

# Synthesis of 1- and 2-substituted thianthrenes

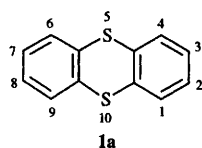
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Lithiation of thianthrene at C-1 allows the synthesis of various 1-substituted thianthrenes for example thianthren-1-ylboronic acid and 1-tributylstannylthianthrene, which undergo palladium-catalysed couplings with aryl halides. 2-Bromothianthrene provides an entry to 2-substituted thianthrenes *via* lithium-halogen exchange then reaction of 2-lithiothianthrene with electrophiles including formation of the 2-boronic acid and 2-tributylstannylthianthrene which were coupled to aryl halides.

## Introduction

Thianthrene **1a** can be easily oxidised to a radical cation chemically,<sup>2</sup> electrochemically<sup>3</sup> or photochemically.<sup>4</sup> Further



oxidation to a dication has also been reported.<sup>5</sup> The tetrathiafulvalene (TTF) system similarly undergoes easy one-electron oxidation; it is this property which makes TTF and substituted analogues popular components for constructing 'organic metals'.<sup>6</sup> With the eventual aim being to examine to what extent thianthrenes too might be useful for the formation of conducting substances, we have looked first at ways in which the heterocycle can be manipulated and derivatives of thianthrene can be synthesised efficiently.

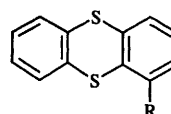
It was known that a limited range of electrophilic substitutions<sup>1</sup> allow access to some 2-mono-substituted thianthrenes, though there is a tendency for 2,7- or sometimes 2,8-disubstitution. 2-Bromothianthrene<sup>7</sup> can be produced relatively easily, though not efficiently, by direct substitution and is an obvious candidate for the further elaboration of 2-mono-substituted thianthrenes. Regioselective lithiation adjacent to ring sulfur has been long known,<sup>8</sup> and was indeed one of the earliest examples of aromatic-CH deprotonation using an alkylolithium: it was employed to synthesise thianthren-1-ylcarboxylic acid<sup>8,9</sup> **1b** and thianthren-1-ylboronic acid<sup>9</sup> **1c**. Gilman used butyllithium and found that the deprotonation required either 24 h of reflux or 40 h at room temperature; no use of thianthren-1-ylolithium has been reported since.

## Results and discussion

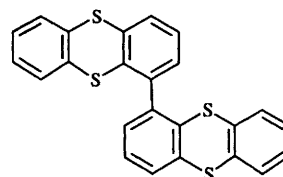
We find that thianthrene can be readily deprotonated in a few minutes by treatment with *tert*-butyllithium at  $-78\text{ }^{\circ}\text{C}$ , the lithiation being completed by bringing the solution briefly to room temperature. The lithiated species thus prepared was converted into the known acids **1b** and **1c**, into 1-bromothianthrene **1d** and 1-iodothianthrene **1e** by reaction with bromine, and iodoperfluorohexane,<sup>10</sup> respectively, and into 1-methylthianthrene **1f** with iodomethane. The 1-tributylstannyl derivative **1g** resulted from reaction with chlorotributylstannane.

Addition of the lithiated heterocycle to benzaldehyde and benzophenone produced **1h** and **1i**, respectively, and the use of dimethylformamide gave the aldehyde **1j**.

The utility of thianthren-1-ylboronic acid in palladium(0) catalysed couplings was demonstrated by its coupling<sup>11</sup> with iodobenzene to give 1-phenylthianthrene **1k** and with 1-

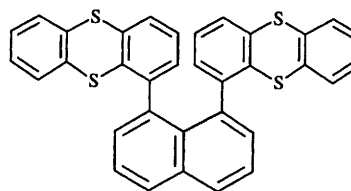


<b>1</b>	R	<b>1</b>	R
<b>b</b>	CO <sub>2</sub> H	<b>h</b>	CH(OH)Ph
<b>c</b>	B(OH) <sub>2</sub>	<b>i</b>	C(OH)Ph <sub>2</sub>
<b>d</b>	Br	<b>j</b>	CHO
<b>e</b>	I	<b>k</b>	Ph
<b>f</b>	Me		
<b>g</b>	SnBu <sub>3</sub>		

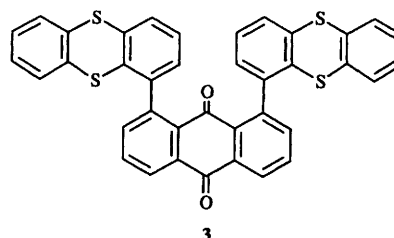


**11**

iodothianthrene giving **11**. The coupling of two mol equiv. of the boronic acid with 1,8-diiodonaphthalene produced **2**. We showed that both thianthren-1-ylboronic acid and 1-tributylstannylthianthrene will couple<sup>12</sup> with displacement of both halogen atoms in 1,8-diiodoanthraquinone,<sup>13</sup> giving **3**.

