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A modular procedure for the synthesis of functionalised β-substituted terthiophene monomers for conducting polymer applications

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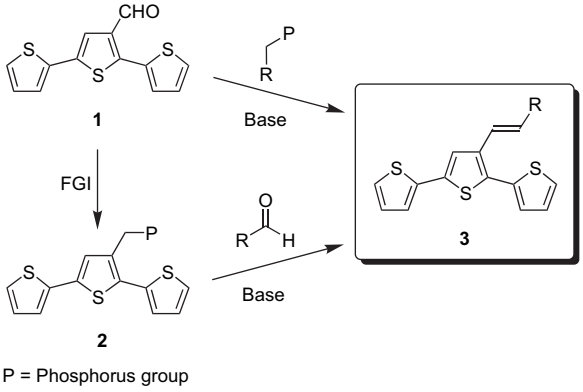
Abstract—An efficient modular strategy has been developed for the synthesis of β-functionalised terthiophene monomers using Suzuki–Miyaura and Wittig/Horner–Emmons chemistries. This paper discusses the problems encountered with converting the β-terthiophene aldehyde building block to the β-terthiophene phosphonium salt and the use of this material in a Wittig condensation. An improved strategy using the β-terthiophene phosphonate building block constructed via Suzuki–Miyaura coupling protocols was developed. We have synthesised and characterised a broad range of functionalised terthiophene materials that have been designed for specific end-use applications. The availability of these building blocks has dramatically increased access to a range of key monomers.

1. Introduction

As a part of our continued efforts to use functionalised conducting polythiophenes for targeted applications we focused on developing a method that would allow rapid construction of highly functionalised monomers. Using a building block approach,[1] we reported that both 3′-formylterthiophene **1** and terthiophene-3′-methylenephosphorus derivative **2** served as ideal platforms from which different monomers, such as **3**, could be accessed using Wittig or Horner–Emmons chemistries (Scheme 1). This methodology eliminated the need to design new syntheses for each different target monomer. Recent work has been directed at obtaining practical quantities of phosphonium salt of type **2**; unfortunately, this proved to be problematic for several reasons. These difficulties were overcome by the design and synthesis of the phosphonate derivative of **2**. The current paper describes synthetic routes to these phosphorus derivatives and the implementation of this building block approach in the synthesis of a variety of desirable functionalised monomers.



Scheme 1.

2. Results

2.1. Synthesis of terthiophene-methylene phosphonium salt building block

Since 3′-formylterthiophene[2] could be easily prepared on a 50–100 g scale, it was envisaged that functional group interconversion (FGI) of the aldehyde group would provide an easy route to the terthiophene phosphonium salt building block. As reported previously,[1] reduction of aldehyde **1** with sodium borohydride proceeded smoothly to give the alcohol **4** (Scheme 2). Analysis of the alcohol by ^{1}H NMR

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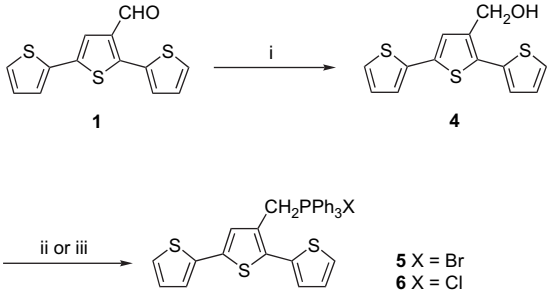
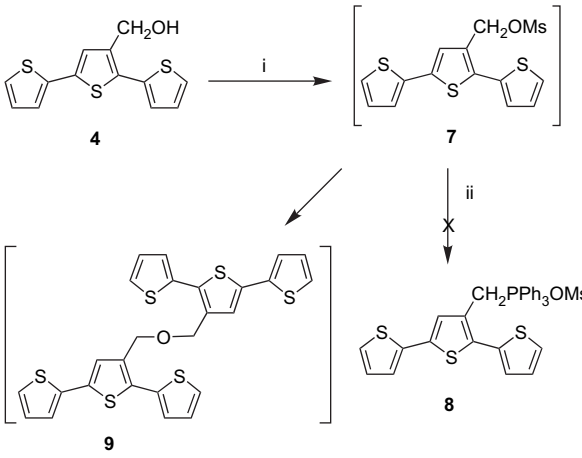
spectroscopy indicated the aromatic protons of the thiophene rings and two new up-field signals. These signals at 4.76 and 1.80 ppm were attributed to the methylene protons and the hydroxyl group, respectively. Following known procedures to form aryl phosphonium salts directly from aryl methylene alcohols,[3,4] a solution of **4** in benzene was heated in the presence of triphenylphosphine hydrogen bromide (PPh_3.HBr) to give the desired bromide salt **5**, albeit in surprisingly poor yield (34%) (Method A). Attempts to improve the yield by employing a mild two-step procedure proved tedious and provide only marginally better yields. Treatment of the alcohol **4** at low temperature with thionyl chloride presumably affords 3′-(chloromethyl)terthiophene. Attempts to isolate and purify this chloride before proceeding to the following step were unsuccessful; the chloride was unstable and decomposed on handling. Instead, the crude chloride was heated in the presence of triphenylphosphine in benzene and after cooling and crystallisation afforded the chloride phosphonium salt **6** in 52% yield (Method B).



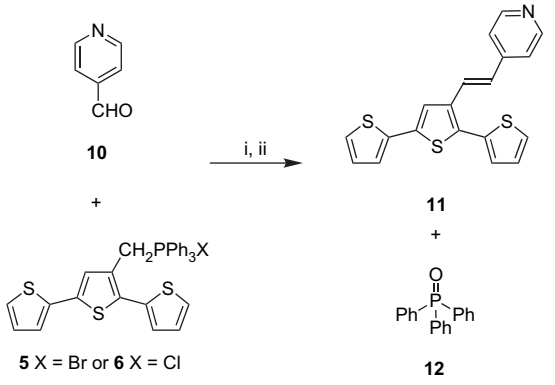
Scheme 2. Reagents and conditions: (i) $NaBH_4$, THF, EtOH, 84%; (ii) Method A: $PPh_3 \cdot HBr$, benzene, reflux, 34% or (iii) Method B: (a) $SOCl_2$, pyridine, 0 °C; (b) PPh_3, reflux, 52%.

Because of the unexpected difficulty in synthesising phosphonium salts **5** and **6**, we believed a closer examination of these reactions was warranted. Since 3′-(chloromethyl)-terthiophene could not be isolated, we sought to form a leaving group that could be detected by NMR spectroscopy and aid in determining the effectiveness of this step. Attempts to convert **4** under standard conditions[5] (Scheme 3) to the mesylate confirmed our concerns. Analysis of the crude product by ^1H NMR indicated a relatively simple spectrum, however, the key methyl signal expected from the mesylate group of **7** could not be detected. Apart from some minor shifts in the aromatic region the only noticeable change was an up-field shift of the methylene signal from 4.76 ppm of **4** to 4.64 ppm in the product. Attempts to purify and isolate this product for further characterisation were unsuccessful as the oily substance readily decomposed when subjected to column chromatography. Based on the ^1H NMR data of the crude compound, we concluded that the bis-terthiophene ether **9** was formed. Formation of only **9** under these mild conditions may explain the low yields from the earlier phosphonium salt syntheses described in Scheme 2.

With access to phosphonium salts **5** and **6**, we decided to evaluate the reactivity of these salts in typical Wittig reactions. The need to develop and study functionalised monomers that have the capacity to co-ordinate transition metal ions directed our attention to pyridyl complexes (see later, Section 2.3.). Reaction of either **5** or **6** with the commercially available 4-pyridylaldehyde **10** under Wittig conditions produced geometric isomers and the by-product triphenylphosphine oxide **12** (Scheme 4). This crude material was then subjected to iodine in dichloromethane to enable isomerisation of the cis-isomer to the all trans-product. However, given the similar physical properties of *trans*-**11** and triphenylphosphine oxide, attempts to isolate **11** using chromatographic or even recrystallisation techniques were unfruitful. The synthetic difficulties in obtaining the phosphonium salts and the purification problems of the subsequent Wittig reaction led us to devise an alternative building block (Scheme 4).



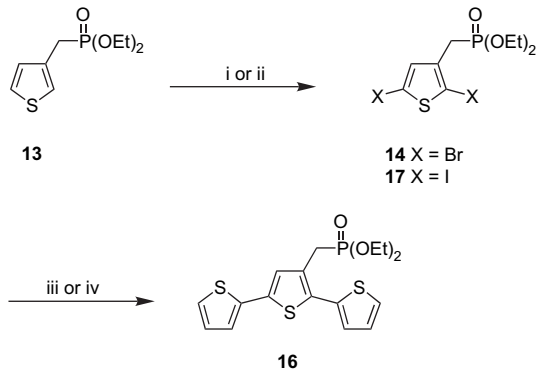
Scheme 3. Reagents and conditions: (i) MsCl, 0 °C, THF, pyridine; (ii) PPh_3, reflux.



Scheme 4. Reagents and conditions: (i) DBU, THF; (ii) I_2, CH_2Cl_2.

