Photochemical Coupling between Halogenoheterocyclic and Heterocyclic Derivatives

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The photochemical reaction between 5-iodo-heteroaryl derivatives **1a–d** and both 3-heteroaryl allylic alcohols (**2a–b**) and acetates (**3a–b**) have been investigated. The presence of an alcoholic function was not compatible with photochemical coupling since compounds **1a–d** were photoreduced in the presence of an alcohol. In contrast, the acetates **3a, b** gave the expected coupling products. The presence of a weak electron-withdrawing group on the alkene induced an inverted regiochemistry giving only aryl–aryl coupling products. The same behaviour was observed using 2-(3-acetoxyprop-1-ynyl)thiophene **8**, in which case only the product deriving from aryl–aryl coupling was again observed. When 2-prop-1-ynylthiophene **11** was used as starting material, the some product resulting from attack on the methyl group **13** was observed. Photochemical coupling between 2-thienylacetonitrile (**14**) and halogenothienyl derivatives **1b, c** gave no reaction product. In contrast, the irradiation of methyl 2-thienylacetate **15** and methyl 2-(2-thienyl)propionate (**17**) in the presence of **1b, c** did give the corresponding coupling products.

Because of their therapeutic potential, interest in organic compounds showing photodynamic properties is considerable.[1,2] We described such a group of heterocyclic compounds recently,[3–5] the synthesis of which we now report.

Earlier,[6] we reported that 5-iodothienyl derivatives couple with arylalkenes and arylalkynes in a reaction which worked very well when the alkene had an α-alkyl substituent.[7] However, with arylalkynes we obtained a mixture of regioisomeric products.[6]

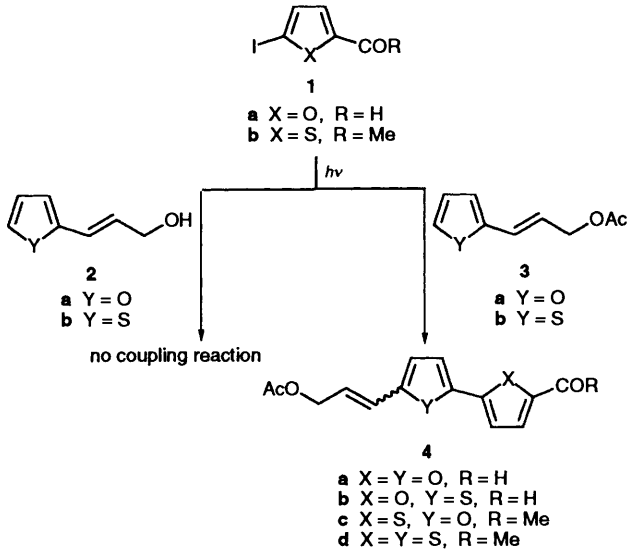
Here[8] we report our results of a study of the reactivity of halogenofuryl and halogenothienyl derivatives in the presence of a weak electron-withdrawing group such as CH_2OAc. In the knowledge that an electron-donating group (alkyl) favours the coupling reaction, while a strong electron-withdrawing group inhibits it completely, we wished to explore the possibility of a weak electron-withdrawing group depressing the reactivity of the alkene or alkyne moiety and thus leading to selective photocoupling of the aromatic part of the molecule.

In our previous work on photochemical arylation of halogenoheterocycles, we found that 5-iodothienyl derivatives couple with thiophene, 2-methylthiophene and 2-bromothiophene.[8,9] Although our results showed that both electron-donating (Me) and electron-withdrawing groups (Br) allowed photochemical aryl–aryl coupling, we were unable to isolate any coupling products of 5-iodothienyl derivatives with nitrobenzene, benzonitrile or methyl benzoate.[11]

Here, we present our results for the photochemical coupling between 5-iodothienyl derivatives and both 2-cyanomethylthiophene and methyl 2-thienylacetates. These substrates were used in order to establish whether the presence of a carbon atom between the heteroaromatic ring and the electron-withdrawing groups could modify the reactivity of the substrate or whether the presence of some substituents in the substrates prevented photochemical coupling.

