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Synthesis of 'thianthrene dimer' by the coupling reaction of stannylthianthrenes in the presence of copper catalysts

Hiroyuki Morita *, Yasutaka Oida, Takamine Ariga, Satoru Fukumoto, Md. Chanmiya Sheikh *, Takayoshi Fujii, Toshiaki Yoshimura *

Department of Applied Chemistry, Faculty of Engineering, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan

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ABSTRACT

The coupling reaction of 1-tributylstannylthianthrene (**5**) and 2-tributylstannylthianthrene (**7**) in the presence of copper catalysts at rt afforded the thianthrene dimer 1,1′-bithianthrene (**3**), 2,2′-bithianthrene (**8**), and 1,2′-dithianthrene (**9**) in high yields. Also we obtained thianthrene oxide dimer (*R*,*R*) (*S*,*S*)-1-(10-*S*-monoxythianthrene-1-yl)thianthrene-10-*S*-monoxide (**12**) and (*R*,*S*) (*S*,*R*)-1-(10-*S*-monoxythianthrene-1-yl)thianthrene-10-*S*-monoxide (**13**) from 1-tributylstannyl-10-*S*-monoxythianthrene (**10**) under the same reaction condition. The final structural conformation of **3**, **8**, **9**, and **12** was performed by X-ray crystallographic analysis. Further, the solvent effects in the coupling reactions were also examined.

1. Introduction

It has been known that thianthrene derivatives are folded along the S–S axis, and consequently exist as 'butterfly structures', which contain a boat-form similar to a 1,4-dithiin by X-ray crystallographic analyses for both thianthrene itself and several oxidized thianthrenes.[1–4] To dates, only a limited number of reports in the chemistry of thianthrene, such as its oxidation to sulfoxides and sulfones, and its imination to derivatives,[5] have appeared in the literatures. Recently, Bonchio et al.[6] and Adam and Golsch[7] reported that the importance of steric and electronic effects on both the rate and the site of further oxidation of thianthrene or its 5-oxide to their oxides under several oxidation conditions. From these results, it is envisaged that a direct interaction was operated between the substituents on the two sulfur atoms both sterically and electronically. Therefore, in the course of the study of thianthrene derivatives with a regulation functionality of a new class of functionalized materials, we investigated cis/trans isomerization of several 5,10-disubstituted thianthrene derivatives. Recently, we reported the syntheses and structural analyses of 10-monoxy and dioxy-5-*N*-substituted iminothianthrene derivatives and the stereochemical change on their sulfur atom under acidic and thermal conditions.[8] In the report, we indicated the inversion of sulfinyl group by substitution of H_2O on the hydroxysulfonium sulfur atom at the 10-position formed by protonation in the course of hydrolysis in concentrated H_2SO_4, which also shows evident that the trans form seems to be less easily attacked by H_2O than the cis form because of unfavorable steric hindrance by the hydrogen of *peri*-position. Hence, we suggested that the interaction between substituents of *peri*-position and substituents on sulfur atom influence the 'flip–flap' inversion.

Previously, Lovell and Joule.[9a] reported on electrophilic aromatic substitution of thianthrene under various electrophiles and the steric effect was found to be important on the reactivity and regioselectivity in the thianthrene system. To clarify the steric effects of *peri* substituents and also neutral interaction of the conformational change, we have attempted to synthesize thianthrene derivatives having substituents on *peri*-position. Recently, Ogawa et al.[9b] reported the synthesis of 1,9′-disubstituted thianthrene by Negishi coupling reaction. Meanwhile, on the coupling reaction of aryl groups,[10,11] alkynyl,[10] alkenyl,[10,12] and vinyl[13] groups via stannanes in the presence of $Cu(NO_3)_2 \cdot 3H_2O$. It is well known that the protocols were highly effective and versatile, another using copper catalysts, such as $Cu(NO_3)_2 \cdot 3H_2O$ and CuCl, were used in THF or DMF condition.[13,14] In order to reveal the nature of stannylthianthrene, we have prepared their derivatives, and studied the coupling reactions in several solvents in the presence of copper catalyst.

* Corresponding authors. E-mail addresses: moritah@pb.ctt.ne.jp (H. Morita), chansheikh@yahoo.com (M.C. Sheikh), yosimura@eng.u-toyama.ac.jp (T. Yoshimura).

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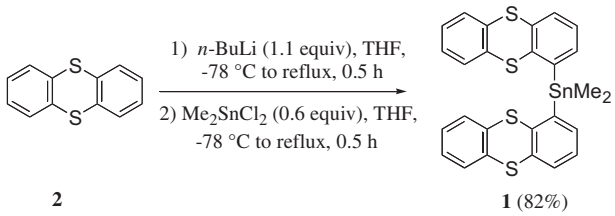
2. Results and discussion

2.1. Synthesis of stannyl compound 1 and studies the coupling reaction of 1 in the presence of copper catalysts

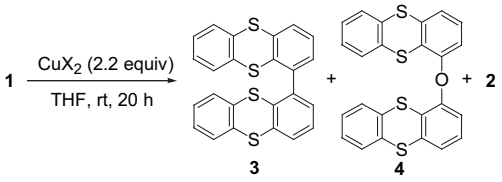
Dimethylbis(thianthren-1-yl)tin (**1**) was prepared from thianthrene (**2**) where **2** was prepared by the reaction of diphenyl sulfide with sulfur and $AlCl_3$. Initially, the solution briefly to reflux completed the lithiation of *peri*-position nine, which afforded **1** in 82% yield after successive addition of Me_2SnCl_2 (Scheme 1).



Scheme 1. Synthesis of stannyl compound **1** via the lithiation of **2**.

Subsequently, the coupling reactions of **1** were carried out in the presence of $Cu(NO_3)_2\cdot 3H_2O$ or $Cu(OTf)_2$ in THF at rt under nitrogen or ambient atmosphere to give 1,1′-bithianthrene **3**. The results are shown in Table 1.

Table 1
The coupling reaction of **1** in the presence of copper catalysts



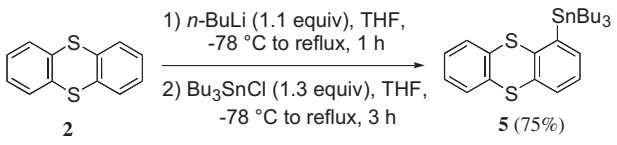
Entry	CuX_2	Atmosphere	Product[a] (yield%)		
			3	**4**	**2**
1	$Cu(NO_3)_2\cdot 3H_2O$	Ambient	12	3	72
2	$Cu(OTf)_2$	Ambient	23	47	15
3	$Cu(OTf)_2$	Nitrogen	21	26	53

[a] Isolated yields (not optimized).