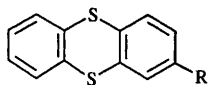


**2**

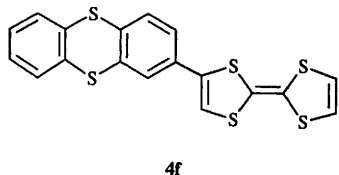


**3**

The Grignard derivative from 2-bromothianthrene did not react in a straightforward manner with benzaldehyde, a mixture of thianthrene, the anticipated alcohol **4a** and its corresponding



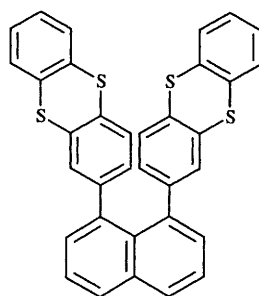
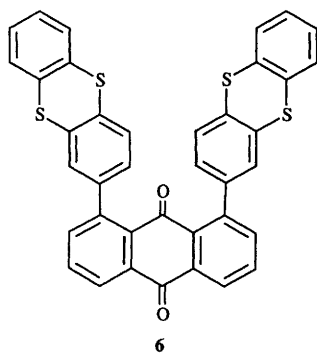
<b>4</b>	R
<b>a</b>	CH(OH)Ph
<b>b</b>	CO.Ph
<b>c</b>	B(OH) <sub>2</sub>
<b>d</b>	SnBu <sub>3</sub>
<b>e</b>	CHO



ketone **4b** was obtained. Lithiation by reaction of 2-bromothianthrene with butyllithium proceeded smoothly, however, as exemplified by the subsequent reaction of thianthren-2-yllithium with trimethyl borate, producing the known **4c**<sup>14</sup> and with tributyltin chloride giving **4d**.

No isomerisation to the more stable 1-lithio-isomer was observed when a solution containing the 2-lithiated thianthrene was maintained at  $-78^{\circ}\text{C}$ , however, if the solution was brought to room temperature for 30 min isomerisation did occur. For example, quenching with *N,N*-dimethylformamide (DMF) under the former conditions gave 2-formylthianthrene **4e**, exclusively, in 72% yield, while following a regime including 30 min at room temperature before quenching, gave a mixture of thianthren-2-yl- and thianthren-1-ylcarbaldehydes in a ratio of 5:2.

The 2-bromide was also coupled with tributylstannyl-tetrathiafulvalene<sup>15</sup> producing **4f**. In analogy with the couplings carried out in the thianthren-1-yl series, the coupling of two mol equiv. of thianthren-2-ylboronic acid and two mol equiv. of 2-tributylstannylthianthrene, with 1,8-diiodonaphthalene and 1,8-diiodoanthraquinone, respectively, produced **5** and **6**. We shall be reporting separately on some of the interesting electrochemical properties of compounds such as

**5****6**

**2, 3, 5** and **6** which have two thianthrene rings held in proximity by a pillaring aromatic unit.

## Experimental

### General

Thin layer chromatography was carried out on Merck silica gel F<sub>254</sub> 0.255 mm plates, and spots were visualised, where appropriate, by UV fluorescence at 254 or 297 nm or by spraying with phosphomolybdic acid in ethanol (PMA). Flash column chromatography was performed using Merck Kieselgel 60 (230–400 mesh) silica. Tetrahydrofuran was dried by distillation from potassium-benzophenone; diethyl ether (referred to as ether) was pre-dried over calcium chloride before refluxing over sodium-benzophenone; toluene and dichloromethane were dried by distillation from calcium hydride; *N,N*-dimethylformamide was dried over 4 Å molecular sieves. Solutions of lithium diisopropylamide monotetrahydrofuran, butyl- and *tert*-butyl-lithium and methylmagnesium bromide were purchased from the Aldrich chemical company and used without titration. All other chemicals were purified using standard procedures as required. Organic solutions were dried over magnesium sulfate. UV spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer, path length 1 cm. IR spectra were recorded on an ATI Mattson Genesis Series FTIR spectrometer. <sup>1</sup>H NMR spectra were recorded on a Varian AC 300E NMR spectrometer operating at 300 MHz or a Varian Gemini 200 spectrometer operating at 200 MHz. All chemical shifts are reported in parts per million downfield from tetramethylsilane. Peak multiplicities are denoted by s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) or by a combination of these, e.g. dd (double doublet), with coupling constants (*J*) given in Hz. <sup>13</sup>C NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 75 MHz. Mass spectra were recorded on a Fisons VG Trio 2000 for electron impact (EI) and chemical ionisation (CI) conditions. Fast atom bombardment (FAB) spectra and accurate mass measurements were recorded on a Kratos Concept spectrometer. Melting points were recorded on a Reichert heated stage microscope and are uncorrected.

### 1-Mono-substituted thianthrenes

**Lithiation of thianthrene; 1-lithiothianthrene.** To a stirred suspension of thianthrene **1a** in tetrahydrofuran at  $-78^{\circ}\text{C}$  under an atmosphere of argon was added *tert*-butyllithium. After addition was complete the mixture was allowed to warm to room temperature. The resulting red solution was stirred for 30 min before being re-cooled to  $-78^{\circ}\text{C}$  for the addition of electrophiles. Reactions were carried out on one of three scales: *Scale A* [thianthrene (1.00 g, 4.63 mmol) in THF (20 cm<sup>3</sup>) with *tert*-butyllithium (3.00 cm<sup>3</sup> of a 1.7 M solution in pentane, 5.1 mmol)], *Scale B* [thianthrene (2.00 g, 9.26 mmol) in THF (40 cm<sup>3</sup>) and *tert*-butyllithium (8.00 cm<sup>3</sup> of a 1.7 M solution in pentane, 13.6 mmol)], or *Scale C* [thianthrene (0.5 g, 2.3 mmol) in THF (10 cm<sup>3</sup>) and *tert*-butyllithium (2.00 cm<sup>3</sup> of a 1.7 M solution in pentane, 3.4 mmol)]. For individual work-up procedures see below.