Results and Discussion

Initial experiments were conducted with 3-(2-furyl)- and 3-(2-thienyl)-allylic alcohols **2a, b** and the corresponding acetates **3a, b** as photochemical partners of the halogenofuryl and halogenothienyl derivatives **1a** and **1b**. Irradiation of **1a** and **1b** in the presence of **2a, b** gave no coupling product (Scheme 1), a result in agreement with our previous observations; in fact, neither 2-thienylmethanol nor 2-(thienyl)ethanol gave coupling product.[11] Probably hydrogen abstraction from the alcohol, a competitive reaction in this case was able to quench the lowest excited triplet state of **1a, b**. The formation of reduction products of **1a, b**, detected by GC–MS, confirmed this hypothesis. In contrast, use of the corresponding acetates **3a, b** gave products deriving from photoarylation of the heterocyclic ring **4a–d** (Scheme 1, Table 1). In this case, the presence of the acetate function changed the regioselectivity of the reaction, thereby allowing us to synthesize bithienyls, bifuryls and mixed derivatives as *cis–trans* mixtures.



Scheme 1

These results show that a weak electron-withdrawing substituent (CH_2OAc) on the alkene can inhibit attack of the halogenoheterocyclic derivative at the same position of the alkene. Previously, we have described the attack of **1a, b** on the olefinic part of arylalkenes as being due to the stability of the benzilic type intermediate thus formed.[6] Our new results clearly show that the most important factor driving the attack of **1a, b**

Table 1 Photochemical reactivity of **1a**, **b** in the presence of heteroaryllallyl acetates **3**

Substrate	Reagent	Irradiation time (*t*/h)	Product	Yield (%)[a]
1a	**3a**	1	**4a**	22
1a	**3b**	6	**4b**	68
1b	**3a**	1	**4c**	83
1b	**3b**	5	**4d**	66

[a] All yields refer to isolated, chromatographically pure compounds.

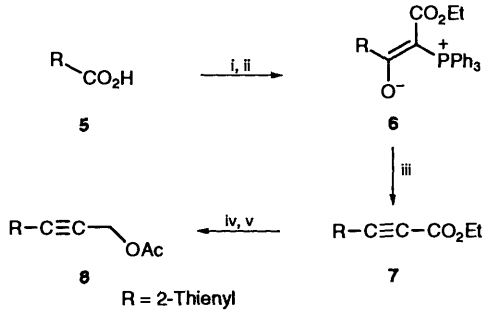
Table 2 Photochemical reactivity of **1a–d** in the presence of **8**

Substrate	Irradiation time (*t*/h)	Conversion	Product	Yield (%)[a]
1a	5.5	100	**9a**	26
1b	6.0	60	**9b**	87
1c	4.5	60	**9c**	55
1d	5.0	74	**9d**	34

[a] All yields refer to isolated, chromatographically pure compounds.

on arylalkenes is the electron density on the carbons that can be attacked.

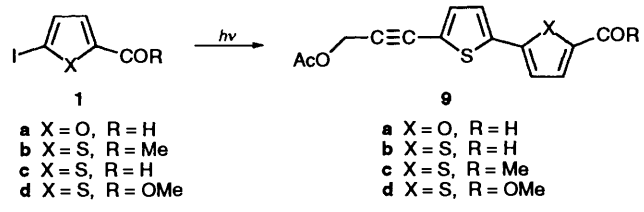
Subsequently, we repeated the reaction with 2-(3-acetoxyprop-1-ynyl)thiophene **8**; we did not use the corresponding alcohol since it had failed to couple with **2a**, **b**. Compound **8** was prepared as follows (see Scheme 2). Thiophene-2-



Scheme 2 *Reagents and conditions:* i, $SOCl_2$; ii, Ph_3PCHCO_2Et, C_6H_6, reflux; iii, 240 °C, 10–14 mmHg; iv, diisobutylaluminium hydride, tetrahydrofuran, −78 °C; v, Ac_2O, pyridine

carboxylic acid **5** was converted into the corresponding acyl chloride which upon treatment with (ethoxycarbonylmethylene)triphenylphosphorane gave the betaine **6**. Thermolysis of this gave ethyl 3-(2-thienyl)propiolate **7**.[12] Which upon reduction with diisobutylaluminium hydride afforded the corresponding alcohol.[13] Acetylation of the latter gave compound **8**.