2.2. Synthesis of terthiophene-methylene phosphonate ester building block

The reaction of carbonyl compounds under Horner–Emmons conditions to construct olefins was investigated as an alternative to the triarylphosphorane chemistry (Scheme 5). It was envisaged that the terthiophene phosphonate **16** could be accessed using Suzuki–Miyaura chemistry as shown in Scheme 5. The known phosphonate **13** was synthesised from 3-methylthiophene following the literature procedures.[6,7] Bromination of **13** was easily achieved using biphasic bromine in aqueous hydrobromic acid and diethyl ether. The dibromophosphonate **14** was purified by distillation to give a dense golden liquid, obtained in an improved yield over the reported method.[8]



Scheme 5. Reagents and conditions: (i) Method A: Br_2, 48% HBr, ether, 0 °C–rt, 67%; (ii) Method B: Py·ICl, MeOH, $HgCl_2$, 86%; (iii) Method C: 2-thiophene boronic acid **15**, $Pd_2(dba)_3$, THF, $^tBu_3P$, K_3PO_4, 70%; (iv) Method D: 2-thiophene boronic acid **15**, $Pd(PPh_3)_4$, aq 1 M Na_2CO_3, DME, 76%.

Utilising the Suzuki-Miyaura conditions developed in the synthesis of 3′-formylterthiophene **1**,[2] an aqueous dimethoxyethane (DME) solution containing the dibromophosphonate **14** was reacted with excess boronic acid **15** and catalytic $Pd(PPh_3)_4$. Unfortunately the reaction afforded a mixture of unreacted starting material **14**, mono-coupled product and the desired terthiophene phosphonate **16** as determined by HPLC and ^1H NMR data. Attempts to drive the reaction to completion by modifying the conditions were unsuccessful. The similar R_f values of the thiophene, bithiophene and terthiophene phosphonate materials prevented separation of these compounds using chromatographic techniques.

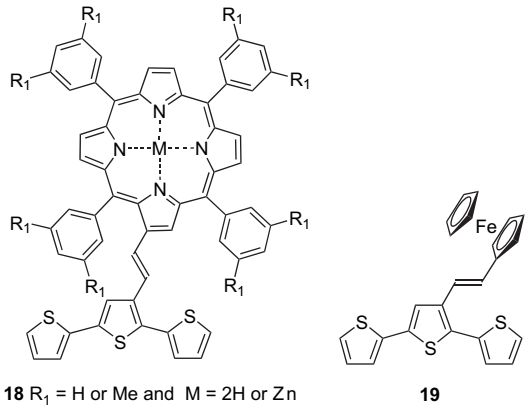
Given the somewhat sluggish reactivity of **14** under this Suzuki–Miyaura coupling protocol, a range of reported modified coupling conditions were investigated.[1] Only the heterogeneous system reported by Littke and Fu[9] allowed the Suzuki reaction of **14** with **15** to be driven to completion. After purification by chromatography and distillation, the terthiophene phosphonate **16** was obtained as a viscous yellow oil in high yield (70%). As with the characterisation of **1**, the long range COSY spectrum enabled the full assignment of all thiophene protons. The AMX spin systems of the two outer thiophene rings were easily determined from the coupling constants, COSY spectrum and the long range coupling correlation between H4′ and H3″. The methylene group is observed as a doublet at 3.31 ppm (J=21.3 Hz) due to coupling with the phosphorus nuclei. The electronic spectrum shows an absorbance maximum at 342 nm, which is consistent for the terthiophene chromophore.

With the new building block **16** in hand, the synthesis of the pyridyl compound **11** was revisited (Scheme 4). Reaction of **10** and **16** under Horner–Emmons conditions gave **11** in good yield and without the complications described previously. Having established the terthiophene phosphonate **16** as the complementary building block to the terthiophene aldehyde **1**, our final objective was to have access to large quantities of the phosphonate. Although the Suzuki coupling reaction (Scheme 5) was successful on a gram scale, attempts to perform the reaction on multi-gram scales using the conditions optimised for **16** were unsuccessful (Method C). Large-scale reactions were again complicated by incomplete consumption of dibromophosphonate **14** and the formation of substantial quantities of the mono-coupled product. The reluctance of **14** to be completely consumed was solved by changing the halide substituents on the phosphonate precursor. The thiophene phosphonate **13** was instead reacted with pyridine–iodine monochloride and mercuric(II) nitrate[10] to afford the diiodo-derivative **17** in excellent yield. Using the typical large-scale Suzuki conditions described previously, terthiophene phosphonate **16** was easily obtained in excellent yield (76%) (Method D). Having developed large-scale syntheses to both the building blocks, we now directed our efforts to synthesising functionalised terthiophene monomers.

2.3. Metallated macrocycles and ligand functionalised terthiophene monomers

As a part of our ongoing efforts to use porphyrins in photovoltaics, sensor and electrocatalysis applications, we recently reported how the architecture of porphyrin/oligothiophene monomers (i.e., compound **18**) was important in understanding and controlling the efficiency of photo-energy conversion.[11]

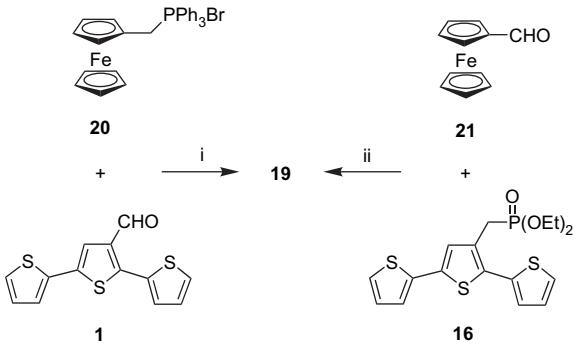
Prior to this research, we were also interested in using ferrocene-appended polythiophenes, such as **19**, for use as redox active biosensors or in electrocatalysis applications (Fig. 1). As an alternative to the three-step literature procedure to (ferrocenylmethylene)triphenylphosphonium iodide,[12] we found that the reaction of ferrocenemethanol with PPh_3·HBr in dry toluene directly gave ferrocene phosphonium salt **20** in essentially quantitative yield: this is in stark contrast to efforts to make terthiophene phosphonium salt **5** via the same procedure. The synthesis of **19** via Wittig olefination gave a mixture of geometric isomers, which were isomerised to the all trans-product (49%).[13] Polymerisation of this monomer gave electroactive films that were found to be effective as a redox sensor for the detection of cytochrome *c* in aqueous solution.[13] The recent availability of practical amounts of **16** has enabled easier access to **19** via the Horner–Emmons reaction of terthiophene phosponate **16** with the commercially available ferrocene aldehyde **21** (Scheme 6). More importantly, the crude reaction is essentially clean as the phosphonate by-products are removed during the aqueous workup and the reaction conditions afford only the trans-product.



18 R_1 = H or Me and M = 2H or Zn

19

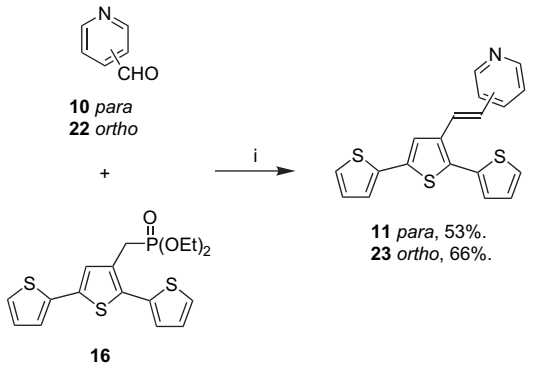
Figure 1.



Scheme 6. Reagents and conditions: (i) Method A: (a) KO^{t}Bu, THF, rt; (b) I_2, DCM, rt, 49%; (ii) Method B: KO^{t}Bu, THF, rt, 62%.

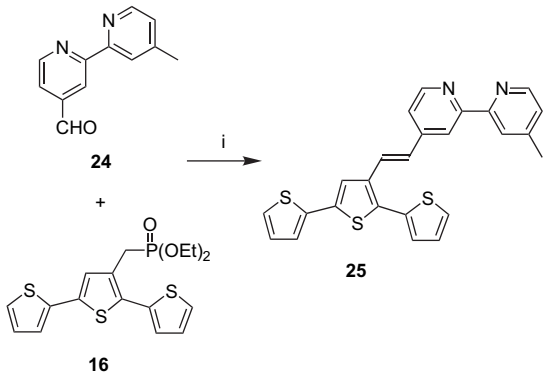
The fabrication of hybrid materials consisting of conducting polythiophenes and transition metal complexes has created a tremendous amount of interest in the field of ECPs.[14–18] Metallopolymers have been synthesised from functionalised monomers, which fit one of the three structurally different morphologies.[18] The simplest approach has been to tether the metal complex to the thiophene backbone via an alkyl linker. The metal system can also be fused directly onto the monomer backbone or, alternatively, inserted into the monomer sequence. The last two methods have been used to produce many metal complex materials, including Cu,[19,20] Ni,[19,21–23] Pd,[23,24] Ru,[25,26] Mo[27] and Au,[23] that exhibit different redox, optical and electronic properties.

In this context, we focused our efforts on the synthesis of terthiophene monomers containing polypyridyl ligands that would be suitable to form metal complexes. As mentioned earlier, condensing the terthiophene phosphonate building block and 4-formylpyridine under Horner–Emmons conditions gave the all *trans*-**11** product in good yield (Scheme 7). Similarly, reaction of **16** with 2-formylpyridine **22** afforded the all *trans-ortho*-product **23** in satisfactory yield. Both the compounds were easily purified by column chromatography and characterised by the usual analytical techniques.



Scheme 7. Reagents and conditions: (i) KO^{t}Bu, THF.