**Thianthren-1-ylcarboxylic acid 1b.** Through a solution of thianthren-1-yllithium (*Scale A*) was bubbled carbon dioxide for 10 min before allowing it to warm to room temperature. Aqueous hydrochloric acid (3 M) was added and tetrahydrofuran evaporated leaving a yellow solid which was washed with water, dried and recrystallised from toluene to give the acid **1b** as a pale yellow-green solid (420 mg, 35%), mp  $224\text{--}225^{\circ}\text{C}$  (lit.,<sup>9</sup>  $224\text{--}225^{\circ}\text{C}$ );  $\nu_{\text{max}}$ (film)/cm<sup>-1</sup> 2959, 1685 (C=O), 1443, 1414, 1255, 1155, 1038, 903 and 748;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm 248 (log  $\epsilon$  4.37), 264 (4.39) and 336 (3.28);  $\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>) 7.39–7.65 (5 H, m, Ar-H), 7.83 (1 H, dd, *J* 7.8 and 1.4, 4-H) and 8.00 (1 H, dd, *J* 7.7 and 1.4, 2-H);  $\delta_{\text{C}}$ (75 MHz, CDCl<sub>3</sub>) 206.00, 167.20, 139.62, 136.28, 135.91, 135.82, 132.96, 130.09, 129.54, 129.12,

129.05, 128.81 and 127.77;  $m/z$  (CI) 278 ( $\text{MNH}_4^+$ , 100%) and 260 ( $\text{MH}^+$ , 40).

**Thianthren-1-ylboronic acid 1c.** To thianthren-1-yllithium (*Scale B*) was added slowly trimethyl borate (6.30  $\text{cm}^3$ , 55.5 mmol). After 15 h at 20 °C aqueous hydrochloric acid (3 M; 25  $\text{cm}^3$ ) was added and product extracted into ether. The ethereal phase was washed with water and brine, dried and the solvent evaporated leaving a white foam which was crystallised from benzene to give thianthren-1-ylboronic acid **1c** as a white solid (1.36 g, 56%), mp 134–137 °C (lit.,<sup>9</sup> 147–148 °C).

**1-Bromothianthrene 1d.** To thianthren-1-yllithium (*Scale B*), bromine (0.70  $\text{cm}^3$ , 2.18 g, 13.7 mmol) was added dropwise and the solution was allowed to warm to room temperature; aqueous saturated ammonium chloride was added, tetrahydrofuran evaporated, and the residue extracted into ether which was then washed with water, brine and aqueous sodium thiosulfate (1 M; 50  $\text{cm}^3$ ), dried and evaporated leaving a residue which on flash chromatography on silica gel with light petroleum (bp 40–60 °C) gave 1-bromothianthrene **1d** as a white solid (1.60 g, 59%), mp 140–143 °C (lit.,<sup>8</sup> 145 °C);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3055, 1544, 1443, 1428, 1394, 1253, 1190, 1111, 1077, 1034, 776, 748 and 700;  $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$  248 (log  $\epsilon$  4.35) and 262 (4.52);  $\delta_{\text{H}}(200 \text{ MHz, CDCl}_3)$  7.10 (1 H, t,  $J$  7.8, 3-H), 7.21–7.35 (2 H, m, Ar-H) and 7.40–7.59 (4 H, m, Ar-H);  $m/z$  (EI) 294, 296 ( $\text{M}^+$ , 82, 90%), 215 (100), 171 (63) and 139 (27).

**1-Iodothianthrene 1e.** To thianthren-1-yllithium (*Scale A*) was added perfluorohexyl iodide (1.50  $\text{cm}^3$ , 3.09 g, 6.94 mmol) dropwise, the solution was allowed to warm to room temperature and then quenched with aqueous saturated ammonium chloride. The solvent was evaporated and the residue extracted into ether which, after washing with water, brine and aqueous sodium thiosulfate (1 M; 25  $\text{cm}^3$ ), was dried and evaporated. Flash chromatography on silica gel with light petroleum (bp 40–60 °C) gave 1-iodothianthrene **1e** as a white solid (744 mg, 47%), mp 95–96 °C (Found: C, 42.0; H, 1.95%;  $\text{M}^+$ , 341.9028.  $\text{C}_{12}\text{H}_7\text{IS}_2$  requires C, 42.1; H, 2.1%;  $M$ , 341.9034);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3050, 2359, 1538, 1449, 1419, 1387, 1110, 1031, 772 and 747;  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  260 (log  $\epsilon$  4.38);  $\delta_{\text{H}}(200 \text{ MHz, CDCl}_3)$  6.94 (1 H, dd,  $J$  7.8 and 7.8, 3-H), 7.28–7.40 (2 H, m, Ar-H), 7.50–7.64 (3 H, m, Ar-H) and 7.81 (1 H, dd,  $J$  7.8 and 1.1, 2-H);  $\delta_{\text{C}}(75 \text{ MHz, CDCl}_3)$  140.60, 138.25, 135.92, 135.74, 135.30, 128.99, 128.82, 128.77, 128.20, 128.18, 127.92 and 98.46;  $m/z$  (EI) 342 ( $\text{M}^+$ , 15), 215 (40), 171 (100), 139 (37), 127 (70) and 69 (80).

**1-Methylthianthrene 1f.** To thianthren-1-yllithium (*Scale A*) was added iodomethane (1.15  $\text{cm}^3$ , 18.5 mmol) and the reaction mixture allowed to warm to room temperature overnight. Evaporation of solvent left a residue which was extracted into dichloromethane; the extract was washed with water then brine, dried and evaporated. Chromatography on silica gel with hexane yielded 1-methylthianthrene **1f** as a waxy white solid (400 mg, 38%), mp 48–52 °C (Found:  $\text{M}^+$ , 230.0229.  $\text{C}_{13}\text{H}_{10}\text{S}_2$  requires  $M$ , 230.0224);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3054, 2919, 1560, 1447, 1399, 1252, 1181, 1115, 1056, 1031, 773, 748 and 711;  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  244 (log  $\epsilon$  4.28), 260 (4.58) and 284 (3.43);  $\delta_{\text{H}}(200 \text{ MHz, CDCl}_3)$  2.47 (3 H, s, Ar-CH<sub>3</sub>) and 7.10–7.54 (7 H, m, Ar-H);  $m/z$  (EI) 230 ( $\text{M}^+$ , 100%) and 197 (56).

