Facile access to condensed arenothiophenes – preparation of dihydrophenanthrothiophenes and dihydrophenanthro[1]benzothiophenes

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4-Bromo-3-formyl-1,2-dihydronaphthalenes undergo Suzuki cross coupling and Wittig olefination reaction in a one pot procedure. The trienes obtained can be cyclised thermally under concomitant dehydrogenation to dihydrophenanthrothiophenes and dihydrophenanthro[1]benzothiophenes. An X-ray crystal structural analysis was carried out for ethyl (*E*)-3-[1-(1-benzothiophen-3-yl)-3,4-dihydro-2-naphthyl]propenoate.

Keywords: one pot reaction, Wittig-olefination, Suzuki coupling, trienes, electrocyclisation, X-ray crystal structure

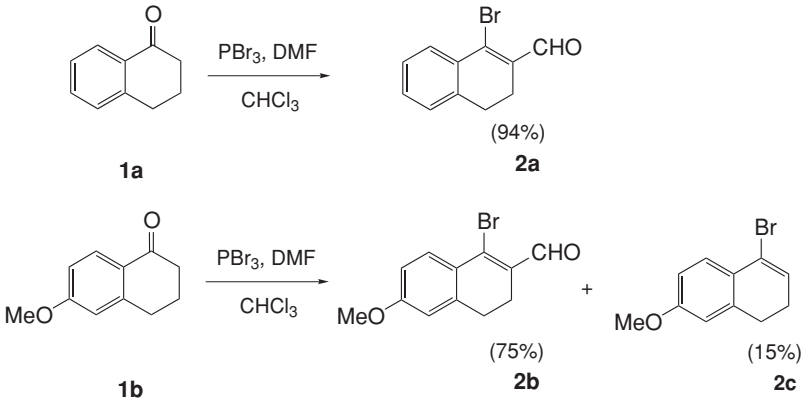
A number of stabilised phosphoranes are inert towards oxygen and water, while maintaining their reactivity towards carbaldehydes.[1] This allows for Wittig olefination reactions in combination with other transformations in one pot procedures. As these phosphoranes also exhibit stability under Pd(0) catalysed C–C bond forming reactions,[2-4] Wittig olefination reactions can be carried out in combination with Sonogashira-,[3] Heck-[3] and Suzuki cross coupling[2] reactions. These protocols have been shown to give ready access to extended pi-systems from haloarenecarbaldehydes.[4] In the present communication, an application of the one pot Suzuki coupling – Wittig olefination routine in combination with a subsequent electrocyclisation for the preparation of arenothiophenes is described. Specifically, thieno containing boronic acids are used for the coupling reaction with bromoformyldihydronaphthalenes to give trienes, in which one of the terminal olefinic moieties is part of a thiophene. Further elaborations of the thienoarenes such as the oxidation to the corresponding thieno *S,S*-dioxides are exemplified.

Tetralone (**1a**) and 6-methoxy-1-tetralone (**1b**) were transformed to 4-bromo-3-formyl-1,2-dihydronaphthalene (**2a**) and to 4-bromo-3-formyl-7-methoxy-1,2-dihydronaphthalene (**2b**) by Arnold-Vilsmeier[5] reaction (Scheme 1). In the case of **1b** a significant amount of 4-bromo-1,2-dihydronaphthalene (**2c**) was obtained.

At the outset, bromodihydronapthalenecarbaldehyde **2a** was reacted in a one-pot Suzuki coupling[6] – Wittig olefination procedure, using the commercially available 2-thienylboronic acid (**3a**), 3-thienylboronic acid (**3b**), and benzo[*b*]thien-3-ylboronic acid (**3c**), benzo[*b*]thien-2-ylboronic acid (**3d**) together with the Wittig reagents, acetylmethylidenetriphenylphosphorane (**4a**), ethoxycarbonyl-methylidenetriphenylphosphorane (**4b**) and benzoylmethylidenetriphenylphosphorane (**4c**). A two phase system was used in the reactions with DME as the organic solvent and aq. Na_2CO_3 as the aqueous medium. In the experiments, bistriphenylphosphinopalladium (II) dichloride [$(PPh_3)_2PdCl_2$][7] was utilised as pre-catalyst for the Suzuki cross-coupling reactions, where further triphenylphosphine (PPh_3) was added as ligand. All combinations gave the desired products in good yield (Table 1). In all cases, only the *E*-isomers were isolated.

2b could be subjected to this one pot Wittig olefination/Suzuki cross coupling protocol with equally good results (Table 1). With benzylidenetriphenylphosphorane, also a semi-stabilised phosphorane was used in the reaction. In this case, the yield was marginally lower and no *E*/*Z*-selectivity was observed, which is normal for Wittig olefinations with semi-stabilised ylides.[8] In the reaction itself, benzyltriphenylphosphonium bromide (**4d**) used as a precursor for the phosphorane, where the aq. Na_2CO_3 solution is sufficient to provide the phosphorane *in situ*.

In order to have some insights in the steric characteristics of the trienes obtained, especially in view of the planned thermal electrocyclisation of the products, an X-ray crystal structural analysis of **5f** was carried out (Fig. 1). Specifically this product was chosen for the X-ray crystal structural analysis, as in previous studies the analogously substituted steroidal system ethyl 16-(benzothien-2-yl)-3-methoxyestra-1,3,5(10),16-tetraene-17-acrylate failed to undergo the subsequent thermal cyclisation. This problem was deemed to stem from steric restrictions within the molecule.[9] From the X-ray of **5f**, it was found that in the crystal the angle between the thienyl ring of **5f** and the averaged plane of the cyclohexadiene ring of the dihydronaphthalene unit is 107.58(2)°.



Scheme 1 Preparation of 4-Bromo-3-formyl-1,2-dihydronaphthalenes by Arnold Vilsmeier reaction.

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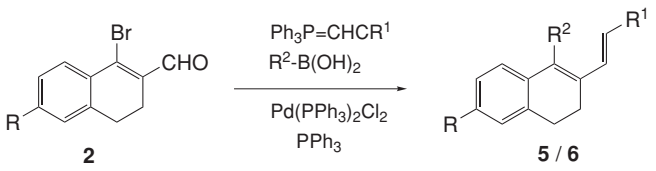
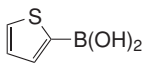
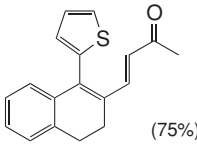
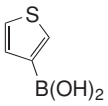
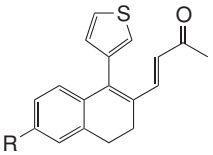
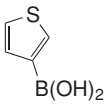
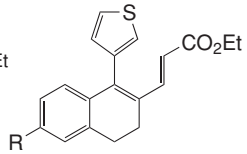
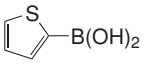
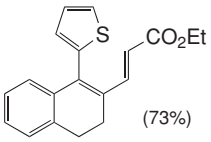
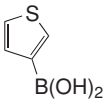
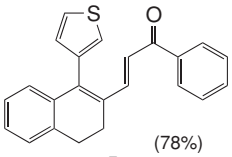
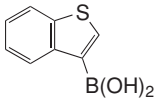
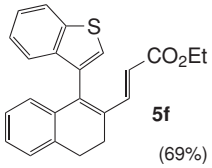
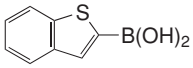
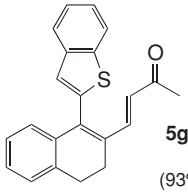
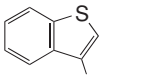
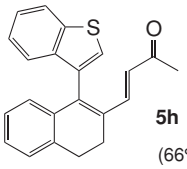
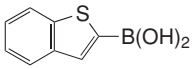
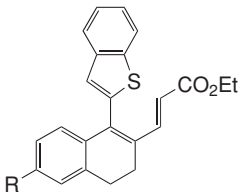
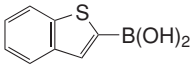
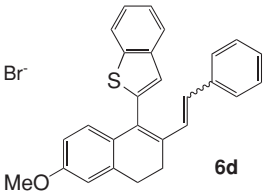
Table 1 One pot Suzuki-Wittig olefination of 4-bromo-3-formyl-1,2-dihydronaphthalenes



Boronic acid	Phosphorane	Product
 **3a**	$Ph_3P=CHCOCH_3$ **4a**	 (75%) **5a**
 **3b**	$Ph_3P=CHCOCH_3$ **4a**	 **5b**: R = H (71%) **6a**: R = OMe (78%)
 **3b**	$Ph_3P=CHCO_2Et$ **4b**	 **5c**: R = H (92%) **6b**: R = OMe (91%)
 **3a**	$Ph_3P=CHCO_2Et$ **4b**	 (73%) **5d**
 **3b**	$Ph_3P=CHCOPh$ **4c**	 (78%) **5e**

Boronic acid	Phosphorane	Product
 **3c**	$Ph_3P=CHCO_2Et$ **4b**	 **5f** (69%)
 **3d**	$Ph_3P=CHCOCH_3$ **4a**	 **5g** (93%)
 **3c**	$Ph_3P=CHCOCH_3$ **4a**	 **5h** (66%)
 **3d**	$Ph_3P=CHCO_2Et$ **4b**	 **5i**: R = H (56%) **6c**: R = OMe (51%)
 **3d**	$Ph_3P^+CH_2Ph\ Br^-$ **4d**	 **6d** *E*/*Z* = 56/44 (51%)

Interestingly, a simple MM2 calculation as anchored within CHEM 3D [CS Chem3D Pro, Molecular Modeling and Analysis, CambridgeSoft, Cambridge, USA, 2001] gave for the energy-minimsed structure a conformation of **5f** similar to that observed in the crystal. Thus, the dihedral angle C3–C4–C3'–C2' is –76.1(2)° as observed in the crystal structure and –75.5° in the calculated model.