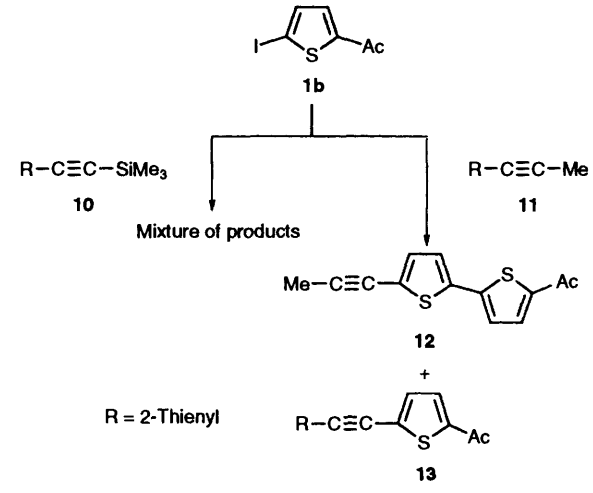
Photochemical coupling between compound **8** and the halogenoheterocycles **1a–d** gave the products shown in Scheme 3 and Table 2. In these reactions, the presence of an electron-



Scheme 3

withdrawing group inhibits the attack of **1a–d** on the triple bond in favour of the formation of arylation products. Compounds **1** underwent only partial conversion, a result, perhaps, of polymer formation on the lamp which prevented effective irradiation of the reaction mixture.

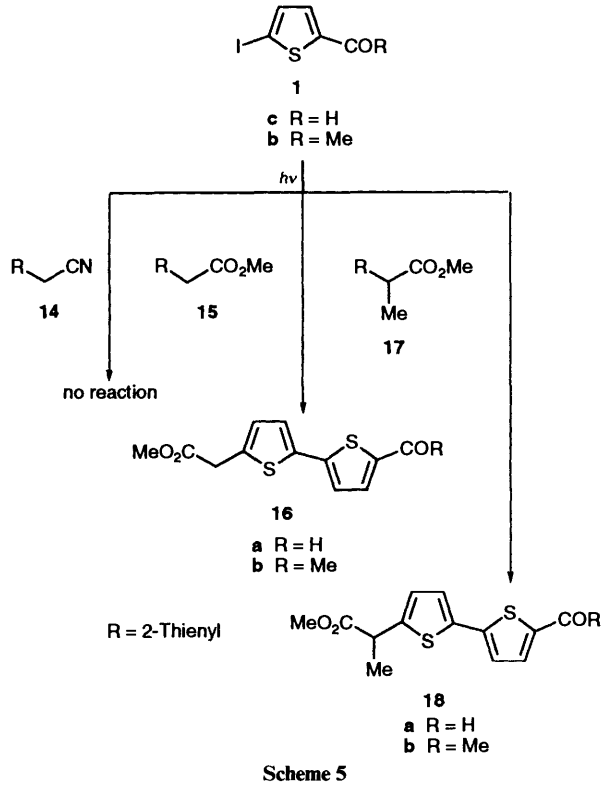
We believe that the above-reported reactions of compound **8** are significant since they are the first in which coupling of a substituted arylalkyne has been reported. While all the reactions of unsubstituted heteroarylalkynes gave mixtures of products,[6] that of **1b** with 2-(trimethylsilylethynyl)thiophene **10** also gave a product deriving from desilylated starting material. Furthermore, the photochemical reaction of **1b** with 2-(prop-1-ynyl)thiophene **11** gave a 1 : 1 mixture of **12** and **13** (Scheme 4).



Scheme 4

In conclusion, **8** is the only compound studied able to give selective photocoupling reaction with **1a–d**.

In related work, the irradiation of **1c** with 2-thienylacetonitrile **14** in acetonitrile, surprisingly, failed to give a reaction product (Scheme 5). Although it is unclear why acetonitrile is,



Scheme 5

generally, the best solvent for these reactions,[14] a simple acetonitrile derivative was ineffective.

Table 3 Photochemical reaction of **1b, c** with thienylacetate derivatives **15, 17**

Substrate	Reagent	Irradiation time (*t*/h)	Product	Yield (%)[a]
1c	**15**	5	**16a**	65
1b	**15**	5	**16b**	60
1c	**17**	4.5	**18a**	47
1b	**17**	4.5	**18b**	45

[a] All yields refer to isolated chromatographically pure product.

