

One pot Suzuki coupling – Wittig olefination reactions

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Bromoarylcarbaldehydes and bromothiénylcarbaldehydes undergo Suzuki cross coupling and Wittig reactions in a one pot procedure to give olefins with extended pi systems. Dihaloarenes can be transformed in a double Wittig – / double Suzuki cross coupling reaction to yield functionalised terphenyls.

Keywords: Suzuki cross-coupling, Wittig olefination, conjugated pi-systems, terphenyls

Numerous conjugated phosphoranes are stable towards water and oxygen.¹ Many of these stabilised phosphoranes react preferentially or exclusively with carbaldehydes,¹ while being otherwise unreactive towards other species. This inertness to other substrates and their tolerance of reaction conditions, such as of acidity/basicity of the medium and reaction temperature, make these phosphoranes useful reagents for olefination reactions with carbaldehydes in combination with other transformations in a one-pot procedure. The authors have already shown that the Wittig olefination can be combined with a [4 + 2]-cycloaddition² of the olefinic product and have demonstrated the possibility of preparing a library of functionalised phosphoranes by transforming haloaroyl- and haloheteroaryl-methylidenetriphenylphosphoranes in Pd(0) catalysed C–C bond reactions, such as Suzuki reactions, Sonogashira- and Heck coupling reactions.³ In this paper, the potential of a combination of Suzuki cross coupling reaction and Wittig olefination with bromoarylcarbaldehydes and bromothiénylcarbaldehydes is investigated.

The reaction of either bromoarenealdehydes **2b**, **2c**, **2e** or of bromothiénylaldehydes **2a**, **2f** with arylboronic acids and conjugated phosphoranes gives access to compounds **4** in good yield (Scheme 1, Table 1). A two phase system was used in these reactions with DME as the organic solvent and aq. Na₂CO₃ as the aqueous medium.

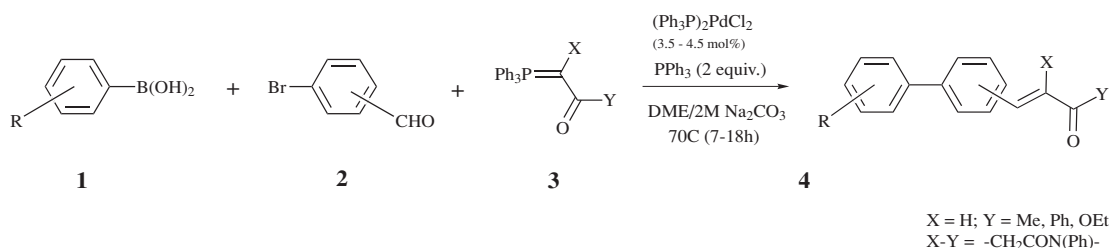
In the experiments, bistriphenylphosphinopalladium (II) dichloride [(PPh₃)₂PdCl₂]⁵ was utilised as pre-catalyst for the Suzuki cross-coupling reactions, where additional

triphenylphosphine (PPh₃) was added as ligand. The transformation also proceeded without the addition of PPh₃, but especially in the case of the two-fold Suzuki coupling reactions, better yields were achieved in the presence of PPh₃.

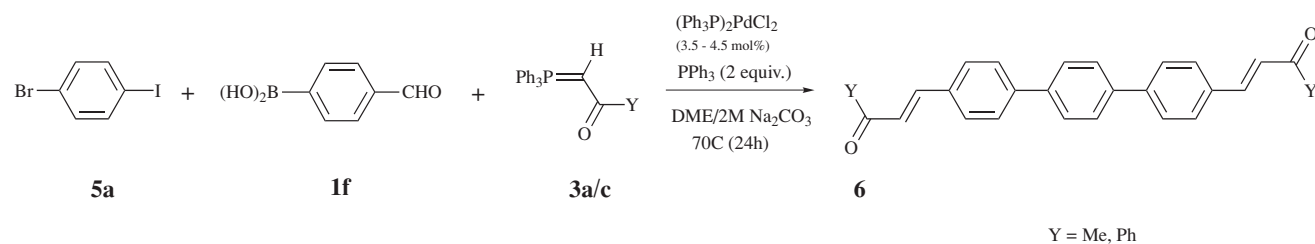
Phosphoranes **3b**, **3d** and **3e** are more reactive towards aldehydes than the benzoylmethylidenetriphenylphosphorane (**3a**) and acetylmethylidenetriphenylphosphorane (**3c**). Thus, **3b**, **3d** and **3e** react with aldehydes exothermally. The evolution of heat is observed especially in their reaction in solventless systems and at high concentrations. While no evolution of heat was observed in the corresponding reaction with **3a** and **3c**. Accordingly, the one-pot Suzuki cross-coupling – Wittig olefination reactions necessitated longer reaction times with **3a** and **3c**.