Next, the products gained from the one pot Wittig olefination – Suzuki cross coupling were to be cyclised thermally. A number of solvents have been used by different authors in triene electrocyclisation reactions, especially when these reactions are carried out at temperatures below 150°C. G. Desimoni *et al.*[9] have looked at the reaction of (1*Z*,3*Z*,5*E*)-1,2,6-triphenylhexa-1,3,5-triene to *cis*-1,5,6-triphenylcyclohexa-1,3-diene as a typical triene-electrocyclisation reaction in 15 different solvents and have found the reaction not to have any significant solvent effect. As the authors needed to carry out the cyclisation reactions at higher temperatures, diphenyl ether was used as solvent, which is not included in the list of solvents investigated by Desimoni *et al.*[10] Diphenyl ether has a number of advantages over decaline, which is normally used for electrocyclic reactions at high temperatures.

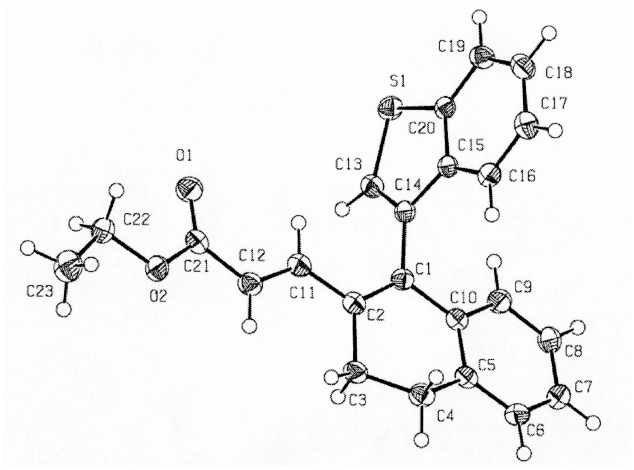
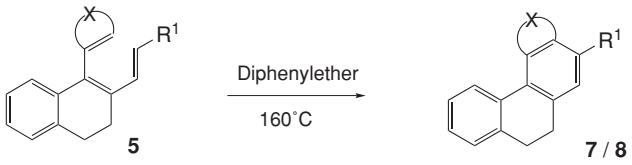


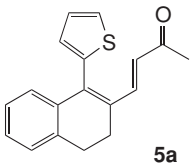
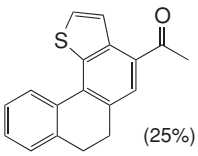
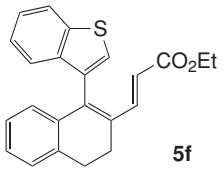
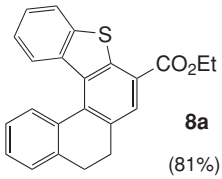
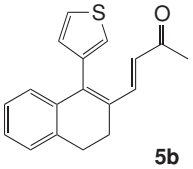
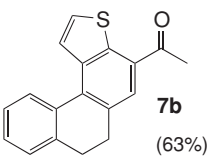
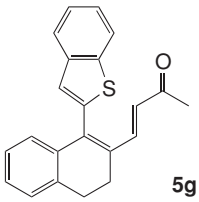
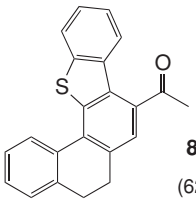
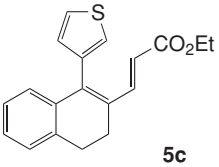
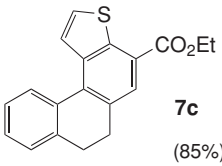
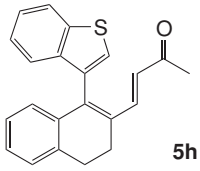
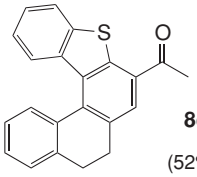
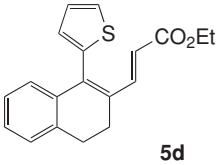
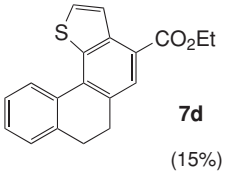
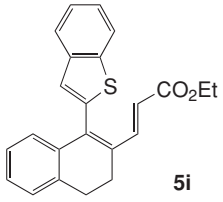
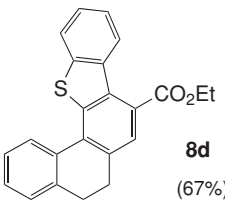
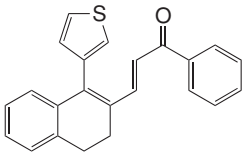
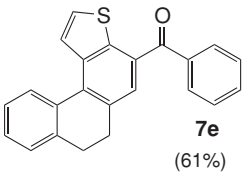
Fig. 1

For one, diphenyl ether solubilises substrates much better than decaline does. This leads to much less polymerisation of the starting materials, which happens quite often in decaline, where the starting material resides in areas of high concentration before it is solubilised completely at higher temperatures. Although diphenyl ether is expected to have higher polarity than decaline, it can be separated from the reaction mixture quite nicely by column filtration with hexane as eluant. As long as the desired product has a functionality, it is not eluted along with the diphenyl ether. Diphenyl ether has the added advantage that its elution through the column can be monitored UV-spectroscopically.

The thermal triene cyclisations of the thienyldienes **5** gave the desired products **7**, usually in good yield (Table 2). A major difference is, however, seen in the cyclisation behaviour of the thien-2-yldienes (*e.g.* of **5a** and **5d**) and the thien-3-yldienes (*e.g.* of **5b**, **5c**, and **5e**). While the former react sluggishly, the cyclisation reactions of the thien-3-yldienes are complete

Table 2 Thermal electrocyclisation of **5**



Starting material	Product	Starting material	Product
 **5a**	 (25%) **7a**	 **5f**	 **8a** (81%)
 **5b**	 **7b** (63%)	 **5g**	 **8b** (62%)
 **5c**	 **7c** (85%)	 **5h**	 **8c** (52%)
 **5d**	 **7d** (15%)	 **5i**	 **8d** (67%)
 **5e**	 **7e** (61%)		

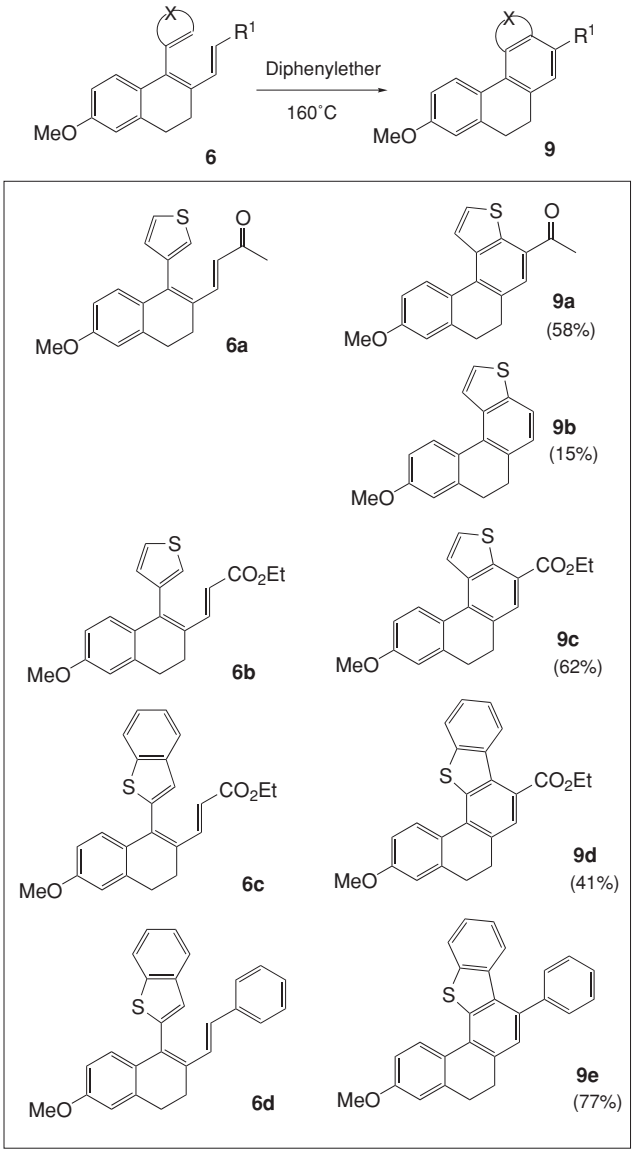
within 12h (at 160°C). Benzothien-3-yl substituted **5f** and **5h** could be cyclised without problem (Table 2), this in sharp contrast to benzothien-3-yl substituted steroidal analogue (see above).[9]

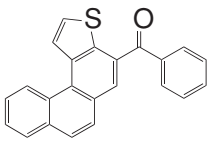
The methoxytetralone derived methoxydihydronaphthalenes **6** could also be cyclised without difficulty (see Table 3). Here, somewhat shorter reaction times were chosen. While the 3-methoxy substituted dihydronaphthalene based trienes crystallise poorly, the cyclised products crystallise readily. Generally, it must be noted that long reaction times (> 24h) lead to fully dehydrogenated by-products (15%), such as to **10** (Fig. 2) in the case of the reaction of **5e**.