**1-Tributylstannylthianthrene 1g.** To thianthren-1-yllithium (*Scale B*), tributyltin chloride (2.80  $\text{cm}^3$ , 10.4 mmol) was added slowly and the resulting colourless solution left to warm to room temperature overnight. Aqueous saturated ammonium chloride was added, tetrahydrofuran evaporated and the aqueous slurry extracted with ether. The ethereal phase was washed with water and brine, dried and evaporated leaving an oil, flash chromatography of which on silica gel with light petroleum (bp 40–60 °C) yielded 1-tributylstannylthianthrene **1g** as a clear colourless oil (2.59 g, 55%) (Found:  $\text{M}^+$ , 506.1121.  $\text{C}_{24}\text{H}_{34}\text{S}_2^{120}\text{Sn}$  requires  $M$ , 506.1124);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3042, 2955, 2924, 2869, 1449, 1373, 1109, 1072, 775 and 747;  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  260 (log  $\epsilon$  4.72);  $\delta_{\text{H}}(300 \text{ MHz, CDCl}_3)$  0.80–

1.70 (27 H, m,  $\text{SnBu}_3$ ) and 7.20–7.60 (7 H, m, Ar-H);  $\delta_{\text{C}}(75 \text{ MHz, CDCl}_3)$  144.30, 143.43, 136.60, 136.32, 135.79, 135.29, 128.98, 128.63, 128.53, 127.62, 127.54, 127.01, 29.14, 27.82, 13.67 and 11.18;  $m/z$  (EI) 506 ( $^{120}\text{M}^+$ , 5%), 449 ( $\text{M}^+ - \text{Bu}$ , 40), 393 (15), 335 (30), 216 (50), 184 (100) and 139 (80).

**Thianthren-1-ylphenylmethanol 1h.** To thianthren-1-yllithium (*Scale C*) was added benzaldehyde (1.00  $\text{cm}^3$ , 9.84 mmol) and the reaction mixture was stirred at –78 °C for 1 h, room temperature for 2 h and then quenched with aqueous hydrochloric acid (3 M; 10  $\text{cm}^3$ ). Dichloromethane was added and the lower aqueous phase separated, washed with brine, dried ( $\text{MgSO}_4$ ) and the solvent removed *in vacuo*. Purification by flash column chromatography on silica gel with toluene as the eluent gave thianthren-1-ylphenylmethanol **1h** as a white foam (480 mg, 64%) (Found:  $\text{M}^+$ , 322.0482.  $\text{C}_{19}\text{H}_{14}\text{OS}_2$  requires  $M$ , 322.0486);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3366br (OH), 3059, 1449, 1407, 1173, 1113, 1030, 748 and 699;  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  246sh (log  $\epsilon$  4.24) and 260 (4.48);  $\delta_{\text{H}}(200 \text{ MHz, CDCl}_3)$  2.83 (1 H, d,  $J$  4.3, C–H), 6.37 (1 H, d,  $J$  4.3, C–OH) and 7.20–7.57 (12 H, m, Ar-H);  $\delta_{\text{C}}(75 \text{ MHz, CDCl}_3)$  143.16, 142.41, 136.58, 136.36, 135.14, 134.42, 129.10, 128.72, 128.66, 128.31, 128.01, 127.90, 127.72, 127.56, 127.16, 126.09 and 73.57;  $m/z$  (CI) 323 ( $\text{MH}^+$ , 12%), 322 (48), 305 (100);  $m/z$  (EI) 322 ( $\text{M}^+$ , 40%), 84 (45) and 49 (100).

**Diphenylthianthren-1-ylmethanol 1i.** To thianthren-1-yllithium (*Scale C*) was added a solution of benzophenone (2.11 g, 11.6 mmol) in tetrahydrofuran (10  $\text{cm}^3$ ) and the reaction mixture allowed to warm to room temperature overnight. Aqueous hydrochloric acid (3 M; 10  $\text{cm}^3$ ) was added, tetrahydrofuran evaporated and the aqueous slurry extracted with ethyl acetate. The organic phase was washed with water and brine, dried ( $\text{MgSO}_4$ ) and evaporated. Flash chromatography on silica gel eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:9) gave thianthren-1-ylidiphenylmethanol **1i** as a white solid (770 mg, 84%), mp 199 °C (Found: C, 75.0; H, 4.4%;  $\text{M}^+$ , 398.0793.  $\text{C}_{25}\text{H}_{18}\text{OS}_2$  requires C, 75.4; H, 4.5%;  $M$ , 398.0799);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3466, 3056, 1447, 1397, 1163, 1112, 1032, 751 and 701;  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  260 (log  $\epsilon$  4.33);  $\delta_{\text{H}}(200 \text{ MHz, CDCl}_3)$  5.48 (1 H, s, OH), 6.62 (1 H, dd,  $J$  7.8 and 1.2, 2-H), 7.08 (1 H, t,  $J$  7.8, 3-H) and 7.18–7.60 (15 H, m, Ar-H);  $m/z$  (EI) 398 ( $\text{M}^+$ , 100%), 381 (25), 182 (25) and 105 (50).