Only in one case did the one-pot procedure fail, namely in the reaction of 5-bromothiénylcarbaldehyde (**2f**) with acetylmethylidenetriphenylphosphorane (**3c**) and benzofuranboronic acid, where the Suzuki coupling reaction did not proceed satisfactorily and a mixture of mostly 4-(5'-bromothien-2'-yl) but-3-en-2-one and the reduced 4-(thien-2'-yl)but-3-en-2-one was produced.

Bishaloarenes and bisheteroarenes can also be subjected to a two-fold Suzuki coupling – Wittig olefination process, when 4-formylphenylboronic acid is used as a building block.⁶ Here, terphenyls conjugated to further pi functional groups can be synthesised readily in one step. The thienyl **6c** is of interest as a new class of fluorescent materials (Scheme 2,



Scheme 1



Scheme 2

* Correspondence.

Table 1 Reaction of bromoarenealdehydes or bromothiénylaldehydes with arylboronic acids and conjugated phosphoranes

<p>Yield 85%; only <i>E</i>-isomer isolated (12h)</p>	<p>Yield 75%; <i>E/Z</i> isomer: 93/7 (8h)</p>
<p>Yield 94%; <i>E/Z</i> 85/15 (10.5h)</p>	<p>Yield 54%; only <i>E</i>-isomer isolated (13h)</p>
<p>Yield 61% (13h)</p>	<p>Yield 81%; only <i>E</i>-isomer isolated (13h)</p>
<p>Yield 59%; based on the purified <i>E</i>-isomer (9h)</p>	<p>Yield 72%; only <i>E</i>-isomer isolated (15h)</p>
<p>Yield 77%; <i>E/Z</i> 95/5 (12h)</p>	<p>Yield 93%; only <i>E</i>-isomer isolated (15h)</p>
<p>Yield 83%; <i>E/Z</i> 93/7 (12h)</p>	<p>Yield 87%; only <i>E</i>-isomer isolated (15h)</p>