The 5,6-dihydrophenanthro[3,4-*b*][1]benzothiophenes and the 5,6-dihydrophenanthro[4,3-*b*][1]benzothiophenes can be oxidised with *m*-CPBA to the corresponding *S*,*S*-dioxides **11** (Scheme 2). The intermittently formed *S*-oxides were not isolated. These areno annelated dibenzothiophene *S*,*S*-dioxides are to be used as model systems for the oxidative desulfurisation[11] of condensed dibenzothiophenes, which are undesired components in fuels.

Highly condensed thienyl systems have been prepared in three steps from commercially available tetralones and thienyl containing boronic acid. The one pot Wittig-Suzuki coupling procedure in combination with a triene cyclisation can be seen to complement nicely annelation methods developed by A. de Meijere *et al.*,[12] which rely on double-Heck or Heck/Stille coupling reactions with a subsequent cyclisation and by T. L. Gilchrist *et al.*, which proceed via sequential Wittig olefination, coupling with organozinc halides and cyclisation.[13]

Table 3 Thermal electrocyclisation of **6**





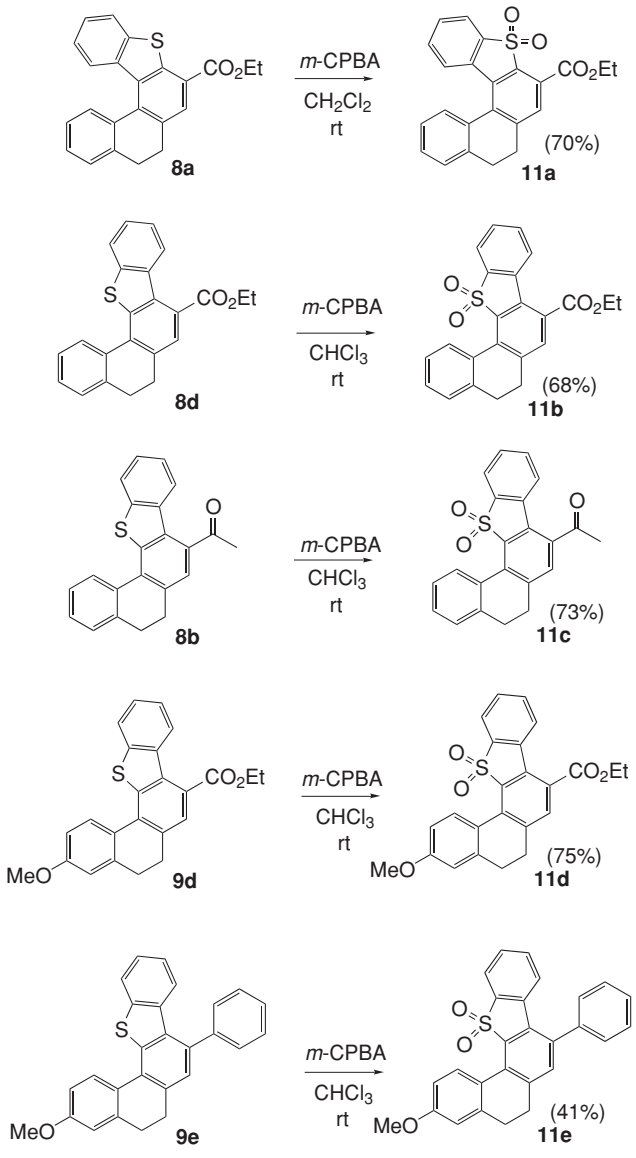
10

Fig. 2

Experimental

General: Melting points were measured on a Yanaco microscopic hotstage and are uncorrected. IR spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2

Scheme 2 Preparation of ring annelated dibenzothiophene-S,S-dioxides



spectrometer (EI, 70 eV, FAB). Column chromatography was carried out on Wakogel 300.

The tetralones **1a** and **1b** (TCI) and the boronic acids **3a**–**3d** (Aldrich) were acquired commercially. While also commercially available, phosphoranes **4a**–**4c**[14] and phosphonium salt **4d**[15] were prepared according to known procedures.

4-Bromo-3-formyl-1,2-dihydronaphthalene (**2a**)[5b,13], *General procedure:* A (Arnold Vilsmeier reaction). To dry DMF (21.9 g, 0.3 mol) in dry $CHCl_3$ (100 ml) was added dropwise phosphorus tribromide (67.7 g, 0.25 mol) at 0°C. The resulting mixture was stirred for 1h. 1-Tetralone (**1a**) (14.6 g, 0.1 mol) was added and the mixture was stirred for 24h at r.t. and thereafter heated under reflux for 3h. Then, the solution was cooled to r.t. and the solvent was removed *in vacuo*. The residue was hydrolysed with ice (100 g) and neutralised with solid sodium hydrogencarbonate. The mixture was extracted with ether (3 × 200 ml). The organic phase was concentrated *in vacuo*, and the residue was subjected to column chromatography on silica gel to give **2a** (22.4 g, 94%) as colourless prisms, m.p. 53–54°C (m.p. 54°C[5b]); δ_H (270 MHz, $CDCl_3$) 2.60–2.65 (2H, m), 2.81–2.87 (2H, m), 7.34–7.91 (4H, m, ArH), 10.26 (1H, s, CHO).

4-Bromo-3-formyl-7-methoxy-1,2-dihydronaphthalene (**2b**)–(**1b** (5.0 g, 28.4 mmol), PBr_3 (6.74 ml, 71.0 mmol, 2.5 equiv) and DMF (6.51 ml, 85.2 mmol, 3 equiv) were reacted according to general procedure A to give 4-bromo-7-methoxy-1,2-dihydronaphthalene (**2c**) as a colourless oil (1.35 g, 15%); ν_{max} (neat)/cm^{-1} 2940, 2832, 1605, 1568, 1490, 1252, 1123, 1040, 815, 670; δ_H (270 MHz, $CDCl_3$) 2.35 (2H, ddd, ^3J = 8.9 Hz, ^3J = 8.1 Hz, ^3J = 4.6 Hz), 2.83 (2H, dd, ^3J = 8.9 Hz, ^3J = 8.1 Hz), 3.81 (3H, s, OCH_3), 6.29 (1H, t, ^3J = 4.6 Hz), 6.67 (1H, d, ^4J = 2.7 Hz), 6.74 (1H, dd, ^3J = 8.4 Hz, ^4J = 2.7 Hz), 7.47 (1H, d, ^3J = 8.4 Hz); δ_C (67.8 MHz, $CDCl_3$) 25.32, 28.17, 55.32, 111.02, 113.49, 121.10, 126.24, 127.90, 127.94, 137.98, 159.48; MS (70 eV) *m/z* (%): 318 (1.4) [$^{81}BrM^+$], 316 (0.8) [$^{79}BrM^+$], 176 (56), 148 (100); and **2b** as a colourless solid (5.69 g, 75%), m.p. 67°C; (Found: M^+, 265.9945. $C_{12}H_{11}{}^{79}BrO_2$ requires M, 265.9942); ν_{max} (KBr)/cm^{-1} 2940, 2860, 1653, 1606, 1585, 1550, 1441, 1252, 1181, 1038, 1003, 955, 802, 578; δ_H (270 MHz, $CDCl_3$) 2.61 (2H, m), 2.81 (2H, m), 3.86 (3H, s, OCH_3), 6.73 (1H, d, ^4J = 2.2 Hz), 6.83 (1H, dd, ^3J = 8.9 Hz, ^4J = 2.2 Hz), 7.83 (1H, d, ^3J = 8.9 Hz), 10.20 (1H, s,CHO); δ_C (67.8 MHz, $CDCl_3$) 22.73, 27.73, 55.49, 112.08, 113.37, 125.97, 130.83, 132.18, 139.21, 141.27, 162.09, 193.04; MS (70 eV) *m/z* (%): 268 (61) [$^{81}BrM^+$], 266 (62) [$^{79}BrM^+$], 158 (85), 115 (100).