**Thianthren-1-ylcarbaldehyde 1j.** To thianthren-1-yllithium (*Scale C*) was added a solution of dimethylformamide (1.00  $\text{cm}^3$ , 12.9 mmol) in tetrahydrofuran (10  $\text{cm}^3$ ) and the reaction mixture was stirred at –78 °C for 1 h, room temperature for 2 h and then quenched with aqueous hydrochloric acid (3 M; 10  $\text{cm}^3$ ). Dichloromethane was added and the lower aqueous phase separated. The organic layer was washed with brine, dried ( $\text{MgSO}_4$ ) and the solvent removed *in vacuo*. Flash chromatography on silica gel eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:9), gave thianthren-1-ylcarbaldehyde **1j** as a clear yellow oil (270 mg, 48%) (Found:  $\text{M}^+$ , 244.0019.  $\text{C}_{13}\text{H}_8\text{OS}_2$  requires  $M$ , 244.0017);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3055, 2927, 2851, 1689, 1572, 1451, 1373, 1234 and 750;  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  252 (log  $\epsilon$  4.38), 286 (3.71) and 346 (3.10);  $\delta_{\text{H}}(200 \text{ MHz, CDCl}_3)$  7.23–7.34 (2 H, m, Ar-H), 7.39 (1 H, t,  $J$  7.7, 3-H), 7.49–7.59 (2 H, m, Ar-H), 7.72 (1 H, dd,  $J$  7.7 and 1.4, 4-H), 7.84 (1 H, dd,  $J$  7.7 and 1.4, 2-H) and 10.58 (1 H, s, CH=O);  $m/z$  (EI) 244 ( $\text{M}^+$ , 100%).

**1-Phenylthianthrene 1k.** Iodobenzene (52 mg, 0.256 mmol) and tetrakis(triphenylphosphine)palladium(0) (88 mg, 0.077 mmol) were stirred together in dimethoxyethane (15  $\text{cm}^3$ ) under nitrogen for 10 min at room temperature. Thianthren-1-ylboronic acid (100 mg, 0.385 mmol) was added, immediately followed by aqueous sodium hydrogen carbonate (1 M; 1.60  $\text{cm}^3$ , 1.6 mmol). The reaction mixture was heated at reflux for 4 h, with vigorous stirring under nitrogen. Solvent was evaporated, water added and the residue was extracted with ether. The ethereal extract was washed with water and brine then dried and evaporated, the product then being purified by flash chromatography on silica gel with ethyl acetate–hexane



(1:9) to yield 1-phenylthianthrene **1k** as a clear colourless oil (47 mg, 63%) (Found:  $M^+$ , 292.0381.  $C_{18}H_{12}S_2$  requires  $M$ , 292.0380);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3054, 3027, 2924, 1442, 1391, 790, 749, 700 and 665;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  262 (log  $\epsilon$  4.31);  $\delta_{\text{H}}(200 \text{ MHz, CDCl}_3)$  7.13–7.60 (12 H, m, Ar-H);  $\delta_{\text{C}}(75 \text{ MHz, CDCl}_3)$  143.01, 140.71, 136.84, 136.47, 135.89, 135.55, 134.47, 134.08, 129.96, 129.80, 129.38, 129.03, 128.75, 128.68, 128.35, 128.29, 128.06 and 127.59;  $m/z$  (CI) 310 ( $\text{MNH}_4^+$ , 30%) and 292 ( $\text{MH}^+$ , 100).

**1-(Thianthren-1-yl)thianthrene 1l.** 1-Iodothianthrene (50 mg, 0.146 mmol) and tetrakis(triphenylphosphine)palladium(0) (5 mg, 0.00433 mmol) were stirred together in dimethoxyethane (10  $\text{cm}^3$ ) under a nitrogen atmosphere for 10 min at room temperature. Thianthrene-1-boronic acid (76 mg, 0.292 mmol) was then added followed by aqueous sodium hydrogen carbonate (1 M; 0.5  $\text{cm}^3$ , 0.5 mmol). After heating at reflux for 4 h, the solvent was evaporated, water added and the product extracted into dichloromethane. The organic extract was washed with brine, dried and the solvent evaporated. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:9), to yield 1-(thianthren-1-yl)thianthrene **1l** as a white solid (51 mg, 81%), mp 249–251 °C (Found  $M^+$ , 429.9981.  $C_{24}H_{14}S_4$  requires  $M$ , 429.9978);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  2922, 2361, 1552, 1432, 1392, 1112, 784 and 748;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  264 (log  $\epsilon$  4.57);  $\delta_{\text{H}}(300 \text{ MHz, CDCl}_3)$  7.15–7.31 (8 H, m, Ar-H), 7.37 (2 H, dd,  $J$  7.6 and 7.7, 3 and 3'-H), 7.56 (2 H, dd,  $J$  7.6 and 1.3, 2 and 2'-H) and 7.63 (2 H, dd,  $J$  7.7 and 1.3, 4 and 4'-H);  $\delta_{\text{C}}(75 \text{ MHz, CDCl}_3)$  140.16, 136.10, 135.92, 135.80, 135.61, 129.38, 129.25, 128.54, 128.47, 127.78, 127.56 and 127.26;  $m/z$  (EI) 430 ( $M^+$ , 100%), 396 (25), 364 (30) and 49 (95).

**1,8-Bis(thianthren-1-yl)naphthalene 2.** 1,8-Diiodonaphthalene (412 mg, 1.09 mmol) and tetrakis(triphenylphosphine)palladium(0) (38 mg, 0.0326 mmol) were stirred together in dimethoxyethane (10  $\text{cm}^3$ ) under argon for 10 min at room temperature. A solution of thianthrene-1-boronic acid (1.693 g, 6.51 mmol) in dimethoxyethane (10  $\text{cm}^3$ ) was then added, followed by aqueous sodium carbonate (2 M; 2.17  $\text{cm}^3$ , 4.34 mmol). After heating at reflux for 24 h, the solvent was evaporated, water added and the product extracted into dichloromethane (2  $\times$  15  $\text{cm}^3$ ). The organic phase was washed with brine, dried and the solvent evaporated leaving a tan foam, flash chromatography of which on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (5:95), yielded 1,8-bis(thianthren-1-yl)naphthalene **2** as a white solid (153 mg, 25%), mp 243–244 °C (Found: C, 73.3; H, 3.5; S, 23.0.  $C_{34}H_{20}S_4$  requires C, 73.3; H, 3.6; S, 23.0%);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3051, 2924, 1449, 1105 and 748;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  242 (log  $\epsilon$  4.57), 262 (4.64) and 290 (4.15);  $\delta_{\text{H}}(300 \text{ MHz, CDCl}_3)$  5.26 (2 H, t,  $J$  7.6, 2  $\times$  thianthren-3-yl-H), 6.80 (4 H, m, Ar-H), 7.22–7.40 (8 H, m, Ar-H), 7.52 (2 H, dd,  $J$  7.55 and 1.3, Ar-H), 7.61 (2 H, dd,  $J$  7.1 and 8.1, Ar-H) and 8.11 (2 H, dd,  $J$  8.2 and 1.1, Ar-H);  $\delta_{\text{C}}(75 \text{ MHz, CDCl}_3)$  142.02, 137.57, 136.92, 135.78, 135.22, 134.13, 133.22, 130.91, 129.63, 129.56, 128.76, 128.66, 127.66, 127.57, 127.13, 125.38 and 125.03;  $m/z$  (EI) 556 ( $M^+$ , 45%), 57 (100).