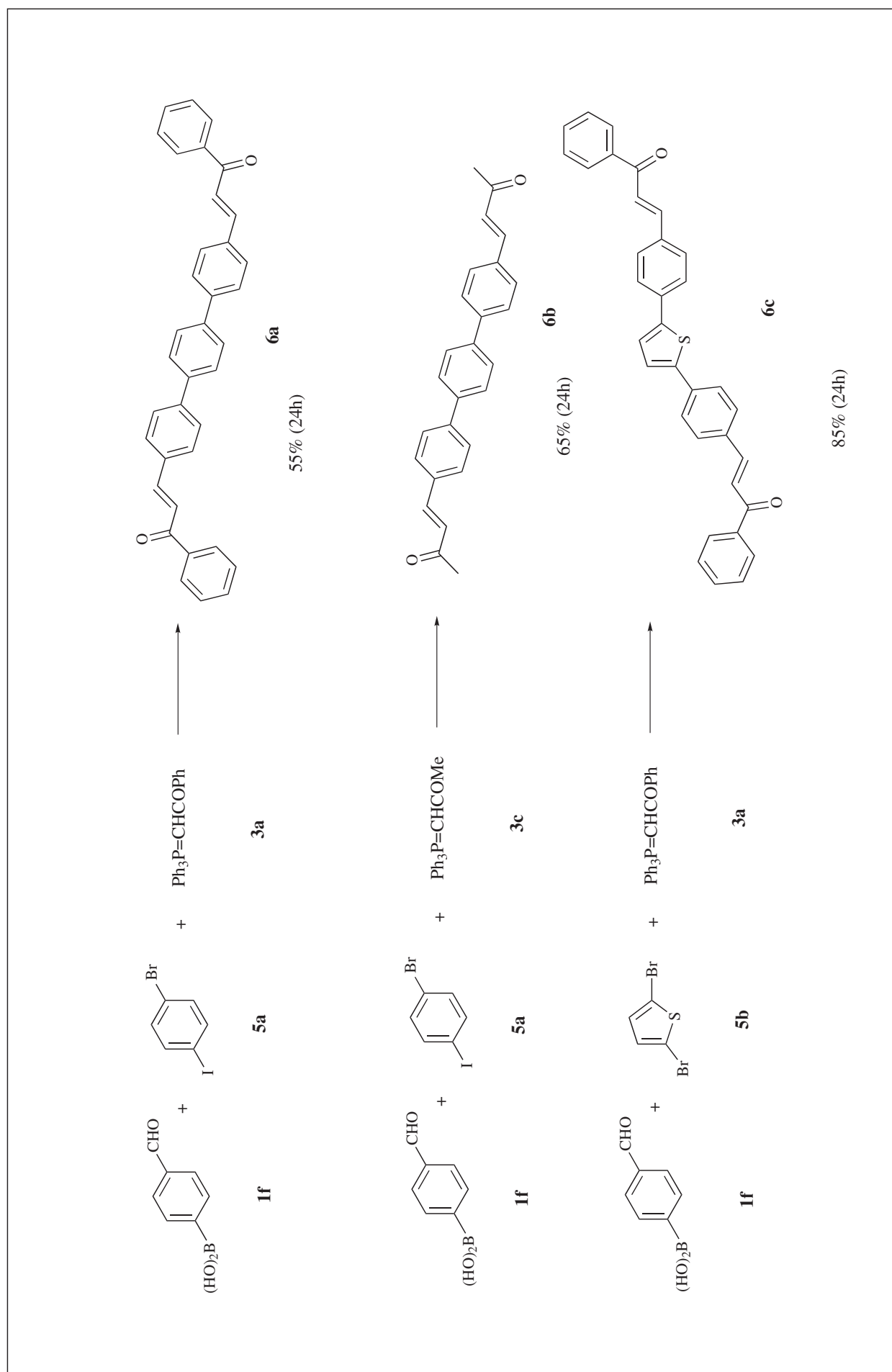
Table 2 Two-fold Suzuki coupling–Wittig defination of bishaloarenes and bisheteroarenes

Table 2). In general, the reaction time (24h) for the two-fold reaction is longer than for the reactions described above.

Most of the products needed to be separated by column chromatography. The terphenyls **4e**, **6a** and **6b** and the quaterphenyl **4f**, however, are sparingly soluble and crystallised from the reaction mixtures. In these cases, after termination of the reaction, water was added and both the organic and the aqueous phase were filtered. The filter cake holds the products and was extracted with hot solvent (chloroform/benzene) to yield the pure product after evaporation of the solvent and crystallisation of the residue from ether. Here, a continuous extraction with a Soxhlet apparatus is of advantage.

As part of our efforts to reduce solvents and waste materials through the development of multi-step one-pot reactions in combination with the use of solventless systems,⁷ studies are currently underway to carry out the transformations presented here in solventless systems.

Experimental

Melting points were measured on a Yanaco microscopic hotstage and are uncorrected. Infrared spectra were measured with a JASCO IR-700 instrument. ¹H (270 MHz and 395.7 MHz) were recorded with a JEOL EX-270 and a JEOL Lambda 400 FT-NMR spectrometer, and, ¹³C (99.45 MHz) with a JEOL Lambda 400 FT-NMR spectrometer. The chemical shifts are relative to TMS (solvent CDCl₃, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2-spectrometer (EI, 70 eV). UV–VIS spectra of **6c** were carried out with a JASCO UV/VIS/NIR V-570 spectrophotometer, the fluorescence spectra with a Hitachi F-4500 Fluorescence Spectrophotometer. Column chromatography was carried out on Wakogel 300. All experiments were purged with argon at the start. 4-Bromothiényl-2-carbaldehyde (**2d**) (Aldrich), 4-bromobenzaldehyde (**2b**) (TCI), bistrisphenylphosphinopalladium(II) dichloride [(PPh₃)₂PdCl₂] (Aldrich) and the boronic acids (Aldrich, TCI) are commercial materials. Bromophenylbenzaldehydes **2c** and **2e** were synthesised by Suzuki cross coupling reaction of 4-formylphenylboronic acid (**1f**) with 1,2-bromiodobenzene (Aldrich) and 1,4-bromiodobenzene (**5a**), respectively. The phosphoranes **3a**,^{8a} **3b**,^{8b} **3c**,^{8a} **3d**,^{8c} and 5-bromothiénylcarbaldehyde (**2f**)⁹ were prepared according to literature procedures. Compound **4b** (Table 1) is a known compound.¹⁰