(E)-4-[1-(2-Thienyl)-3,4-dihydro-2-naphthyl]but-3-en-2-one (**5a**), *General procedure* B: A mixture of 4-bromo-3-formyl-1,2-dihydronaphthalene (**2a**) (474 mg, 2.0 mmol), acetylmethylidene-triphenylphosphorane (**4a**) (1.2 g, 4.0 mmol), 2-thienylboronic acid (**3a**) (500 mg, 4.0 mmol), $(PPh_3)_2PdCl_2$ (35 mg, $5{\cdot}10^{-2}$ mmol) and triphenylphosphine (20 mg, 7.6 . 10^{-5} mol) in DME (5 ml) and 2M aq. Na_2CO_3 (3 ml) was kept at 70°C for 12h. Thereafter, the mixture was poured into water (20 ml) and extracted with chloroform (3 × 15 ml). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give a residue which was purified by column chromatography on silica gel (hexane/ether 2:1) to give **5a** (420 mg, 75%) as yellow plates; m.p. 157°C; (Found: M^+ 280.0918. $C_{18}H_{16}OS$ requires M, 280.0922); ν_{max} (KBr)/cm^{-1} 3056, 2940, 1674, 1576, 1314, 1282, 1245, 1181, 985, 768, 698; δ_H (270 MHz, $CDCl_3$) 2.23 (3H, s, CH_3), 2.65 (2H, dd, ^3J = 7.3 Hz, ^3J = 5.9 Hz), 2.93 (2H, dd, ^3J = 7.3 Hz, ^3J = 5.9 Hz), 6.31 (1H, d, ^3J = 16.2 Hz), 6.95–7.25 (6H, m), 7.46 (1H, m), 7.50 (1H, d, ^3J = 16.2 Hz); δ_C (99.45 MHz, $CDCl_3$) 24.55, 26.93, 27.64, 126.63, 126.89, 127.00, 127.25, 127.30, 127.60, 128.62, 129.56, 134.93, 135.92, 136.70, 137.96, 142.86, 199.00; MS (70 eV) *m/z* (%): 280 (34) [M^+], 237 (100) [M^+-CH_3CO], 221 (39), 203 (30), 165 (19). (Found: C, 77.19; H, 5.76. $C_{18}H_{16}OS$ requires C, 77.11; H, 5.75%).

(E)-4-[1-(3-Thienyl)-3,4-dihydro-2-naphthyl]but-3-en-2-one (**5b**): Prepared as **5a** but using 3-thienylboronic acid: Yellow plates, m.p. 167°C; (Found: MH^+, 281.0999. $C_{18}H_{17}OS$ requires M, 281.1000); ν_{max} (KBr)/cm^{-1} 1672, 1575, 1354, 1283, 1181, 987; δ_H (270 MHz, $CDCl_3$) 2.18 (3H, s, CH_3), 2.63 (2H, dd, ^3J = 8.6 Hz, ^3J = 6.2 Hz), 2.93 (2H, dd, ^3J = 8.6 Hz, ^3J = 6.2 Hz), 6.29 (1H, d, ^3J = 15.9 Hz), 6.84 (1H, d, ^3J = 7.6 Hz), 6.99 (1H, dd, ^3J = 4.9 Hz, ^4J = 1.4 Hz), 7.06–7.46 (5H, m), 7.42 (1H, d, ^3J = 15.9 Hz), δ_C (67.8 MHz, $CDCl_3$) 24.41, 26.90, 27.81, 125.63, 125.70, 126.59, 126.85, 127.35, 127.57, 128.52, 129.82, 132.91, 135.70, 136.99, 137.64, 140.31, 143.34, 199.01; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 281 (100) [MH^+], 237 (44). (FAB, MH^+). (Found: C, 77.11; H, 5.75. $C_{18}H_{16}OS$ requires C, 77.11; H, 5.75%).

Ethyl (E)-3-[1-(3-thienyl)-3,4-dihydro-2-naphthyl]propenoate (**5c**): Prepared according to general procedure B: slowly crystallising oil; (Found: MH^+, 311.1100. $C_{19}H_{19}O_2S$ requires MH^+, 311.1106); ν_{max} (neat)/cm^{-1} 3098, 3062, 2952, 1705, 1611, 1450, 1366, 1300, 1166, 1039, 855, 794, 770, 670; δ_H (270 MHz, $CDCl_3$) 1.26 (3H, t, ^3J = 7.0 Hz), 2.62 (2H, dd, ^3J = 9.7 Hz, ^3J = 7.3 Hz), 2.92 (2H, dd, ^3J = 9.7 Hz, ^3J = 7.3 Hz), 4.17 (2H, q, ^3J = 7.0 Hz), 6.04 (1H, d, ^3J = 15.9 Hz), 6.83 (1H, d, ^3J = 7.3 Hz), 6.96 (1H, dd, ^3J = 5.1 Hz, *J* 1.3 Hz), 7.06–7.20 (4H, m), 7.42 (1H, dd, ^3J = 5.1 Hz, *J* = 2.7 Hz), 7.59 (1H, d, ^3J = 15.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.27, 24.43, 27.81, 60.19, 117.48, 125.51, 125.62, 126.51, 127.24, 127.49, 128.26, 189.79, 132.55, 135.79, 136.88, 137.51, 139.43, 144.03, 167.51; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 311 (100) [MH^+], 265 (44), 237 (80).

Ethyl (E)-3-[1-(2-thienyl)-3,4-dihydro-2-naphthyl]propenoate (**5d**): Prepared to general procedure B: colourless solid, m.p. 98°C; (Found: MH^+, 311.1102. $C_{19}H_{19}O_2S$ requires MH^+, 311.1106); ν_{max} (KBr)/cm^{-1} 3112, 2970, 2926, 1707, 1614, 1309, 1180, 976, 856, 844, 766, 711; δC (67.8 MHz, $CDCl_3$) 14.26, 24.60, 27.65, 60.25, 118.16, 126.56, 126.72, 126.96, 127.16, 127.54, 128.39, 129.55, 134.62, 136.02, 136.59, 136.86, 137.90, 143.59, 167.35; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 311 (48) [MH^+], 237 (22). (Found: C, 73.62; H, 5.83. $C_{19}H_{18}O_2S$ requires C, 73.52; H, 5.84%.)

Phenyl (E)-2-[2-(3-thienyl)-3,4-dihydro-2-naphthyl]vinyl ketone (**5e**): Prepared according to general procedure B: slowly solidifying oil; (Found: MH^+, 343.1159. $C_{23}H_{19}OS$ requires MH^+, 343.1157); ν_{max} (KBr)/cm^{-1} 3064, 2936, 1659, 1569, 1450, 1305, 1212, 1189, 1305, 1212, 1189, 1080, 1020, 912; δ_H (270 MHz, $CDCl_3$) 2.75 (2H, m), 2.97 (2H, m), 6.86 (1H, d, ^3J = 7.6 Hz), 6.97 (1H, dd, ^3J = 5.1 Hz, ^4J = 1.4 Hz), 7.05–7.56 (8H, m), 7.11 (1H, d, ^3J = 15.4 Hz), 7.73 (1H, d, ^3J = 15.4 Hz), 7.92 (2H, m); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 343 (57) [MH^+], 237 (28).

Ethyl (E)-3-[1-(3-benzothiophenyl)-3,4-dihydro-2-naphthyl] propenoate (**5f**): Prepared according to general procedure B: pale yellow crystals; m.p. 154°C; (Found: MH^+, 361.1270. $C_{23}H_{21}O_2S$: requires MH^+, 361.1262); ν_{max} (KBr)/cm^{-1} 3062, 2936, 1705, 1613, 1304, 1270, 1176, 1030, 979, 774, 756, 734; δ_H (270 MHz, $CDCl_3$) 1.20 (3H, t, CH_3, ^3J = 7.0 Hz), 2.66–2.75 (2H, m), 2.99–3.07 (2H, m), 4.11 (2H, q, OCH_2, ^3J = 7.0 Hz), 6.07 (1H, d, ^3J = 15.9 Hz), 6.67 (1H, d, ^3J = 7.6 Hz), 6.98 (1H, m), 7.14–7.38 (6H, m), 7.45 (1H, d, ^3J = 15.9 Hz), 7.92 (1H, d, ^3J = 8.1 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.23, 24.35, 27.91, 60.21, 118.03, 122.70, 123.32, 124.29, 124.54, 126.65, 126.67, 127.31, 127.33, 128.40. 132.87, 134.41, 135.08, 136.57, 138.20, 139.29, 140.00, 143.46, 167.29; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 361 (51) [MH^+], 287 (29). (Found: C, 76.72; H, 5.62. $C_{23}H_{20}O_2S$ requires C, 76.64; H, 5.59%).