As shown in Table 1, the coupling reaction of **1** in the presence of $Cu(NO_3)_2\cdot 3H_2O$ gave thianthrene dimer 1,1′-dithianthrene (**3**) as a coupling target compound in 12% yield with 1,1′-dithianthrenyl ether (**4**) in 3% and destannylated product **2** in 72% yield (entry 1). The similar reaction in the presence of $Cu(OTf)_2$ gave **2** and **3** in 15% and 23% yields, respectively. In this case **4** was obtained as a main product in 47% yield (entry 2). Further, the reaction was also carried out under nitrogen to give **4** in 26% yield (entry 3). Hence, it is considered that the oxygen in **4** did not derive from ambient atmosphere and **4** is the characteristic product by this reaction in the presence of $Cu(OTf)_2$. These three reactions gave the target compound **3** in low yields. It is probably due to the difficulty of attacking to stannyl compound **1** by copper catalysts because of unfavorable steric hindrance by both side's thianthrene structures. Therefore, it is suggested that the stannyl compound, 1-tributylstannylthianthrene (**5**)[9a] seemed to be easily attacked by copper catalysts.

2.2. Synthesis of stannylthianthrene derivatives (5, 7) and studied their coupling reaction in the presence of various copper catalysts

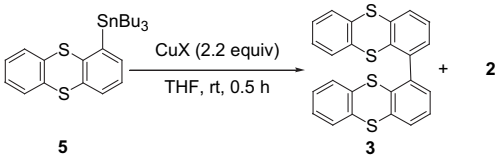
We have prepared stannylthianthrene **5** by the reaction of lithiated thianthren and Bu_3SnCl in 75% yield (Scheme 2).



Scheme 2. Synthesis of stannylthianthrene **5** via the lithiation of **2**.

Then, the reactions of **5** were carried out in the presence of copper catalysts, such as $Cu(NO_3)_2\cdot 3H_2O$, $Cu(OTf)_2$ or CuOTf in THF at rt under ambient atmosphere. Herein CuOTf was used as a catalyst to compare copper of the monovalent and divalent. The results are summarized in Table 2.

Table 2
The coupling reaction of **5** in the presence of copper(I) or (II) catalyst



Entry	CuX	Yield[a] (%)	
		3	**2**
1	$Cu(NO_3)_2\cdot 3H_2O$	54	41
2	$Cu(OTf)_2$	76	14
3	CuOTf	47	50

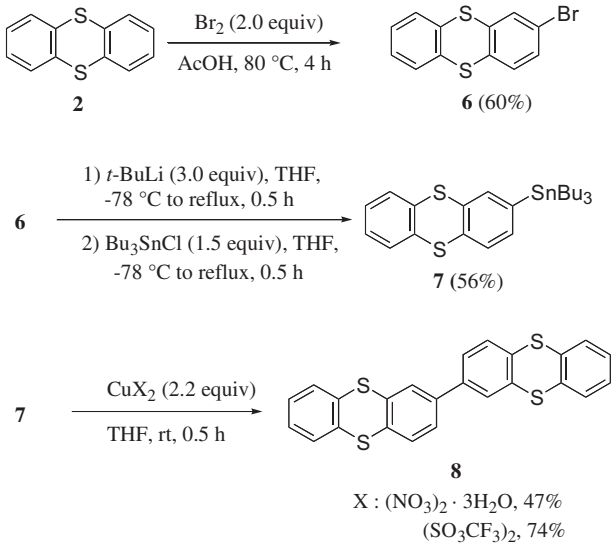
[a] Isolated yields (not optimized).

As shown in Table 2, the coupling reaction in the presence of $Cu(NO_3)_2\cdot 3H_2O$ afforded thianthrene coupling compound **3** in 54% yield, and also gave destannylated product **2** in 41% yield (entry 1). The coupling reaction of **5** resulted a better yield and shorter reaction time in comparison with the case of Table 1. We then examined the reaction in the presence of $Cu(OTf)_2$ under similar conditions and the best result was obtained in shorter time (entry 2). The reaction in the presence of CuOTf afforded **2** and **3** in 50% and 47% yields, respectively (entry 3). The results clearly indicate that in the case of CuOTf only gave half yield of **3** in comparison with the case of $Cu(OTf)_2$ (entries 2 and 3). Hence, we comprehended that the coupling reaction prefers to copper(II) catalysts to copper(I) catalysts and it is seems that **5** was easily attacked by copper catalysts than **1**. Using the compound **5** also extremely shortens the reaction time.

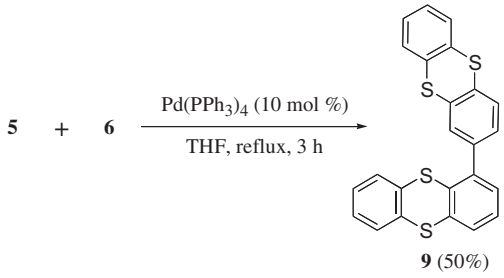
Furthermore, we attempted to synthesize 2,2′-dithianthrene (**8**) using stepwise route. Initially, we have prepared 2-bromothianthrene (**6**)[9] by the reaction of **2** with Br_2/AcOH in 60% yield, and **6** was lithiated with *t*-BuLi, and followed by the reaction with Bu_3SnCl to afford 2-tributylstannylthianthrene (**7**)[9a] in 56% yield. Finally, the stannyl compound **7** was employed to synthesize the compound **8** (Scheme 3). The coupling reaction in the presence of $Cu(NO_3)_2\cdot 3H_2O$ or $Cu(OTf)_2$ gave the target coupling compound **8** in 47% and 74% yields, respectively.

In the Stille coupling reaction, only 1,2′-dithianthrene (**9**) is expected as a cross-coupling product, therefore we carried out the reaction of **5** with **6** using $Pd(PPh_3)_4$ as a catalyst (Scheme 4). Only the cross-coupling product **9** was obtained expectedly in 50% yield.

