

0957-4166(95)00074-7

New Axially Chiral Sulfur Compounds: Synthesis and Conformational Stability of Enantiopure 4,4'-Biphenanthrene-3,3'-dithiol and Related Atropisomeric Derivatives

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Abstract: Enantiopure (R)- and (S)-4,4'-biphenanthrene-3,3'-dithiol **1a** has been prepared for the first time through a synthetic procedure involving in the key step a stereoconservative Newman-Kwart thermorearrangement of the *bis*-N,N-dimethylthiocarbamoyl ester of (R)- and (S)-biphenanthrol **2b**, respectively. The atropisomeric conformations of **1a** are not interconverted even at temperatures as high as 285° C, whereas the related biphenanthrothiophene **3** is completely racemized in a few minutes at 250° C. The axially chiral backbone of **1a** has been incorporated in a set of novel C₂ symmetry sulfur reagents suitable for a variety of stereoselective reactions.

In recent years 1,1'-binaphthalene-2,2'-dithiol **4a** has been used as the precursor of a series of different C₂-symmetry chiral auxiliaries of high efficiency and wide applicability.¹ Good to excellent stereoselectivities have been recorded with these reagents in several processes including Diels-Alder reaction², carbanion addition³, sulfide oxidation.⁴ Quite recently, it has been demonstrated that rhodium(I) complexes containing the parent dithiol **4a** or the relevant dimethylsulfide **4b** as ligands are efficient catalysts for the highly regioselective hydroformylation of styrene.⁵ Modest enantioselectivities (up to 15%) were recorded using enantiopure compounds in this process.

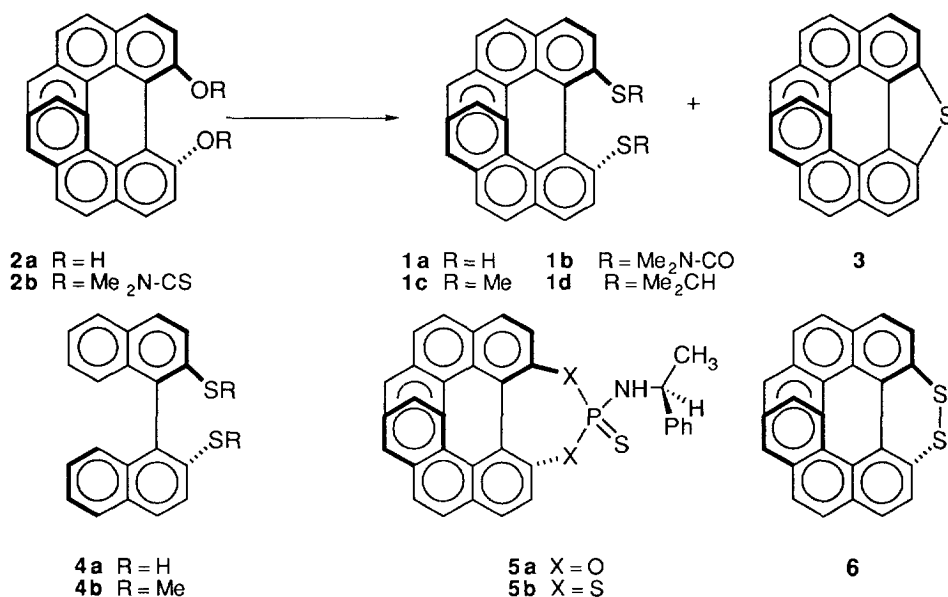
We reasoned that introduction of one more phenyl group onto the aromatic backbone of these derivatives, *i.e.* changing from binaphthalene to biphenanthrene, would supply increased conformational stability to the axially chiral arrangement of the diaryl framework and possibly favour a higher asymmetric bias in the reactions involving these chiral auxiliaries. This led us to address our synthetic efforts towards the so far unknown 4,4'-biphenanthrene-3,3'-dithiol **1a** and its derivatives. Here we provide a practical method for the preparation of **1a** in enantiopure form starting from enantiopure **2a** for which we have as well devised a convenient method of resolution.

For the synthesis of the parent compound we exploited our previous experiences on the corresponding binaphthyl derivative⁶ (Scheme 1). 3-Phenanthrol, obtained from phenanthrene by sulfonation and alkali fusion,⁷ was subjected to oxidative coupling in the presence of α -methylbenzylamine-copper(II) complex⁸ affording racemic 4,4'-biphenanthrene-3,3'-diol **2a**. This was deprotonated with NaH and then treated with dimethylthiocarbamoyl chloride to afford in high yield the corresponding N,N-dimethyldithiocarbamate **2b**. Upon heating at 275-285°C for a few minutes, this ester suffered a Newman-Kwart rearrangement leading to a mixture of the transposed carbamate **1b** (65-75%) and biphenanthro[3,4-*b*;4',3'-*d*]thiophene **3** (20-25%) which were separated by flash chromatography. The desired dithiol **1a** was eventually obtained in 90% yield by

treatment of **1b** with LiAlH_4 . The product is quite stable in the solid state, but in solution oxidation to disulfide **6** occurs to a variable extent.

Thiophene formation in the rearrangement step is not unexpected since such a product is also formed in the preparation of 1,1'-binaphthalene-2,2'-dithiol and in some instances it is the main or even the exclusive product of the thermorearrangement.⁹ The extent of its formation seems dependent, *inter alia*, on the crystalline nature of the starting binaphthalene dithiocarbamate.¹⁰ No evidence of conformational polymorphism has been noticed in the present case.

Scheme 1



Following several unsuccessful attempts to resolve the racemic dithiol **1a**, we addressed our efforts to the resolution of the relevant diol **2a**. This choice was more successful and resolution was readily achieved by fractional crystallisation of the thiophosphamidate adduct with α -methylbenzylamine **5a** (Scheme 1).⁶ The fairly large difference in the solubilities of the diastereomeric adducts allowed a complete separation after two crystallizations from benzene. The less soluble diastereoisomer was levorotatory and, upon treatment with LiAlH_4 , released (-)-4,4'-biphenanthrene-3,3'-diol **2a** in quantitative yield in more than 97% enantiomeric purity, as confirmed by HPLC on Chiracel OD of the relevant dimethyl ether. The absolute configuration of this enantiomer has been established by its CD spectrum to be (R). This contrasts with the original attribution⁷ and agrees with more recent observations of other authors.¹¹ Processing the mother liquors led to the recovery of almost enantiopure (S)-**2a** in high yield. On the whole, this method of resolution was quite efficient providing in high chemical yield both the antipodes in not less than 97% enantiomeric purity.