**1,8-Bis(thianthren-1-yl)-9,10-anthraquinone 3.** This compound was prepared by two methods, which, for comparison, are both described here.

*Method A.*—1,8-Diiodoanthraquinone (0.316 g, 0.687 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.048 g, 0.0412 mmol) were stirred together in dimethoxyethane (10  $\text{cm}^3$ ) under nitrogen for 10 min at room temperature. Thianthrene-1-boronic acid (1.786 g, 6.87 mmol) in dimethoxyethane (10  $\text{cm}^3$ ) was added then aqueous sodium carbonate (2 M; 1.37  $\text{cm}^3$ , 2.75 mmol). After heating at reflux for 24 h, the solvent was evaporated, water added and the residue extracted with dichloromethane which was washed with brine, dried and evaporated leaving a brown solid, which was purified by flash chromatography on silica gel, eluting with toluene–light

petroleum (bp 40–60 °C) (80:20), to yield 1,8-bis(thianthren-1-yl)-9,10-anthraquinone **3** as an orange–yellow solid (0.212 g, 49%), mp > 230 °C decomp. (Found: C, 71.3; H, 3.2; S, 19.7.  $C_{38}H_{20}O_2S_4$  requires C, 71.7; H, 3.2; S, 20.0%);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3056, 2922, 1675, 1574, 1325, 1251 and 742;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  260 (log  $\epsilon$  4.89) and 332 (3.73);  $\delta_{\text{H}}(300 \text{ MHz, CDCl}_3)$  7.01–7.59 (16 H, m, Ar-H), 7.83 (2 H, t,  $J$  7.7, Ar-H) and 8.48 (2 H, dd,  $J$  7.8 and 1.2, Ar-H);  $\delta_{\text{C}}(75 \text{ MHz, CDCl}_3)$  183.83, 183.64, 140.91, 140.66, 137.36, 136.07, 135.44, 134.64, 134.01, 133.89, 133.11, 132.51, 128.59, 128.42, 128.17, 127.73, 127.67, 127.42, 127.30 and 127.09;  $m/z$  (CI) 654 ( $\text{MNH}_4^+$ , 100%) and 637 ( $\text{MH}^+$ , 20).

*Method B.*—A solution of 1-tributylstannylthianthrene (550 mg, 1.09 mmol), 1,8-diiodoanthraquinone (100 mg, 0.217 mmol), bis(triphenylphosphine)palladium(II) chloride (30 mg, 0.0427 mmol) and copper(I) iodide (62 mg, 0.326 mmol) in dimethylformamide (10  $\text{cm}^3$ ) was stirred at room temperature under an atmosphere of argon for 2 h. The reaction mixture was diluted with ether (100  $\text{cm}^3$ ), filtered through a pad of Celite, washed with water and brine, dried and solvent removed *in vacuo*. Chromatography on silica gel with toluene–light petroleum (bp 40–60 °C) (80:20) yielded **3** (77 mg, 56%), identical with that prepared in *Method A*.

## 2-Mono-substituted thianthrenes

**2-Benzoylthianthrene 4b and phenylthianthren-2-ylmethanol 4a.** A solution of 2-bromothianthrene<sup>7</sup> (587 mg, 1.99 mmol) in tetrahydrofuran (20  $\text{cm}^3$ ) was added to magnesium turnings (72 mg, 2.98 mmol) under nitrogen. After stirring and heating at reflux for 1 h the mixture was cooled to 0 °C. Benzaldehyde (0.20  $\text{cm}^3$ , 1.99 mmol) was added and the reaction mixture heated at reflux for 30 min before being poured on to ice, acidified with aqueous hydrochloric acid and extracted with dichloromethane. The extract was washed with water, dried and evaporated leaving a clear lime coloured oil. Flash chromatography on silica gel with toluene yielded firstly thianthrene (107 mg, 25%), then 2-benzoylthianthrene **4b** as white crystals (131 mg, 21%), mp 141–142 °C (Found:  $M^+$ , 320.0325.  $C_{19}H_{12}OS_2$  requires  $M$ , 320.0330);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3056, 1658 (C=O), 1446, 1279 and 729;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  252 (log  $\epsilon$  4.48) and 336 (3.50);  $\delta_{\text{H}}(200 \text{ MHz, CDCl}_3)$  7.24–7.31 (2 H, m, Ar-H), 7.43–7.80 (9 H, m, Ar-H) and 7.87–7.91 (1 H, d,  $J$  2.2, Ar-H);  $m/z$  (CI) 338 ( $\text{MNH}_4^+$ , 20%) and 321 ( $\text{MH}^+$ , 100);  $m/z$  (EI) 320 ( $M^+$ , 20%), 105 (100) and 77 (72), and lastly phenylthianthren-2-ylmethanol **4a** as a clear lime-coloured oil (177 mg, 28%) (Found:  $M^+$ , 322.0486.  $C_{19}H_{14}OS_2$  requires  $M$  322.0486);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3358br (OH), 3059, 1447, 1024 and 749;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  260 (log  $\epsilon$  4.61);  $\delta_{\text{H}}(200 \text{ MHz, CDCl}_3)$  2.65 (1 H, d,  $J$  4.0, C–H), 5.74 (1 H, d,  $J$  4.0, C–OH) and 7.15–7.53 (12 H, m, Ar-H);  $m/z$  (CI) 305 ( $\text{MH}^+ - \text{H}_2\text{O}$ , 100%),  $m/z$  (EI) 322 ( $M^+$ , 15%), 84 (70) and 49 (100).