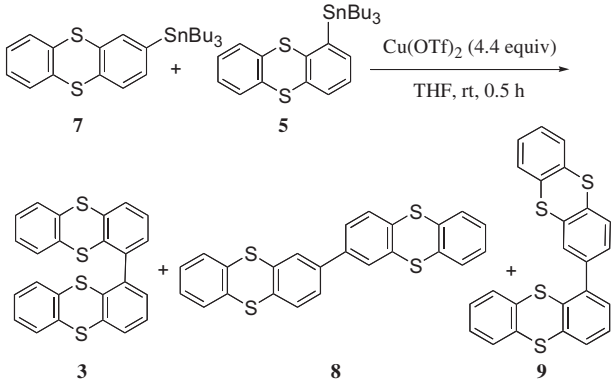
In addition, the cross-coupling reaction between **5** and **7** was also carried out in the presence of $Cu(OTf)_2$ in THF at rt under ambient atmosphere (Scheme 5). The ratio of the three products was estimated by ^1H NMR to be found **3**: **8**: **9**=1.0: 1.8: 1.3. This ratio also seems to indicate the steric factor on the coupling reaction of the formed radical. As a result, the steric repulsion at 1-positon of thianthrene seems to be larger than 2-position.



Scheme 3. Synthetic path of 2,2′-bithianthrene (**8**) from **2**.



Scheme 4. The coupling reaction of **5** and **6** in the presence of $Pd(PPh_3)_4$.

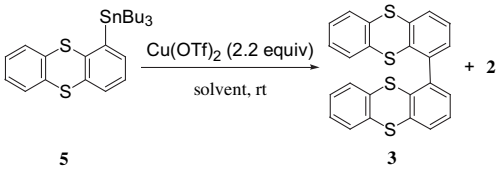


Scheme 5. The coupling reaction of **5** and **7** in the presence of $Cu(OTf)_2$.

2.3. Solvent effect in the coupling reaction of 5 in the presence of copper(II) catalyst

Under the optimized reaction conditions, several solvents were examined. Table 3 shows the effect of solvent on the $Cu(OTf)_2$–catalyzed coupling reaction. Inspection of Table 3 clearly shows the yields of thianthrene dimer, **3** are high and in cases of DMF (entry 1), DMSO (entry 2), and acetone (entry 3) the reaction times were very short within 30 min. In the case of alcohol solvents, such as methanol or ethanol was used, the reaction rates were slow and the starting material **5** remained after 30 min (entry 4). Although the reaction time was prolonged the yield of thianthrene dimer **3** was not good.

Table 3
Effect of the solvent on reaction time and yield of the coupling reaction



Entry	Solvent (*Z* value)	Time (h)	Product[a] (yield%)	
			3	**2**
1	DMF (68.5)	0.5	78	11
2	DMSO (68.4)	0.5	78	10
3	Acetone (65.5)	0.5	74	14
4	MeOH (83.6)	0.5	32	29
5	EtOH (79.6)	0.5	59	33
6	$CHCl_3$ (63.2)	0.5	0	—
7	H_2O (94.6)	0.5	0	—

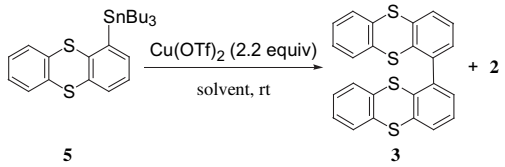
[a] Isolated yields (not optimized).

We propose that the solvent effects of the reactions were involved in *Z* value of solvent polarity parameter.[15] The lower the *Z* value is the better yield of the thianthrene dimer **3** and the shorter the reaction time. Therefore, the coupling reaction in ethanol (entry 5) gave thianthrene dimer **3** in a better yield and shorter reaction time in comparison with that in methanol (entry 4). No reaction was detected using chloroform or water (entries 6 and 7). Based on the results, we propose that in this coupling reaction, inorganic catalyst (copper catalyst) and organic compound (**5**) were required; therefore, solubility of both copper catalysts and **5** is necessary to obtain thianthrene dimer **3** in better yield. In order to obtain the clue, further the coupling reaction was carried out in the mixed solvent. The results are summarized in Table 4. As shown in Table 4, the coupling reaction in mixed solvent, DMSO/$CHCl_3$ (1:1) gave the thianthrene dimer **3** in 75% yield (entry 1). Successively, we studied the reaction in H_2O/acetone (1:5) as a mixed solvent to give **3** and **2** in 55% and 30% yield, respectively (entry 2). The compound **3** was obtained in worse yield than the reaction in only acetone. Increasing the ratio of water in mixed solvent, H_2O/acetone (1:3) gave **3** and **2** in 30% and 41% yields, respectively (entry 3). Thus, we suggest that *Z* value of the mixed solvent increased when H_2O was contained, which decrease the yield of **3**. From these results, it is considered that the coupling reactions proceeded when both **5** and $Cu(OTf)_2$ were dissolved into the solvent. Hence, the coupling reaction did not proceed in only H_2O or only chloroform as a solvent (Table 3).

2.4. Synthesis of thianthrene oxide dimer 12 and 13 from 5

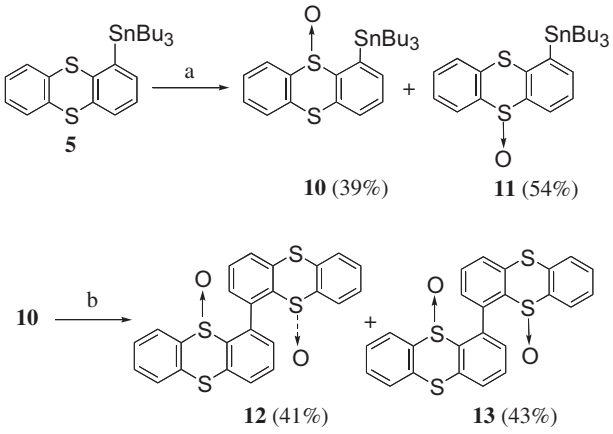
In our initial experiment, we attempted to synthesize the thianthrene oxide dimers, (*R*,*S*) (*S*,*R*)-1-(10-*S*-monoxythianthrene-1-yl)thianthrene-10-*S*-monoxide (**12**) or (*R*,*R*) (*S*,*S*)-1-(10-*S*-monoxythianthrene-1-yl)thianthrene-10-*S*-monoxide (**13**) from thianthrene dimer **3**. When **3** was allowed to react with 3-chloroperbenzoic acid (*m*-CPBA) at 0 °C in CH_2Cl_2, the reaction proceed smoothly and crude ^1H NMR spectrum showed that the crude product of their oxide dimers contain an inseparable by-product. Seeking more convenient and shorter synthetic route we have finally used the stepwise route. The diastereomeric mixture of thianthrene oxide dimers, *meso* **12**, and racemic **13** were synthesized by the one step reaction of 1-tributylstannyl-10-*S*-monoxythianthrene (**10**) with $Cu(OTf)_2$ in DMF where **10** was prepared by the oxidation reaction of **5** with *m*-CPBA at 0 °C temperature (Scheme 6). The stereomeric assignment was performed as follows: the compound **12** showed 14 different proton NMR signals while

Table 4
Effect of the mixed solvents on reaction time and yield of the coupling reaction



Entry	Solvent	Product[a] (yield%)	
		3	**2**
1	DMSO/$CHCl_3$ (1:1)	75	12
2	H_2O/acetone (1:5)	55	30
3	H_2O/acetone (1:3)	30	41

[a] Isolated yields (not optimized).