For the preparation of enantiopure **1b**, a pyrex vial containing neat enantiopure (-)-(R)-**2b** was immersed for 22 min into a glycerol bath heated at 280-285°C. Under these carefully controlled conditions the substrate was quantitatively converted into a mixture of (+)-(R)-**1b** (70-5%) and **3** (20-25%). After chromatographic

separation, the carbamoyl groups of (+)-(R)-**1b** were removed with LiAlH_4 to afford (-)-(R)-**1a**. The enantiomeric purity of this product could be easily determined on the corresponding thiophosphamidate adduct with (S)- α -methylbenzylamine **5b**. This showed only one set of signals in the $^1\text{H-NMR}$ spectrum corresponding to a single diastereoisomer. Thus, it has been established that no appreciable loss of enantiomeric purity occurs in the formation of (R)-**1b** from (R)-**2b** at 285°C . This result confirms^{6,12} that, when properly performed, the Newmann-Kwart rearrangement is a stereoconservative reaction despite the harsh conditions required.

On the contrary, the thiophene **3** isolated after the thermorearrangement of different samples of enantiopure **2b** was always devoid of optical activity¹³ in spite of its heptaheterohelicene structure. Accordingly, HPLC analysis of these samples on a chiral stationary phase revealed two equivalent peaks corresponding to the two enantiomers of **3**. It is worth to note that also the analogue thiophene derived from binaphthalene has been never obtained in optically active form even when prepared from enantiopure precursors.⁶ In that case, however, we did neither succeed to observe separate peaks on chiral HPLC, probably because racemization of this product is a fast process at room temperature in solution. Easy atropisomerization is a common trait of binaphthyl-fused five-membered ring heterocycles¹⁴ which are conformationally labile due to the relatively small pitch of the pentahelicene helix.¹⁵

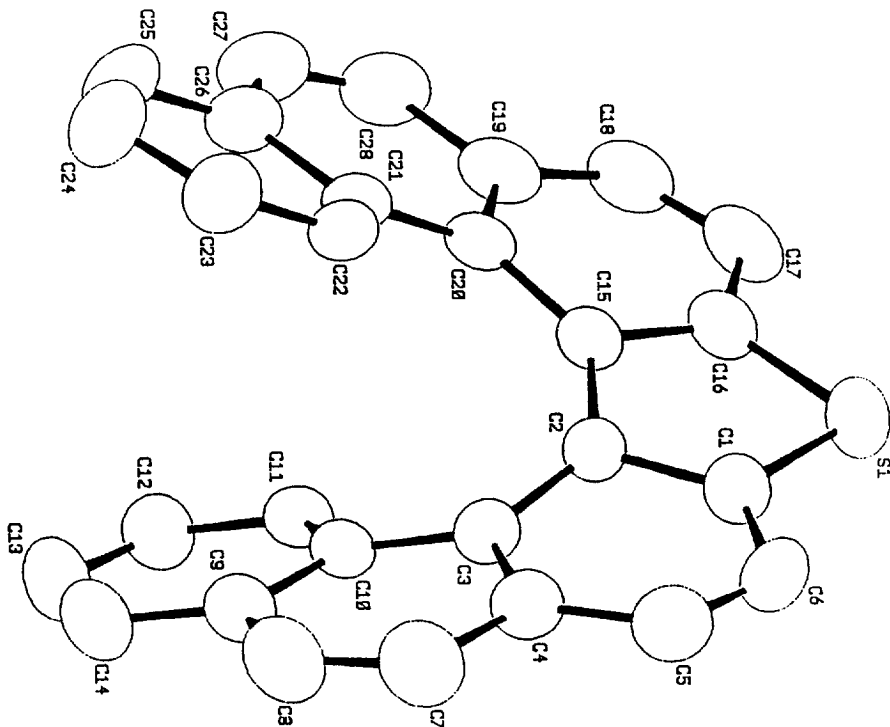
The formation of **3** could take place from the rearranged *S,S*-bis-carbamate **1b** as well as from a mixed *O,S*-carbamate, an elusive intermediate in the thermorearrangement, through an intramolecular nucleophilic aromatic substitution involving attack of a nucleophilic sulfur center onto the substituted 2'-carbon. Racemization might occur either at this stage or after thiophene formation. Some clue into the racemization pathway could be obtained from the following experiments. Upon heating for 30 min at 260°C , an enantiopure sample of **1b** gave racemic **3** in modest yield, while unreacted **1b** did not suffer any racemization. No loss of enantiomeric purity of **2b** was noticed when some unreacted substrate was recovered after the Newmann-Kwart thermorearrangement. An optically active sample of **3** (20% e.e. by HPLC), obtained from fractional crystallisation of the TAPA¹⁶ complex prepared from the racemic thiophene, underwent complete racemization upon heating 20 min at 250°C . All these results support the view that racemization does not precede, but follow after thiophene formation. This conclusion is confirmed by the observation that thermal racemization of heptahelicene occurs within minutes at $290\text{--}300^\circ\text{C}$.¹⁷ This process is even more facile when one or more phenyl rings of the basic structure are substituted by a heteroaromatic five-membered ring.¹⁵

Well shaped crystals of compound **3** could be grown from methylene chloride/hexane and this allowed to determine its geometry by X-ray structure analysis. The ORTEP view of the crystal structure is reported in Fig. 1. The product shows the expected helical conformation with the two terminal phenyl rings which are almost facing each other. The contact distance between C_{11} and C_{22} is 3.22 \AA and the dihedral angles between the best planes of the adjacent rings, starting from the terminal phenyl, are 8.19, 11.00, 9.94, 10.01, 11.97 and 8.49° , respectively. The dihedral angle between the best planes of the terminal phenyl rings which follows from the sum of these contributions is 59.6° . This provides the measure of the deviation from the planarity of the heptaheterohelicene structure. An almost identical value (58.5°) has been determined for the same angle in the case of hexahelicene.¹⁸ Bond lengths and distances are in the normal range for a diarylthiophene derivative¹⁴ and a slight distortion from planarity of the heterocyclic ring is apparent.