In contrast compounds **1b, c** when irradiated in the presence of methyl 2-thienylacetate **15**, gave the corresponding coupling products **15a, b** in good yields (Scheme 5, Table 3), no photoisomerization by-products being formed.[15]

Methyl 2-(2-thienyl)propionate **17** when irradiated in the presence of **1b, c** gave the corresponding coupling products **16a, b**, although in lower yields than when using compound **15** (Table 3). This reaction is of potential interest in the synthesis of non-steroidal anti-inflammatory drugs.

In conclusion, the halogenoheterocycles **1a–d** when irradiated in the presence of arylalkenes and arylalkynes substituted with weak electron-withdrawing groups showed that such substituents can change the selectivity in photochemical coupling reactions. Furthermore, we have shown that compounds **14** and **15** gave completely different photochemical behaviour when irradiated in the presence of **1a–d**.

Experimental

Starting materials.—5-Iodo-2-furaldehyde **1a** was obtained through reaction of 5-bromo-2-furaldehyde with KI.[16] 5-Bromo-2-furaldehyde was prepared by reaction of 2-furaldehyde with bromine in 1,2-dichloroethane.[17] 5- Iodothiophene-2-carbaldehyde **1c** was prepared from thiophene-2-carbaldehyde by reduction with $NaBH_4$, iodination of the resulting alcohol with iodine and HgO, followed by its oxidation to the corresponding aldehyde with pyridinium chlorochromate.[10] 2-Acetyl-5-iodothiophene **1b** was prepared by treating 2-iodothiophene with Ac_2O and H_3PO_4[18] and 2-iodothiophene by iodination of thiophene with iodine and HgO.[19] Methyl 5-iodothiophene-2-carboxylate was prepared by iodination of methyl thiophene-2-carboxylate[20] with iodine and iodic acid.[21] 2-(3-Acetoxyprop-1-enyl)furan **3a** was obtained by reduction of 3-(2-furyl)acrylic acid with $LiAlH_4$ and acetylation of the product; 2-(3-acetoxyprop-1-enyl)thiophene **3b** was similarly prepared. 2-(Prop-1-ynyl)thiophene **11** was obtained by treatment of 2-(prop-1-enyl)thiophene with bromine to give a dibromide and subsequent reaction of this with Bu^{t}OK. 2-(Prop-1-enyl)thiophene was obtained by a Wittig reaction between thiophene-2-carbaldehyde and ethyl-(triphenyl)phosphonium iodide in the presence of BuLi.[22] 2-Thienylacetonitrile **14** was commercially available (Fluka). Methyl 2-thienylacetate **15** was obtained from the corresponding acid through reaction with MeOH in the presence of sulfuric acid. Methyl 2-(2-thienyl)propionate **17** was obtained by metallation of methyl 2-thienylacetate with lithium diisopropylamide in tetrahydrofuran at −30 °C and subsequent reaction of the product with methyl iodide.[23]

(E,Z)-5-(3-*Acetoxyprop*-1-*enyl*)-5′-*acetyl*-2,2′-*bithienyl* **4d** (*General Procedure*).—Compound **1b** (1 g) and **3b** (5 g) were dissolved in acetonitrile (300 cm^3) and the solution was purged with nitrogen for 1 h. It was then irradiated in an immersion apparatus with a 500 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water jacket. After 5 h, the mixture was diluted with chloroform (500 cm^3), washed with aqueous $Na_2S_2O_3$ (0.05 mol dm^{-3}), dried (Na_2SO_4) and evaporated under reduced pressure to yield a crude product which was chromatographed on SiO_2. Elution with hexane–EtOAc (4:1) gave pure **4d** (800 mg, 66%) as a very dense oil (Found: 58.6; H, 4.7. $C_{15}H_{14}O_3S_2$ requires C, 58.80; H, 4.61%); δ_H 7.65 (1 H, d, *J* 4), 7.3–6.9 (3 H, m), 6.72 (1 H, d, *J* 16), 6.2 (1 H, m), 4.68 (2 H, m), 2.55 (3 H, s) and 2.08 (3 H, s); ν_{max}/cm^{-1} 1732, 1653, 1449, 1433, 1431, 1361, 1310, 1272, 1250, 1240, 1227, 1194, 1029, 953 and 906; *m*/*z* 307 (14%), 306 (85), 264 (30), 263 (14), 247 (15), 235 (16), 231 (19), 203 (43), 190 (10), 181 (11), 180 (100), 171 (24), 165 (33), 152 (39), 127 (14), 115 (10), 113 (25) and 97 (17).