Scheme 6. Synthesis of thianthrene oxide dimer **12** and **13**. Reagents: (a) *m*-CPBA (1.0 equiv) in CH_2Cl_2, 0 °C, 1 h; (b) $Cu(OTf)_2$ (2.2 equiv) in DMF, rt, 30 min.

the compound **13** showed only seven different proton signals to show C_2 symmetry and these *R*,*R* or *S*,*S* isomer of **13**. HRMS of both compounds showed the same molecular ion. The structure of **12** was confirmed also by X-ray crystallographic analysis.

2.5. X-ray crystallographic analysis of 3, 4, 8, 9, and 12

Since X-ray crystal structures of **3**, **4**, **8**, **9**, and **12** are new compounds, hence, the structure of **3**, **4**, **8**, **9**, and **12** were confirmed by single crystal X-ray crystallographic analysis. An ORTEP drawing and some selected bond lengths and angles are listed in Figs. 1–5.

3. Conclusion

In conclusion, we have prepared thianthrene dimer **3**, **8**, and **9** from the stannyl compound **5** and **7** by the coupling reaction in the presence of copper catalysts and thianthrene oxide dimer **12** and **13** were obtained from stannyl oxide compound **10** under the same condition. Further, the solvent effect in coupling reactions of **5** was also examined and it was observed that when *Z* value is lower the thianthrene dimer **3** was formed in better yield and a short reaction time. Now we are succeedingly studying the synthesis and reactivity of thianthrene dimer including heteroatom.

4. Experimental section

4.1. General

All melting points were uncorrected using a micro melting point apparatus. IR spectra were recorded on a HORIBA FT-71 spectrometer.

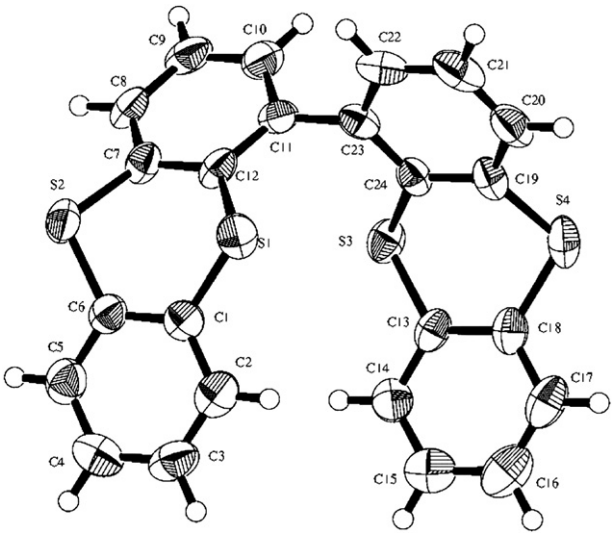


Fig. 1. An ORTEP drawing of **3** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: S(1)–C(1), 1.774 (5); S(1)–C(12), 1.764 (4); S(2)–C(6), 1.765 (5); S(2)–C(7), 1.766 (5); S(3)–C(13), 1.772 (5); S(3)–C(24), 1.768 (5); S(4)–C(18), 1.771 (5); S(4)–C(19), 1.771 (5); C(11)–C(23), 1.501 (7); C(12)–S(1)–C(1), 101.91 (2); C(6)–S(2)–C(7), 102.37 (2); C(24)–S(3)–C(13), 101.77 (2); C(18)–S(4)–C(19), 101.68 (2).

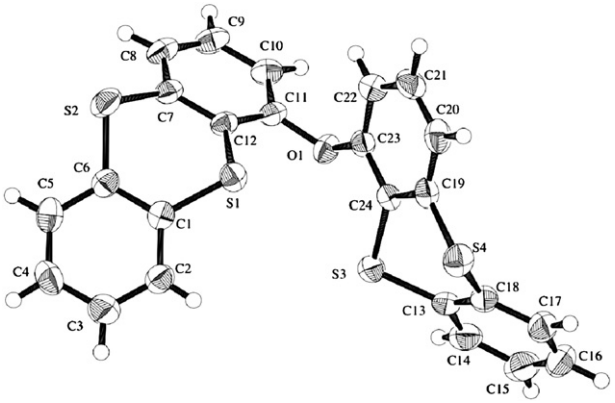


Fig. 2. An ORTEP drawing of **4** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: S(1)–C(1), 1.768 (3); S(1)–C(12), 1.770 (3); S(2)–C(6), 1.769 (3); S(2)–C(7), 1.772 (3); S(3)–C(13), 1.777 (3); S(3)–C(24), 1.771 (3); S(4)–C(18), 1.770 (3); S(4)–C(19), 1.773 (3); O(1)–C(11), 1.393 (3); O(1)–C(23), 1.393 (3); C(1)–S(1)–C(12), 101.0 (1); C(6)–S(2)–C(7), 101.2 (1); C(13)–S(3)–C(24), 100.3 (1); C(18)–S(4)–C(19), 100.4 (1); O(1)–C(11)–C(10), 118.5 (3); O(1)–C(11)–C(12), 120.4 (1); O(1)–C(23)–C(22), 121.6 (3); O(1)–C(23)–C(24), 116.9 (2); C(11)–O(1)–C(23), 117.4 (2).

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a JMN-A400 spectrometer in $CDCl_3$ using TMS as the internal standard. All the reactions were monitored by TLC, and the products were separated by column chromatography using Silica Gel 60 and by preparative-layer chromatography using Silica Gel 60 PF_{254} with UV or PMA and DNP detection. Also, silica gel used for preparative thin layer chromatography (PLC) was Merck Kieselgel 60 PF_{254}. Mass spectra were obtained on a JEOL-JMS-D300 mass spectrometer. Elemental analyses were performed by using a Yanaco CHN-coder MT-5. The X-ray crystallographic analyses were performed on Rigaku AF7R four-circle difractometer using graphite monochromate Mo Kα radiation. All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., and Aldrich Chemical Co. All the reagents were the highest quality and were further purified by distillation, or re-crystallization.