The use of a bipyridyl ligand system in metal complexes is well known and therefore compound **25** was considered an ideal target. Reaction of bipyridyl-mono-aldehyde **24**[28] with the phosphonate **16** under the conditions described previously produced the bipyridyl-terthiophene **25** in excellent yield (88%) as a yellow microcrystalline solid (Scheme 8). As expected, the aromatic region in the ^{1}H NMR spectrum of this compound is extremely congested. However, using coupling constants and the long range COSY experiment it was possible to fully assign all the signals. As in all the cases where the terthiophene phosphonate was used, only the trans-product was observed. Currently, the syntheses of a variety of metal–ligand complexes are being explored.



Scheme 8. Reagents and conditions: (i) KO^{t}Bu, THF, 88%.

2.4. Cross-linked polymers for studying electronic properties

Polythiophenes that are cross-linked through the β-position have been of interest since the early 1990s. It is well known that the regiochemistry and architecture of the monomer play a dramatic role in determining the electronic, physical and chemical properties of the resultant polymer.[29] However, the advantages or disadvantages of using cross-linked materials in homopolymers and copolymers are not well understood.

Early work by Tanaka and Kumei showed that the cross-linked monomer 3′,3′-bis-(2,2′:5′,2″-terthiophene) upon electrochemical polymerisation formed materials with increased electroactive properties with respect to polyterthiophene.[30] In their efforts to develop nanowire materials, Tour and colleagues used oligothiophene monomer **26** rigidly linked via a spirobicyclic system to control the 3-D geometry of the resulting polymer.[31] Cherioux and colleagues,[32] and more recently Liu and colleagues, have investigated the properties of polymers derived from star-shaped monomers, such as **27** (Fig. 2).[33] While Roncali and colleagues have elegantly shown that β-thiophene monomers linked via polyethers act as pseudo-crown ethers in the presence of cations.[34]

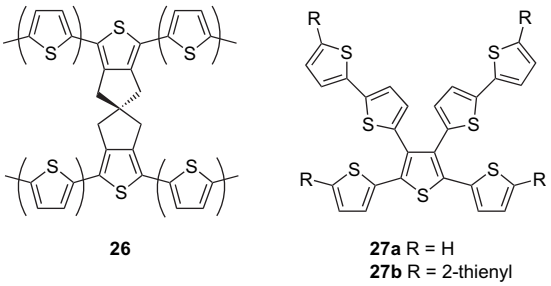
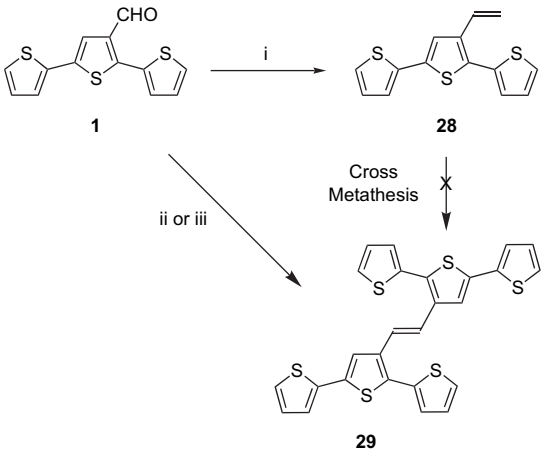


Figure 2.

Interest has also been directed at cross-linked polymers containing alkene or alkyne linkers, as these materials have been suggested as low band gap polymers.[35] Although the computational and physical data for these thiophene monomers are encouraging, conclusive experimental results for these polymer materials are needed. Marani and Emtezami's[36] previous efforts to chemically oxidise a number of α- and β-vinyl cross-linked thiophene monomers resulted in poor films. Our group and others have also found that the electrochemical polymerisation of similar styryl linked 3-thienyl substituted monomers produces electro-inactive homopolymers.[37–39]

Based on our earlier success with the electrochemistry of styryl-substituted β-terthiophenes,[2] we expected that the block monomer bis-(terthiophene)alkene **29** would eliminate these problems observed with thiophene derivatives. Initially, it was envisioned that cross-metathesis of alkene **28** would provide the target **29** (Scheme 9). The alkene **28** has been previously accessed via the palladium catalysed reaction of 3′-bromoterthiophene with vinylmagnesium bromide.[40] In this case, **28** was generated by Wittig condensation of the aldehyde **1** with triphenylphosphinemethylene ylide to give the identical product in excellent yield (90%). Surprisingly, treatment of **28** with Grubb's first generation ruthenium catalyst ((Ph=$RuCl_2(PCy_3)_2$) under argon in DCM or even at elevated temperatures in toluene did not result in the formation of any metathesis product.



Scheme 9. Reagents and conditions: (i) PPh_3MeI, KO^{t}Bu, THF, 90%; (ii) Method A: $TiCl_4$, Zn, THF, reflux, 66%; (iii) Method B: **16**, KO^{t}Bu, THF, rt, 86%.

A successful synthesis of bis-(terthiophene)alkene **29** was achieved following McMurray coupling[41] protocols (Method A). The reaction of the low-valent titanium reagent, generated from the in-situ reduction of $TiCl_4$, with 3′-formyl-2,2′:5′,2″-terthiophene **1** afforded the *trans*-alkene **29** in good yield (66%) (Method A). Surprisingly, no cis-isomer was detected in the crude sample by ^{1}H NMR spectroscopy. The C_{2v} symmetry of pure **29** is evident from the relatively simple ^{1}H NMR spectrum. The vinylic protons are present as a singlet at 7.29 ppm. The two AMX spin systems of the outer thiophene rings were fully assigned using proton coupling constants and long range coupling correlation between H4″ and H3‴.[2] The low resolution mass spectrum of **29** indicated a relatively strong parent ion at M^+ 520 (95%), supporting the formation of a stable radical cation species. The UV–vis spectrum shows three absorption bands that occur at 251, 317 and 348 nm. The lower and higher absorption bands are reminiscent of the thiophene and terthiophene chromophores, respectively, while the centre band is presumably a result of the conjugative linker connecting the central thiophene moieties.

To obtain practical quantities of **29** for further studies and device testing, large-scale McMurray reactions were performed, however, they provided poor yields. Access to both terthiophene building blocks allowed the condensation between **1** and **16** providing bis-(terthiophene)alkene in excellent yield (86%) (Method B). Interestingly, neither this route nor the McMurray coupling afforded any detectable amount of the cis-isomer.

A comparison of the X-ray structure for *trans*-1,2-bis-(2′,2″:5″,2‴-terthiophen)-3‴-yl)ethene **29** to that reported previously for *trans*-1-((2′,2″:5″,2‴-terthiophen)-3‴-yl)-2-(4⁗-cyanophenyl)ethene **30**[2] shows some differences. Most noticeable is that four of the thiophene rings and the vinylic bond of structure **29** (Fig. 3) are essentially co-planar, thereby allowing significant π orbital overlap through these rings. The two remaining thiophene rings are twisted by an angle of 45.2°, presumably to compensate for the steric congestion caused by the proximity of the vinylic protons. The mean plane through the atoms of the central thiophene ring and the cyano-substituted aryl ring of **30** was calculated to have a dihedral angle of 26.5°. Interestingly, the central

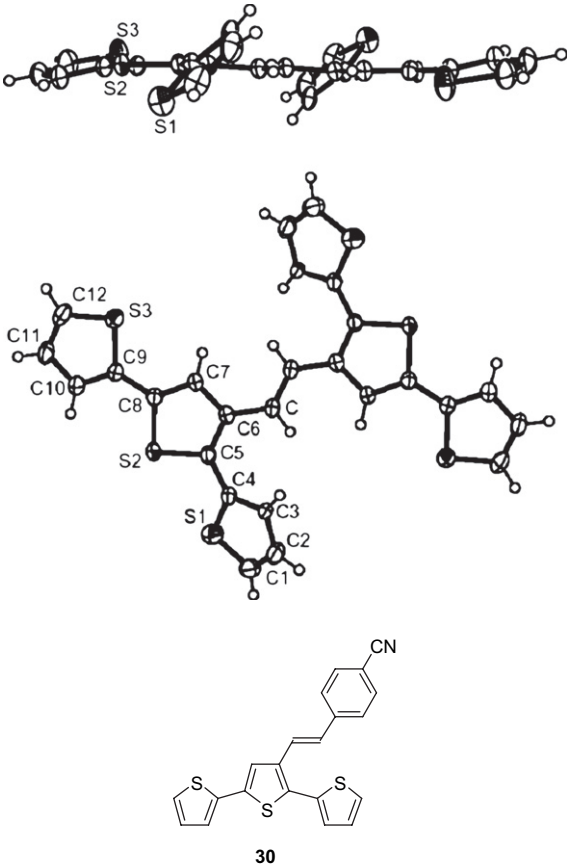
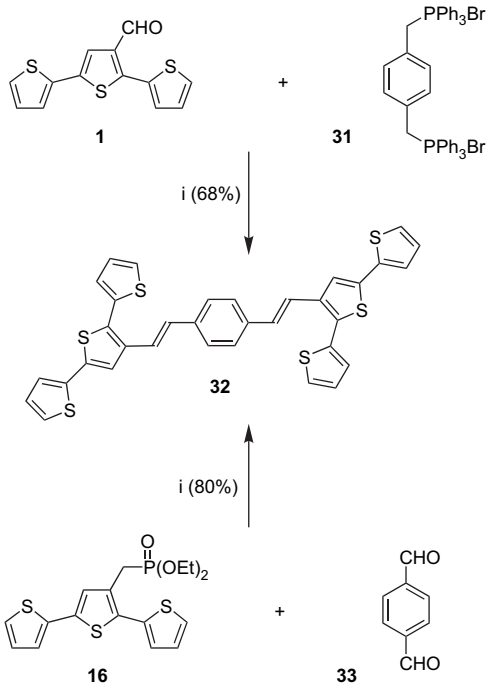


Figure 3. Side view and top view ORTEP diagrams of compound **29** and structure of compound **30**.

bis-(thienyl)ethene unit of **29** is essentially planar having a dihedral angle of only 7.7°.