Due to its C_2 symmetry, compound **3** shows a very characteristic $^1\text{H-NMR}$. Eight completely resolved signals corresponding to two AB and one AA'BB' systems were observed between 6.34 and 8.14 ppm. The

remarkable upfield shift of the H(C₂₃) and H(C₁₂) resonance is the consequence of the diamagnetic ring-current induced by the partially overlapping terminal phenyl rings on the underlying protons.

Figure 1



Selected bond lengths

S-C(1)	1.735(3)	C(25)-C(26)	1.398(4)
S-C(16)	1.725(3)	C(26)-C(27)	1.442(4)
C(1)-C(2)	1.411(3)	C(27)-C(28)	1.324(5)
C(2)-C(15)	1.476(3)	C(28)-C(19)	1.433(4)
C(15)-C(16)	1.401(3)	C(19)-C(18)	1.406(4)
C(15)-C(20)	1.437(3)	C(18)-C(17)	1.340(4)
C(20)-C(21)	1.447(3)	C(17)-C(16)	1.408(4)
C(21)-C(22)	1.415(3)	C(22)-C(23)	1.371(4)

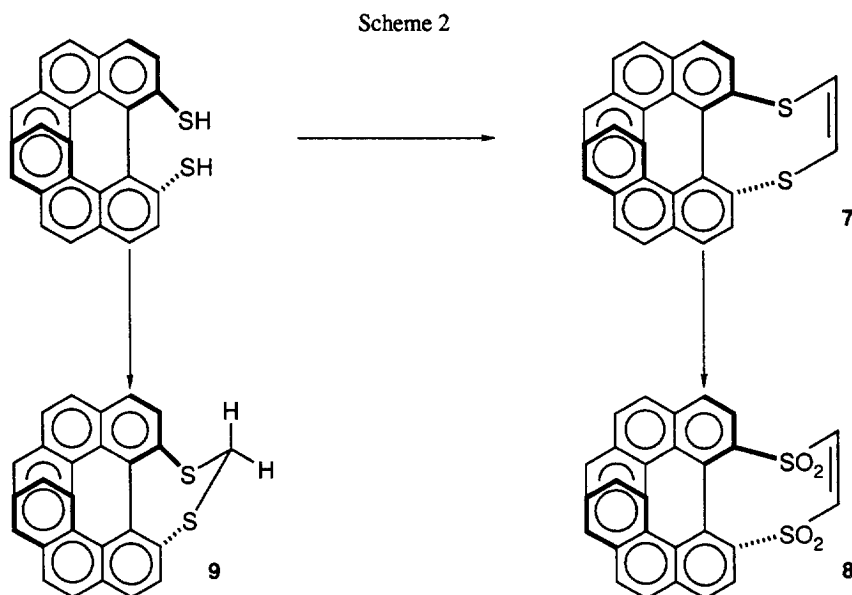
Selected bond angles

C(1)-S-C(16)	91.0(1)
S-C(16)-C(15)	113.8(2)
S-C(16)-C(15)	113.8(2)
C(2)-C(15)-C(16)	110.4(2)
C(2)-C(15)-C(16)	110.4(2)
C(1)-C(2)-C(15)	110.1(2)
C(3)-C(2)-C(15)	133.3(2)
C(2)-C(15)-C(20)	132.2(2)
C(1)-C(2)-C(3)	116.5(2)

Figure 1. X-Ray crystal structure (hydrogens omitted) of compound 3. C₂₈H₁₆S, M = 384.5, monoclinic, space group P2_{1/a} (No. 14), *a* = 14.841(2) Å, *b* = 10.881(3) Å, *c* = 11.902(2) Å, *V* = 1875.5(6) Å³, *Z* = 4, *D*_c = 1.36 g cm⁻³, Mo-K_α radiation, λ = 0.71073 Å, μ(Mo-K_α) = 1.75 cm⁻¹; the final *R* and *R*_w values are 0.049 and 0.056, respectively, for 2594 absorption-corrected reflections with *F* > 3σ(*F*).

The dithiol **1a** was converted into the relevant dimethyl and diisopropyl thioethers **1c** and **1d**, respectively, by alkylation with the suitable halides. Preliminary tests have confirmed the ability of these sulfides as well as of the parent dithiol **1a** to act as sulfur donor ligands towards rhodium(I) centres producing complexes which are active catalysts in the hydroformylation of styrene under mild conditions.¹⁹

Treatment of the sodium salt of **1a** with (*Z*)-1,2-dichlorethylene gave 4,4'-biphenanthro[3,4-*e*; 4',3'-*g*]dithiocine **7** which was oxidised with *m*-chloroperbenzoic acid to give the corresponding tetroxide **8** (Scheme 2). Cycloaddition of **8** with excess furan (toluene, 180°C, 2h) resulted in a mixture of two isomers. By comparison with the products obtained in the analogue reaction with the binaphthalene derived dienophile, they were identified as the *exo*- and *endo*- cycloadducts in a 6:4 ratio (NMR analysis). Reaction of furan with binaphthodithiocine dioxide proceeded with the same stereoselectivity, but at a higher rate².



Treatment of **1a** with dimethoxymethane in the presence of BF₃ etherate afforded biphenanthro[3,4-*d*; 4',3'-*f*]dithiepine **9** which can be regarded as a chiral C₂-symmetry synthon of the formyl anion (Scheme 2). The anion of **9**, obtained by deprotonation with BuLi, reacted sluggishly with benzaldehyde affording in low yield a mixture of several products where the expected carbinol was present only as a minor component.

These results show that biphenanthrenedithiol **1a** behaves similarly to the corresponding binaphthalene derivative as to general reactivity, but that remarkable differences exist in the chemical behaviour of the reagents derived therefrom. Changing the binaphthalene framework into biphenanthrene seems to exert a marginal effect on the stereochemical outcomes of the processes investigated, but renders the sulfur reagents more reluctant to react.

Biphenanthro[3,4-*b*; 4',3'-*d*]thiophene **3** is itself a valuable source of new biphenanthrene derivatives.²⁰ Oxidation with *m*-chloroperbenzoic acid converts **3** into an almost equimolar mixture of the corresponding mono- and di- oxides, **10a** and **10b** respectively, which can be isolated in pure form by flash chromatography. Application of **10a** as a chiral oxidation reagent and of **10b** as an intermediate in the

preparation of non symmetrically disubstituted biphenanthrene derivatives through ring opening or cycloaddition reactions can be easily envisaged.