(E)-4-[1-(Benzothiophen-2-yl)-3,4-dihydro-2-naphthyl]but-3-en-2-one (**5g**): Prepared according to general procedure B: pale yellow, slowly solidifying oil; m.p. 54°C; [(Found: MH^+, 331.1161. $C_{22}H_{19}OS$ requires: MH^+, 331.1157 (FAB)); ν_{max} (KBr)/cm^{-1} 1664, 1579, 1433, 1355, 1255, 1173, 969, 748; δ_H (270 MHz, $CDCl_3$) 2.16 (3H, s, $COC\underline{H}_3$), 2.68 (1H, dd, ^3J = 9.7 Hz, ^3J = 7.3 Hz), 2.95 (1H, dd, ^3J = 9.7 Hz, ^3J = 7.3 Hz), 6.35 (1H, d, ^3J = 15.9 Hz), 7.01–7.45 (8H, m), 7.57 (1H, d, ^3J = 15.9 Hz), 7.81–7.89 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 24.51, 27.17, 27.59, 122.21, 123.74, 124.58, 124.65, 126.34, 126.71, 127.34, 127.62, 127.73, 128.77, 135.29, 135.35, 136.57, 137.58, 138.67, 139.62, 140.84, 142.39, 198.97; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 331 (3.9) [MH^+], 287 (39) [M^+-$COCH_3$].

(E)-4-[1-(Benzothiophen-3-yl)-3,4-dihydro-2-naphthyl]but-3-en-2-one (**5h**): Prepared according to general procedure B: colourless solid, m.p. 160°C; (Found: M^+, 330.1076. $C_{22}H_{18}OS$ requires: M^+, 330.1078); ν_{max} (KBr)/cm^{-1} 3064, 2936, 1659, 1602, 1426, 1288, 1253, 972, 771, 759, 731; δ_H (270 MHz, $CDCl_3$) 2.03 (3H, s, $COCH_3$), 2.67–2.97 (2H, m), 3.00–3.08 (2H, m,), 6.31 (1H, d, ^3J = 16.2 Hz), 6.70 (1H, d, ^3J = 8.1 Hz), 6.97 (1H, m), 7.16–7.40 (7H, m), 7.93 (1H, d, ^3J = 8.1 Hz); δC (67.8 MHz, $CDCl_3$) 24.28, 26.77, 27.86, 122.76, 123.30, 124.42, 124.70, 126.58, 126.71, 127.17, 127.35, 127.41, 128.63, 132.95, 134.59, 135.02, 136.68, 138.97, 139.20, 139.88, 142.81, 199.00; MS (EI, 70 eV) *m/z* (%): 330 (19) [M^+], 287 (100) [M^+-$COCH_3$].

Ethyl (E)-3-[1-(benzothiophen-2-yl)-3,4-dihydro-2-naphthyl] propenoate (**5i**): Prepared according to general procedure B: Colourless solid, m.p. 140°C; (Found: M^+, 360.1181. $C_{23}H_{20}O_2S$ requires: M^+, 360.1184); ν_{max} (KBr)/cm^{-1} 1710, 1615, 1304, 1175, 747; δ_H (270 MHz, $CDCl_3$) 1.23 (3H, t, CH_3, ^3J = 7.0 Hz), 2.67 (1H, dd, ^3J = 9.7 Hz, ^3J = 7.0 Hz), 2.95 (1H, dd, ^3J = 9.7 Hz, ^3J = 7.0 Hz), 4.15 (2H, q, $OC\underline{H}_2$, ^3J = 7.0 Hz), 6.12 (1H, d, ^3J = 15.8 Hz), 7.08–7.86 (9H, m), 7.71 (1H, d, ^3J = 15.8 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.27, 24.49, 27.57, 60.34, 118.71, 121.40, 122.15, 123.73, 124.42, 124.47, 124.79, 126.31, 126.64, 127.26, 127.56, 128.55,

134.97, 135.39, 136.44, 138.60, 139.69, 143.18, 167.26; MS (EI, 70 eV) *m/z* (%): 360 (28) [M^+], 287 (100).

(E)-4-[6-Methoxy-1-(3-thienyl)-3,4-dihydro-2-naphthyl]but-3-en-2-one (**6a**): A mixture of **2b** (534 mg, 2.0 mmol), 3-thienylboronic acid (**3b**) (384 mg, 3.0 mmol) and acetylmethylidenetriphenylphosphorane (**4a**) (1.3 g, 4.0 mmol), $(PPh_3)_2PdCl_2$ (35 mg, $5{\cdot}10^{-2}$ mmol) and triphenylphosphine (20 mg, 7.6×10^{-5} mol) in DME (8 ml) and an aq. 1.5 M Na_2CO_3 solution (6 ml) is heated at 65°C for 10h. Thereafter, the cooled solution is diluted with water (20 ml) and extracted with chloroform (3×20 ml). The organic is dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue is subjected to column chromatography on silica gel (hexane/ether/$CHCl_3$ 3:1:1) to give **6a** (484 mg, 78%) as a colourless solid, m.p. 138°C; (Found: MH^+, 311.1110. $C_{19}H_{19}O_2S$ requires: MH^+, 311.1106 [FAB]); ν_{max} (KBr)/cm^{-1} 1671, 1571, 1428, 1275, 1250, 1181, 1155, 1113, 1082, 1036, 986, 852, 811, 794, 655; δ_H (270 MHz, $CDCl_3$) 2.17 (3H, s, $COC\underline{H}_3$), 2.61 (2H, dd, ^3J = 9.5 Hz, ^3J = 7.0 Hz), 2.90 (2H, dd, ^3J = 9.5 Hz, ^3J = 7.0 Hz), 3.81 (3H, s, OCH_3), 6.25 (1H, d, ^3J = 15.9 Hz), 6.62 (1H, dd, ^3J = 8.6 Hz, ^4J = 2.7 Hz), 6.77 (1H, s), 6.79 (1H, d, ^3J = 8.6 Hz), 6.98 (1H, dd, ^3J = 4.9 Hz, ^4J = 1.1 Hz), 7.19 (1H, dd, ^3J = 3.0 Hz, ^4J = 1.1 Hz), 7.43 (1H, d, ^3J = 15.9 Hz), 7.44 (1H, m); δ_C (67.8 MHz, $CDCl_3$) 24.24, 26.81, 28.25, 55.30, 111.38, 113.31, 125.51, 125.57, 125.89, 128.84, 129.18, 129.80, 130.54, 137.79, 139.07, 140.32, 143.67, 159.85, 199.11; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 311 (9.6) [MH^+].

Ethyl (E)-3-[6-methoxy-1-(3-thienyl)-3,4-dihydro-2-naphthyl] propenoate (**6b**): prepared as **6a** using ethoxycarbonylmethyliden-etriphenylphosphorane (**4b**): colourless solid, m.p. 94°C; (Found: M^+, 340.1137. Calcd. for $C_{20}H_{20}O_3S$: M^+, 340.1133); ν_{max} (KBr)/cm^{-1} 2938, 1703, 1599, 1306, 1272, 1243, 1174, 1039, 849; δ_H (270 MHz, $CDCl_3$) 1.23 (3H, t, CH_3, ^3J = 7.3 Hz), 2.59 (1H, dd, ^3J = 10.0 Hz, ^3J = 7.6 Hz), 2.88 (1H, dd, ^3J = 10.0 Hz, ^3J = 7.6 Hz), 3.81 (3H, s, OCH_3), 4.16 (2H, q, ^3J = 7.3 Hz), 5.98 (1H, d, ^3J = 15.7 Hz), 6.61 (1H, dd, ^3J = 8.6 Hz, ^4J = 3.0 Hz), 6.75 (1H, s), 6.76 (1H, d, ^3J = 6.7 Hz), 6.96 (1H, dd, ^3J = 4.9 Hz, ^4J = 1.3 Hz), 7.17 (1H, dd, J = 3.0 Hz, ^4J = 1.3 Hz), 7.41 (1H, dd, ^3J = 4.9 Hz, J = 3.0 Hz), 7.56 (1H, d, ^3J = 15.7 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.29, 24.29, 28.25, 55.29, 60.11, 111.26, 113.27, 116.29, 125.41, 125.53, 128.94, 129.06, 129.77, 130.23, 137.68, 138.92, 139.02, 144.25, 159.64, 167.71; MS (EI, 70 eV) *m/z* (%): 340 (67) [M^+], 267 (100).