We considered whether materials where the key component was conjugatively positioned between two monomer linkers, such as type **32**, could result in polymeric systems with superior electronic properties (Scheme 10). Reaction of **1** with the bis-phosphonium salt **31** under Wittig conditions gave the product in good yields (68%) (Method A). However, we also found the cross-linked material **32** could be made in better yield (80%) by the reaction of **19** with commercially available *p*-terephthaldehyde **33** (Method B).



Scheme 10. Reagents and conditions: (i) KO^{t}Bu/THF.

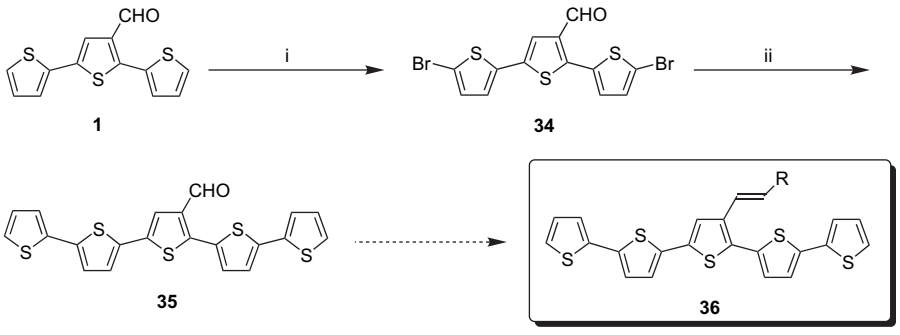
Irrespective of the method used, analysis of the crude ^{1}H NMR spectrum revealed that only one of the three possible geometric isomers was present; this was determined to be the all *trans*,*trans*-product **32** based on the vinylic coupling constant (16.2 Hz). Surprisingly, the C_{2v} symmetry of **32** provides a very simple ^{1}H NMR spectrum that along with coupling constants and long range COSY data enabled full assignment of all signals. The other spectroscopic data is in full agreement with the structure of **32**. Interestingly, the presence of the additional styryl component of **32** compared to compound **29** is clearly observed in the UV–vis absorption spectra. In addition to the similar absorption bands found in compound **29**, the presence of the shoulder seen at 490 nm in the visible region is presumably caused by the extensive conjugated system connecting the two terthiophene rings.

Electrochemical studies with bis-terthiophene alkene **29** and its fabrication into photovoltaic devices have provided some information on polymer opto-electronic properties. Homopolymers of **29** provide materials that are electroactive. However, the best photovoltaic response was found to be achieved from a blend of **29** with terthiophene, rather than-homopolymers derived from either poly-**29** or polyterthiophene.[42] These preliminary results suggest that careful control of conjugative cross-linking in the polymer can be used to alter polymer architecture and opto-electronic properties.

2.5. Synthesis of the building block homologue, pentathiophene aldehyde

Initial efforts were directed at expanding the modular approach used to construct the building blocks **1** and **16** to access the analogous compounds, such as the pentathiophene aldehyde **35**. The reaction of 3-formyl-2,5-dibromothiophene with bithiophene-2-boronic acid under Suzuki conditions unfortunately gave complex mixtures of unreacted starting material, mono-coupled product, bithiophene (i.e., deboronylation by-product) and small amounts of the desired pentathiophene. Attempts to effectively isolate the various products by chromatographic or recrystallisation methods were problematic.[43]

As an alternative, the stepwise thiophene elongation of the initial terthiophene aldehyde **1** was explored as a route to **35** (Scheme 11). Following Bäuerle and co-workers' protocols,[44] terthiophene aldehyde **1** was subjected to NBS in DMF to give the dibromide **34** in high yield (80%). The proton NMR spectrum of **34** is simple, consisting of an aldehyde signal downfield at 10.02 ppm, a singlet at 7.48 ppm for H4′ and two AB quartet spin systems between 7.13 and 6.95 ppm (J=3.9 Hz) for the remaining four β-thiophene protons. Suzuki coupling of the terthiophene dibromide **34** with thiophene boronic acid under conditions as described for **1** and **16** proceeded smoothly with the complete consumption of **34** as indicated by TLC. This crude material was recrystallised to give the



Scheme 11. Reagents and conditions: (i) NBS, DMF, darkness, 80%; (ii) 2-thiophene boronic acid **15**, $Pd(PPh_3)_4$, DME, 1 M aq Na_2CO_3, 71%.

analogous pentathiophene aldehyde **35** as a deep red solid in good yield (71%). Analysis of the ^{1}H NMR spectrum of **35** was, as expected, extremely complex in the aromatic region. Most distinguishable are the two singlets at 10.14 and 7.55 ppm that were identified as the aldehyde proton and H4″, respectively. With the aid of coupling constants and long range COSY experiments the proton NMR spectrum of **35** was assigned. We have recently shown that the pentathiophene aldehyde reacts in a similar fashion to the terthiophene aldehyde allowing access to a *meso*-bis-pentathiophene porphyrin analogue[11] of interest in photovoltaic studies.[45]

3. Conclusion

The modular strategy described in the present work allows the rapid and efficient construction of the building blocks, terthiophene aldehyde and terthiophene-methylene phosphonate, by employing Suzuki–Miyaura coupling methodology. As shown in this paper, this approach is extremely versatile. Irrespective of whether the coupling partner is commercially available, had to be synthesised or has the desired chemical reactivity, all the target monomers could ultimately be obtained in good yields and purity. As a result, a range of functionalised terthiophene monomers have been generated for study in specific conducting polymer applications. In addition, these types of monomeric materials[46] are of current interest as novel materials for use in plastic electronics. The synthesis of the pentathiophene aldehyde analogue was also achieved by applying this modular approach. Current work is directed at using β-functionalised thiophene boronic acids in the Suzuki–Miyaura coupling reaction to give second generation building blocks with tuned physical, chemical and electronic properties. The results of this work will be published in the near future.

4. Experimental

4.1. General

Melting points were determined on a Reichert Hot Stage apparatus and are uncorrected. Microanalyses were performed by Campbell Microanalytical Laboratory (Dunedin, New Zealand). Nuclear Magnetic Resonance (NMR) spectra were measured at 400 MHz (^{1}H), 100.6 MHz (^{13}C) and 300 MHz (^{1}H), 75 MHz (^{13}C) on a Bruker Avance 400 and 300 Ultrashield spectrometers. All NMR spectra were recorded in deuterochloroform unless otherwise stated, with reference to tetramethylsilane. Signals are described in terms of chemical shifts, multiplicity, intensity, coupling constants and assignment. The following abbreviations have been used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or br (broad). COSY experiments were used to assign signals in ^{1}H NMR spectra.

Analytical Thin Layer Chromatography (TLC) was carried out using Merck (Art. 1.05554) silica gel 60 F_{254} pre-coated on aluminium sheets. Flash and column chromatography were performed using Merck Kieselgel 60 as adsorbent. Both the chromatographic techniques used increasing proportions of ethyl acetate in petroleum ether as eluting solvent, unless stated otherwise. Fractions were monitored by TLC and appropriate fractions were combined.

Anhydrous tetrahydrofuran was obtained by distillation from benzophenone ketyl, while anhydrous CH_2Cl_2 was distilled off calcium hydride. Reactions requiring anhydrous reagents or solvents were carried out under an inert atmosphere of nitrogen or argon.

4.1.1. 3′-(Hydroxymethyl)-2,2′:5′,2″-terthiophene (4). A stirred solution of 3′-formyl-2,2′:5′,2″-terthiophene **1**[2] (500 mg, 1.81 mmol) in ethanol (10 mL) and THF (5 mL) at rt was treated with sodium borohydride (48 mg, 1.27 mmol). After 3 h the reaction mixture was quenched with ice-cold water (20 mL), then treated with a solution of 1 M HCl (40 mL) and extracted with CH_2Cl_2 (3×40 mL). The organic extracts were combined and washed with water (60 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a faint yellow oily/solid. This material was then subjected to column chromatography with gradient elution (EtOAc/toluene) to afford a solid that was recrystallised from ether/petroleum ether to give the *alcohol* **4** as fluffy pale yellow crystals (423 mg, 84%), mp 85 °C. ^{1}H NMR (400 MHz) δ 7.35 (dd, 1H, J=5.1, 1.2 Hz, H5); 7.25 (s, 1H, H4′); 7.24 (dd, 1H, J=5.1, 1.2 Hz, H5″); 7.22 (dd, 1H, J=3.6, 1.2 Hz, H3); 7.19 (dd, 1H, J=3.6, 1.2 Hz, H3″); 7.10 (dd, 1H, J=5.1, 3.6 Hz, H4); 7.03 (dd, 1H, J=5.1, 3.6 Hz, H4″); 4.76 (s, 2H, CH_2OH); 1.80 (br s, 1H, CH_2OH). ^{13}C NMR (100.6 MHz) δ 138.1, 136.8, 135.9, 134.7, 132.1, 128.0, 127.9, 126.5, 126.1, 125.7, 124.7, 123.7, 59.1. IR (KBr) 3078, 2954, 2924, 2854, 1459, 1421, 1379, 1320, 1226, 1177, 1030, 833, 699 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} nm/(log ε) 253 (4.10), 348 (4.32). LRMS (EI) m/z 280 (15), 279 (17), 278 (M^+, 100%), 261 (28), 245 (19), 216 (12), 127 (11). Anal. Calcd for $C_{13}H_{10}OS_3$: C, 56.08; H, 3.62; S, 34.55. Found: C, 56.29; H, 3.74; S, 34.43.