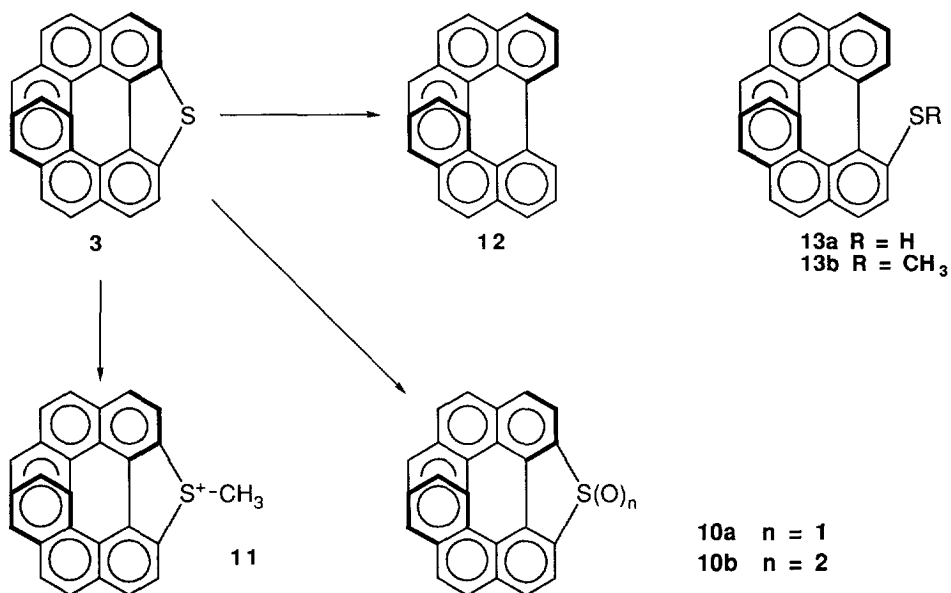
Alkylation of **3** with methyl iodide in the presence of silver tetrafluoroborate gave the *S*-methyl thiophenium salt **11** in 60% isolated yield. This product has a great tendency to restore the starting thiophene by transferring the methyl group. It reacts immediately with oxygen nucleophiles like water, acetate ion and dimethylacetamide to afford *O*-methylated derivatives. Alkylation at carbon takes place on ethyl acetoacetate and reaction with the lithium dianion of phenylacetic acid affords 2-phenylpropionic acid. Deprotonation of **11** with BuLi and quenching of the relevant sulfonium ylide with benzaldehyde did not give the expected phenyloxirane, but led to a complex mixture of products.

Reaction of **3** with an excess of lithium metal in THF brought about cleavage of the thiophene ring resulting, after quenching with a protic reagent, in a net desulfurisation of the substrate and in the production of 4,4'-biphenanthrene **12** as the unique reaction product. Use of a lower amount of lithium (4 equivalents) afforded a 4:1 mixture of **12** and thiol **13a**. Surprisingly, compound **12** was again the main product when the reaction was quenched with methyl iodide. In this case a fair amount of methylthiobiphenanthrene **13b** could be also isolated.

These results are fairly different from the ones observed in the same reactions of binaphthothiophene²⁰ and are probably related to the lower grade of conformational mobility of **3** as compared with the corresponding binaphthalene derivative. While the latter should be able to attain a double lithium bridging in the anionic intermediate,²¹ this situation may be precluded to **3** by its heptahelicene structure.

In conclusion, we have provided here useful synthetic procedures for the preparation of a series of novel atropisomeric sulfur reagents based on the biphenanthrene chiral backbone and have highlighted several potential applications of these derivatives which will be the subject of future investigations.

Scheme 3



Experimental section

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data were recorded with a Varian VXR 5000 spectrometer (300 and 121.5 MHz, respectively), using TMS as an internal standard. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. Melting points were determined on a Buchi 510 apparatus and are uncorrected. Mass spectra were recorded with a HP 5988A spectrometer. (S)-(-)-Dichloro-N-(methylbenzyl)phosphorothioamide was prepared as described in ref.6.

Resolution of 3,3'-dihydroxy-4,4'-biphenanthrene (2a). A solution of (S)-(-)-dichloro-N-(methylbenzyl)phosphorothioamide (2 g, 5.17 mmol.) in pyridine (70 mL) was added dropwise at room temperature under nitrogen atmosphere to a stirred solution of racemic 3,3'-dihydroxy-4,4'-biphenanthrene (1.47 g, 5.17 mmol) in pyridine (30 mL). After warming at gentle reflux for 5 h, the reaction mixture was cooled to room temperature and a dilute solution of sulphuric acid was added. The solution was extracted with dichloromethane (2x100 mL), the organic layers were collected, washed with water and dried (Na_2SO_4). Removal of the solvent afforded a 1/1 mixture of (R,S)-(-) and (S,S)-(+)-4,4'-biphenanthryl-3,3'-diyl-N-(S)- (methylbenzyl) thiophosphoramidate (**5a**) (2.94 g, 95%) as a white crystalline powder. This mixture (4 g) was dissolved in refluxing benzene (20 mL) and, after 24 h, the precipitate was filtered. A further crystallization of these crystals from benzene gave (R,S)-(-)-**5a** as colourless needles (0.98 g, 32%): mp 258–9°C (benzene); $[\alpha]_{\text{D}}^{25}$ -853.6 ($c=1.1$, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 1.54 (d, $J=1.2$ Hz, - CH_3), 3.71 (m, -NH-), 4.91 (m, -CH-), 6.20–8.10 (series of m, Ar, 21H); $^{31}\text{P-NMR}$ (CDCl_3) δ 80.10 (s); IR (KBr disk) 3350(m), 2975(w), 1615(m), 1400(m), 1245(s), 1065(s), 950(s), 835(s), 755(s); m/z 567.6 (M+), 497.6 (100%), 421.8 (27%), 388.3 (33%), 267.1 (38%).

Removal of the solvent from the mother liquor gave a solid which was crystallized from refluxing benzene (40 mL). The white crystals were filtered to obtain (S,S)-(+)-**5a** (0.95 g, 31%) mp 234–235°C (benzene); $[\alpha]_{\text{D}}^{25}$ +724.3 ($c=1.1$, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 1.64 (d, $J=1.2$ Hz, - CH_3), 3.80 (m, -NH-), 4.85 (m, -CH-), 6.20–8.10 (series of m, Ar, 21H); $^{31}\text{P-NMR}$ (CDCl_3) δ 78.90 (s); IR (KBr disk) 3350(m), 2975(w), 1615(m), 1400(m), 1245(s), 1065(s), 950(s), 835(s), 755(s); m/z 567.6 (M+), 497.6 (100%), 421.8 (20%), 388.3 (39%), 267.1 (48%).