(E,Z)-5-(3-*Acetoxyprop*-1-*enyl*)-5′-*formyl*-2,2′-*bifuryl* **4a**.—Very dense oil (Found: C, 64.5; H, 4.8. $C_{14}H_{12}O_5$ requires C, 64.61; H, 4.65%); δ_H 9.55 (1 H, s), 7.3–5.9 (6 H, m), 4.66 (2 H, m) and 2.06 (3 H, s); ν_{max}/cm^{-1} 1734, 1671, 1526, 1450, 1368, 1250, 1232, 1019, 959, 786 and 754; *m*/*z* 260 (51%), 218 (54), 217 (59), 203 (11), 202 (76), 201 (16), 200 (12), 189 (32), 175 (34), 161 (15), 153 (27), 150 (41), 145 (12), 144 (8), 143 (8), 131 (9), 123 (8), 122 (12), 121 (7), 116 (8), 115 (31), 103 (8), 97 (100) and 91 (12).

(E,Z)-5-[5,(3-*Acetoxyprop*-1-*enyl*)-2-*thienyl*]-2-*furaldehyde* **4b**.—Very dense oil (Found: C, 61.0; H, 4.5. $C_{14}H_{12}O_4S$ requires C, 60.86; H, 4.38%); δ_H 9.51 (1 H, s), 7.28 (1 H, d, *J* 4), 7.21 (1 H, d, *J* 4), 7.11 (1 H, m), 6.85 (1 H, m), 6.74 (1 H, d, *J* 4), 6.53 (1 H, d, *J* 4), 4.07 (2 H, m) and 2.01 (3 H, s); ν_{max}/cm^{-1} 1733, 1668, 1578, 1537, 1500, 1444, 1387, 1363, 1238, 1029, 961, 798, 763, 759, 735, 699 and 603; *m*/*z* 276 (50%).

(E,Z)-5-[5-(3-*Acetoxyprop*-1-*enyl*)-2-*furyl*]-2-*acetylthiophene* **4c**.—Very dense oil (Found: C, 61.5; H, 5.0. $C_{15}H_{14}O_4S$ requires C, 62.05; H, 4.86%); δ_H 7.58 (1 H, d, *J* 4), 7.31 (1 H, m), 6.7–6.0 (4 H, m), 4.72 (2 H, m), 2.53 (3 H, s) and 2.09 (3 H, s); ν_{max}/cm^{-1} 1731, 1652, 1600, 1499, 1430, 1362, 1273, 1244, 1017, 958 and 927; *m*/*z* 290 (4%), 289 (10), 288 (63), 246 (48), 231 (12), 230 (16), 229 (100), 228 (21), 217 (10), 187 (10), 186 (16), 85 (26) and 83 (36).

Photochemical Reaction of **1b** *with* 2-(*Prop*-1-*ynyl*)*thiophene*.—Compound **1b** (400 mg) and compound **11** (1.5 g) were dissolved in acetonitrile (300 cm^3) **11**. The general procedure for **4d** was then followed with irradiation for 5.5 h. After removal of the solvent, the crude product was chromatographed on SiO_2. Elution with benzene gave pure **12** (180 mg, 49%) and **13** (180 mg, 49%). **12**: m.p. 93–94 °C (lit.,[24] 93–94.5 °C) (Found: C, 67.6; H, 4.6. Calc. for $C_{13}H_{10}S_2$: C, 67.79; H, 4.38%); δ_H 7.50 (1 H, d, *J* 4), 7.22 (2 H, m), 7.03 (2 H, d, *J* 4), 2.60 (3 H, 2 s) and 2.12 (3 H, s); ν_{max}/cm^{-1} 2225, 1660, 1430, 1360, 1275, 1075 and 910 cm^{-1}; **13**: Syrup (Found: C, 67.9; H, 4.5. $C_{13}H_{10}S_2$ requires C, 67.79; H, 4.38%); δ_H 7.38 (2 H, m), 7.0 (3 H, m), 2.40 (3 H, s) and 2.20 (2 H, s); ν_{max}/cm^{-1} 2225, 1660, 1450, 1410, 1360, 1275 and 855.