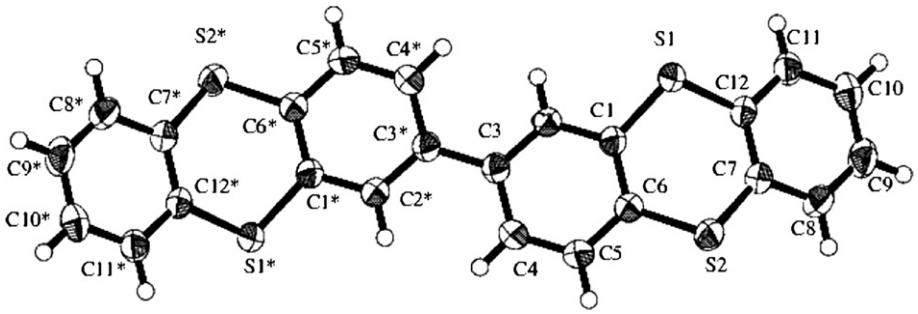


Fig. 3. An ORTEP drawing of **8** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: S(1)–C(1), 1.712 (2); S(1)–C(12), 1.767 (2); S(2)–C(6), 1.755 (2); S(2)–S(7), 1.771 (2); C(3)–C(3*), 1.485 (4); C(1)–S(1)–C(12), 103.31 (9); C(6)–S(2)–C(7), 103.23 (10); C(2)–C(3)–C(3*), 121.1 (2); C(3*)–C(3)–C(4), 121.9 (2).

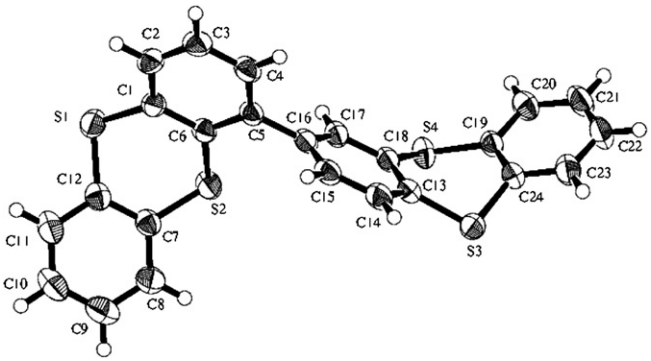


Fig. 4. An ORTEP drawing of **9** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: S(1)–C(1), 1.768 (2); S(1)–C(12), 1.774 (2); S(2)–C(6), 1.774 (2); S(2)–C(13), 1.765 (2); S(3)–C(13), 1.766 (2); S(3)–C(24), 1.772 (2); S(4)–C(18), 1.773 (2); S(4)–C(19), 1.767 (2); C(5)–C(16), 1.496 (2); C(1)–S(1)–C(12), 101.59 (8); C(6)–S(2)–C(7), 101.86 (8); C(13)–S(3)–C(24), 101.05 (8); C(18)–S(4)–C(19), 100.95 (8); C(4)–C(5)–C(16), 118.6 (2); C(5)–C(16)–C(15), 119.7 (2); C(5)–C(16)–C(17), 121.1 (2); C(6)–C(5)–C(16), 122.5 (1).

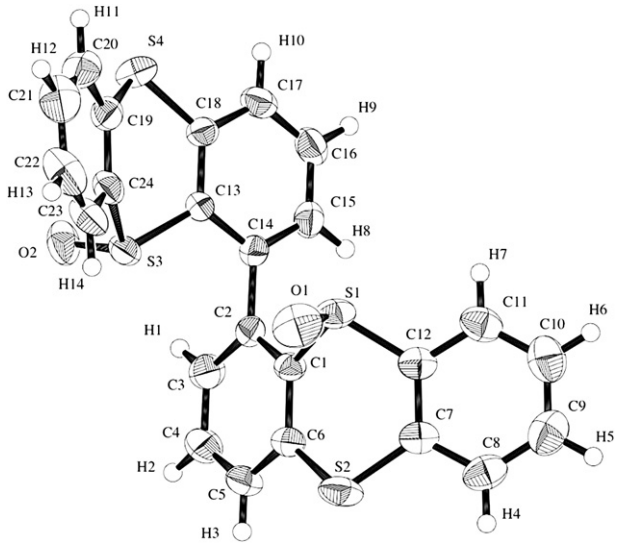


Fig. 5. An ORTEP drawing of **12** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: S(1)–C(1), 1.788 (2); S(1)–C(12), 1.786 (3); S(1)–O(1), 1.475 (2); S(2)–C(6), 1.762 (3); S(2)–C(7), 1.768 (3); C(2)–C(14), 1.499 (3); S(3)–O(2), 1.490 (2); S(3)–C(13), 1.782 (2); C(24)–S(3) 1.784 (3); S(4)–C(19), 1.753 (3); S(4)–C(18), 1.756 (2); C(1)–S(1)–O(1), 106.9 (1); C(12)–S(1)–O(1), 108.1 (1); C(1)–S(1)–C(12), 97.3 (1); C(6)–S(2)–C(7), 101.4 (1); C(13)–S(3)–O(2), 106.4 (1); C(13)–S(3)–C(24), 98.6 (1); C(24)– S(3)–O(2), 106.7 (1); C(19)–S(4)–C(18), 102.7 (1).

4.2. Lithiation of thianthrene; 1-lithiothianthrene

To a stirred solution of thianthrene **2** (1.00 g, 4.62 mmol) in THF (35 mL) was added 1.6 M *n*-BuLi (3.2 mL, 5.09 mmol) at −78 °C under N_2. After heating to reflux for 30 min, the reaction mixture was re-cooled to −78 °C, which was used for the reaction of electrophiles successively.

4.3. Preparation of dimethylbis(thianthren-1-yl)tin (1)

To a stirred solution of thianthren-1-yllithium (4.62 mmol) in THF (6 mL) was added Bu_2SnCl_2 (609 mg, 2.77 mmol) at −78 °C under N_2. After heating at reflux for 30 min, the solvent was evaporated, and $CHCl_3$ was added. Then, the organic layer was washed with H_2O and aqueous saturated NH_4Cl, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed by the column on silica gel with hexane/AcOH (10:1) to give dimethylbis(thianthren-1-yl)tin **1** (1.10 g, 82%) as a colorless solid; mp 129–130 °C (from hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 6H), 7.14–7.25 (m, 8H), 7.33–7.35 (m, 2H), 7.48–7.53 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.9, 127.3, 127.6, 127.7, 128.6, 128.7, 129.5, 136.1; IR (KBr) 1373, 748 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{20}S_4Sn$: 577.9470; found: *m*/*z* 577.9468.