4-(4'-Methoxyphenyl)-2-(2''-benzoylthienyl)thiophene (4a) General Procedure A: A mixture of **2a** (350 mg, 1.8 mmol), **1a** (347 mg, 2.3 mmol), **3a** (1.05 g, 2.7 mmol), bistrisphenylphosphinopalladium (II) dichloride [(PPh₃)₂PdCl₂] (45 mg, 6.4·10⁻² mmol), triphenylphosphine (34 mg, 0.12 mmol) in DME (8 ml) and 2M aq. Na₂CO₃ (4 ml) was kept at 70°C for 12h. The mixture was cooled, diluted with water (50 ml) and extracted with chloroform (2 × 30 ml). The organic phase was dried over anhydrous MgSO₄ and concentrated *in vacuo*. The residue was chromatographed on silica gel (ether/hexane/chloroform 1:4:1) to yield **4a** (498 mg, 85%) as pale yellow crystals, m.p. 179°C (hexane/ether 1:1); (Found: M⁺ 320.0869. C₂₀H₁₆O₂S requires M, 320.0871); ν_{\max} (KBr)/cm⁻¹ 3090, 1658, 1596, 1509, 1280, 1256, 1199, 1177, 1012, 825, 775; δ_{H} (270 MHz, CDCl₃) 3.85 (3H, s, OCH₃), 6.96 (2H, d, ³J 8.4 Hz), 7.38 (1H, d, ³J 15.4 Hz), 7.43 (1H, bs), 7.47 – 7.63 (6H, m), 7.95 (1H, d, ³J 15.4 Hz), 8.02 (d, ³J 8.4 Hz); δ_{C} (99.45 MHz, CDCl₃) 55.34, 114.31, 120.87, 122.20, 127.43, 127.70, 128.41, 128.63, 130.68, 132.78, 137.23, 138.12, 143.19, 159.28, 189.82; MS (70 eV) *m/z* (%): 320 (100) [M⁺], 289 (19), 243 (15), 215 (18). (Found: C, 74.51; H, 5.06. C₂₀H₁₆O₂S requires C, 74.97; H, 5.03).

Further selected physical and spectral data

4-(4''-Methoxybiphenyl)buten-2-one (4c): Colourless prisms, m.p. 184°C; (Found: M⁺ 252.1552. C₁₇H₁₆O₂ requires M, 252.1150); ν_{\max} (KBr)/cm⁻¹ 2956, 2836, 1657, 1599, 1498, 1358, 1293, 1254, 1192, 1036, 977, 840, 808; δ_{H} (270 MHz, CDCl₃) 2.40 (3H, s, CH₃), 3.86 (3H, s, OCH₃), 6.74 (1H, d, ³J 16.7 Hz), 6.98 (2H, d, ³J 8.4 Hz), 7.51 – 7.65 (7H, m); MS (70 eV) *m/z* (%) 252 (72).