**Metal–halogen exchange of 2-bromothianthrene; 2-lithiothianthrene.** To a stirred solution of 2-bromothianthrene (1.00 g, 3.39 mmol) in tetrahydrofuran (20  $\text{cm}^3$ ) at –78 °C under argon was added butyllithium (1.6 M solution in hexane; 2.54  $\text{cm}^3$ , 4.06 mmol). The solution was maintained at –78 °C for 1 h before addition of the electrophile.

**Thianthren-2-ylboronic acid 4c.** Trimethyl borate (1.50  $\text{cm}^3$ , 13.2 mmol) was added dropwise to 2-lithiothianthrene and the resulting solution allowed to warm to room temperature overnight, aqueous hydrochloric acid (3 M; 15  $\text{cm}^3$ ) added and the whole extracted with ether. The product was then extracted into aqueous sodium hydroxide (10%; 6  $\times$  15  $\text{cm}^3$ ) then the aqueous layer was acidified and the resulting white precipitate collected and dried to give thianthren-2-ylboronic acid (364 mg, 41%), mp *ca.* 145 °C, after recrystallisation mp 215–216 °C (lit.,<sup>11</sup> 169 °C, then 214–215 °C).

**2-Tributylstannylthianthrene 4d.** Tributyltin chloride (1.10  $\text{cm}^3$ , 4.08 mmol) was added dropwise to 2-lithiothianthrene and the resulting solution was allowed to warm to room temperature overnight and was then quenched with saturated

aqueous ammonium chloride. Extraction with ether, followed by washing with water, brine, drying and evaporation gave the crude product, which was dissolved in warm hexane (40 cm<sup>3</sup>) and then washed with acetonitrile (4 × 20 cm<sup>3</sup>), evaporation producing 2-tributylstannylthianthrene **4d** as a clear colourless oil (591 mg, 35%) (Found: M<sup>+</sup>, 506.1124. C<sub>24</sub>H<sub>34</sub>S<sub>2</sub><sup>120</sup>Sn requires M, 506.1124); ν<sub>max</sub>(neat)/cm<sup>-1</sup> 3056, 2955, 2925, 2869, 2359, 1443, 1108, 811 and 747; λ<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/nm (log ε 4.61); δ<sub>H</sub>(300 MHz; CDCl<sub>3</sub>) 0.85–1.70 (27 H, m, SnBu<sub>3</sub>) and 7.22–7.67 (7 H, m, Ar-H); δ<sub>C</sub>(75 MHz, CDCl<sub>3</sub>) 141.89, 136.05, 135.84, 135.52, 135.15, 134.90, 128.78, 128.73, 128.11, 127.68, 127.57, 127.54, 29.02, 27.34, 13.65 and 9.75; m/z (EI) 506 (<sup>120</sup>M<sup>+</sup>, 20%), 449 (M<sup>+</sup> – Bu, 40), 393 (30), 335 (42), 216 (70), 184 (100), 139 (28) and 57 (45).

**Thianthren-2-ylcarbaldehyde 4e.** To a solution of 2-bromothianthrene (0.50 g, 1.69 mmol) in tetrahydrofuran (10 cm<sup>3</sup>) at –78 °C under an atmosphere of nitrogen was added butyllithium (1.30 cm<sup>3</sup> of a 1.6 M solution in hexane; 2.08 mmol). After stirring at –78 °C for 3 h dimethylformamide (1.0 cm<sup>3</sup>, 12.9 mmol) was added and the reaction was maintained at –78 °C for a further hour, allowed to warm to room temperature and then quenched with aqueous hydrochloric acid (3 M; 10 cm<sup>3</sup>). Ethyl acetate was added and the aqueous phase separated. The organic layer was washed with brine, dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo*. Flash chromatography on silica gel eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:9), gave thianthren-2-ylcarbaldehyde **4e** as a clear yellow oil (260 mg, 63%) (Found: M<sup>+</sup>, 244.0015. C<sub>13</sub>H<sub>8</sub>OS<sub>2</sub> requires M, 244.0017); ν<sub>max</sub>(film)/cm<sup>-1</sup> 2849, 1695, 1580, 1447, 1195, 1104 and 749; λ<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/nm 250 (log ε 4.35), 278 (4.20), 308 (3.77) and 342 (3.41); δ<sub>H</sub>(200 MHz, CDCl<sub>3</sub>) 7.24–7.34 (2 H, m, Ar-H), 7.45–7.53 (2 H, m, Ar-H), 7.61 (1 H, d, J 8.0, 4-H), 7.74 (1 H, dd, J 8.0 and 1.7, 3-H), 7.94 (1 H, d, J 1.7, 1-H) and 9.96 (1 H, s, CH=O); m/z (CI) 262 (MNH<sub>4</sub><sup>+</sup>, 60%), 245 (MH<sup>+</sup>, 75) and 244 (100).

