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Selective Palladium-Catalysed *ipso* Arylation of α,α-Disubstituted Benzo[*b*]thien-2-ylmethanols with Aryl Bromides using PCy_3 as Ligand

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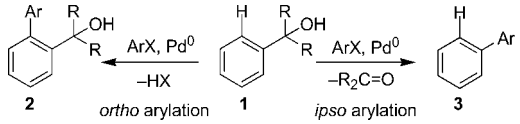
α,α-Diphenylbenzo[*b*]thien-2-ylmethanol was treated with a series of aryl bromides in the presence of palladium(II) acetate and tricyclohexylphosphane to give the appropriate 2-aryl-benzo[*b*]thiophenes in good to excellent yield with concomitant formation of benzophenone. The reaction was successfully extended to α,α-diphenylbenzo[*b*]thien-3-ylmethanol, although in certain cases the transformation was biased by concurrent *ortho* arylation.

Introduction

Transition-metal catalysed carbon–carbon bond forming reactions are an indispensable tool for synthetic chemists.[1,2] Processes accompanied by the cleavage of a carbon–hydrogen or a carbon–carbon bond have attracted particular attention from the atom-economic and sustainability points of view.[3] The selectivity of coupling reactions proceeding by C–H activation usually originates in the coordinating effect of an adjacent functional group; hence, these reactions are also known as *ortho* arylation reactions (Scheme 1).[4–6]



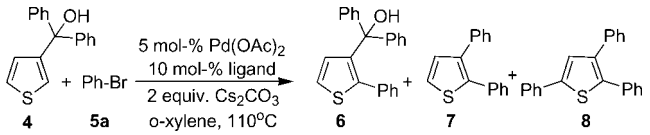
Scheme 1. The *ortho* and *ipso* arylation of aryl carbinols.

Catalytic processes involving C–C bond cleavage by β-carbon elimination lead to the selective introduction of the aryl moiety into the *ipso* position. In such processes, the bond to break is typically between a tertiary alcohol and an sp^2- or sp-hybridized carbon. Ethynyl carbinols, for example, were successfully converted into diarylacetylenes with concomitant loss of a ketone molecule in a palladium-catalysed transformation,[7,8] whereas in the presence of rhodium catalysts, their dimerization was selectively observed.[9]

In the palladium-catalysed transformation of α,α-disubstituted arylmethanols with aryl halides, *ortho* arylation and *ipso* coupling are usually competing reactions.[10] In certain cases, however, these transformations might proceed sequentially to give rise to highly substituted products.[11] In order to achieve selective *ipso* coupling, one typically must block the *ortho* positions in the starting carbinol by substitution. Exceptions to this rule are 2-thienyl and 2-furyl carbinols that, according to Miura, give 2-phenyl heterocycles exclusively when reacted with chlorobenzene.[12] This reaction was successfully extended to the preparation of 2-arylthiophenes and 5-aryl-2,2′-bithiophenes.[13] As part of our ongoing studies on the palladium-catalysed functionalization of heterocyclic compounds, we attempted to extend Miura's procedure to 3-thienyl carbinols and benzo[*b*]thiophenylmethanol derivatives. The principal aim of our research was to establish reaction conditions for which the *ipso*-arylated heterocyclic product is formed with high selectivity.

Results and Discussion

The first set of experiments were designed to establish whether the reaction of 3-thienyl carbinols and aryl halides proceeds at the *ipso* position, as in the case of the analogous 2-thienyl derivatives, and to determine if the competing *ortho* arylation reaction also takes place to a considerable extent. Our carbinol of choice was α,α-diphenylthien-3-ylmethanol (**4**) and it was treated with bromobenzene (**5a**) in the presence of palladium acetate, different phosphanes, and cesium carbonate (Scheme 2). The reactions were monitored and the products were identified by GC–MS.



Scheme 2. The coupling of α,α-diphenylthien-3-ylmethanol (**4**) and bromobenzene.