To release the free diol **2a**, LiAlH_4 (0.40 g, 10.60 mmol.) was added portionwise over 15 minutes to a mechanical stirred solution of diastereopure (R,S)-**5a** (1.0 g, 1.66 mmol.) in dry THF (30 mL) at 0°C under nitrogen atmosphere. After 2 h at rt, water was added and the solution was neutralized with dilute HCl. The solution was rotoevaporated and the residue extracted with dichloromethane (2x80 mL). The organic layers were collected, washed with water and dried (Na_2SO_4). Removal of the solvent in vacuo afforded in 95% yield colorless crystalline (-)-(R)-3,3'-dihydroxy-4,4'-biphenanthrene (**2a**): mp 245–247°C (CH_2Cl_2 /petroleum ether); $[\alpha]_{\text{D}}^{25}$ -69.6 ($c=0.5$, CHCl_3); enantiomeric purity 99%. Elaboration of the aqueous phase led to recover enantiopure (S)-(-)-phenethylamine in 93% yield, $[\alpha]_{\text{D}}^{25}$ -31.3 ($c=1$, ethanol).

Treatment of (S,S)-**5a** in the same way led to obtain in 95% yield (+)-(S)-**2a**: mp 245–247°C (CH_2Cl_2 /petroleum ether); $[\alpha]_{\text{D}}^{25}$ +69.0 ($c=1.1$, CHCl_3).

(R)-(+)-4,4'-Biphenanthryl-3,3'-diyl-O-O-bis-(N,N-dimethylthio carbamate) (2b). Sodium hydride (5.28 g, 220 mmol of a 50% oil dispersion) was added portionwise over 0.5 h to a vigorously stirred solution of (R)-(-)-**2a** (38.63 g, 100 mmol) in 200 mL of dry DMF, at 0°C under nitrogen atmosphere. After stirring at rt for 15 minutes, N,N -dimethylcarbamoyl chloride (27.19 g, 220 mmol) was added and the yellow suspension was warmed to 85 °C for 1 h. After cooling to room temperature, the mixture was poured into KOH aqueous solution (800 mL). The white precipitate was filtered off, washed several times with water and dissolved in dichloromethane. The organic phase was washed with water and dried (Na_2SO_4). Removal of the solvent and crystallisation of the residue from dichloromethane/petroleum ether afforded (R)-(+)-**2b** as a white solid: 50.41 g (90%), mp 242–3°C; $[\alpha]_{\text{D}}^{25}$ +56.0 ($c=1$, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 2.01 (s, 6H), 2.80 (s, 6H), 7.02 (dt, $J=3.0$, 9.6 Hz, Ar, 2H), 7.43 (dt, $J=0.9$, 9.6 Hz, Ar, 2H), 7.62 (d, $J=8.7$ Hz, Ar, 2H), 7.85 (m, Ar, 6H), 8.01 (d, $J=8.7$ Hz, Ar, 2H), 8.35 (d, $J=8.7$ Hz, Ar, 2H); $^{13}\text{C-NMR}$ (CHCl_3) (aliphatic carbons only) δ 37.16, 42.23; m/z 560.2 (M+), 384.0 (70%), 350.0 (8%), 306.0 (7%), 190.0 (3%), 71.9 (100%).

(R)-(+)-4,4'-Biphenanthryl-3,3'-diyl-S,S-bis-N,N-dimethyl carbamate (1c) and Biphenantro[4,3-b;3',4'-d]thiophene (3). A pyrex vial fitted with a CaCl_2 drying tube, containing (R)-(+)-**2b** (6.51 g, 10.85 mmol) was immersed in a bath containing glycerine at 285 °C for 22 min. After cooling to room temperature the yellow solid was dissolved in dichloromethane and purified by flash chromatography (dichloromethane) to obtain (R)-(+)-**1c** as a white solid (4.68 g, 72%) and **3** as yellow solid (0.83 g, 20%).

1c: mp 243 °C (dichloromethane/petroleum ether); $[\alpha]_{\text{D}}^{25} +301.2$ ($c=1$, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 2.49 (bs, 12H), 6.92 (dt, $J=1.2, 7.8$ Hz, Ar, 2H), 7.35 (dt, $J=0.9, 7.8$ Hz, Ar, 2H), 7.75-7.84 (series of m, Ar, 10H), 8.00 (d, $J=8.1$ Hz, Ar, 2H); $^{13}\text{C-NMR}$ (CHCl_3) (aliphatic carbons only) δ 36.53; m/z 560.2 (M+), 384.0 (62%), 337.0 (8%), 306.0 (6%), 189.0 (3%), 87.9 (100%).

3: mp 241 °C (dichloromethane/petroleum ether); $^1\text{H-NMR}$ (CDCl_3) δ 6.34 (dt, $J=1.2, 6.9$ Hz, Ar, 2H), 7.09 (dt, $J=1.2, 6.9$ Hz, Ar, 2H), 7.52 (d, $J=8.4$ Hz, Ar, 2H), 7.65 (d, $J=8.1$ Hz, Ar, 2H), 7.80 (d, $J=8.7$ Hz, Ar, 2H), 7.93 (d, $J=8.7$ Hz, Ar, 2H), 8.02 (d, $J=8.4$ Hz, Ar, 2H), 8.14 (d, $J=8.4$ Hz, Ar, 2H); m/z 384.0 (M+, 100%), 257.0 (12%), 190.0 (21%), 50.9 (3%).