4.4. Preparation of thianthrene (2)

The suspension of diphenyl sulfide (30.0 g, 0.16 mol) and aluminum chloride (21.0 g, 0.16 mol) in ligroin (100 mL) was heated at 80 °C for 5 h. This reaction mixture was quenched with H_2O and extract was dried up in vacuum after removal of the solvent. The residue was dissolve in $CHCl_3$ and this suspension was filtered with Celite. Then, the solvent was evaporated and dried under vacuum and re-crystallization from CH_2Cl_2/hexane to give thianthrene **2** (15.0 g, 44%) as colorless crystals; mp 153–155 °C (from CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.25 (m, 4H), 7.45–7.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.6, 128.7, 135.5; IR (KBr) 1558, 1540, 1433, 761 cm^{-1}. HRMS (EI) calcd for $C_{12}H_8S_2$: 216.0067; found: *m*/*z* 216.0061.

4.5. Preparation of 1,1′-dithianthrene (3)

To a stirred solution of dimethylbis(thianthren-1-yl)tin **1** (100 mg, 0.17 mmol) in THF (0.2 mL) was added $Cu(OTf)_2$ (137 mg, 0.38 mmol) under ambient atmosphere for 30 min at rt. The solvent was evaporated, and $CHCl_3$ was added. The organic layer was washed with H_2O and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel preparative plate using hexane/CH_2Cl_2 (3:1) to give 1,1′-dithianthrene **3** as colorless crystals (15 mg, 21%); mp 249–251 °C (from CH_2Cl_2/diethylether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.17 (m, 4H), 7.22–7.26 (m, 4H), 7.32 (t, J=7.6 Hz, 2H), 7.50–7.52 (m, 2H),

7.59 (dd, J_1=7.8 Hz, J_2=1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.2, 127.5, 127.7, 128.4, 128.5, 129.2, 129.3, 135.6, 135.7, 135.9, 136.0, 140.1; IR (KBr) 1553, 1449, 1429, 1394, 786, 749, 725, 455 cm^{-1}. Anal. Calcd for $C_{24}H_{14}S_4$: C, 66.94; H, 3.28. Found: C, 67.13; H, 3.29.

4.6. Preparation of 1,1′-dithianthrenyl ether (4)

To a stirred solution of dimethylbis(thianthren-1-yl)tin **1** (100 mg, 0.17 mmol) in THF (0.2 mL) was added $Cu(OTf)_2$ (137 mg, 0.38 mmol) under ambient atmosphere for 30 min at rt. The solvent was evaporated, and $CHCl_3$ was added. Then, the organic layer was washed with H_2O and dried over anhydrous $MgSO_4$. After removal of the solvent the residue was chromatographed on silica gel preparative plate using hexane/CH_2Cl_2 (3:1) to give 1,1′-dithianthrenyl ether **4** as colorless crystals (36.1 mg, 47%); mp 180–181 °C (from CH_2Cl_2/diethylether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (dd, J_1=8.0 Hz, J_2=0.8 Hz, 2H), 7.05 (t, J=7.8 Hz, 2H), 7.12–7.19 (m, 6H), 7.36–7.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.2, 124.2, 127.2, 127.7, 127.8, 128.2, 128.6, 129.1, 134.7, 135.5, 137.4, 153.9; IR (KBr) 1550, 1434, 1414, 1245, 1037, 942, 781, 749 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{14}OS_4$: 445.9927; found: m/z 445.9927.

4.7. Preparation of 1-tributylstannylthianthrene (5)

To a stirred solution of thianthren-1-yllithium (4.62 mmol) in THF (6 mL) was added Bu_3SnCl (1.5 mL, 5.54 mmol) at −78 °C under N_2. After heating at reflux for 3 h, the solvent was evaporated and $CHCl_3$ was added. Then, the organic layer was washed with H_2O and aqueous saturated NH_4Cl, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel using hexane to give 1-tributylstannylthianthrene **5** as a colorless oil (1.75 g, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=7.4 Hz, 9H), 1.17–1.24 (m, 6H), 1.29–1.39 (m, 6H), 1.53–1.61 (m, 6H), 7.16–7.25 (m, 3H), 7.33–7.35 (m, 1H), 7.45–7.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1, 13.6, 27.3, 29.1, 126.9, 127.5, 127.6, 128.4, 128.5, 128.9, 135.2, 135.7, 136.2, 136.5, 143.3, 144.2; IR (KBr) 2956, 2925, 1449 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{34}S_2Sn$: 506.1124; found: m/z 506.1095.

4.8. Preparation of 2-bromothianthrene (6)

Br_2 (0.3 mL, 4.85 mmol) was added dropwise to a stirred suspension of thianthrene **2** (509 mg, 2.35 mmol) in AcOH (10 mL) at rt under N_2. After the addition was completed the mixture was allowed to warm to 80 °C, and the resulted brown solution was stirred for 4 h. Then, the solvent was evaporated and dried in vacuo, the residue was chromatographed on silica gel using hexane and re-crystallized from hexane to give 2-bromothianthrene **6** as a colorless solid (416 mg, 60%); mp 87–89 °C (from hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.26 (m, 2H), 7.30–7.36 (m, 2H), 7.45–7.48 (m, 2H), 7.62 (d, J=2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.4, 127.9, 127.9, 128.8, 128.8, 129.6, 130.6, 131.2, 134.7, 134.8, 135.2, 137.8; IR (KBr) 1420, 1070 cm^{-1}. HRMS (EI) calcd for $C_{12}H_7BrS_2$: 293.9173; found: m/z 293.9171.