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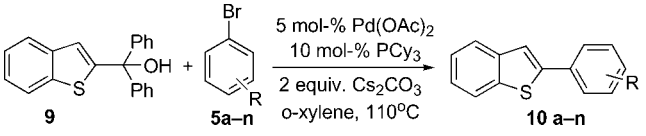
Our experiments revealed that the selectivity of the coupling reaction is quite poor; a mixture of products is furnished in all cases, including *ortho* arylated starting material **6**, 2,3-diphenylthiophene (**7**), and a triphenylthiophene, tentatively identified as 2,3,5-isomer **8** (Table 1). The fact that 3-phenylthiophene was absent from the reaction mixtures suggests that the primary reaction of **4** and **5a** is *ortho* arylation in the 2-position of the thiophene ring. This position is activated both electronically and by the directing effect of the carbinol moiety through complexation to the phenylpalladium intermediate of the catalytic cycle. The coupling of **6** with another molecule of bromobenzene (**5a**) could lead, in principle, to three different products: direct arylation at C-5, *ortho* arylation at C-4, and *ipso* arylation at C3; only the latter product (**7**) was detected. This fact also underlines the importance of the coordination between the phenylpalladium complex and the carbinol in the course of the process. The presence of minor amounts of a triarylated thiophene, with its amount becoming significant only at the later stages of the process, suggests that **7** can undergo direct arylation in the 5-position. This process, also known as the heteroaryl Heck reaction, is well-documented in the literature; the arylation of **7** in the 4-position is far less likely to take place both for steric and electronic reasons. As the data in Table 1 show, the product distribution was only slightly dependent on the coupling conditions. Whereas PCy_3 and dppf (Table 1, Entries 1–4) predominantly led to diarylation products, the use of xantphos or PPh_3 (Table 1, Entries 5 and 6) caused the relative rate of the second (*ipso*) arylation to decrease, which resulted in increased amounts of monoarylated product **6**. A change in the palladium source from $Pd(OAc)_2$ to $[(C_3H_5)PdCl]_2$ or $Pd_2(dba)_3$ had some influence on the activity of the catalyst but not its selectivity (Table 1, Entries 2 and 3). The choice of solvent had very little effect on the process. The coupling worked equally well in high-boiling solvents of apolar (*o*-xylene) or polar (DMA) nature. Preliminary experiments on other 3-thienyl carbinols (dimethyl, pentamethylene) were even more discouraging and usually produced more than three products.

Table 1. Product distribution in the coupling of α,α-diphenylthien-3-ylmethanol (**4**) and bromobenzene (**5a**).

Entry	Ligand	Time [h]	Conversion [%]	**6**	**7**	**8**
1	PCy_3	4	75	4	52	19
		28	90	6	46	38
2[a]		4	55	3	52	0
		22	85	2	69	14
3[b]		4	32	6	26	0
		28	61	0	52	9
4	dppf	4	27	15	12	0
		48	81	16	52	13
5	xantphos	4	26	18	8	0
		48	58	20	32	6
6	PPh_3	4	66	42	20	4
		22	100	6	52	42

[a] $[(C_3H_5)PdCl]_2$ was used instead of $Pd(OAc)_2$. [b] $Pd_2(dba)_3$ was used instead of $Pd(OAc)_2$.

The poor selectivity for *ipso* arylation in the reaction of 3-thienyl carbinols and bromobenzene prompted us to look for other coupling partners.[14] The next reactant of choice was α,α-diphenylbenzo[*b*]thien-2-ylmethanol (**9**, Scheme 3), a compound that was easily prepared from benzo[*b*]thiophene and benzophenone.[15] In **9**, there are two possible sites for coupling: the 2-position for *ipso* coupling and the 3-position for *ortho* arylation. In the first reaction (Table 2, Entry 1), **9** was treated with bromobenzene (**5a**) in *o*-xylene with the use of the same conditions as reported by Miura for thiophene derivatives.[12] The reaction proceeded cleanly and 2-phenylbenzo[*b*]thiophene (**10a**) was formed selectively, which was separated from the byproduct (benzophenone) by column chromatography. Following this encouraging result, a series of other aryl bromides (**5b**–**n**) were also reacted with **9**. All reactions were run to completion, as judged by GC, and led to the selective formation of the corresponding 2-arylbenzo[*b*]thiophene derivatives (**10b**–**n**) (Table 2, Entries 2–14) in good to excellent yield. The *ipso* coupling of **9** worked equally well with electron-rich and electron-deficient aryl halides (compare Table 2, Entries 2–6). The steric effects seemed to play only a minor role, if any, in influencing the yield (compare Table 2, Entries 2 and 3, 4–6, 10–12), although they had some effect on the rate of the coupling. Electron rich and electron poor heterocycles were also efficiently coupled (Table 2, Entries 13, 14).