(R)-(-)-4,4'-Biphenanthrene-3,3'-dithiol (1a). LiAlH_4 (2.27 g, 60 mmol) was added carefully to a solution of **(R)-(+)-1c** (5.60 g, 10 mmol) in 40 ml of dry THF at 0 °C under nitrogen atmosphere. After warming at reflux for 1 h, the reaction mixture was cooled to 0 °C and 10% aqueous hydrochloric acid was added. The mixture was extracted with ether (3x80 mL), the organic layers were collected, washed with water and dried (Na_2SO_4). Removal of the solvent afforded **(R)-(-)-1a** as white solid: (3.76 g, 90%); mp 196 °C (benzene); $[\alpha]_{\text{D}}^{25} -48.3$ ($c=1$, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 3.15 (s, 2H), 6.95 (dt, $J=1.5, 7.8$ Hz, Ar, 2H), 7.38 (dt, $J=1.5, 7.8$ Hz, Ar, 2H), 7.70 (d, $J=8.4$ Hz, Ar, 2H), 7.77-7.86 (series of m, Ar, 6H), 7.94 (d, $J=18.7$ Hz, Ar, 2H), 7.95 (d, $J=8.7$ Hz, Ar, 2H); m/z 418.0 (M+, 85%), 384.0 (100%), 350.0 (55%), 174.9 (91%). Upon standing a few days, a CDCl_3 solution of **(R)-(-)-1** separated a yellow product identified as **(R)-(-)-4,4'-Biphenanthro[4,3-*b*;3',4'-*d*]-1,2-dithiin (6)**: mp 140 °C (benzene); $[\alpha]_{\text{D}}^{25} -80.3$ ($c=0.1$, CH_2Cl_2); $^1\text{H-NMR}$ (CDCl_3) δ 6.26 (d, $J=8.1$ Hz, Ar, 1H), 6.42 (dt, $J=1.2, 6.9$ Hz, Ar, 1H), 6.91 (dt, $J=1.2, 6.9$ Hz, Ar, 1H), 7.20-7.40 (series of m, Ar, 2H), 7.47 (d, $J=8.7$ Hz, Ar, 1H), 7.75 (d, $J=8.1$ Hz, Ar, 1H), 7.90 (d, $J=8.4$ Hz, Ar, 1H). Calcd. for $\text{C}_{28}\text{H}_{16}\text{S}_2$: C, 80.74; H, 3.87; S, 15.39. Found: C, 80.96; H, 4.1; S, 15.12.

(R,S)-(-)- and (S,S)-(+)-4,4'-Biphenanthryl-3,3'-diyl-N-(methylbenzyl)trithiophosphoroamidate (5b). A solution of (S)-(-)-Dichloro-N-(methylbenzyl)phosphorothioamide (2 g, 5.17 mmol) and pyridine (70 mL) was added dropwise with stirring to a solution of racemic **1a** (2.16 g, 5.17 mmol) at room temperature under nitrogen. The solution was refluxed for 6 h. The reaction mixture was washed with dilute sulphuric acid, with water, extracted with dichloromethane (2x100 mL) and dried (Na_2SO_4). Removal of the solvent afforded a 1/1 mixture of **(R,S)-(-)-5b** and **(S,S)-(+)-5b** (2.79 g, 90%) as a white crystalline powder. **(R,S)-(-)-5b**: $^1\text{H-NMR}$ (CDCl_3) δ 1.52 (d, $J=6.9$ Hz, $-\text{CH}_3$), 3.42 (m, $-\text{NH}$), 4.95 (m, $-\text{CH}-$), 6.10-8.20 (series of m, Ar, 21H); $^{31}\text{P-NMR}$ (CDCl_3) δ 105.15 (s). **(S,S)-(+)-5b**: $^1\text{H-NMR}$ (CDCl_3) δ 1.64 (d, $J=6.9$ Hz, $-\text{CH}_3$), 3.42 (m, $-\text{NH}-$), 4.95 (m, $-\text{CH}-$), 6.10-8.20 (series of m, Ar, 21H); $^{31}\text{P-NMR}$ (CDCl_3) δ 104.70 (s).

(R)-(+)-3,3'-Bis(methylthio)-4,4'-biphenanthrene (1b). Methyl iodide (10 mL) in 20 mL of dry methanol was added to a solution of **(R)-(-)-1a** (4.18 g, 10 mmol) in triethylamine (20 mL) at 0 °C under nitrogen atmosphere. After stirring at room temperature for 5 h (the progress of the reaction was monitored by TLC), the solution was neutralized with diluted hydrochloric acid and extracted several times with dichloromethane. The organic layers were collected, washed with water and dried (Na_2SO_4). The solvent was rotoevaporated and the crude product was recrystallized from dichloromethane/petrol ether affording **(R)-(+)-1b**: 96% yield; mp 164-5 °C; $^1\text{H-NMR}$ (CDCl_3) δ 2.45 (s, 6H), 6.88 (dt, $J=1.2, 8.7$ Hz, Ar, 2H), 7.34 (dt, $J=0.9, 8.7$ Hz, Ar, 2H), 7.63 (d, $J=8.4$ Hz, Ar, 2H), 7.74 (d, $J=9.0$ Hz, Ar, 2H), 7.79 (d, $J=7.8$ Hz, Ar, 2H), 7.85 (d, $J=8.7$ Hz, Ar, 2H), 7.90 (d, $J=9.0$ Hz, Ar, 2H), 8.10 (d, $J=9.0$ Hz, Ar, 2H); $[\alpha]_{\text{D}}^{25} +50.6$ ($c=1$, CHCl_3); m/z 446.6 (M+), 400.6 (100%), 354.6 (25%), 188.3 (31%), 67.1 (33%). In the same way racemic **1a** by treatment with 2-bromopropane gave **1d**: 90% yield; mp 234-6 °C (dichloromethane/petroleum ether); $^1\text{H-NMR}$ (CDCl_3) δ 0.83 (d, $J=6$ Hz, 6H), 1.05 (d, $J=6$ Hz, 6H), 3.38 (m, 2H), 6.88 (dt, $J=1.2, 8.6$ Hz, Ar, 2H), 7.36 (dt, $J=0.9, 8.6$ Hz, Ar, 2H), 7.65-7.85 (series of m, Ar, 10H), 8.00 (d, $J=8.4$ Hz, Ar, 2H); m/z 502.7 (M+), 500.7 (100%), 358.7 (27%), 288.3 (30%), 167.1 (13%).