**4-(Thianthren-2-yl)-2-(1,3-dithiol-2-ylidene)-1,3-dithiole 4f.** 2-Bromothianthrene (138 mg, 0.468 mmol) and tetrakis(triphenylphosphine)palladium(0) (54 mg, 0.0468 mmol) were stirred together in toluene (10 cm<sup>3</sup>) for 10 min at room temperature under argon. A solution of tributylstannyl-tetrathiafulvalene (231 mg, 0.469 mmol) in toluene (10 cm<sup>3</sup>) was then added and the mixture heated at reflux for 5 h. After cooling and washing with water, the dried solution was evaporated and the residue purified by flash chromatography on alumina with ethyl acetate–hexane (1:9) yielding 4-(thianthren-2-yl)-2-(1,3-dithiol-2-ylidene)-1,3-dithiole **4f** as an orange solid (47 mg, 24%), mp 218–219 °C (Found: M<sup>+</sup>, 417.9105. C<sub>18</sub>H<sub>10</sub>S<sub>6</sub> requires M, 417.9107); ν<sub>max</sub>(film)/cm<sup>-1</sup> 3064, 2924, 1444 and 749; λ<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/nm 269 (log ε 4.53), 320 (4.34) and 417 (3.61); δ<sub>H</sub>(200 MHz; CDCl<sub>3</sub>) 6.34 (2 H, s, 4' and 5'-H), 6.53 (1 H, s, 5-H), 7.22–7.30 (3 H, m, Ar-H) and 7.41–7.54 (4 H, m, Ar-H); m/z (EI) 418 (M<sup>+</sup>, 30%), 240 (50), 102 (100) and 76 (68).

**1,8-Bis(thianthren-2-yl)naphthalene 5.** 1,8-Diiodonaphthalene (0.153 g, 0.403 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.028 g, 0.0242 mmol) were stirred together in dimethoxyethane (10 cm<sup>3</sup>) under nitrogen for 10 min at room temperature. A solution of thianthren-2-ylboronic acid (0.418 g, 1.61 mmol) in dimethoxyethane (10 cm<sup>3</sup>) was added followed by aqueous sodium hydrogen carbonate (1 M; 2.4 cm<sup>3</sup>, 2.40 mmol). After heating at reflux for 24 h, the solvent was evaporated, water added and the residue extracted with dichloromethane. The organic phase was washed with brine, dried and the solvent evaporated to yield a brown solid, purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (5:95), to yield 1,8-bis(thianthren-2-yl)naphthalene **5** as a white solid (59 mg, 26%), mp 203–204 °C (Found: M<sup>+</sup>, 556.0433. C<sub>34</sub>H<sub>20</sub>S<sub>4</sub>

requires M, 556.0433); ν<sub>max</sub>(film)/cm<sup>-1</sup> 3050, 2360, 1445, 1108 and 745; λ<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/nm 242 (log ε 4.61), 260 (4.61) and 302 (4.25); δ<sub>H</sub>(300 MHz, CDCl<sub>3</sub>) 6.70–6.88 (2 H, m, Ar-H), 6.98–7.20 (4 H, m, Ar-H), 7.26–7.50 (10 H, m, Ar-H), 7.59 (2 H, dd, J 7.8 and 7.3, naphthalenyl 3- and 6-H) and 8.00 (2 H, d, J 8.1, naphthalenyl 2- and 7-H); δ<sub>C</sub>(75 MHz, CDCl<sub>3</sub>) 142.44, 138.53, 135.82, 135.39, 135.26, 133.69, 132.88, 130.51, 130.26, 129.08, 128.84, 128.45, 128.07, 127.57, 127.48, 127.25 and 125.28; m/z (CI) 574 (MNH<sub>4</sub><sup>+</sup>, 100%), 557 (MH<sup>+</sup>, 20).

**1,8-Bis(thianthren-2-yl)-9,10-anthraquinone 6.** A solution of 2-tributylstannylthianthrene (549 mg, 1.09 mmol), 1,8-diiodoanthraquinone (100 mg, 0.217 mmol), bis(triphenylphosphine)palladium(II) chloride (30 mg, 0.0427 mmol) and copper(I) iodide (62 mg, 0.326 mmol) in dimethylformamide (10 cm<sup>3</sup>) was stirred at room temperature under argon for 24 h. The reaction mixture was diluted with ether (100 cm<sup>3</sup>), filtered through a pad of Celite, washed with water then brine, dried and evaporated. Chromatography on silica gel with ethyl acetate–light petroleum (bp 40–60 °C) (85:15) yielded 1,8-bis(thianthren-2-yl)-9,10-anthraquinone **6** as an orange–yellow solid (79 mg, 57%), mp 158–160 °C (Found: M<sup>+</sup>, 636.0342. C<sub>38</sub>H<sub>20</sub>O<sub>2</sub>S<sub>4</sub> requires M, 636.0346); ν<sub>max</sub>(film)/cm<sup>-1</sup> 3055, 1674, 1575, 1445, 1429, 1326, 1248, 1108, 975, 912, 824, 801 and 744; λ<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/nm 262 (log ε 4.99) and 318 (4.01); δ<sub>H</sub>(300 MHz, CDCl<sub>3</sub>) 7.17 (2 H, dd, J 8.0 and 1.8, Ar-H), 7.29 (4 H, m, Ar-H), 7.41–7.60 (10 H, m, Ar-H), 7.76 (2 H, dd, J 7.7 and 7.7, Ar-H) and 8.36 (2 H, dd, J 7.7 and 1.1, Ar-H); δ<sub>C</sub>(75 MHz, CDCl<sub>3</sub>) 185.95, 183.12, 141.79, 140.42, 137.39, 135.52, 135.46, 135.32, 134.73, 134.19, 134.06, 132.61, 128.77, 128.72, 128.42, 128.20, 128.12, 127.85, 127.75 and 126.92; m/z (FAB) 636 (M<sup>+</sup>, 100%).

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