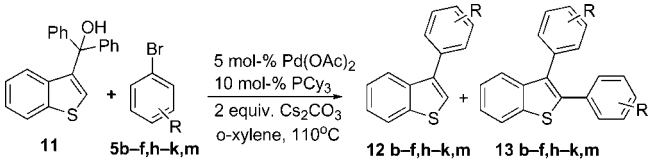
Scheme 3. The coupling of α,α-diphenylbenzo[*b*]thien-2-ylmethanol (**9**) and aryl bromides.

Table 2. The palladium-catalysed coupling of α,α-diphenylbenzo-[*b*]thien-2-ylmethanol (**9**) and aryl bromides **5a**–**n**.

Entry	Reagent	Time [h]	Yield [%]
1	1-bromobenzene (**5a**)	8	77 (**10a**)
2	2-chloro-1-bromobenzene (**5b**)	22	74 (**10b**)
3	4-chloro-1-bromobenzene (**5c**)	19	97 (**10c**)
4	2-bromotoluene (**5d**)	20	76 (**10d**)
5	3-bromotoluene (**5e**)	46	95 (**10e**)
6	4-bromotoluene (**5f**)	22	78 (**10f**)
7	4-bromoanisole (**5g**)	20	67 (**10g**)
8	2-fluoro-1-bromobenzene (**5h**)	20	91 (**10h**)
9	4-fluoro-1-bromobenzene (**5i**)	46	51 (**10i**)
10	1-bromonaphthalene (**5j**)	17	69 (**10j**)
11	2-bromonaphthalene (**5k**)	22	73 (**10k**)
12	9-bromoanthracene (**5l**)	46	68 (**10l**)
13	2-bromothiophene (**5m**)	46	95 (**10m**)
14	3-bromopyridine (**5n**)	22	70 (**10n**)

By following the coupling reactions with GC–MS, we were unable to detect the formation of the appropriate *ortho*-arylated or 2,3-diarylated benzo[*b*]thiophene derivatives, a finding that underlines the excellent selectivity of the process. We also carried out some preliminary experiments on the α,α-dimethyl and α,α-pentamethylene analogues of **9**, but the coupling of these derivatives was far less selective; therefore, in the next set of experiments the

diphenyl carbinol moiety was shifted to the 3-position of the benzo[*b*]thiophene frame. α,α-Diphenylbenzo[*b*]thien-3-ylmethanol (**11**, Scheme 4) was prepared from 3-bromobenzo[*b*]thiophene[16] and benzophenone, in a similar method to **9**. In **11**, there are also two likely sites for coupling: the electronically activated 2-position for *ortho* arylation (the primary reaction of 3-thienyl carbinols) and the 3-position for *ipso* coupling (the only reaction route observed for 2-benzothienyl carbinols). The coupling experiments were carried out under the same previously used conditions. Mixtures of **11**, 2 equiv. of the appropriate aryl halide, the catalyst consisting of 5 mol-% $Pd(OAc)_2$ and 10 mol-% PCy_3, and 2 equiv. of cesium carbonate were heated in *o*-xylene (Scheme 3). The reactions were monitored by GC–MS and run until **11** was consumed.



Scheme 4. The coupling of α,α-diphenylbenzo[*b*]thien-3-ylmethanol (**11**) and aryl bromides.