4,4'-Biphenanthro[4,3-*e*;3',4'-*g*]-1,4-dithiocine (7). Sodium (0.45 g, 19.57 mmol) was slowly dissolved in ethanol (50 mL) and (Z)-dichloroethylene (1.30 mL, 9.26 mmol) and 4,4'-biphenanthrene-3,3'-dithiol **7** (0.37 g, 8.88 mmol) were added sequentially. The reaction mixture was refluxed for 5 h and then cooled to room temperature. Water (200 mL) was added and the mixture was extracted with dichloromethane (2x100 mL). The organic layer was washed with water, dried (Na_2SO_4) and evaporated to afford **7** as a colorless solid: 0.35 g; 90% yield; mp 251 °C; $^1\text{H-NMR}$ (CDCl_3) δ 6.34 (s, 2H), 6.75 (dt, $J=1.5, 6.9$ Hz, Ar, 2H), 6.95 (d, $J=8.4$ Hz, Ar, 2H), 7.22 (dt, $J=1.5, 7.2$ Hz, Ar, 2H), 7.67 (dd, $J=1.5, 7.8$ Hz, Ar, 2H),

7.70 (d, $J = 8.7$ Hz, Ar, 2H), 7.85 (d, $J = 9.0$ Hz, Ar, 2H), 7.99 (d, $J = 8.1$ Hz, Ar, 2H), 8.20 (d, $J = 8.1$ Hz, Ar, 2H); m/z 442.0 (M⁺), 397.0 (100%), 365.0 (25%), 190.0 (25%), 57.9 (22%).

4,4'-Biphenanthro[4,3-*e*;3',4'-*g*]-1,4-dithiocine 1,1,4,4-tetraoxide (8). A solution of **7** (0.25 g, 0.58 mmol) and *m*-chloroperbenzoic acid (85%, 0.86 g, 4.98 mmol) in chloroform (60 mL) was refluxed for 24 h. Water was added, the organic layer was separated and washed with a saturated solution of sodium metabisulfite and sodium bicarbonate. The organic solution was dried (Na₂SO₄) and evaporated to give a colorless solid which was purified by flash chromatography (petroleum ether-dichloromethane) to give **8** as colorless crystals (0.23 g, 80%): mp 351 °C; ¹H-NMR (CDCl₃) δ 6.47 (d, $J = 8.7$ Hz, Ar, 2H), 6.71 (dt, $J = 1.1, 6.9$ Hz, Ar, 2H), 7.14 (s, 2H), 7.20 (dt, $J = 1.2, 6.9$ Hz, Ar, 2H), 7.62 (dd, $J = 1.2, 7.8$ Hz, Ar, 2H), 7.80 (d, $J = 8.4$ Hz, Ar, 2H), 7.85 (d, $J = 8.4$ Hz, Ar, 2H), 8.36 (d, $J = 8.1$ Hz, Ar, 2H), 8.62 (d, $J = 8.1$ Hz, Ar, 2H); m/z 506.0 (M⁺, 51%), 384.0 (16%), 351.0 (100%), 187.1 (11%), 175.0 (93%).

4,4'-Biphenanthro[3,4-*e*;4',3'-*g*]-1,3-dithiepine (9). To a solution of **1a** (3.70 g, 8.88 mmol) and dimethoxymethane (0.70 g, 8.88 mmol) in 70 mL of dry dichloromethane, boron trifluoride etherate (1.26 g, 8.88 mmol) was added dropwise under argon at 0 °C. The reaction mixture was stirred for 4 h at 0 °C and for 3 h at room temperature. The solution was washed with 5% KOH (2x15 mL) and water (3x10 mL) and dried over anhydrous sodium sulfate. Concentration of the filtrate in vacuo provided **9** as a colorless solid (90%): mp 297 °C (CH₂Cl₂); ¹H-NMR (CDCl₃) δ 4.40 (s, 2H), 6.20 (d, $J = 8.7$ Hz, Ar, 2H), 6.60 (dt, $J = 1.5, 6.9$ Hz, Ar, 2H), 7.00 (dt, $J = 0.9, 6.6$ Hz, Ar, 2H), 7.45 (d, $J = 6.6$ Hz, Ar, 2H), 7.50 (d, $J = 6.6$ Hz, Ar, 2H), 7.71 (d, $J = 8.7$ Hz, Ar, 2H), 8.08 (s, 4H); m/z 430.6 (M⁺, 85%), 384.0 (100%).

4,4'-Biphenanthro[4,3-*b*;3',4'-*d*]thiophene S-oxide (10a) and 4,4'-Biphenanthro[4,3-*b*;3',4'-*d*]thiophene S,S-dioxide (10b). 3-Chloroperoxybenzoic acid (1.03 g, 2.99 mmol, 50% purity) in dichloromethane (20 mL) was added dropwise to a solution of **3** (1.15 g, 2.99 mmol) in dichloromethane (20 mL) at -20 °C. The mixture was allowed to warm to room temperature slowly and stirring was continued overnight. The organic solution was washed several times with saturated NaHCO₃ aqueous solution and dried over Na₂SO₄. The solvent was rotoevaporated and the crude product was purified by flash chromatography (dichloromethane) affording **10a** as the first eluted compound: 40% yield; mp. 245-6 °C; ¹H-NMR (CDCl₃) δ 6.30 (dt, $J = 1.5, 7.2$ Hz, Ar, 1H), 6.36 (dt, $J = 1.5, 6.9$ Hz, Ar, 1H), 7.05 (dt, $J = 1.2, 6.0$ Hz, Ar, 1H), 7.08 (dt, $J = 1.5, 6.0$ Hz, Ar, 1H), 7.40 (d, $J = 8.4$ Hz, Ar, 1H), 7.42 (d, $J = 8.4$ Hz, Ar, 1H), 7.51 (m, Ar, 2H), 7.72 (m, Ar, 4H), 7.97 (d, $J = 7.8$, Ar, 1H), 8.04 (d, $J = 8.1$, Ar, 1H), 8.14 (d, $J = 8.1$ Hz, Ar, 1H), 8.25 (d, $J = 7.8$ Hz, Ar, 1H); m/z 400.5 (M⁺, 100%), 257.0 (45%), 190.0 (20%), 50.9 (23%). **10b**: 40% yield; mp. 233-6 °C; ¹H-NMR (CDCl₃) δ 6.34 (t, $J = 7.8$ Hz, Ar, 2H), 7.07 (t, $J = 7.5$ Hz, Ar, 2H), 7.39 (d, $J = 8.4$ Hz, Ar, 2H), 7.49 (d, $J = 8.4$ Hz, Ar, 2H), 7.71 (m, Ar, 4H), 8.03 (m, Ar, 4H); m/z 416.5 (M⁺, 100%), 257.0 (22%), 190.0 (11%), 50.9 (53%).