Ethyl 3-(2-*Thienyl*)*propiolate* **7**.—Thiophene-2-carboxylic acid **5** (20 g, 0.16 mol) was treated with $SOCl_2$ (57 cm^3) under reflux for 2 h. Evaporation under reduced pressure of the remaining $SOCl_2$ left the corresponding acyl chloride (20 g, 0.14 mol) which was dissolved in dry benzene (150 cm^2) and added dropwise to a solution of (ethoxycarbonylmethylidene)triphenylphosporane (76 g, 0.22 mol) in dry benzene (500 cm^3). The mixture was refluxed for 12 h. After cooling, the mixture was filtered and the solvent removed under reduced pressure. The betaine, dissolved in chloroform, was filtered through SiO_2 and then crystallized twice from EtOAc to give pure **6** (46 g, 0.1 mol); δ_H 7.91 (1 H, dd, *J* 3.7 and 1.2), 7.75 (5 H, m), 7.5–7.4 (11 H, m), 7.02 (1 H, dd, *J* 4.9 and 3.7), 3.71 (2 H, q, *J* 7) and 0.66 (3 H, t, *J* 7). Pyrolysis of the betaine **6** in a Kugelrohr apparatus under

reduced pressure (10 mmHg) at 240 °C gave pure title compound **7** (16 g, 0.09 mol, 64%) as a dense oil; δ_H 7.46 (1 H, dd, *J* 4 and 1), 7.44 (1 H, dd, *J* 5 and 1), 7.03 (1 H, dd, *J* 5 and 4), 4.27 (2 H, q, *J* 7) and 1.33 (3 H, t, *J* 7); δ_C 137.0, 131.57, 129.0, 119.94, 112.78, 85.30, 62.42 and 14.27; ν_{max}/cm^{-1} 2205, 1697, 1367, 1267, 1245, 1211, 1180, 1168, 1157, 1136, 1092, 1057, 1043, 1015, 748, 746, 695 and 677; *m/z* 181 (3%), 180 (32), 136 (13), 135 (99), 109 (8), 108 (100), 82 (3), 81 (10), 77 (7), 69 (9) and 63 (23).

2-(3-*Acetoxyprop*-1-*ynyl*)*thiophene* **8**.—A 1 mol dm^{-3} solution of diisobutylaluminium (92 mmol) in CH_2Cl_2 was added to a solution of compound **7** (7 g, 40 mmol) dissolved in anhydrous tetrahydrofuran (500 cm^3) at −78 °C, under Ar. This mixture was stirred at −78 °C for 2 h and then at room temperature overnight. It was then treated first with saturated aqueous NH_4Cl (50 cm^3) and then with 10% HCl until pH 4–5 was reached. After this the mixture was extracted with Et_2O. After the extract had been washed with 10% HCl and brine it was dried (Na_2SO_4) and evaporated to yield a pure alcohol (5 g, 36 mmol, 90%) as a dense oil; δ_H 7.24 (1 H, dd, *J* 5 and 1), 7.19 (1 H, dd, *J* 4 and 1), 6.95 (1 H, dd, *J* 5 and 4), 4.48 (2 H, s) and 1.83 (1 H, br s); ν_{max}/cm^{-1} 2225, 1421, 1357, 1265, 1190, 1080, 1045, 1020, 847, 832 and 702. The alcohol, dissolved in pyridine (114 cm^3), was treated with Ac_2O (114 cm^3) for 48 h, after which work-up gave a crude product. This was chromatographed on SiO_2 with hexane–EtOAc (4:1) as eluent to give pure title compound **8** (5.8 g, 32 mmol, 90%) (Found: C, 60.1; H, 4.7. $C_9H_8O_2S$ requires C, 59.98; H, 4.47%); δ_H 7.26 (1 H, dd, *J* 5 and 1), 7.23 (1 H, dd, *J* 4 and 1), 6.95 (1 H, dd, *J* 5 and 4), 4.89 (2 H, s) and 2.10 (3 H, s); ν_{max}/cm^{-1} 2230, 1741, 1426, 1375, 1359, 1223, 1196, 1118, 1026, 849 and 705.