Unlike the case of 2-benzothienyl carbinols, the reaction of **11** with aryl bromides usually led to the concomitant formation of 3-arylbenzo[*b*]thiophenes (**12**) and 2,3-diarylbenzo[*b*]thiophenes (**13**). In contrast to the recent results of Miura and coworkers where the palladium-catalysed coupling of α,α-dimethylbenzo[*b*]thien-3-ylmethanol and some aryl bromides was reported to give 2,3-diarylbenzo[*b*]thiophenes in the presence of the bulky P(biphenyl-2-yl)(*t*Bu)$_2$ ligand,[14] in our case the major product was generally *ipso*-coupled 3-aryl derivative **12**, which was separated from the byproducts by column chromatography (Table 3). By following the coupling reactions by GC–MS, we established that the **12/13** ratio varies only a little in the course of the process, which suggests that *ortho* arylation (at C-2) and *ipso* arylation (at C-3) are competing processes for **11**. In contrast to this finding, Miura's analogous process was reported to follow a C-2 arylation, C-3 arylation sequence.[14] Analysis of the data presented in Table 3 reveals that it is difficult to establish any marked trends in the product distribution. The yield of the 3-arylbenzo[*b*]thiophenes ranges from good to poor and it is interesting to note that 2-fluoro-1-bromobenzene (**5h**) gave 2,3-bis(2′-fluorophenyl)benzo[*b*]thiophene (**13h**) exclusively. From a preparative point of view, the utility of this reaction is limited to selected aryl bromides. A possible future extension of the transformation is the identification of such catalyst systems that improve its selectivity either towards *ipso* arylation, or towards the formation of 2,3-diarylbenzo[*b*]thiophenes.

Table 3. The palladium-catalysed coupling of α,α-diphenylbenzo[*b*]thien-3-ylmethanol (**11**) and aryl bromides **5b**–**f**,**h**–**k**,**m**.

Entry	Reagent	**12**[a]	**13**[a]
1	2-chloro-1-bromobenzene (**5b**)	94 (91, **12b**)	6
2	4-chloro-1-bromobenzene (**5c**)	89 (86, **12c**)	11
3	2-bromotoluene (**5d**)	71 (67, **12d**)	29
4	3-bromotoluene (**5e**)	55 (51, **12e**)	45
5	4-bromotoluene (**5f**)	65 (50, **12f**)	35
6	2-fluoro-1-bromobenzene (**5h**)	0	100 (51, **13h**)
7	4-fluoro-1-bromobenzene (**5i**)	60 (32, **12i**)	40
8	1-bromonaphthalene (**5j**)	85 (44, **12j**)	0[b]
9	2-bromonaphthalene (**5k**)	90 (55, **12k**)	0[b]
10	2-bromothiophene (**5m**)	47 (37, **12m**)	53

[a] **12**:**13** Ratios were determined by GC–MS from the reaction mixtures. Numbers in parentheses refer to the yield of isolated product. [b] Dibromonaphthalene is formed as a byproduct.

Conclusions

In summary, we reacted α,α-disubstituted thienylmethanol and benzo[*b*]thienylmethanol derivatives with a series of aryl bromides in the presence of a palladium(II) acetate/tricyclohexylphosphane catalyst system. Although the coupling reactions proceeded readily, the synthetic utility of some of the studied transformations is limited by the fact that coupling through C–C bond fission (*ipso* arylation) and through C–H activation (*ortho* arylation) might be competing processes, which can lead to product mixtures. Starting from α,α-diphenylbenzo[*b*]thien-2-ylmethanol, we prepared a series of 2-arylbenzo[*b*]thiophenes with high selectively in good to excellent yields, whereas in case of α,α-diphenylbenzo[*b*]thien-3-ylmethanol, a varying selectivity was observed in the coupling, which decreased the yield of 3-arylbenzo[*b*]thiophenes in most cases at the expense of the formation of 2,3-diarylbenzo[*b*]thiophenes.

Experimental Section

General Remarks: Melting points were determined with a hotplate and are uncorrected. The ^{1}H and ^{13}C NMR ($CDCl_3$) spectra were recorded with a Bruker DRX-250 spectrometer. For ^{1}H NMR spectra the residual peak of $CHCl_3$ (δ = 7.26 ppm) was used as the internal reference, whereas for ^{13}C NMR spectra the central peak of $CDCl_3$ (δ = 77.0 ppm) was used as the reference. The IR spectra (KBr pellet) were obtained with a Bruker IFS-55 FTIR spectrometer. GC–MS measurements were carried out with an Agilent 6890N instrument (HP-5 capillary column: 30.0 m × 250 μm × 0.25 μm). Silica gel (0.040–0.063 mm) was used for flash column chromatography.