4.9. Preparation of 2-tributylstannylthianthrene (7)

To a stirred solution of 2-bromothianthrene **6** (358 mg, 1.82 mmol) in THF (35 mL) at rt under N_2 was added 1.7 M t-BuLi (3.2 mL, 5.45 mmol). After heating at reflux for 30 min, the reaction mixture was cooled to rt. To thianthren-2-yllithium was added Bu_3SnCl (0.7 mL, 2.72 mmol). After heating at reflux for 3 h, the solvent was evaporated, and $CHCl_3$ was added. The organic layer was washed with H_2O and aqueous saturated NH_4Cl, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel using hexane to give 2-tributylstannylthianthrene **7** as a colorless oil (515 mg 56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86–0.90 (m, 9H), 1.03–1.07 (m, 6H), 1.26–1.37 (m, 6H), 1.48–1.55 (m, 6H), 7.20–7.24 (m, 2H), 7.30 (dd, J_1=7.6 Hz, J_2=0.8 Hz, 1H), 7.41–7.50 (m, 3H), 7.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.7, 13.6, 27.3, 29.0, 127.5, 128.1, 128.6, 128.7, 134.9, 135.1, 135.5, 135.7, 135.8, 136.0, 141.8. HRMS (EI) calcd for $C_{24}H_{34}S_2Sn$: 506.1124; found: m/z 506.1120.

4.10. Preparation of 2,2′-dithianthrene (8)

To a stirred solution of 2-tributylstannylthianthrene **7** (79.0 mg, 0.16 mmol) in THF (0.2 mL) was added $Cu(OTf)_2$ (122.9 mg, 0.34 mmol) under ambient atmosphere for 30 min at rt. The solvent was evaporated, and $CHCl_3$ was added. The organic layer was washed with H_2O, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel preparative plate using hexane/CH_2Cl_2 (3:1) to give 2,2′-dithianthrene **8** as colorless crystals (25.1 mg, 74%); mp 232–234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.27 (m, 4H), 7.41 (dd, J_1=8.2 Hz, J_2=1.8 Hz, 2H), 7.47–7.53 (m, 6H), 7.66 (d, J=2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.2, 127.0, 127.8, 127.8, 128.7, 128.8, 129.0, 135.1, 135.2, 135.4, 136.4, 139.4; IR (KBr) 1529, 1442, 1353, 806, 756, 407 cm^{-1}. Anal. Calcd for $C_{24}H_{14}S_4$: C, 66.94; H, 3.29. Found: C, 65.65; H, 3.56.

4.11. Preparation of 1,2′-dithianthrene (9)

To a stirred solution of 1-tributylstannylthianthrene **5** (30.0 mg, 0.06 mmol) and 2-bromothianthrene **6** (24.0 mg, 0.08 mmol) in THF (10 mL) was added $Pd(PPh_3)_4$ (6.9 mg, 0.01 mmol) at reflux under N_2 for 3 h. The reaction mixture was filtered and $CHCl_3$ was added. The organic layer was washed with H_2O, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel preparative plate using hexane/CH_2Cl_2 (3:1) to give 1,2′-dithianthrene **9** as colorless crystals (12.8 mg, 50%); mp 163 °C (from CH_2Cl_2/diethylether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.30 (m, 7H), 7.36 (dd, J_1=7.6 Hz, J_2=1.6 Hz, 1H), 7.48–7.54 (m, 5H), 7.57 (d, J=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.2, 127.6, 127.8, 127.9, 128.2, 128.5, 128.6, 128.7, 128.8, 128.9, 129.1, 129.4, 134.9, 135.1, 135.4, 135.5, 135.6, 135.7, 136.2, 139.8, 140.9; IR (KBr) 3047, 1438, 751 cm^{-1}. Anal. Calcd for $C_{24}H_{14}S_4$: C, 66.94; H, 3.28. Found: C, 65.62; H, 3.90.

4.12. Oxidation of 1-tributylstannylthianthrene (5) with 3-chloroperbenzoic acid (*m*-CPBA)

To a stirred solution of 1-tributylstannylthianthrene **5** (214 mg, 0.42 mmol) in $CHCl_3$ (6 mL) was added *m*-CPBA (73.0 mg, 0.42 mmol) and the reaction mixture was stirred for 1 h at 0 °C and quenched with water. Then, $CHCl_3$ was added and the organic layer was washed with H_2O, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel using hexane/AcOEt (10:1) to give 1-tributylstannyl-10-*S*-monoxythianthrene **10** (85.1 mg, 39%) and 1-tributylstannyl-5-*S*-monoxythianthrene **11** (120 mg, 54%).

*4.12.1. 1-Tributylstannyl-10-S-monoxythianthrene (**10**).* Colorless oil; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.86 (t, J=7.2 Hz, 9H), 1.14–1.18 (m, 6H), 1.27–1.37 (m, 6H), 1.48–1.58 (m, 6H), 7.32–7.37 (m, 1H), 7.41 (td, J_1=7.6 Hz, J_2=0.9 Hz, 1H), 7.52 (td, J_1=7.6 Hz, J_2=0.9 Hz 1H), 7.61 (dd, J_1=7.6 Hz, J_2=1.2 Hz, 1H), 7.63 (dd, J_1=7.8 Hz, J_2=1.0 Hz, 1H), 7.67 (dd, J_1=7.2 Hz, J_2=1.2 Hz, 1H), 7.84 (dd, J_1=8.0 Hz, J_2=1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.1, 13.7, 27.4, 29.2, 124.1, 128.0, 128.6, 128.9, 129.0, 129.3, 129.4, 129.6, 137.0, 140.4, 141.9, 145.1; IR

(KBr) 2954, 2919, 1443, 1075, 753 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{34}OS_2Sn$: 522.1073; found: *m*/*z* 522.1053.

*4.12.2. 1-Tributylstannyl-5-S-monoxythianthrene (**11**).* Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=7.2 Hz, 9H), 1.19–1.24 (m, 6H), 1.29–1.38 (m, 6H), 1.51–1.60 (m, 6H), 7.40 (td, J_1=7.6 Hz, J_2=1.2 Hz, 1H), 7.43–7.59 (m, 4H), 7.85–7.88 (m, 1H), 7.91 (dd, J_1=7.8 Hz, J_2=1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0, 13.6, 27.3, 29.0, 124.1, 124.2, 127.6, 128.3, 128.7, 128.9, 129.5, 135.9, 137.5, 141.2, 142.3, 144.9; IR (KBr) 2955, 2925, 1442, 1081, 753 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{34}OS_2Sn$: 522.1073; found: *m*/*z* 522.1072.