Ethyl (E)-3-[6-methoxy-1-(benzothiophen-2-yl)-3,4-dihydro-2-naphthyl]propenoate (**6c**): Prepared as **6a** using ethoxycarbonylmethylidenetriphenylphosphorane (**4b**) and 1-benzothien-2-ylboronic acid (**3d**): pale yellow solid; m.p. 165°C; (Found: M^+, 390.1295. $C_{24}H_{22}O_3S$ requires: M^+, 390.1290); ν_{max} (KBr)/cm^{-1} 2992, 1706, 1602, 1307, 1267, 1250, 1181, 1039, 815, 753; δ_H (270 MHz, $CDCl_3$) 1.23 (3H, t, ^3J = 7.0 Hz), 2.65 (2H, dd, ^3J = 10.0 Hz, ^3J = 7.3 Hz), 2.90 (2H, dd, ^3J = 10.0 Hz, ^3J = 7.3 Hz), 3.80 (3H, s, OCH_3), 4.15 (2H, q, ^3J = 7.0 Hz), 6.06 (1H, d, ^3J = 15.7 Hz), 6.61 (1H, dd, ^3J = 8.6 Hz, ^4J = 2.7 Hz), 6.76 (1H, d, ^4J = 2.7 Hz), 6.95 (1H, d, ^3J = 8.6 Hz), 7.21 (1H, s), 7.33–7.40 (2H, m), 7.70 (1H, d, ^3J = 15.7 Hz), 7.79–7.86 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 14.28, 24.41, 28.08, 55.33, 60.22, 111.37, 113.34, 117.60, 122.14, 123.72, 124.39, 124.43, 126.20, 128.60, 129.19, 132.56, 135.00, 138.54, 138.85, 139.70, 140.15, 143.39, 159.88, 167.44; MS (EI, 70 eV) *m/z* (%): 391 (36) [MH^+], 317 (64), 266 (100).

4-Benzothien-2'-yl-7-methoxy-3-(phenylethenyl)-1,2-dihydronaphthalene (**6d**): A mixture of **2b** (534 mg, 2.0 mmol), 1-benzothien-2-ylboronic acid (**3d**) (695 mg, 3.9 mmol), benzyltriphenylphosphonium bromide (**4d**) (1.9 g, 4.4 mmol), $(PPh_3)_2PdCl_2$ (35 mg, 5×10^{-2} mmol) and triphenylphosphine (20 mg, 7.6×10^{-5} mol) in DME (8 ml) and an aq. 1.5 M Na_2CO_3 solution (10 ml) is heated at 65°C for 15h. Thereafter, the cooled solution is diluted with water (20 ml) and extracted with chloroform (3×20 ml). The organic is dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue is subjected to column chromatography on silica gel (hexane/ether/$CHCl_3$ 20:1:1). Partial evaporation of the solvent *in vacuo* and dilution of the remainder with hexane gave pure *E*–**6d** (32 mg) a colourless solid, m.p. 136°C; (Found: M^+, 394.1395. $C_{27}H_{22}OS$ requires: M^+, 394.1391); ν_{max} (KBr)/cm^{-1} 3014, 2930, 2830, 1605, 1581, 1490, 1432, 1305, 1277, 1253, 1153, 1036, 810, 749, 724, 697; δ_H (270 MHz, $CDCl_3$) 2.27 (2H, m), 2.72 (2H, m), 3.80 (3H, s, OCH_3), 6.40 (1H, d, ^3J = 12.1 Hz), 6.46 (1H, d, ^3J = 12.1 Hz), 6.63 (1H, dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz), 6.70 (1H, d, ^4J = 2.4 Hz), 7.04 (1H, d, ^3J = 8.4 Hz), 7.20–7.41 (8H, m), 7.75–7.85 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 28.57, 29.11, 55.27, 111.03, 113.08, 122.16, 123.43, 124.17, 126.00, 127.06, 127.66, 127.94, 128.88, 129.02, 129.64, 131.34, 136.01, 138.27, 138.51, 139.87, 140.70, 141.07, 158.92; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 394 (23) [M^+]. The remainder of the solvent was evaporated to *E*/*Z*–**6d** with a total amount of *E*/*Z*–**6d** of 402 mg (1.03 mmol, 51%, *E*/*Z* 56/44).

4-Acetyl-6,7-dihydrophenanthro[3,4-b]thiophene (**7b**), *General procedure* C: Thermal cyclisation of **5b**. **5b** (150 mg, 0.54 mmol) in diphenyl ether (2.2 ml) was heated at 160°C for 18h. Thereafter, the reaction mixture was subjected to column chromatography on silica gel (first hexane, to elute the diphenyl ether, then hexane/ether 5:1) to give 4-acetyl-6,7-dihydrophenanthro[3,4-*b*]thiophene (**7b**) (95 mg, 64%) as a pale yellow solid, m.p. 177°C; (Found: MH^+, 279.0839. $C_{18}H_{15}OS$ requires: MH^+, 279.0844 [FAB]); ν_{max} (KBr)/cm^{-1} 2940, 1659, 1538, 1500, 1367, 1277, 1205, 712 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 2.78 (3H, s, CH_3), 2.88 (2H, mc), 3.00 (2H, mc), 7.34 (3H, m), 7.64 (1H, d, ^3J = 4.9 Hz), 7.76 (1H, s), 7.83 (1H, d, ^3J = 4.9 Hz), 8.02 (1H, m); δ_C (67.8 MHz, $CDCl_3$) 26.34, 29.42, 29.60, 122.90, 126.75, 127.55, 128.04, 128.08, 128.39, 129.05, 131.40, 133.99, 134.77, 135.64, 137.50, 138.30, 139.86, 196.92; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 279 (47) [MH^+]. (Found: C, 77.88; H, 5.07. $C_{18}H_{14}OS$ requires: C, 77.66; H, 5.07%).

4-Ethoxycarbonyl-6,7-dihydrophenanthro[3,4-b]thiophene (**7c**): Prepared as **7b**: colourless solid, m.p. 92°C; (Found: M^+, 308.0868. $C_{19}H_{16}O_2S$ requires: M^+, 308.0871); ν_{max} (KBr)/cm^{-1} 2970, 1696, 1277, 1208, 1058, 1035, 830, 777, 708; δ_H (270 MHz, $CDCl_3$) 1.46 (3H, t, ^3J = 7.0 Hz), 2.85 (2H, mc), 2.96 (2H, mc), 4.51 (2H, q, OCH_2, ^3J = 7.0 Hz), 7.29–7.43 (3H, m), 7.53 (1H, d, ^3J = 5.7 Hz), 7.95 (1H, d, ^3J = 5.7 Hz), 8.00 (1H, d, ^3J = 7.6 Hz), 8.06 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 14.54, 29.40 (2C), 61.35, 122.61, 122.81, 126.66, 126.93, 127.84, 128.01, 128.18, 129.77, 134.10, 134.93, 135.10, 137.26, 139.82, 140.23, 167.23; MS (FAB, 3-nitrobenzyl alcohol) *m/z (*%): 308 (100) [M^+], 263 (23), 154 (44).

4-Ethoxycarbonyl-6,7-dihydrophenanthro[4,3-b]thiophene (**7d**): Prepared as **7b**: colourless oil; (Found: MH^+, 279.0848. $C_{18}H_{15}OS$ requires: MH^+, 279.0844); ν_{max} (KBr)/cm^{-1} 2924, 2854, 1670, 1543, 1428, 1351, 1262, 1103, 1034, 970, 861, 797, 761 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 2.68 (3H, s, CH_3), 2.83 (2H, mc), 2.95 (2H, mc), 7.26–7.41 (3H, m), 7.55 (1H, d, ^3J = 5.7 Hz), 7.80 (1H, s), 8.35 (1H, d, ^3J = 7.8 Hz), 8.37 (1H, d, ^3J = 5.7 Hz); δ_C (67.8 MHz, $CDCl_3$) 28.21, 29.09, 29.65, 124.96, 126.20, 126.83, 128.20, 128.38, 128.48, 128.63, 130.51, 133.38, 134.00, 134.21, 138.14, 139.57, 198.87; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 279 (6.4) [MH^+].

8-Ethoxycarbonyl-5,6-dihydrophenanthro[3,4-b][1] benzothiophene (**8a**): A solution of **5f** (191 mg, 0.53 mmol) in diphenyl ether (1.1 ml) was heated at 160° for 14h. The dark brown solution was subjected directly to column chromatography on silica gel (hexane / ether/ $CHCl_3$ 5 : 1 : 1) to give **8a** (155 mg, 81%); (Found: 358.1034. Calcd. for $C_{23}H_{18}O_2S$: 358.1027); ν_{max} (KBr)/cm^{-1} 2934, 1703, 1299, 1253, 1228, 1055, 1039, 760; δ_H (270 MHz, $CDCl_3$) 1.40 (3H, t, CH_3, ^3J = 7.0 Hz), 2.77–2.89 (4H, m), 4.42 (2H, q, OCH_2, ^3J = 7.0 Hz), 7.05–7.33 (5H, m), 7.78 (1H, d, ^3J = 7.8Hz), 7.88 (1H, d, ^3J = 7.1 Hz), 7.98 (1H, s), 8.24 (1H, d, ^3J = 8.1 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.26, 29.32, 29.36, 61.20, 118.65, 122.25, 122.36, 122.71, 124.74, 125.54, 126.36, 127.55, 127.71, 128.87, 129.50, 132.71, 134.09, 136.63, 137.25. 139.64. 141.02, 141.79, 165.99; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 358 (8.9) [M^+].