General Procedure for the Preparation of 2-Arylbenzo[*b*]thiophenes (10a–n): In a flame-dried Schlenk flask, **9** (60 mg, 0.189 mmol), the appropriate aryl halide (2 equiv.), PCy_3 (5.3 mg, 0.0189 mmol, 10 mol-%), $Pd(OAc)_2$ (2.1 mg, 0.00949 mmol, 5 mol-%), Cs_2CO_3 (0.123 g, 0.378 mmol), and *o*-xylene (6 mL) were mixed under an atmosphere of argon and heated in an oil bath at 110 °C. After complete conversion of the starting material (monitored by GC) and cooling of the mixture to ambient temperature, water (20 mL) was added, and the reaction mixture was extracted with dichloromethane. The combined organic extracts were dried with $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, gradient from 100:0 to 80:20).

2-Phenylbenzo[*b*]thiophene (10a):[17] White solid, 31 mg (77%).

2-(2-Chlorophenyl)benzo[*b*]thiophene (10b): White solid, 34 mg (74%). M.p. 67.5–69 °C. ^{1}H NMR (250 MHz): δ = 7.30–7.43 (m, 4 H), 7.51–7.54 (m, 1 H), 7.60–7.63 (m, 2 H), 7.82–7.89 (m, 2 H) ppm. ^{13}C NMR (62.5 MHz): δ = 122.0, 123.8, 124.4, 124.5, 124.6, 126.9, 129.2, 130.5, 131.9, 132.8, 133.2, 139.8, 140.1, 140.3 ppm. IR: $\tilde{\nu}$ = 2963, 1261, 832, 802, 747, 723 cm^{-1}. MS (EI): *m*/*z* (%) = 224 (100) [M]$^+$, 208 (30), 133 (2), 86 (8), 63 (6), 51 (6). $C_{14}H_9ClS$ (209.51): calcd. C 68.71, H 3.71; found C 68.66, H 3.97.

2-(4-Chlorophenyl)benzo[*b*]thiophene (10c):[18] White solid, 41 mg (97%).

2-(*o*-Tolyl)benzo[*b*]thiophene (10d):[19] White solid, 32 mg (76%).

2-(*m*-Tolyl)benzo[*b*]thiophene (10e):[17] White solid, 40 mg (95%).

2-(*p*-Tolyl)benzo[*b*]thiophene (10f):[21] Light yellow solid, 33 mg (78%).

2-Anisylbenzo[*b*]thiophene (10g):[20] White solid, 35 mg (67%).

2-(2′-Fluorophenyl)benzo[*b*]thiophene (10h): White solid, 29 mg (91%). M.p. 55–56 °C. ^{1}H NMR (250 MHz): δ = 7.13–7.24 (m, 2 H), 7.26–7.39 (m, 3 H), 7.66–7.73 (m, 2 H), 7.78–7.86 (m, 2 H) ppm. ^{13}C NMR (62.5 MHz): δ = 116.2, 116.6, 122.0, 123.5, 123.8, 124.5, 124.6, 129.3, 129.5, 137.3, 139.4, 140.4, 157.6, 161.6 ppm. MS (EI): *m*/*z* (%) = 228 (100) [M]$^+$, 208 (5), 196 (10), 183 (30), 170 (5), 157 (8), 144 (3), 133 (3). $C_{14}H_9FS$ (228.15): calcd. C 73.45, H 3.89, S 13.85; found C 73.66, H 3.97, S 14.05.

2-(4′-Fluorophenyl)benzo[*b*]thiophene (10i): White solid, 39 mg (51%). M.p. 162–164 °C. ^{1}H NMR (250 MHz): δ = 6.91 (t, J = 8.6 Hz, 2 H), 7.05–7.16 (m, 3 H), 7.46 (dd, J_1 = 5.1 Hz, J_2 = 8.8 Hz, 2 H), 7.55 (d, J = 6.9 Hz, 1 H), 7.61 (d, J = 7.0 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz): δ = 115.8, 116.1, 119.4, 122.2, 123.5, 124.4, 124.6, 128.2, 130.5, 139.4, 140.6, 143.0 ppm. IR: $\tilde{\nu}$ = 3059, 1510, 1261, 821, 744 cm^{-1}. MS (EI): *m*/*z* (%) = 228 (100) [M]$^+$, 208 (5), 183 (30). $C_{14}H_9FS$ (228.15): C 73.66, H 3.97; found C 73.38, H 4.12.

2-(1′-Naphthyl)benzo[*b*]thiophene (10j):[21] White solid, 34 mg (69%).

2-(2′-Naphthyl)benzo[*b*]thiophene (10k):[23] White solid, 36 mg (73%).