S-Methyl-4,4'-biphenanthro[4,3-*b*;3',4'-*d*]thiophenium tetrafluoroborate (11). Methyl iodide (10 mL) was added dropwise to a stirred solution of **3** (3.8 g, 10 mmol) and silver tetrafluoroborate (1.1 eq) in dry 1,2-dichloroethane at room temperature under nitrogen atmosphere. After stirring for 24 h, the precipitated silver iodide was filtered off and washed with 1,2-dichloroethane (2x50 mL). The organic phases were collected and the solvent was evaporated to obtain a yellow solid which was crystallized from dichloromethane-ether to give **11**: 60% yield; mp 188-9 °C; ¹H-NMR (CDCl₃) δ 4.08 (s, 3H), 6.86 (dt, $J = 1.2, 7.8$ Hz, Ar, 1H), 6.90 (dt, $J = 1.2, 7.8$ Hz, Ar, 1H), 7.68 (dt, $J = 1.2, 6.8$ Hz, Ar, 1H), 7.72 (dt, $J = 1.2, 6.8$ Hz, Ar, 1H), 7.75 (d, $J = 8.4$ Hz, Ar, 1H), 7.86 (d, $J = 8.4$ Hz, Ar, 1H), 7.81 (m, Ar, 2H), 8.48 (m, Ar, 4H), 8.86 (m, Ar, 4H); Anal. Calcd. for C₂₉H₁₉F₄SB: C, 71.62; H, 3.94; Found: C, 71.40; H, 3.88.

4,4'-Biphenanthrene (12). **3-Mercapto-4,4'-biphenanthrene (13a).** **3-Methylthio-4,4'-biphenanthrene (13b).** The thiophene **3** (2g, 5.20 mmol) was added to a suspension of lithium (0.63 g of a 25% oil dispersion, 22.69 mmol) in dry THF (20 mL) at 0 °C under nitrogen atmosphere. After stirring 24 h at room temperature, the dark solution was cooled down to 0 °C and quenched with either methanol (0.5 mL) or with methyl iodide (1.5 g, 10.56 mmol) in anhydrous THF (45 mL). The solution was allowed to warm to room temperature and the solvent was rotoevaporated. Diluted hydrochloric acid was added and the solution was extracted several times with dichloromethane. The organic layers were collected, washed with water and dried (Na₂SO₄). The solvent was rotoevaporated and the crude product was purified by flash chromatography (n-hexane/dichloromethane 10:1). **12**: mp 101-4 °C; ¹H-NMR (CDCl₃) δ 6.98 (t, $J = 6.9$ Hz, Ar, 2H), 7.33 (m, Ar, 2H), 7.41 (m, Ar, 2H), 7.59 (t, $J = 7.2$ Hz, Ar, 2H), 7.88 (m, Ar, 6H), 8.03 (t, $J = 7.5$, Ar, 4H); m/z 354.0 (M⁺, 100%), 239.0 (22%), 326.0 (15%), 162.9 (13%), 149.9 (9%). **13a**: mp 166 °C; ¹H-NMR (CDCl₃) δ 3.05 (s, 1H), 6.80 (dt, $J = 1.2, 8.4$ Hz, Ar, 1H), 7.10 (dt, $J = 1.2, 8.4$ Hz, Ar, 1H), 7.25 (d, $J = 8.4$ Hz, Ar, 1H), 7.32 (t, $J = 8.4$ Hz, Ar, 1H), 7.44 (d, $J = 9.4$ Hz, Ar, 1H), 7.60 (d, $J = 9.0$ Hz, Ar, 1H),

7.72 (t, $J = 8.4$ Hz, Ar, 1H), 7.78-7.95 (series of m, Ar, 8H), 8.08 (d, $J = 9.0$ Hz, Ar, 1H), 8.15 (d, $J = 9.0$ Hz, Ar, 1H); m/z 386.5 (M⁺), 353.5 (100%), 253.0 (35%), 191.5 (21%), 114.9 (10%). **13b**: mp 166 °C; ¹H-NMR (CDCl₃) δ 2.20 (s, 3H), 6.85 (dt, $J = 1.2, 8.7$ Hz, Ar, 1H), 7.20 (dt, $J = 1.2, 8.7$ Hz, Ar, 1H), 7.28 (d, $J = 8.4$ Hz, Ar, 1H), 7.34 (t, $J = 9.0$ Hz, Ar, 1H), 7.41 (d, $J = 9.0$ Hz, Ar, 1H), 7.58 (d, $J = 8.4$ Hz, Ar, 1H), 7.70 (t, $J = 8.4$ Hz, Ar, 1H), 7.78 (d, $J = 8.7$ Hz, Ar, 2H), 7.88 (m, Ar, 4 H), 7.94 (d, $J = 8.4$ Hz, Ar, 1H), 8.30 (d, $J = 8.4$ Hz, Ar, 1H), 8.10 (d, $J = 9.0$ Hz, Ar, 1H), 8.20 (d, $J = 9.10$ Hz, Ar, 1H); m/z 400.0 (M⁺), 382.0 (12%), 353.0 (65%), 191.0 (21%), 174.9 (100%).

X-Ray data collection and structure determination.

Selected bond distances and angles are listed in Figure 1. Crystal data and other experimental details are summarized in the caption to fig.1. The diffraction experiment was carried out on a Philips PW 1100 diffractometer in the ω -2 θ scan mode at room temperature using Mo-K α radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator in the incident beam. Maximum 2 θ was 56° and hlk ranges were: -19/19; 0/14 and 0/15, respectively. Of the 4520 unique reflections collected, 2594 were considered observed with $F > 3\sigma(F)$. The structure was phased by the SHELX 86 program and refined by blocked full-matrix least-squares using the SHELX 76 program. Anisotropic thermal factors were refined for all the non-hydrogen atoms. The hydrogen atoms were located on a DF map and isotropically refined. The final conventional R factor for the 2594 unique observed reflections was 0.0494, R_w 0.0561 with $W = 1/[\sigma^2(F) + 0.0088F^2]$. Full structural details have been deposited with the Cambridge Crystallographic centre.

Acknowledgements.

We thank C.N.R.-Progetti Finalizzati (Rome) and MURST (Rome) for financial support. We are indebted with Dr. Orlandoni (Enichem Research Centre, Porto Torres) for registering mass spectra.

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