4.1.2. ((2,2′:5′,2″-Terthiophen)-3′-yl)methylene phosphonium bromide (5). A stirred solution of 3′-hydroxymethyl-2,2′:5′,2″-terthiophene **4** (200 mg, 0.72 mmol) in dry benzene (15 mL) at rt was treated with $PPh_3\cdot HBr$ (247 mg, 0.72 mmol) with vigorous stirring. The mixture was then heated at reflux for 10 h, then cooled and diluted with petroleum ether (50 mL). The precipitate was collected and dried under vacuum to give a yellow/grey powder **5** (149 mg, 34%), mp 247–248 °C. ^{1}H NMR (400 MHz) δ 7.82–7.73 (m, 3H, ArH); 7.73–7.58 (m, 12H, ArH); 7.22 (dd, 1H, J=5.2, 1.1 Hz, H5″); 7.19 (dd, 1H, J=5.1, 1.1 Hz, H5); 7.03 (dd, 1H, J=3.6, 1.1 Hz, H3); 6.96 (dd, 1H, J=5.1, 3.6 Hz, H4); 6.92 (dd, 1H, J=5.2, 3.6 Hz, H4″); 6.72–6.80 (m, 2H, H4′, H3″); 5.57 (d, 2H, $J_{H,P}$=13.8 Hz, CH_2PPh$_3$). ^{13}C NMR (100.6 MHz) δ 137.2 (d, $J_{C,P}$=2.7 Hz), 135.2 (d, $J_{C,P}$=2.9 Hz), 134.7, 134.6, 134.2 (d, $J_{C,P}$=9.9 Hz), 133.0 (d, $J_{C,P}$=2.5 Hz), 130.3 (d, $J_{C,P}$=12.6 Hz), 128.0, 127.9, 127.8, 126.9, 126.3 (d, $J_{C,P}$=2.7 Hz, C4′), 125.3, 124.4, 123.9 (d, $J_{C,P}$=9.0 Hz), 117.5 (d, $J_{C,P}$=85.6 Hz), 25.6 (d, $J_{C,P}$=48.1 Hz). Anal. Calcd for $C_{31}H_{24}BrPS_3$: C, 61.69; H, 4.01; S, 15.94. Found: C, 61.67; H, 3.89; S, 16.10.

4.1.3. ((2,2′:5′,2″-Terthiophen)-3′-yl)methylene triphenylphosphonium chloride (6). An ice-cold solution of 3′-hydroxymethyl-2,2′:5′,2″-terthiophene **4** (248 mg, 0.89 mmol) and dry pyridine (0.50 mL, 6.24 mmol, 493 mg) in anhydrous CH_2Cl_2 (50 mL) was treated dropwise with distilled

thionyl chloride (0.26 mL, 3.56 mmol, 424 mg, 4 equiv). After 30 min, analysis by TLC indicated that all the starting material had been consumed and the reaction mixture was quenched with ice water (50 mL). The reaction mixture was washed with 10% sodium bicarbonate solution (2×30 mL), saturated copper sulfate solution (20 mL), water (60 mL) and dried ($MgSO_4$). Attempts to purify the material by chomatographic means resulted in decomposition and thus the chloride was used immediately in the next step. The mixture of the crude chloride and triphenylphosphine (701 mg, 2.67 mmol, 3 equiv based on alcohol) dissolved in dry benzene (30 mL) was heated under reflux for 16 h. After this period the reaction mixture was cooled, petroleum ether (30 mL) was added and then cooled in ice. The precipitate that formed was collected and recrystallised from CH_2Cl_2/ether to give the *terthiophene phosphonium salt* **6** as yellow cream crystals (257 mg, 52% based on alcohol used), mp 275 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.41 (d, 2H, $J_{H,P}$=13.9 Hz, CH_2PPh$_3$); 6.75 (br d, 1H, $J_{H,P}$=1.3 Hz, H4′); 6.82 (br dd, 1H, J=3.5 Hz, H3″); 6.98 (dd, 1H, J=5.2, 3.6 Hz, H4″); 7.02 (dd, 1H, J=5.1, 3.6 Hz, H4); 7.09 (dd, 1H, J=3.6, 1.1 Hz, H3); 7.27 (dd, 1H, J=5.1, 1.1 Hz, H5); 7.31 (dd, 1H, J=5.2, 1.1 Hz, H5″); 7.62–7.71 (m, 12H, ArH); 7.79–7.86 (m, 3H, ArH). ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 25.6 (d, $J_{C,P}$=48.1 Hz), 117.5 (d, $J_{C,P}$=85.6 Hz), 123.9 (d, $J_{C,P}$=9.0 Hz), 124.4, 125.3, 126.3 (d, $J_{C,P}$=2.7 Hz), 126.9, 127.8, 127.9, 128.0, 130.3 (d, $J_{C,P}$=12.6 Hz), 133.0 (d, $J_{C,P}$=2.5 Hz), 134.2 (d, $J_{C,P}$=9.9 Hz), 134.6, 134.7, 135.2 (d, $J_{C,P}$=2.9 Hz), 137.2 (d, $J_{C,P}$=2.7 Hz). Anal. Calcd for $C_{31}H_{24}ClPS_3$: C, 66.59; H, 4.33; S, 17.20. Found: C, 66.33; H, 4.03; S, 17.11.

4.1.4. Diethyl ester (2,5-dibromo-3-thienylmethyl)phosphonic acid (14). A solution of bromine (28.7 g, 9.3 mL, 0.180 mol) in 48% hydrobromic acid (26 mL) was added dropwise over 15 min to a vigorously stirred solution of the phosphonate **13**[7] (20.8 g, 0.085 mol) in 48% aqueous hydrobromic acid (26 mL) and ether (20 mL) cooled at 0 °C. The reaction was allowed to gradually warm to rt and left to stir for 45 min. The mixture was then diluted with CH_2Cl_2 (200 mL) and water (150 mL) and the aqueous phase removed. The organic layer was washed with 10% sodium hydrogen carbonate solution (5×75 mL), 10% sodium thiosulfate solution (50 mL), water (2×75 mL) and dried ($MgSO_4$). The solvent was removed under reduced vacuum to give a dark brown viscous oil, which was vacuum distilled (156–158 °C/0.03 mmHg) with a Vigreux column to afford product **14** as a golden liquid (22.5, 67%) (98% purity by HPLC) (lit.[8] 131–135 °C/0.08 Torr). ^{1}H NMR (400 MHz) δ 6.98 (d, 1H, $J_{H,P}$=1.3 Hz, H4); 4.05 (dq, 4H, OCH_2CH$_3$); 3.07 (d, 2H, $J_{H,P}$=21.1 Hz, ThCH_2P); 1.256 (dt, 6H, OCH$_2$CH_3). ^{13}C NMR (100.6 MHz) δ 32.2 (d, $J_{C,P}$=9.2 Hz), 131.5 (d, $J_{C,P}$=2.9 Hz), 111.0 (d, $J_{C,P}$=2.5 Hz), 110.6 (d, $J_{C,P}$=13.7 Hz), 62.4 (d, $J_{C,P}$=6.7 Hz), 27.8 (d, $J_{C,P}$=141.9 Hz), 16.4 (d, $J_{C,P}$=6.0 Hz). UV–vis ($CHCl_3$) λ_{max} nm/(log ε) 247 (4.94).

4.1.5. Diethyl ester (2,5-diiodo-3-thienylmethyl)phosphonic acid (17). A stirred mixture of the phosphonate **13** (10 g, 0.043 mol), Py·ICl[10] (21.65 g, 0.090 mol, 2.1 equiv) in methanol (105 mL) was treated with $Hg(NO_3)_2\cdot H_2O$ (29.95 g, 0.085 mol) at rt and in the dark. It was left for 2.5 h and then diluted with brine (300 mL). The mixture was extracted with CH_2Cl_2 (4×80 mL), dried ($MgSO_4$) and concentrated. The crude product was vacuum distilled (192 °C/0.01 mmHg) with a Vigreux column to give **17** as a faint yellow oil (17.86 g, 86%). ^{1}H NMR (400 MHz) δ 7.11 (d, 1H, $J_{H,P}$=1.3 Hz, H4); 4.05 (dq, 4H, OCH_2CH$_3$); 3.11 (d, 2H, $J_{H,P}$=21.1 Hz, ThCH_2P); 1.25 (dt, 6H, OCH$_2$CH_3). ^{13}C NMR (100.6 MHz) δ 138.7 (d, J=9.1 Hz), 138.3 (d, J=3.0 Hz), 79.9 (d, $J_{C,P}$=15.1 Hz), 76.5 (d, $J_{C,P}$=3.0 Hz), 62.4 (d, $J_{C,P}$=7.0 Hz), 30.2 (d, $J_{C,P}$=141.8 Hz), 16.4 (d, $J_{C,P}$=6.0 Hz). IR (NaCl) 3433, 1733, 1636, 1526, 1389, 1242, 1162, 1096, 1026, 992, 969, 846, 782, 644 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} nm/(log ε) 268 (4.95). LRMS (EI) *m/z* 486 (M$^+$, 11), 359 (100%), 349 (31), 331 (24), 303 (60), 239 (39), 95 (22), 80 (12). HRMS (EI) M$^+$ calcd for $C_9H_{13}I_2O_3PS$ 485.8412. Found 485.8410.