4.13. Coupling reaction of 1-tributylstannyl-10-S-monoxythianthrene (10) using $Cu(OTf)_2$

To a stirred solution of 1-tributylstannyl-10-*S*-monoxythianthrene **10** (30 mg, 0.06 mmol) in DMF (0.1 mL) was added $Cu(OTf)_2$ (45.8 mg, 0.13 mmol) and the reaction mixture was stirred for 0.5 h under ambient atmosphere and quenched with water. Then, $CHCl_3$ was added and the organic layer was washed with H_2O, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel preparative plate using AcOEt/$CHCl_3$ (10:1) to give (*R*,*S*) (*S*,*R*)-1-(10-*S*-monoxythianthrene-1-yl)thianthrene-10-*S*-monoxide **12** (5.4 mg, 41%) and (*R*,*R*) (*S*,*S*)-1-(10-*S*-monoxythianthrene-1-yl)thianthrene-10-*S*-monoxide **13** (5.6 mg, 43%).

*4.13.1. (R,S) (S,R)-1-(10-S-Monoxythianthrene-1-yl)thianthrene-10-S-monoxide (**12**).* Colorless crystals; mp 291–293 °C (from CH_2Cl_2/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J_1=1.2 Hz, J_2=7.6 Hz, 1H), 7.36–7.40 (m, 2H), 7.48–7.56 (m, 3H), 7.59–7.65 (m, 2H), 7.69 (dd, J_1=1.2 Hz, J_2=7.6 Hz, 1H), 7.75–7.79 (m, 2H), 7.83 (dd, J_1=1.6 Hz, J_2=7.8 Hz, 1H), 7.75–7.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.3, 127.4, 127.5, 128.3, 128.6, 129.1, 129.3, 129.5, 129.7, 130.1, 130.2, 130.3, 130.4, 130.6, 131.4, 131.6, 131.9, 132.6, 133.2, 134.0, 135.8, 136.9, 139.9, 140.1; IR (KBr) 1558, 1540, 1028, 668, 611 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{14}O_2S_4$: 461.9877; found: *m*/*z* 461.9874.

*4.13.2. (R,R) (S,S)-1-(10-S-Monoxythianthrene-1-yl)thianthrene-10-S-monoxide (**13**).* Colorless crystals; mp 298–300 °C (from CH_2Cl_2/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 4H), 7.52–7.56 (m, 2H), 7.62–7.63 (m, 4H), 7.80 (d, *J*=7.6 Hz, 2H), 7.87–7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.3, 128.6, 129.2, 130.3, 130.6, 130.6, 131.7, 133.2, 133.3, 136.0, 140.0; IR (KBr) 1551, 1559, 1034, 754, 668 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{14}O_2S_4$: 461.9877; found: *m*/*z* 461.9853.

4.14. X-ray crystal structure analysis of 3, 4, 8, 9, and 12

The single crystals were obtained by re-crystallization from hexane/CH_2Cl_2. Diffraction data were measured with ω–2θ scan technique at 296 K on a Rigaku AFC7R diffractometer using graphite monochromated Mo Kα radiation (λ=0.7107). The data were corrected for Lorentz and polarization effects. The respective structure were solved by using direct methods (SIR 92)[16] and expanded using Fourier techniques (DIRDIF).[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985) and (1999). Crystallographic data analysis has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC No. 674016–674020, for **3**, **4**, **8**, **9**, and **12**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223 336 030; e-mail: deposite@ccdc.cam.ac.uk).

*4.14.1. 1,1′-Bithianthrene (**3**).* X-ray crystal data; empirical formula: $C_{24}H_{14}S_4$; formula weight 430.61; crystal system=triclinic; space group $P\bar{1}$ (#2); lattice parameters: *a*=10.209 (4) Å; *b*=21.182 (6) Å, *c*=10.155 (4) Å; α=97.65 (3)°, β=111.03 (2), γ=97.17 (3); *V*=1995 (1) $Å^3$; *Z*=4; μ (Mo Kα)=4.83 cm^{-1}; 12,221 reflections measured, 505 unique (R_{int}=0.047); final *R* value 0.058. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.26 and −0.27 $e^-/Å^3$, Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 674017.

*4.14.2. 1,1′-Dithianthrenyl ether (**4**).* X-ray crystal data; empirical formula: $C_{24}H_{14}OS_4$; formula weight 446.61; crystal system=triclinic; space group $P\bar{1}$ (#2); lattice parameters: *a*=11.290 (3) Å; *b*=12.198 (2) Å, *c*=8.240 (2) Å; α=92.70 (2)°, β=93.33 (2), γ=117.65 (3); *V*=1000.0 (5) $Å^3$; *Z*=2; μ (Mo Kα)=4.89 cm^{-1}; 6123 reflections measured, 318 unique (R_{int}=0.039); final *R* value 0.048. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.26 and −0.27 $e^-/Å^3$, Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 674016.

*4.14.3. 2,2′-Bithianthrene (**8**).* X-ray crystal data; empirical formula: $C_{24}H_{14}S_4$; formula weight 430.61; crystal system=monoclinic; space group $P\bar{1}$ (#14); lattice parameters: *a*=11.118 (5) Å; *b*=6.262 (3) Å, *c*=14.400 (2) Å; β=106.65 (2); *V*=960.5 (5) $Å^3$; *Z*=4; μ (Mo Kα)=10.04 cm^{-1}; 3188 reflections measured, 127 unique (R_{int}=0.037); final *R* value 0.051. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.23 and −0.16 $e^-/Å^3$, Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 674019.

*4.14.4. 1,2′-Dithianthrene (**9**).* X-ray crystal data; empirical formula: $C_{24}H_{14}S_4$; formula weight 430.61; crystal system=triclinic; space group $P\bar{1}$ (#2); lattice parameters: *a*=10.714 (2) Å; *b*=12.588 (3) Å, *c*=7.775 (1) Å; α=104.14 (2)°, β=102.30 (1), γ=92.02 (2); V=989.2 (3) $Å^3$; *Z*=2; μ (MoKα)=4.88 cm^{-1}; 6053 reflections measured, 253 unique (R_{int}=0.035); final *R* value 0.051. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.29 and −0.18 $e^-/Å^3$, Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 674020.

*4.14.5. (R,S) (S,R)-1-(10-S-Monoxythianthrene-1-yl)thianthrene-10-S-monoxide (**12**).* X-ray crystal data; empirical formula: $C_{24}H_{14}O_2S_4$; formula weight 462.61; crystal system=monoclinic; space group C2/c(#15); lattice parameters: *a*=36.36 (2) Å; *b*=7.682 (3) Å, *c*=15.68 (1) Å; β=107.18 (1), V=4184 (5) $Å^3$; *Z*=7; μ (Mo Kα)=4.14 cm^{-1}; 6630 reflections measured, 271 unique (R_{int}=0.040); final *R* value 0.053. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.57 and −0.25 $e^-/Å^3$, Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 674018.

Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.04.057.

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