N-Phenyl-3-(4''-methoxybiphenyl)methylidene-4(H)-maleimide (4d): Colourless solid, m.p. 227°C; (Found: MH⁺ 370.1444. C₂₄H₂₀O₃N requires M, 370.1443); ν_{\max} (KBr)/cm⁻¹ 1768, 1706, 1647, 1598, 1498, 1381, 1249, 1173, 700, 669; δ_{H} (270 MHz, CDCl₃) 3.81 (2H, d, ⁴J 2.1 Hz), 3.87 (3H, s, OCH₃), 7.02 (2H, d, ³J 8.7 Hz), 7.37 – 7.70 (11H, m), 7.77 (1H, t, ⁴J 2.1 Hz); δ_{C} (99.45 MHz, CDCl₃) 34.42, 55.39, 114.46, 122.39, 126.48, 127.20, 128.20, 128.58,

129.15, 130.85, 131.04, 132.34, 135.13, 143.20, 159.85, 162.01, 170.01, 173.09; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 370 (2.6) [MH⁺]; (Found: C, 76.81; H, 5.18; N, 3.72. C₂₄H₁₉NO₃·0.25H₂O requires: C, 77.09; H, 5.26; N, 3.74)

Ethyl 3-(4''-methoxy-p-terphenyl)acrylate (4e): Colourless crystals, mp. 330°C* (ether) (Found: M⁺ 358.1570. C₂₄H₂₂O₃ requires M, 358.1569); ν_{\max} (KBr)/cm⁻¹ 1706, 1631, 1599, 1491, 1309, 1288, 1253, 1202, 1176, 1035, 813; δ_{H} (270 MHz, CDCl₃) 1.31 (3H, t, ³J 7.1 Hz), 3.86 (3H, s, OCH₃), 4.28 (2H, q, ³J 7.1 Hz), 6.48 (1H, d, ³J 15.9 Hz), 7.00 (2H, d, ³J 8.6 Hz), 7.49 – 7.76 (m, 11H); MS (70 eV) *m/z* (%): 358 (46), 277 (48), 58 (100). *Shows three unidentified mesophases at 260 – 307°C; at 307 – 327°C and 327 – 330°C.

Ethyl 3-(quaterphenyl)acrylate (4f): Colorless crystals, 346°C (ether); (Found: M⁺ 404.1773. C₂₉H₂₄O₂ requires M, 404.1776); ν_{\max} (KBr)/cm⁻¹ 1713, 1633, 1484, 1311, 1176, 816, 764; δ_{H} (270 MHz, CDCl₃) 1.36 (3H, t, ³J 7.0 Hz), 4.29 (2H, q, ³J 7.0 Hz), 6.49 (1H, d, ³J 15.9 Hz), 7.31 – 7.77 (18H, m); MS (70 eV) *m/z* (%): 404 (19) [M⁺], 358 (65), 306 (100).

Ethyl 3-(4'-phenylthien-2'-yl)isobut-2(3)-enoate (4g): m.p. 89°C (hexane/ether 1:1); (Found: M⁺ 272.0876. C₁₆H₁₆O₂S requires M, 272.0871); ν_{\max} (KBr)/cm⁻¹ 3094, 2984, 1704, 1614, 1265, 1242, 1184, 1122, 1109, 741; δ_{H} (270 MHz, CDCl₃) 1.36 (3H, t, ³J 7.0 Hz), 2.24 (3H, d, ⁴J 1.3 Hz), 4.28 (2H, q, ³J 7.0 Hz), 7.27 – 7.63 (7H, m), 7.87 (1H, d, ⁴J 1.3 Hz); δ_{C} (99.45 MHz, CDCl₃) 14.28, 14.35, 60.98, 123.89, 125.58, 126.37, 127.54, 128.90, 130.50, 131.37, 135.17, 139.98, 142.47, 168.45; MS (70 eV) *m/z* (%): 272 (100) [M⁺], 243 (18), 227 (21), 198 (60). (Found: C, 70.50; H, 5.88. C₁₆H₁₆O₂S requires C, 70.77; H, 5.92).

4-(4''-Methoxy-m-terphenyl)but-3-en-2-one (4h): A slowly crystallising solid; (Found: M⁺ 328.1460; C₂₃H₂₀O₂ requires M, 328.1463); ν_{\max} (KBr)/cm⁻¹ 3026, 2928, 2836, 1667, 1607, 1516, 1476, 1250, 1178, 909, 833; δ_{H} (270 MHz, CDCl₃) 2.37 (3H, s, CH₃), 3.78 (3H, s, OCH₃), 6.68 (1H, d, ³J 16.2 Hz), 6.75 (2H, d, ³J 8.3 Hz), 7.06 (2H, d, ³J 8.3 Hz), 7.17 (2H, d, ³J 8.1 Hz), 7.30 – 7.41 (6H, m), 7.47 (1H, d, ³J 16.2 Hz); MS (70 eV) *m/z* (%): 328 (100) [M⁺], 145 (39).