4.1.6. Suzuki coupling to form diethyl ester (3′-methylene-2:2′,5′:2″-terthiophene)phosphonic acid (16). *Method C*. A mixture of dibromophosphonate **14** (1.00 g, 2.55 mmol), tri(*tert*-butyl)phosphine (0.18 mL, 146 mg, 0.722 mmol), 2-thienylboronic acid **15** (653 mg, 5.10 mmol, 2 equiv) and anhydrous K_3PO_4 (1.30 g, 6.12 mmol, 2.4 equiv) in dry THF (25 mL) was stirred vigorously at rt to give a homogeneous slurry before tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$] (35 mg, 0.038 mmol, 1.5 mol %) was added. The reaction mixture was then heated for 2 h under reflux, when analysis of the mixture by HPLC indicated that the reaction had ceased. The mixture was then charged with additional tri(*tert*-butyl)phosphine (0.18 mL, 146 mg, 0.722 mmol) and 2-thienylboronic acid **15** (326 mg, 2.55 mmol, 1 equiv) and heated for another 2 h. The crude mixture was then diluted with CH_2Cl_2 and filtered. The organic mixture was then subjected to normal aqueous workup and the solvent removed under reduced pressure to afford a dark brown oil. This material was subjected to column chromatography to give a crude yellow oil, which was further purified by vacuum distillation (~260–270 °C/0.03 mmHg) to give the *terthiophene phosphonate* **16** as a yellow viscous oil (0.714 g, 70%). ^{1}H NMR (400 MHz) δ 7.35 (dd, 1H, J=5.2, 1.2 Hz, H5); 7.32–7.30 (m, 1H, H3); 7.23 (s, 1H, H4′); 7.23 (dd, 1H, J=5.1, 1.1 Hz, H5″); 7.18 (dd, 1H, J=3.6, 1.1 Hz, H3″); 7.10 (dd, 1H, J=5.2, 3.6 Hz, H4); 7.02 (dd, 1H, J=5.1, 3.6 Hz, H4″); 4.07 (q, 4H, OCH_2CH$_3$); 3.31 (d, 2H, $J_{H,P}$=21.3 Hz, ThCH_2P); 1.28 (br t, 6H, OCH$_2$CH_3). ^{13}C NMR (100.6 MHz) δ 136.7, 135.9 (d, $J_{C,P}$=2.3 Hz), 131.9 (d, $J_{C,P}$=11.5 Hz), 128.2 (d, $J_{C,P}$=9.4 Hz), 127.8, 127.1, 126.8 (d, $J_{C,P}$=2.8 Hz), 126.2, 124.7, 123.9, 62.3 (d, $J_{C,P}$=6.6 Hz), 27.4 (d, $J_{C,P}$=141.5 Hz), 16.4 (d, $J_{C,P}$=6.1 Hz). IR (KBr) 3464, 3075, 2984, 2908, 2362, 1509, 1438, 1394, 1247, 1053, 1025, 965, 841, 697 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} nm/(log ε) 249 (4.06), 342 (4.27). LRMS (FAB) *m/z* 399 (MH$^+$, 84%), 398 (M$^+$, 100%), 371 (4.3), 343 (3.6), 261 (32), 227 (5), 203 (3), 179 (3). HRMS (EI) M$^+$ calcd for $C_{17}H_{19}O_3PS_3$ 398.0234. Found 398.0230.

Method D. A mixture of the boronic acid **15** (7.90 g, 0.062 mmol, 3 equiv), di-iodophosphonate **17** (10.0 g, 0.071 mol) DME (180 mL) and 1 M Na_2CO_3 solution (130 mL) was stirred vigorously at rt. To this was added $Pd(PPh_3)_4$ (1.19 g, 1.03 mmol, 5 mmol %) and the reaction mixture was heated under reflux for 12 h. The mixture was then cooled and the DME removed under reduced pressure. The residual mixture was diluted with water (100 mL) and

extracted with CH_2Cl_2 (4×120 mL). The organic extracts were combined and washed with water (2×70 mL), dried ($MgSO_4$) and concentrated. The crude product was subjected to Kugelrohr distillation (208 °C/0.01 mmHg) to give a yellowish oil (6.25 g, 76%).

4.1.7. (Ferrocenemethylene)triphenylphosphonium bromide (20). A stirred solution of hydroxymethylferrocene (790 mg, 3.66 mmol) in dry benzene (20 mL) was treated with finely ground $PPh_3 \cdot HBr$ (1.24 g, 3.60 mmol, 0.98 equiv) at rt. The reaction mixture was heated at 50 °C for 2 h, then cooled and the yellow precipitate was collected and washed with petroleum ether (2×30 mL). The solid was dried under vacuum (P_2O_5) to give the *ferrocene phosphonium salt* **20** as fluffy yellow crystals (1.84 g, 94%), mp 223–224 °C decomp. ^{1}H NMR (400 MHz) δ 4.01 (br s, 2H, CH); 4.10 (br s, 2H, CH); 4.40 (s, 5H, Cp); 5.09, d, 2H, $^2J_{H,P}$=11.7 Hz, CH_2PPh_3); 7.62–7.88 (m, 15H, ArH). ^{13}C NMR (100.6 MHz) δ 27.5 (d, $J_{C,P}$=45.8 Hz), 68.7, 69.9, 70.5, 73.7, 118.0 (d, $J_{C,P}$=84.6 Hz), 130.1 (d, $J_{C,P}$=12.6 Hz), 134.2 (d, $J_{C,P}$=9.9 Hz), 134.8 (d, $J_{C,P}$=2.8 Hz). LRMS (FAB) *m/z* 462 (36), 461 (M^+−Br, 100%), 200 (16), 199 (87). Anal. Calcd for $C_{29}H_{26}BrFeP$: C, 64.35; H, 4.84; P, 5.72. Found: C, 64.32; H, 4.86; P, 5.70.

4.1.8. Synthesis of *trans*-(*E*)-1-((2′,2″:5″,2‴-terthiophen)-3″-yl)-2-(ferrocenyl)ethene (19). *Method B*. A stirred solution of the ferrocene aldehyde **21** (500 mg, 2.34 mmol) and terthiophene phosphonate **16** (1.02 g, 2.57 mmol, 1.1 equiv) in dry THF (20 mL) was slowly treated at rt with KO^{t}Bu (283 mg, 257 mmol, 1.1 equiv). The reaction was exothermic and was left to stir for 2 h. After this period the reaction mixture was quenched with water (20 mL), acidified with 1 M solution of HCl (50 mL) and extracted with CH_2Cl_2 (3×60 mL). The organic extracts were combined, dried ($MgSO_4$) and pre-adsorbed onto silica. This crude material was subjected to rapid silica filtration to give the product, which was further purified by recrystallisation from ether/petroleum ether (charcoal) (650 mg, 62%), mp 165 °C (lit.[13] mp 165 °C).

4.1.9. General Horner–Emmons reaction procedure. A stirred mixture of the appropriate aldehyde **10**, or **22** (10 equiv) and diethyl ester (3′-methylene-2:2′,5′:2″-terthiophene)phosphonic acid **16** (1 equiv, ~600–750 mg) in anhydrous THF (30 mL) was treated with KO^{t}Bu (1 equiv). The reaction mixture was stirred at rt for 4 h. The mixture was quenched with water (20 mL) and acidified with a 1 M HCl (70 mL) solution. The mixture was diluted with CH_2Cl_2 (50 mL) and neutralised with saturated Na_2CO_3 solution. The organic layer was removed and the aqueous extracted with a further portion of CH_2Cl_2 (30 mL), then combined and dried ($MgSO_4$). The crude product was pre-adsorbed onto alumina and subjected to column chromatography using gradient elution with CH_2Cl_2/petroleum ether.

4.1.9.1. *trans*-(*E*)-1-((2′,2″:5″,2‴-Terthiophen)-3″-yl)-2-(4‴-pyridyl)ethene (11). The required fractions were concentrated under vacuum to give a solid that was recrystallised from absolute ethanol/pentane to afford *product* **11** as bright yellow fluffy crystals (307 mg, 53%), mp 128–129 °C. ^{1}H NMR (400 MHz) δ 8.62–8.50 (m, 2H, pyridyl H_A); 7.54 (d, 1H, *J*=16.2 Hz, vinyl H1); 7.43 (dd, 1H, *J*=5.1, 1.2 Hz, H5‴); 7.42 (s, 1H, H4″); 7.36–7.30 (m, 2H, pyridyl H_B); 7.27 (dd, 1H, *J*=5.1, 1.2 Hz, H5′); 7.22 (dd, 1H, *J*=3.6, 1.2 Hz, H3′); 7.20 (dd, 1H, *J*=3.6, 1.2 Hz, H3‴); 7.15 (dd, 1H, *J*=5.1, 3.6 Hz, H4‴); 7.05 (dd, 1H, *J*=5.1, 3.6 Hz, H4′); 6.93 (d, 1H, *J*=16.2 Hz, vinyl H2). ^{13}C NMR (100.6 MHz) δ 150.1, 144.7, 136.5, 136.3, 135.3, 134.5, 133.7, 128.0 (2×CH), 127.4 (2×CH), 127.0, 125.8, 125.1, 124.4, 121.9, 120.8. IR (KBr) 3431, 1623, 1590, 1500, 1415, 969, 831, 812, 696, 678 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} nm/(log ε) 311 (4.24), 349 (sh) (4.03). LRMS (EI) *m/z* 353 (13), 352 (21), 351 (M^+, 100%), 350 (17), 318 (19), 273 (18), 240 (8), 127 (10). Anal. Calcd for $C_{19}H_{13}NS_3$: C, 64.92; H, 3.73; N, 3.98. Found: C, 64.21; H, 3.54; N, 3.95.