2-(9′-Anthryl)benzo[*b*]thiophene (10l): Light yellow solid, 43 mg (68%). M.p. 226.5–228 °C. ^{1}H NMR (250 MHz): δ = 7.41–7.52 (m, 7 H), 7.90–7.97 (m, 4 H), 8.06 (d, J = 8.3 Hz, 2 H), 8.57 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz): δ = 122.2, 123.6, 124.3, 124.5, 125.3, 126.1, 126.2, 126.5, 127.2, 128.3, 128.3, 128.4, 131.1, 131.4, 134.1, 140.1 ppm. IR: $\tilde{\nu}$ = 3050, 3027, 1440, 886, 824, 746 cm^{-1}. MS (EI): *m*/*z* (%) = 310 (100) [M]$^+$, 276 (10), 154 (50). $C_{22}H_{14}S$ (310.24): C 85.12, H 4.55; found C 85.04, H 4.38.

2-(2′-Thienyl)benzo[*b*]thiophene (10m):[22] White solid, 38 mg (95%).

2-(3′-Pyridyl)benzo[*b*]thiophene (10n): Light yellow solid, 28 mg (70%). M.p. 118.5–120.5 °C. ^{1}H NMR (250 MHz): δ = 7.33–7.39 (m, 3 H), 7.61 (s, 1 H), 7.92–7.87 (m, 2 H), 7.96 (d, J = 9.5 Hz, 1 H), 8.58 (d, J = 5.0 Hz, 1 H), 8.99 (d, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz): δ = 120.7, 122.3, 123.6, 123.8, 124.8, 124.9, 130.3, 133.5, 139.7, 140.2, 140.4, 147.4, 149.1 ppm. IR: $\tilde{\nu}$ = 3052, 1662, 1524, 831, 803, 745, 726 cm^{-1}. MS (EI): *m*/*z* (%) = 211 (100) [M]$^+$, 79 (25), 51 (4). $C_{13}H_9NS$ (211.14): C 73.90, H 4.29, N 6.63; found C 73.66, H 4.33, N 6.30.

General Procedure for the Preparation of 3-Arylbenzo[*b*]thiophenes

In a flame-dried Schlenk flask, **11** (100 mg, 0.316 mmol), the appropriate aryl halide (2 equiv.), $PCy_3{\cdot}HBF_4$ (11.4 mg, 0.316 mmol, 10 mol-%), $Pd(OAc)_2$ (3.5 mg, 0.0158 mmol, 5 mol-%), Cs_2CO_3 (0.206 g, 0.632 mmol), and *o*-xylene (7 mL) were mixed under an atmosphere of argon and heated in an oil bath at 110 °C. After complete conversion of the starting material (by GC–MS) and cooling of the mixture to ambient temperature, water (20 mL) was added, and the reaction mixture was extracted with dichloromethane. The combined organic extracts were dried with $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, gradient from 100:0 to 80:20).

3-(2′-Chlorophenyl)benzo[*b*]thiophene (12b): Colourless oil, 42 mg (91%), ^{1}H NMR (250 MHz): δ = 7.36–7.45 (m, 6 H), 7.52–7.58 (m, 2 H), 7.92–7.96 (m, 1 H) ppm. ^{13}C NMR (62.5 MHz): δ = 122.7, 123.2, 124.2, 124.4, 125.4, 126.7, 128.9, 129.1, 129.9, 130.0, 132.0, 133.8, 138.3, 139.7 ppm. IR: $\tilde{\nu}$ = 3023, 1231, 827, 792, 753, 731 cm^{-1}. MS (EI): *m*/*z* (%) = 224 (100) [M]$^+$, 208 (35), 165 (45). $C_{14}H_9ClS$ (244.65): calcd. C 68.71, H 3.71; found C 69.04, H 4.05.

2,3-Bis(2′-chlorophenyl)benzo[*b*]thiophene (13b): MS (EI): *m*/*z* (%) = 354 (75) [M]$^+$, 318 (25), 284 (45), 207 (100).