2-(4''-Methoxyphenyl)-5-(but-1''-en-3''-on-1''-yl)thiophene (4i): Bright yellow needles, m.p. 158°C; (Found: M⁺ 258.0716. C₁₅H₁₄O₂S requires M, 258.0715); ν_{\max} (KBr)/cm⁻¹ 1656, 1635, 1604, 1505, 1446, 1258, 1178, 1025, 969, 824, 796; δ_{H} (270 MHz, CDCl₃) 2.34 (3H, s, CH₃), 3.80 (3H, s, OCH₃), 6.49 (1H, d, ³J 15.7 Hz), 6.92 (2H, d, ³J 8.6 Hz), 7.17 (1H, d, ³J 4.0 Hz), 7.25 (1H, d, ³J 4.0 Hz), 7.55 (2H, d, ³J 8.6 Hz), 7.59 (1H, d, ³J 15.7 Hz); MS (70 eV) *m/z* (%): 258 (82) [M⁺], 243 (100). (Found: C, 69.68; H, 5.48. C₁₅H₁₄O₂S requires C, 69.93; H, 5.46).

2-[2''-(4''-Methoxyphenyl)thien-5''-yl]vinylphenylketone (4k): Light yellow crystals; m.p. 158°C; (Found: M⁺ 320.0870. C₂₀H₁₆O₂S requires M, 320.0871); ν_{\max} (KBr)/cm⁻¹ 2954, 1650, 1588, 1574, 1256, 1221, 1033, 964, 812, 692; δ_{H} (270 MHz, CDCl₃) 3.86 (3H, s, OCH₃), 6.94 (2H, d, ³J 8.9 Hz), 7.19 (1H, d, ³J 4.5 Hz), 7.29 (1H, d, ³J 14.9 Hz), 7.32 (1H, d, ³J 4.5 Hz), 7.47 – 7.62 (5H, m), 7.93 (1H, d, ³J 14.9 Hz), 8.02 (2H, m), δ_{C} (99.45 MHz) 55.40, 114.49, 119.85, 123.20, 127.37, 127.63, 128.37, 128.56, 132.64, 133.82, 137.18, 137.44, 138.63, 147.99, 160.06, 189.80; MS (70 eV) *m/z* (%) = 320 (100) [M⁺], 243 (26).

4-(4''-Methoxyphenyl)-2-(2''-acetylenyl)thiophene (4l): Pale yellow crystals, mp. 141°C. (Found: M⁺ 258.0714. C₁₅H₁₄O₂S requires M, 258.0715); ν_{\max} (KBr) cm⁻¹ 3096, 1669, 1614, 1508, 1255, 1180, 1025, 973, 825, 761; δ_{H} (270 MHz, CDCl₃) 2.35 (3H, s, CH₃), 3.84 (3H, s, OCH₃), 6.55 (1H, d, ³J 15.9 Hz), 6.78 (1H, s), 6.93 (2H, d, ³J 6.9 Hz), 7.40 (1H, bs), 7.47 (2H, d, ³J 6.9 Hz), 7.64 (1H, d, ³J 15.9 Hz); MS (70 eV) *m/z* (%): 258 (100) [M⁺], 243 (85). (Found: C, 69.62; H, 5.46. C₁₅H₁₄O₂S requires C, 69.93; H, 5.46%).

2-[2''-(o-Tolyl)thien-5''-yl]vinylphenylketone (4m): Pale yellow oil; (Found: M⁺ 304.0921. C₂₀H₁₆OS requires M, 304.0922); ν_{\max} (KBr)/cm⁻¹ 3058, 1658, 1589, 1448, 1353, 1280, 1216, 1014; δ_{H} (270 MHz, CDCl₃) 2.47 (3H, s, CH₃), 7.05 – 8.03 (12H, m), 7.89 (1H, d, ³J 17.0 Hz); MS (70 eV) *m/z* (%) = 304 (70) [M⁺], 271 (25), 214 (100), 185 (42), 157 (19), 137 (47).