5-[5-(3-*Acetoxyprop*-1-*ynyl*)-2-*thienyl*]-2-*furaldehyde* **9a** (*General Procedure*).—Compound **1a** (1 g) and compound **8** (4 g) were dissolved in acetonitrile (300 cm^3) and the procedure for **4d** was then followed, with irradiation for 5.5 h, to give the pure title compound **9a** (320 mg, 26%) as a very dense oil (Found: C, 61.2; H, 3.9. $C_{14}H_{10}O_4S$ requires C, 61.30; H, 3.67%); δ_H 9.61 (1 H, s), 7.50 (1 H, d, *J* 5.5), 7.35 (1 H, d, *J* 4), 7.30 (1 H, d, *J* 5.5), 7.27 (1 H, d, *J* 4), 4.95 (2 H, s) and 2.12 (3 H, s); ν_{max}/cm^{-1} 2225, 1738, 1671, 1596, 1577, 1533, 1495, 1431, 1412, 1387, 1374, 1357, 1337, 1304, 1257, 1250, 1195, 1152, 1115, 1086, 1062, 1024, 970, 925 and 854.

5-(3-*Acetoxyprop*-1-*ynyl*)-5′-*acetyl*-2,2′-*bithienyl* **9c**.—Very dense oil (Found: C, 59.3; H, 4.2. $C_{15}H_{12}O_3S_2$ requires C, 59.19; H, 3.9%); δ_H 7.53 (1 H, d, *J* 4), 7.12 (3 H, m), 4.88 (2 H, s), 2.50 (3 H, s) and 2.10 (3 H, s); ν_{max}/cm^{-1} 2405, 1738, 1654, 1509, 1454, 1430, 1411, 1357, 1271, 1241 and 1026.

5′-(3-*Acetoxyprop*-1-*ynyl*)-2,2′-*bithienyl*-5-*carbaldehyde* **9b**.—Very dense oil (Found: C, 57.3; H, 3.6. $C_{14}H_{10}O_3S_2$ requires C, 57.91; H, 3.47%); δ_H 9.84 (1 H, s), 7.64 (1 H, d, *J* 4), 7.22 (1 H, d, *J* 4), 7.19 (1 H, d, *J* 4), 7.16 (1 H, d, *J* 4), 4.90 (2 H, s) and 2.11 (3 H, s); ν_{max}/cm^{-1} 2825, 2225, 1738, 1660, 1571, 1539, 1509, 1457, 1430, 1376, 1357, 1321, 1244, 1215, 1196, 1188, 1176, 1160, 1142, 1090, 1046, 1024, 906 and 804.

Methyl 5′-(3-*Acetoxyprop*-1-*ynyl*)-2,2′-*bithienyl*-5′-*carboxylate* **9d**.—Very dense oil (Found: C, 56.1; H, 4.0. $C_{15}H_{12}O_4S_2$ requires C, 56.24; H, 3.78%); δ_H 7.74 (1 H, d, *J* 4), 7.53 (1 H, d, *J* 4), 7.27 (1 H, d, *J* 5.5), 7.22 (1 H, d, *J* 5.5), 4.99 (2 H, s), 3.88 (3 H, s) and 2.14 (3 H, s); ν_{max}/cm^{-1} 2225, 1734, 1713, 1644, 1598, 1524, 1511, 1457, 1434, 1410, 1374, 1356, 1331, 1298, 1267, 1261, 1243, 1190, 1147, 1098, 1050, 966, 926, 906, 855, 816 and 810.