4.1.9.2. *trans*-(*E*)-1-((2′,2″:5″,2‴-Terthiophen)-3″-yl)-2-(2‴-pyridyl)ethene (23). The required fractions were concentrated under vacuum to give a solid that was recrystallised from ether/pentane to afford *product* **23** as pale yellow micro-crystals (392 mg, 66%), mp 119 °C. ^{1}H NMR (400 MHz) δ 8.60–8.56 (m, 1H, pyridyl H6‴); 7.82 (d, 1H, *J*=16.0 Hz, vinyl H1); 7.65–7.62 (m, 1H, pyridyl H4‴); 7.47 (s, 1H, H4″); 7.42–7.39 (m, 1H, pyridyl H3‴); 7.39 (dd, 1H, *J*=5.1, 1.1 Hz, H5′); 7.26 (dd, 1H, *J*=5.1, 1.2 Hz, H5‴); 7.22 (dd, 1H, *J*=3.6, 1.1 Hz, H3′); 7.21 (dd, 1H, *J*=3.6, 1.2 Hz, H3‴); 7.15–7.13 (m, 1H, pyridyl H5‴); 7.13 (dd, 1H, *J*=5.1, 3.6 Hz, H4′); 7.11 (d, 1H, *J*=16. Hz, vinyl H2); 7.04 (dd, 1H, *J*=5.1, 3.6 Hz, H4‴). ^{13}C NMR (100.6 MHz) δ 155.7, 149.7, 136.6, 136.4, 136.1, 135.8, 134.9, 133.3, 129.9, 128.0 (2×CH), 127.3, 126.7, 125.4, 124.9, 124.1, 122.3, 122.0, 121.6. IR (KBr) 3443, 3056, 1629, 1584, 1469, 1430, 967, 817, 697 cm^{-1}. LRMS (EI) *m/z* 352 (27), 351 (M^+, 85%), 350 (51), 319 (23), 318 (100), 272 (25), 268 (53), 79 (32). Anal. Calcd for $C_{19}H_{13}NS_3$: C, 64.92; H, 3.73; N, 3.98. Found: C, 64.74; H, 3.69; N, 4.04.

4.1.10. *trans*-(*E*)-1-((2′,2″:5″,2‴-Terthiophen)-3″-yl)-2-(4⁗-(4⁗′-methyl-2⁗,2⁗′-bipyridyl))ethene (25). A mixture of 4-formyl-4′-methyl-2,2′-bipyridine **24** (300 mg, 1.51 mmol) and terthiophene phosphonate **16** (665 mg, 1.66 mmol) dissolved in dry THF (25 mL) was treated with KO^{t}Bu (188 mg, 1.68 mmol) and was left to stir at rt for 5 h. The reaction mixture was subjected to the normal aqueous workup as described for the pyridyl-terthiophene isomers. The crude product was adsorbed onto alumina and subjected to column chromatography, first gradient elution with chloroform/petroleum ether, followed with 10% methanol/chloroform. The necessary fractions were combined, concentrated and the product recrystallised from CH_2Cl_2/petroleum ether (charcoal) to give *title compound* **25** as a yellow microcrystalline solid (388 mg, 88%), mp 158–159 °C. ^{1}H NMR (400 MHz) δ 8.63 (d, 1H, *J*=5.1 Hz, pyridyl H6⁗); 8.55 (d, 1H, *J*=4.9 Hz, pyridyl H6⁗′); 8.42 (br s, 1H, pyridyl H3⁗); 8.24 (br s, 1H, pyridyl H3⁗′); 7.62 (d, 1H, *J*=16.2 Hz, vinyl H1); 7.44–7.41 (m, 2H, H4″ and H5‴); 7.38 (m, 1H, pyridyl H5⁗); 7.28 (dd, 1H, *J*=5.1, 1.0 Hz, H5′); 7.24–7.20 (m, 2H, H3′ and H3‴); 7.16–7.13 (m, 2H, pyridyl H5⁗′ and H4′); 7.057 (d, 1H, *J*=16.2 Hz, vinyl H2); 7.056 (dd, 1H, *J*=5.1, 3.6 Hz, H4‴); 2.45 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz) δ 156.8, 155.8 (2×CH), 149.4, 149.0, 148.1, 145.7, 136.45, 136.41, 135.5, 134.7, 133.6, 128.0 (2×CH), 127.4, 126.9, 125.8, 125.1, 124.8, 124.3, 122.1, 122.0, 120.2, 118.9, 21.2. IR

(KBr) 3434, 3052, 1629, 1592, 1545, 1460, 964, 841, 828, 670 cm^{-1}. LRMS (EI) *m/z* 444 (14), 443 (28), 442 (M^+, 100%), 441 (29), 409 (6), 359 (10), 315 (14), 170 (28). Anal. Calcd for $C_{25}H_{18}N_2S_3$: C, 67.84; H, 4.10; N, 6.33. Found: C, 67.98; H, 4.18; N, 6.63.

4.1.11. 3′-Vinyl-2:2′,5′:2″-terthiophene (28). A slurry of triphenylphosphonium methyl bromide (2.65 g, 7.42 mmol, 4.1 equiv) in dry THF (45 mL) at 0 °C was treated dropwise with a solution of *n*-BuLi in THF (2.5 M, 2.7 mL, 6.75 mmol) and stirred for 2 h. The reaction mixture was then allowed to warm to rt and stirred for a further 2 h, before a solution of terthiophene aldehyde **1** (500 mg, 1.81 mmol) in dry THF (20 mL) was added dropwise. After a further 2 h of stirring at rt, the reaction mixture was quenched by the addition of 1 M HCl (50 mL) and then concentrated under reduced pressure to remove the solvent. This residue was diluted with water (50 mL) and then extracted with CH_2Cl_2 (2×50 mL). The organic layers were combined, washed with water (20 mL), dried ($MgSO_4$) and concentrated under vacuum to give a dark yellow oil. This crude material was adsorbed onto silica and subjected to column chromatography with gradient elution CH_2Cl_2/petroleum ether (with increasing concentration of CH_2Cl_2). The appropriate fractions were combined, concentrated and kept under high vacuum for several hours to give the desired *alkene* **28** as a bright yellow oil (478 mg, 90%). The proton NMR spectrum of this material is consistent with the compound that was made by Kagan and Liu via the Kumada coupling route.[40] UV–vis ($CHCl_3$) λ_{max} nm/(log ε) 251 (4.23), 347 (4.29).

4.1.12. *trans*-(*E*)-1,2 Bis((2′,2″:5″,2‴-terthiophen)-3″-yl)ethene (29). *Method A*. A stirred solution of $TiCl_4$ (11.7 mL, 0.105 mol, 20.25 g) in dry THF (150 mL) at rt was treated with portions of zinc dust (4.63 g, 0.071 mol). This mixture was then heated at reflux for 15 min before a solution of the terthiophene aldehyde **1** (1.00 g, 3.62 mmol) in dry THF (25 mL) was added dropwise. After 17 h the reaction mixture was cooled and cold water (50 mL) was added slowly. The mixture was then diluted CH_2Cl_2 (100 mL) and a 1 M solution of HCl (70 mL) was added and the mixture stirred for 30 min. The organic layer was then separated and the aqueous layer extracted with CH_2Cl_2 (3×50 mL). The organic layers were combined, then dried ($MgSO_4$) and the solvent removed under reduced pressure to give bright yellow solid. This crude material was then pre-adsorbed onto silica gel and subjected to column chromatography. The column was first eluted with 10% CH_2Cl_2/petroleum ether to remove some high R_f materials, then with toluene to allow isolation of the crude product. Recrystallisation from CH_2Cl_2/petroleum ether gave *alkene* **29** as yellow/greenish needles (625 mg, 66%), mp 202–203 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.05 (dd, 2H, *J*=5.1, 3.6 Hz, H4‴); 7.15 (dd, 2H, *J*=5.2, 3.6 Hz, H4′); 7.230 (dd, 2H, *J*=3.6, 1.2 Hz, H3′); 7.235 (dd, 2H, *J*=3.6, 1.2 Hz, H3‴); 7.28 (dd, 2H, *J*=5.1, 1.2 Hz, H5‴); 7.285 (s, 2H, H1 and H2); 7.38 (s, 2H, H4″); 7.43 (dd, 2H, *J*=5.2, 1.2 Hz, H5′). ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 122.8, 124.0 (2×CH) 124.8, 125.5, 127.0, 127.6, 128.4 (2×CH), 132.2, 135.5, 136.5, 136.9, 137.0. IR (KBr) 1431, 1416, 1350, 1276, 1167, 1049, 991, 960, 847, 831, 814, 691 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} nm/(log ε) 251 (4.48), 317 (4.73), 348 (4.66). LRMS (EI) *m/z* 520 (M^+, 95), 243 (40), 179 (44), 178 (100%), 165 (43), 73 (52), 57 (64), 55 (55), 43 (57), 41 (50). Anal. Calcd for $C_{26}H_{16}S_6$: C, 59.96; H, 3.10; S, 36.94. Found: C, 59.89; H, 3.12; S, 36.95.