2-[6''-Fluorobiphenyl]vinylphenylketone (4n): Colourless oil; (Found: M⁺ 302.1104. C₂₁H₁₅OF requires M, 302.1107); ν_{\max} (KBr)/cm⁻¹ 3060, 2924, 1663, 1604, 1484, 1450, 1332, 1215, 1015, 982, 756; δ_{H} (270 MHz, CDCl₃) 7.13 – 7.65 (10H, m), 7.73 (2H, d, ³J 8.2 Hz), 7.86 (1H, d, ³J 15.9 Hz), 8.04 (2H, m); MS (70 eV) *m/z* (%) = 302 (100) [M⁺], 225 (13), 207 (31), 190 (32).

2,5-Bis(2''-benzoylthienyl)thiophene (6c): General procedure B: A mixture of 4-bromo-1-iodobenzene (**5a**) (242 mg, 1.0 mmol), 4-formylphenylboronic acid (**1f**) (600 mg, 4.0 mmol), benzoylmethylidenetriphenylphosphorane (**3a**) (2.28 g, 6.0 mmol), [(PPh₃)₂PdCl₂]

(30 mg, $4.3 \cdot 10^{-2}$ mmol), and triphenylphosphine (23 mg, $8.6 \cdot 10^{-2}$ mmol) in DME (7 ml) and 2M aq. Na_2CO_3 solution (3 ml) was heated at 70°C for 24h. The cooled solution was then diluted with water and extracted with ether. Both the organic and the aqueous phase were filtered. The remaining filter cake was extracted with hot chloroform. The filtrate resulting from the hot extraction was concentrated *in vacuo*. Ether was added to the concentrated solution (100 ml). The precipitate was filtered and washed with ether to give **6c** (420 mg, 85%) as metallic-yellow crystals, mp. 214°C (ether); (Found: MH^+ 497.1574. $\text{C}_{34}\text{H}_{25}\text{O}_2\text{S}$ requires MH, 497.1575). ν_{max} (KBr)/ cm^{-1} 1659, 1598, 1333, 1219, 1017, 802, 772, 686; δ_{H} (270 MHz, CDCl_3) 7.41 (2H, s), 7.47 – 7.65 (8H, m), 7.67 (8H, bs), 7.82 (2H, d, 3J 16.3 Hz), 8.03 (4H, d, 3J 7.4 Hz); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) = 497 (MH^+ , 4.9); UV λ_{max} = 394.5 nm (lge 4.62, $c = 10^{-5}$ in CH_2Cl_2); $F\lambda_{\text{max}}$ = 513.8 nm (excitation at $\lambda = 394$ nm, $c = 10^{-6}$ in CH_2Cl_2)

Further selected physical and spectral data: 4,4''-Bis(benzoylphenyl)-*p*-terphenyl (**6a**) as shiny silver flakes, m.p. 328°C (ether)*; ν_{max} (KBr)/ cm^{-1} 3062, 1662, 1640, 1602, 1340, 1311, 1286, 1219, 1013, 979, 805, 772, 688; δ_{H} (270 MHz, CDCl_3) 7.50 – 7.75 (16H, m), 7.73 (4H, s), 7.87 (2H, d, 3J 15.9 Hz), 8.05 (4H, d, 3J 8.4 Hz); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) = 491 (MH^+ , 0.3), 415 ($\text{MH}^+ - \text{C}_6\text{H}_5$, 0.8). *shows an unidentified mesophase between 312°C and 328°C .

4,4''-Bis(acetylphenyl)-*p*-terphenyl (**6b**): shiny silver flakes; mp 325°C (dec.)* (ether); ν_{max} (KBr)/ cm^{-1} 1662, 1259, 979, 803; δ_{H} (270 MHz, CDCl_3) 2.41 (6H, s, 2 CH_3), 6.77 (2H, d, 3J 16.2 Hz), 7.56 (2H, d, 3J 16.2 Hz), 7.64 (4H, d, 3J 8.4 Hz), 7.70 (4H, d, 3J 8.4 Hz), 7.72 (4H, s); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) = 367 (MH^+ , 1.9). * shows unidentified mesophase between 296°C and 325°C .

Received 2 July 2004; accepted 12 September 2004
Paper 04/2621

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