; $\alpha=83.625(18)$; $\beta=76.563(17)$; $\gamma=87.14(2)°$; $V=2659.3(16)$ Å^3; $T=120$ K; $Z=2$; 27569 reflections measured; 9042 unique ($R_{int}=0.1054$); $Goof=1.045$; final R_1 and wR_2 (all reflections) were 0.1081 and 0.3730.

*Dibutyl Chryseno[1,2-b : 7,8-b']dihiophene-3,9-dicarboxylate (**20**)*

Reaction time: 64 h at 20 °C. 250 mg (0.459 mmol) of **18** was used with DDQ (255 mg, 1.1 mmol), dichloromethane (300 mL), and methanesulfonic acid (3 mL, added after addition of dichloromethane). Yield: 123 mg (50 %) of yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.50$ (s, 1H), 8.99 (d, 1H, $J=9.2$ Hz), 8.37 (m, 2H), 7.70 (d, 1H, $J=5.5$ Hz), 4.53 (t, 2H, $J=6.9$), 1.93 (m, 2H), 1.60 (m, 2H), 1.07 ppm (t, 3H, $J=7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=167.1$, 136.1, 129.8, 129.5, 127.1, 126.3, 126.1, 126.0, 124.9, 124.7, 124.2, 124.0, 65.5, 31.0, 19.6, 14.0 ppm. HRMS: m/z: calcd for $C_{32}H_{28}O_4S_2$: 540.1429 $[M]^+$; found: 540.1453. Elemental analysis calcd (%) for $C_{32}H_{28}O_4S_2$: C 71.08, H 5.22; found: C 70.89, H 5.20.

*Dimethyl Benzo[1,2-b : 3,4-b']dithiophene-1,5-dicarboxylate (**23**) and Thieno[3,2-g]-1H-2-benzothiopyran-1-one-10-carboxylic acid (**24**)*

23: Yield (from **22**): 310 mg (34 %) of brown needles (the compound was separated from **24** by chromatography on a silica gel column with dichloromethane as eluent). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.77$ (d, 1H, $J=5.5$ Hz), 7.59 (d, 1H, $J=5.5$ Hz), 7.56 (d, 1H, $J=5.5$ Hz), 7.47 (d, 1H, $J=5.5$ Hz), 3.99 (s, 3H), 3.98 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=168.8$, 166.3, 138.7, 135.2, 135.0, 134.3, 132.1, 127.6, 126.6, 123.7, 121.0, 120.1, 53.0, 52.9 ppm. Crystals suitable for X-ray crystallography were obtained by slow evaporation of a solution in DCM. Crystallographic data: $C_{14}H_{10}O_4S_2$; orthorhombic; space group $Pca2(1)$; $a=17.3421(10)$; $b=7.5256(4)$; $c=19.9689(11)$ Å; $V=2606.1(2)$ Å^3; $T=100$ K; $Z=8$; 51728 reflections measured; 6936 unique ($R_{int}=0.0659$); $Goof=1.059$; final R_1 and wR_2 (all reflections) were 0.0458 and 0.1237.

24: Yield: 80 mg (10 %) of yellow needles. ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=8.34$ (s, 1H), 8.19 (d, 1H, $J=5.5$ Hz), 7.65 (d, 1H, $J=5.5$ Hz), 7.52 (d, 1H, $J=9.6$ Hz), 7.43 ppm (d, 1H, $J=6.9$ Hz). ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta=185.3$, 169.6, 144.2, 138.1, 135.6, 134.7, 129.8, 126.1, 124.6, 124.2, 122.9, 120.5 ppm. HRMS: m/z: calcd for $C_{12}H_6O_3S_2$: 261.9724 $[M]^+$; found: 261.9716.

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