Method B. A vigorously stirred mixture of the terthiophene aldehyde (**1**) (1.61 g, 5.83 mmol) and terthiophene phosphonate **16** (2.44 g, 6.12 mmol, 1.05 equiv) in dry THF (100 mL) was slowly treated with KO^{t}Bu (687 mg, 6.12 mmol) over a 10 min period at rt under an inert atmosphere. The reaction was then left to stir at rt for 3 h by which time a yellow precipitate had formed. The mixture was diluted with water (60 mL) and the yellow solid collected. The crude solid was dissolved in hot toluene, dried ($MgSO_4$) and passed through a plug of silica. The filtrate was concentrated and the residue recrystallised from CH_2Cl_2/petroleum ether (charcoal) to afford *alkene* **29** as bright yellow crystals (2.60 g, 86%).

4.1.13. *trans*,*trans*-(1‴′,4‴′-Bis-[2-((2′,2″:5″,2‴-terthiophen)-3″-yl)vinyl]benzene (32). *Method A*. A stirred slurry of the bis-phosphonium salt **31** (300 mg, 0.380 mmol) and terthiophene aldehyde **1** (215 mg, 0.779 mmol) in dry THF (10 mL) and CH_2Cl_2 (10 mL) was treated with freshly sublimed KO^{t}Bu (128 mg, 1.14 mmol, 3 equiv) at 0 °C. The reaction was allowed to warm to rt and stirred for 5 h. The mixture was diluted with CH_2Cl_2 (20 mL), then 1 M HCl (50 mL) was added and vigorously stirred for 10 min. The organic layer was removed and washed with water (50 mL), dried ($MgSO_4$) and concentrated under vacuum to give a yellow solid. The crude material was adsorbed onto silica and subjected to column chromatography beginning with 50% toluene/petroleum ether, then gradually increasing to toluene. This material was recrystallised from CH_2Cl_2/petroleum ether (charcoal) to give *product* **32** as yellow powdery solid (162 mg, 68%), mp 229–230 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.10 (dd, 2H, *J*=5.1, 3.6 Hz, H4′); 7.11 (d, 2H, *J*=16.2 Hz, vinylic); 7.19 (dd, 2H, *J*=5.1, 3.6 Hz, H4‴); 7.27 (dd, 2H, *J*=3.6, 1.2 Hz, H3‴); 7.29 (dd, 2H, *J*=3.6, 1.2 Hz, H3′); 7.34 (dd, 2H, *J*=5.1, 1.2 Hz, H5′); 7.44 (d, 2H, *J*=16.2 Hz, vinylic); 7.47 (dd, 2H, *J*=5.1, 1.2 Hz, H5‴); 7.52 (s, 2H, H3″); 7.38 (s, 4H, aryl H). ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 121.8, 122.5, 124.6, 125.4, 127.0, 127.2, 127.4, 128.3, 128.4, 130.3, 132.0, 135.4, 136.4, 136.8, 137.0, 137.2. IR (KBr) 1512, 1420, 1309, 1232, 1175, 1069, 1045, 950, 834, 815, 690 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} nm/(log ε) 246 (4.39), 279 (4.09), 345 (4.84), 456 (4.65). LRMS (EI) *m/z* 460 (19), 459 (30), 458 (M^+, 100%), 304 (13), 303 (31), 69 (15), 57 (20), 55 (19), 43 (20), 41 (18). Anal. Calcd for $C_{34}H_{22}S_6$: C, 65.56; H, 3.56; S, 30.88. Found: C, 65.32; H, 3.40; S, 31.01.

Method B. A vigorously stirred mixture of the terephthaldicarboxaldehyde **33** (300 mg, 2.24 mmol) and terthiophene phosphonate **16** (2.04 g, 5.12 mmol, 2.3 equiv) in dry THF (50 mL) was slowly treated with KO^{t}Bu (552 mg, 4.94 mmol) and then left to stir at rt for 3 h. After this period the reaction mixture was quenched with water (30 mL), treated with 1 M solution of HCl (100 mL) to give a yellow precipitate. This solid was filtered and dissolved in CH_2Cl_2 (500 mL) with gentle heating. The solution was washed with water (80 mL) and then organic layer was dried ($MgSO_4$). This crude solid was dissolved in a minimum

amount of toluene and passed through a pad of silica using rapid silica filtration to remove the first band of intensely yellow material. The appropriate concentrations were concentrated to afford a yellow solid, which was recrystallised from CH_2Cl_2/petroleum ether (charcoal) to give *product* **32** (1.11 g, 80%) as a bright yellow solid.

4.1.14. 5,5″-Dibromo-3′-formyl-2,2′:5′,2″-terthiophene (34). To a stirred solution of 3′-formyl-2:2′,5′:2″-terthiophene **1** (2.76 g, 10 mmol) in DMF (130 mL) kept in the dark at rt was added NBS (3.74 g, 21 mmol) and was left to stir for 5 h. After this period a yellow precipitate had formed. The mixture was poured into ice-cold water and filtered. The yellow solid was then dried (P_2O_5) under vacuum and recrystallised chloroform/ether to give the *dibromide* **9** as bright yellow fluffy crystals (3.47 g, 80%), mp 163 °C. ^{1}H NMR (300 MHz) δ 10.02 (s, 1H, CHO); 7.48 (s, 1H, H4′); 7.12 (A part of ABq, 1H, J=3.9 Hz, H4 or H3); 7.08 (B part of ABq, 1H, J=3.9 Hz, H3 or H4); 7.01 (A part of ABq, 1H, J=3.9 Hz, H4″); 6.96 (B part of ABq, 1H, J=3.9 Hz, H3″). ^{13}C NMR (75 MHz) δ 184.4, 144.4, 137.8, 136.7, 136.1, 133.3, 131.2, 130.9, 129.5, 125.2, 123.0, 115.9, 112.9. IR (KBr) ν_{max}/cm^{-1} 3099, 3084, 1673, 1509, 1434, 1422, 1374, 1324, 1301, 1233, 1225, 1215, 1190, 1168, 1065, 981, 975, 954, 850, 842, 804, 779, 746, 735, 690. UV–vis ($CHCl_3$) λ_{max} nm/(log ε) 264 (4.29), 332 (4.19), 374 (sh) (4.14). EIMS m/z 437 (8), 436 (61), 434 (M^+, 100%), 408 (9), 406 (15), 355 (14), 327 (42), 311 (22), 309 (20), 246 (22), 205 (10), 201 (15), 123 (15), 69 (17). Anal. Calcd for $C_{13}H_6Br_2OS_3$: C, 35.96; H, 1.39; S, 22.16. Found: C, 36.06; H, 1.19; S, 22.55.

4.1.15. 3″-Formyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (35). A stirred mixture of 5,5″-dibromo-3′-formyl-2,2′:5′,2″-terthiophene **34** (0.803 g, 1.85 mmol) and tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] (1.28 mg, 0.11 mmol, 6 mmol %) in DME (15 mL) was added to 2-thiophene boronic acid **15** (0.710 g, 5.55 mmol) and a solution of 1 M Na_2CO_3 (11 mL). The reaction mixture was heated under reflux for 7 h during which time a red precipitate formed. After this period the reaction mixture was cooled, the DME removed under reduced pressure and the aqueous layer extracted with CH_2Cl_2 (2×70 mL). The organic layers were then combined, washed with water (50 mL) and dried (Drydisk). The filtrate was then diluted with an equal volume of petroleum ether and passed through a pad of silica with further elution with 75% CH_2Cl_2/petroleum ether to collect an intense red band and to remove baseline impurities. This crude material was adsorbed onto silica and subjected to column chromatography eluting with 50% toluene/petroleum ether, 75% toluene/petroleum ether, 1% EtOAc/toluene and 4% EtOAc/toluene. The appropriate fractions were combined and concentrated to give a solid that was recrystallised from CH_2Cl_2/petroleum ether (charcoal) to afford the *pentathiophene aldehyde* **35** as deep red crystals (0.578 g, 71%), mp 178 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 10.14 (s, 1H, CHO); 7.55 (s, 1H, H4″); 7.33 (dd, 1H, J=5.1, 1.1 Hz, H5); 7.32–7.26 (m, 3H, J=3.9 Hz, H3, H4′, H5⁗); 7.24 (d, 2H, J=3.9 Hz, H3′, H3⁗); 7.18 (A part of ABq, 1H, J=3.8 Hz, H3‴); 7.14 (B part of ABq, 1H, J=3.8 Hz, H4‴); 7.08 (dd, 1H, J=5.1, 3.6 Hz, H4); 7.06 (dd, 1H, J=5.1, 3.6 Hz, H4⁗). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 185.1, 145.6, 141.3, 138.3, 138.2, 137.1, 136.8, 134.7, 131.3, 130.6, 127.7, 128.6, 126.3, 126.2, 125.7, 125.3, 125.2, 125.0, 124.8, 123.2. ν_{max}/cm^{-1} 3064, 1655, 1495, 1424, 1386, 1354, 1221, 1203, 1166, 1056, 1047, 833, 786, 690. UV–vis ($CHCl_3$) λ_{max} nm/(log ε) 257 (4.42), 369 (sh) (4.47), 412 (4.54). EIMS m/z 442 (27), 441 (28), 440 (M^+, 100%), 412 (15), 358 (4), 220 (9), 209 (6), 127 (29), 69 (7). Anal. Calcd for $C_{21}H_{12}OS_5$: C, 57.24; H, 2.74; S, 36.38. Found: C, 57.25; H, 2.59; S, 36.46.

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Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, no. CCDC-652064. Copies of the data can be obtained free of charge on application to CCDC, University Chemical Lab, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk). Processing data and the selected crystal data for compound **29** can be found in the Supplementary data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.08.022.

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