Methyl 5′-*Formyl*-2,2′-*bithienyl*-5-*ylacetate* **16a**: *General Procedure*.—Compound **1c** (1 g) and compound **15** were dissolved in acetonitrile (300 cm^3) and the procedure for **4d** was then followed. Chromatography of the product on SiO_2, eluting with hexane–EtOAc (3:1), gave the pure title compound **16a** (670 mg, 60%) as a viscous oil (Found: C, 54.3; H, 3.6. $C_{12}H_{10}O_3S_2$ requires C, 54.12; H, 3.78%); δ_H 9.80 (1 H, s), 7.61 (1 H, d, *J* 4), 7.2 (2 H, m), 6.86 (1 H, d, *J* 3), 3.81 (2 H, s) and 3.71 (3 H, s); δ_C 183.23, 142.07, 137.98, 129.08, 128.71, 127.23, 126.37, 126.17, 125.49, 124.55, 35.63, 29.91 and 14.30; ν_{max}/cm^{-1} 1733, 1661, 1434, 1333, 1249, 1238, 1222, 1172, 1052, 1009, 906 and 810; *m/z* 268 (3%), 267 (4), 266 (29), 209 (10), 208 (12), 207 (100), 179 (6), 178 (2), 177 (4), 135 (3), 134 (5) and 103 (3); λ_{max}(EtOH)/nm 350 (ε/dm^3 mol^{-1} cm^{-1} 7493) and 276 (4141).

Methyl 5′-*Acetyl*-2,2′-*bithienyl*-5-*acetate* **16b**.—Viscous oil (Found: C, 55.6; H, 4.5. $C_{13}H_{12}O_3S_2$ requires C, 55.69; H, 4.31%); δ_H 7.51 (1 H, d, *J* 4), 7.10 (2 H, m), 7.05 (1 H, d, *J* 4), 3.90 (2 H, s), 3.68 (3 H, s) and 2.49 (3 H, s); δ_C 190.99, 171.70, 133.87, 133.58, 129.09, 128.54, 127.06, 125.79, 125.26, 124.40, 35.52, 26.67 and 14.33; ν_{max}/cm^{-1} 1731, 1652, 1467, 1450, 1447, 1432, 1370, 1358, 1273, 1254, 1243, 1176, 1042, 1012, 928, 906 and 813; *m/z* 282 (10%), 281 (17), 280 (98), 267 (3), 266 (4), 265 (30), 223 (4), 222 (5), 221 (34), 208 (2), 207 (5), 206 (7), 181 (9), 180 (13), 179 (100), 178 (23), 176 (30), 145 (4), 135 (9), 134 (21), 121 (11), 103 (8), 89 (8), 69 (6) and 59 (5); λ_{max}(EtOH)/nm 343 (ε/dm^3 mol^{-1} cm^{-1} 7258), 275 (3575) and 248 (4323).

Methyl (R,S)-2-(5′-*formyl*-2,2′-*bithienyl*-5-*yl*)*propionate* **18a**.—Viscous oil (Found: C, 5.9; H, 4.4. $C_{13}H_{12}O_3S_2$ requires C, 55.69; H, 4.31%); δ_H 9.82 (1 H, s), 7.63 (1 H, d, *J* 4), 7.18 (2 H, d, *J* 4), 6.88 (1 H, d, *J* 4), 3.71 (3 H, s), 3.45 (1 H, q, *J* 7) and 1.58 (3 H, d, *J* 7); ν_{max}/cm^{-1} 2820, 1732, 1661, 1605, 1567, 1511, 1465, 1432, 1378, 1322, 1170, 1084, 1051, 986, 906, 880 and 853; *m/z* 282 (3%), 281 (4), 280 (25), 223 (10), 222 (14), 221 (100), 160 (8), 147 (6), 110 (4) and 69 (3).

Methyl (R,S)-2-(5′-*Acetyl*-2,2′-*bithienyl*-5-*yl*)*propionate* **18b**.—Viscous oil (Found: C, 57.0; H, 5.0. $C_{14}H_{14}O_3S_2$ requires C, 57.12; H, 4.79%); δ_H 7.53 (1 H, d, *J* 4), 7.1 (m, 3 H), 3.70 (3 H, s), 3.45 (1 H, q, *J* 7), 2.50 (3 H, s) and 1.56 (3 H, d, *J* 7); ν_{max}/cm^{-1} 1737, 1657, 1519, 1470, 1437, 1380, 1362, 1321, 1279, 1180, 1174, 1076, 1034, 930, 908, 879 and 856; *m/z* 296 (4%), 295 (5), 294 (33), 279 (7), 235 (100), 207 (5), 148 (4), 147 (8) and 110 (4).

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