8-Acetyl-5,6-dihydrophenanthro[4,3-b][1]benzothiophene (**8b**): Prepared as **8a**: grey solid; m.p. 72°C; (Found: M^+, 328.0926. $C_{22}H_{16}OS$ requires: M^+, 328.0922); ν_{max}(KBr)/cm^{-1} 1687, 1440, 1259, 1234, 1107, 738; δ_H (270 MHz, $CDCl_3$) 2.80 (3H, s, $COC\underline{H}_3$), 2.84–2.90 (2H, m), 2.97–3.01 (2H, m), 7.29–7.49 (6H, m), 7.90 (1H, m), 8.05 (1H, d, ^3J = 8.4 Hz), 8.42 (1H, d, ^3J = 8.1Hz); δ_C (67.8 MHz, $CDCl_3$) 29.08, 29.68, 31.33, 122.43, 123.73, 124.24, 124.51, 125.91, 126.77 (2C), 128.19, 128.27, 131.67, 131.85, 133.50, 133.72, 136.14, 136.69, 136.80, 139.28, 139.60, 204.67; MS (EI, 70 eV) *m/z* (%): 328 (100) [M^+], 313 (87) [M^+-CH_3], 284 (46).

8-Acetyl-5,6-dihydrophenanthro[3,4-b][1]benzothiophene (**8c**): Prepared as **8a**: light brownish solid, m.p. 226°C; (Found: M^+, 328.0919. $C_{22}H_{16}OS$ requires: M^+, 328.0922); ν_{max} (KBr)/cm^{-1} 2944, 1661, 1536, 1360, 1297, 1252, 1224, 968, 761, 747, 727, 609; δ_H (270 MHz, $CDCl_3$) 2.79 (3H, s, $COCH_3$), 2.83 (4H, bs), 7.17–7.43 (5H, m), 7.91 (1H, d, ^3J = 8.1 Hz), 7.96 (1H, s), 7.99 (1H, d, ^3J = 8.1 Hz), 8.34 (1H, d, ^3J = 8.1 Hz); δ_C (67.8 MHz, $CDCl_3$) 26.57, 29.57, 29.76, 122.76, 123.02, 124.94, 125.87, 126.61, 127.81, 128.44, 128.79, 129.03, 129.26, 132.86, 133.28, 133.66, 136.71, 137.90, 139.63, 139.89, 143.22, 197.08. MS (EI, 70 eV) *m/z* (%): 328 (100) [M^+], 313 (39) [M^+–CH_3], 284 (51) [M^+–C_2H_4O], 282 (53).

8-Ethoxycarbonyl-5,6-dihydrophenanthro[3,4-b][1] benzothiophene (**8d**): Prepared as **8a**: yellow, slowly solidifying oil; (Found: M^+, 358.1024. $C_{23}H_{18}O_2S$ requires: M^+, 358.1028); ν_{max} (neat)/cm^{-1} 2924, 1728, 1260, 1119, 911, 738; δ_H (270 MHz, $CDCl_3$) 1.38 (3H, t, CH_3, ^3J = 7.0 Hz), 2.73–2.78 (2H, m), 2.85–2.90 (2H,

m), 4.48 (2H, q, OCH_2, ^3J = 7.0 Hz), 7.29–7.78 (6H, m), 7.54 (1H, s), 8.22 (1H, m), 8.32 (1H, d, ^3J = 7.8 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.98, 29.73, 30.19, 122.81, 124.98, 125.29, 126.65, 126.95, 127.41, 127.46, 128.15, 128.85, 128.98, 133.05, 133.10, 134.17, 134.47, 137.23, 138.18, 140.08, 138.18, 140.08, 140.34, 169.87; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 358 (100) [M^+], 313 (37), 285 (35).

4-Acetyl-9-methoxy-6,7-dihydrophenanthro[3,4-b]thiophene (**9a**): Prepared as **8a**: colourless solid, m.p. 196°C; (Found: M^+, 308.0867. $C_{19}H_{16}O_2S$ requires: M^+, 308.0871); ν_{max} (KBr)/cm^{-1} 1659, 1611, 1535, 1494, 1349, 1305, 1276, 1240, 817, 716, 638; δ_H (270 MHz, $CDCl_3$) 2.77 (3H, s, $COCH_3$), 2.86 (2H, dd, ^3J = 10.3 Hz, ^3J = 3.5 Hz), 2.97 (2H, dd, ^3J = 10.3 Hz, ^3J = 3.5 Hz), 3.89 (3H, s, OCH_3), 6.87–6.95 (2H, m), 7.62 (1H, d, ^3J = 5.9 Hz), 7.86–7.96 (2H, m), 7.92 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 26.31, 29.54, 29.83, 55.37, 111.88, 113.68, 122.29, 126.86, 127.63, 128.31, 129.43, 131.05, 133.75, 135.74, 137.01, 141.79, 159.65, 196.86 (C=O); MS (EI, 70 eV) *m/z* (%) 308 (100) [M^+], 293 (46) [M^+–CH_3], 265 (7.5) [M^+–$COCH_3$].

4-Ethoxycarbonyl-9-methoxy-6,7-dihydrophenanthro[3,4-b]thiophene (**9c**): Prepared as **8a**: colourless solid, m.p. 114°C; (Found: M^+, 338.0978. $C_{20}H_{18}O_3S$ requires: M^+, 338.0977); ν_{max} (KBr)/cm^{-1} 3084, 2938, 2830, 1699, 1609, 1586, 1570, 1546, 1504, 1306, 1283, 1235, 1209, 1181, 1036, 851, 825, 768, 722, 707; δ_H (270 MHz, $CDCl_3$) 2.83 (2H, dd, ^3J = 9.2 Hz, ^3J = 5.4 Hz), 2.94 (2H, dd, ^3J = 9.2 Hz, ^3J = 5.4 Hz), 3.89 (3H, s, OCH_3), 4.50 (2H, q, OCH_2, ^3J = 7.0 Hz), 6.86–6.95 (2H, m), 7.61 (1H, d, ^3J = 5.9 Hz), 7.90–7.95 (2H, m), 8.08 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 14.52, 29.29, 29.95, 55.40, 61.21, 111.80, 113.61, 121.72, 122.81, 126.93, 126.97, 129.13, 129.43, 133.97, 135.17, 136.77, 140.24, 141.66, 159.46, 166.19 (C=O); MS (EI, 70 eV) *m/z* (%): 338 (100) [M^+].

8-Ethoxycarbonyl-3-methoxy-5,6-dihydrophenanthro[4,3-b][1]benzothiophene (**9d**): Prepared as **8a**: colourless solid, m.p. 125°C; (Found: M^+, 388.1140. $C_{24}H_{20}O_3S$ requires: M^+, 388.1133); ν(KBr)/cm^{-1} 2936, 1713, 1602, 1260, 1243, 1199, 1165, 1125, 812, 769, 753, 741; δ_H (270 MHz, $CDCl_3$) 1.48 (3H, t, ^3J = 7.0 Hz), 2.84–2.87 (2H, m), 2.95–2.98 (2H, m), 3.90 (3H, s, OCH_3), 4.57 (2H, q, OCH_2, ^3J = 7.0 Hz), 6.90 (1H, d, ^4J = 2.7 Hz), 6.97 (1H, dd, ^3J = 8.6 Hz, ^4J = 2.7 Hz), 7.41–7.47 (2H, m), 7.62 (1H, s), 7.87 (1H, d, ^3J = 7.0 Hz), 8.30–8.37 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 14.29, 29.52 (2C), 55.35, 61.67, 111.42, 114.07, 122.11, 122.22, 123.69, 124.26, 124.72, 126.36 (2C), 126.67, 126.70, 127.42, 132.51, 133.96, 135.50, 139.70, 141.43, 159.37, 169.22; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 389 (10) [MH^+], 388 (17) [M^+].

3-Methoxy-8-phenyl-5,6-dihydrophenanthro[4,3-b][1]benzothiophene (**9e**): Prepared as **8a**: colourless oil; (Found: M^+, 392.1231. $C_{27}H_{20}OS$ requires: M+, 392.1235); ν_{max} (KBr)/cm^{-1} 2934, 1610, 1501, 1438, 1260, 1042, 750 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 2.79–2.82 (2H, m), 2.87–2.90 (2H, m), 3.82 (3H, s, OCH_3), 6.83–7.45 (m, 10H), 7.23 (1H, s), 7.75 (1H, d, ^3J = 7.3 Hz), 8.31 (1H, d, ^3J = 8.6 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 392 (100) [M^+].

4-Benzoylphenanthro[3,4-b]thiophene (**10**): Solid, m.p. 188°C; (Found: M^+, 338.0761; $C_{23}H_{14}OS$ requires: M^+, 338.0765); ν_{max} (KBr)/cm^{-1} 1648, 1588, 1569, 1475, 1396, 1267, 1233, 1015, 811, 770, 752, 681, 663; δ_H (270 MHz, $CDCl_3$) 7.31–7.84 (10H, m), 7.78 (1H, s), 8.16–8.19 (2H, m), 8.25 (1H, d, ^3J = 8.4 Hz); δ_C (67.8 MHz, $CDCl_3$) 112.85, 119.05, 121.66, 124.49, 125.99, 126.62, 126.77, 128.40, 133.04, 135.54, 135.87, 138.77, 139.05, 144.96, 152.12, 190.26; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 339 (23) [MH^+]

8-ethoxycarbonyl-5,6-dihydrophenanthro[3,4-b][1]benzothiophene S,S-dioxide (**11a**): A solution of **8a** (125 mg, 0.35 mmol) and *m*-CPBA (30w%, 436 mg) in CH_2Cl_2 (15 ml) was stirred for 168h at rt. The mixture was poured into a sat. aq. Na_2CO_3 solution (150 ml) and the resulting mixture was stirred for 45 min. Thereafter, it was extracted with chloroform (3 × 30 ml). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/ether/$CHCl_3$ 2:1:1) gave **11a** (96 mg, 70%) as a colourless solid, m.p.173°C; (Found: M^+, 390.0927. $C_{23}H_{18}O_4S$ requires: M^+, 390.0926); ν_{max} (KBr)/cm^{-1} 2972, 1719, 1588, 1460, 1434, 1310, 1255, 1223, 1162, 1128, 772, 644, 541; δ_H (270 MHz, $CDCl_3$) 1.51 (3H, t, ^3J = 7.3 Hz, CH_3), 2.73–2.99 (4H, m), 4.55 (2H, q, OCH_2, ^3J = 7.3 Hz), 7.21–7.49 (5H, m), 7.79–7.87 (3H, m), 7.96 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 14.09, 28.81, 29.58, 62.46, 122.24, 124.73, 125.81, 126.26, 128.13, 129.06, 129.67, 129.98, 130.35 (2C), 130.89, 131.47, 132.31, 137.96, 138.62, 138.83, 139.78, 146.47, 163.49; MS (EI, 70 eV) *m/z* (%): 390 (100) [M^+], 345 (25), 252 (64).

8-Ethoxycarbonyl-5,6-dihydrophenanthro[4,3-b][1]benzothiophene S,S-dioxide (**11b**): Prepared as **11a**: Pale yellow solid; m.p. 185°C; (Found: M^+, 390.0920. $C_{23}H_{18}O_4S$ requires: M^+, 390.0926); ν_{max} (KBr)/cm^{-1} 2974, 1732, 1443, 1302, 1251, 1197, 1161, 1019, 782, 746; δ_H (270 MHz, $CDCl_3$) 1.46 (3H, t, ^3J = 7.0 Hz), 2.83–2.92 (4H, m), 4.52 (2H, q, ^3J = 7.0 Hz), 7.30–7.62 (5H, m), 7.69 (1H, s), 7.84 (1H, m), 7.92 (1H, m), 8.81 (1H, dd, ^3J = 7.6 Hz, ^4J = 0.8 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.15, 29.01, 29.84, 62.35, 121.78, 124.59, 127.49, 127.68, 128.03, 129.59, 129.76, 130.14, 130.21 (2C), 130.37, 133.05, 133.58, 135.67, 136.58, 137.51, 139.45, 142.32, 167.94; MS (EI, 70 eV) *m/z* (%): 390 (100) [M^+], 345 (24), 252 (39).

8-Acetyl-5,6-dihydrophenanthro[4,3-b][1]benzothiophene S,S-dioxide (**11c**):Prepared as **11a**: colourless solid; m.p. 221°C; [Found: MH^+, 361.0897. $C_{22}H_{17}O_3S$ requires: MH^+, 361.0898 (FAB)]; ν_{max} (KBr)/cm^{-1} 2946, 2836, 1699, 1445, 1297, 1159, 1127, 790, 756, 606, 580, 554, 502; δ_H (270 MHz, $CDCl_3$) 2.74 (3H, s, $COCH_3$), 2.84–2.93 (4H, m), 7.31–7.67 (9H, m), 7.44 (1H, s), 7.85 (1H, m), 8.81 (1H, dd, ^3J = 8.9 Hz, ^4J 1.1 Hz); δ_C (67.8 MHz, $CDCl_3$) 29.01, 30.00, 31.45, 122.07, 124.16, 127.54, 128.04, 128.46, 129.48, 129.74, 130.10, 130.19, 130.40 (2C), 133.76, 135.66, 135.96, 136.69, 137.51, 139.30, 142.65, 203.36; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 361 (31) [MH^+], 360 (18) [M^+].

8-Ethoxycarbonyl-3-methoxyphenanthro[4,3-b][1]benzothiophene (**11d**): Prepared as **11a**: colourless solid, m.p. 246°C; (Found: M^+, 420.1031. $C_{24}H_{20}O_5S$ requires: M^+, 420.1031); ν_{max} (KBr)/cm^{-1} 2946, 1731, 1599, 1505, 1300, 1268, 1198, 1156, 1132, 1038, 908, 854, 830, 753; δ_H (270 MHz, $CDCl_3$) 1.45 (3H, t, ^3J = 7.0 Hz), 2.80–2.90 (4H, m), 3.88 (3H, s, OCH_3), 4.51 (2H, q, OCH_2, ^3J = 7.0 Hz), 6.83 (1H, d, ^4J = 2.7 Hz), 6.99 (1H, dd, ^3J = 8.9 Hz, ^4J = 2.7 Hz), 7.50–7.61 (2H, m), 7.66 (1H, s), 7.85 (1H, m), 7.92 (1H, m), 8.78 (1H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz,$CDCl_3$) 29.46, 29.81, 55.32, 62.25, 112.02, 114.17, 121.73, 123.02, 124.70, 126.76, 129.93, 130.19, 130.28, 131.31, 132.99, 133.53, 134.78, 136.64, 137.55, 141.47, 141.63, 160.92, 168.00; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%): 421 (8.9) [MH^+], 420 (9.4) [M^+]. (Found: C, 68.44; H, 4.77. $C_{18}H_{14}OS$ requires: C, 68.55; H, 4.79%).

3-Methoxy-8-phenyl-5,6-dihydrophenanthro[4,3-b][1]benzothiophene S,S-dioxide (**11e**): Prepared as **11a**: (Found: M^+, 424.1127. $C_{27}H_{20}O_3S$ requires: M^+, 424.1133); ν_{max} (KBr)/cm^{-1} 2924, 2852, 1614, 1450, 1296, 1261, 1160, 1128 753, 704; δ_H (270 MHz, $CDCl_3$) 2.85 (4H, bs), 3.89 (3H, s, OCH_3), 6.65 (1H, d, ^3J = 8.1 Hz), 6.85 (1H, d, ^4J = 2.7 Hz), 7.01 (1H, dd, ^3J = 8.1 Hz, ^4J = 2.7 Hz), 7.16–7.36 (5H, m), 7.31 (1H, s), 7.39–7.53 (3H, m), 8.82 (1H, d, ^3J = 8.9Hz); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 425 (1.7) [MH^+], 424 (1.9) [M^+].

X-ray crystal data and structure determination of **5f**: $C_{23}H_{20}O_2S$, *M*r 360.47, triclinic, space group P-1(#2), a = 7.997(2) Å b = 10.399(3) Å c = 11.780(3) Å α = 73.63(2)°, β = 75.50(1)°, γ = 82.40(2)°, V 908.0(3) Å^3, Z = 2, D_{calc} = 1.32 g cm^{-3}, μ(CuKα) 16.87 cm^{-1}; F(000) = 380, λ= 1.54187 Å. Data were collected using a crystal size 0.26 × 0.22 × 0.10 mm^3 on a Rigaku Raxis-Rapid imaging plate diffractometer. A total of 10054 reflections were collected for $4.0 < \Theta < 68.2°$ and $-9 \le h \le 9$, $-12 \le k \le 12$, $-14 \le l \le 14$. There were 3055 independent reflections and 2702 reflections with $I > 2\sigma(I)$ were used in the refinement. Multi scan absorption correction was applied (T. Higashi, Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan, 1995), T_{min} = 0.677, T_{max} = 0.845. The structure was solved by direct methods (SIR 97)[16] and refined using CRYSTALS.[17] The final R indices were [$I > 2.00\sigma(I)$] R_1 = 0.037, and (all data) R = 0.041 and wR_2 = 0.119. The goodness-of-fit on F^2 1.007 and the largest difference peak and hole was 0.32 and –0.30 e Å^{-3}. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 269473).

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