3-(4′-Chlorophenyl)benzo[*b*]thiophene (12c): Colourless oil, 40 mg (86%). ^{1}H NMR (250 MHz): δ = 7.23 (s, 1 H), 7.38–7.43 (m, 3 H), 7.46–7.53 (m, 3 H), 7.84–7.93 (m, 2 H) ppm. ^{13}C NMR (62.5 MHz): δ = 122.6, 123.0, 123.7, 124.5, 124.6, 128.7, 128.9, 129.1, 129.9, 130.8, 131.7, 134.4, 136.8, 140.7 ppm. IR: $\tilde{\nu}$ = 3052, 1523, 1190, 829, 782, 751, 727, 677 cm^{-1}. MS (EI): *m*/*z* (%) = 244 (100) [M]$^+$, 208 (30), 165 (30). $C_{14}H_9ClS$ (244.65): calcd. C 68.71, H 3.71; found C 68.88, H 3.59.

2,3-Bis(4′-chlorophenyl)benzo[*b*]thiophene (13c): MS (EI): *m*/*z* (%) = 354 (100) [M]$^+$, 318 (20), 305 (5), 284 (70), 253 (10), 207 (25).

3-(*o*-Tolyl)benzo[*b*]thiophene (12d): White solid, 28 mg (67%). M.p. 178–179 °C. ^{1}H NMR (250 MHz): δ = 2.20 (s, 3 H), 7.30–7.48 (m, 8 H), 7.92–7.96 (d, J = 7.4 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz): δ = 20.2, 122.7, 123.2, 123.7, 124.1, 124.2, 125.7, 127.9, 130.2, 130.5, 135.4, 137.1, 137.5, 139.0, 139.9 ppm. IR: $\tilde{\nu}$ = 3031, 1521, 1483, 802 cm^{-1}. MS (EI): *m*/*z* (%) = 224 (100) [M]$^+$, 208 (35), 76 (10). $C_{15}H_{12}S$ (224.17): calcd. C 80.31, H 5.39; found C 79.83, H 5.15.

2,3-Bis(*o*-tolyl)benzo[*b*]thiophene (13d): MS (EI): *m*/*z* (%) = 314 (100) [M]$^+$, 221 (32), 207 (29), 142 (20).

3-(*m*-Tolyl)benzo[*b*]thiophene (12e): Colourless oil, 22 mg (51%). ^{1}H NMR (250 MHz): δ = 2.44 (s, 3 H), 7.22–7.23 (m, 1 H), 7.38–7.12 (m, 6 H), 7.89–7.94 (m, 2 H) ppm. ^{13}C NMR (62.5 MHz): δ = 21.5, 122.9, 123.0, 123.2, 124.3, 124.4, 125.8, 128.3, 128.6, 129.4, 135.9, 137.9, 138.2, 138.4, 140.6 ppm. IR: $\tilde{\nu}$ = 3029, 1539, 1499, 828, 742 cm^{-1}. MS (EI): *m*/*z* (%) = 224 (100) [M]$^+$, 208 (20), 76 (5). $C_{15}H_{12}S$ (224.17): calcd. C 80.31, H 5.39; found C 79.90, H 5.45.

2,3-Bis(*m*-tolyl)benzo[*b*]thiophene (13e): MS (EI): *m*/*z* (%) = 314 (100) [M]$^+$, 298 (20), 284 (30), 134 (15).

3-(*p*-Tolyl)benzo[*b*]thiophene (12f): White solid, 22 mg (50%). M.p. 122.5–123.5 °C. ^{1}H NMR (250 MHz): δ = 2.46 (s, 3 H), 7.25 (d, J = 7.5, 2 H), 7.39–7.43 (m, 3 H), 7.52 (d, J = 8.0 Hz, 2 H), 7.92–7.97 (m 2 H) ppm. ^{13}C NMR (62.5 MHz): δ = 21.3, 122.9, 123.0, 124.2, 124.3, 126.8, 128.6, 129.4, 133.1, 137.3, 138.0, 138.1, 140.7 ppm. IR: $\tilde{\nu}$ = 3025, 2918, 1541, 1494, 845, 822, 805, 761, 733 cm^{-1}. MS (EI): *m*/*z* (%) = 224 (100) [M]$^+$, 208 (15), 134 (5). $C_{15}H_{12}S$ (224.17): calcd. C 80.31, H 5.39; found C 79.98, H 5.05.

2,3-Bis(*p*-tolyl)benzo[*b*]thiophene (13f): MS (EI): *m*/*z* (%) = 314 (100) [M]$^+$, 298 (30), 284 (35), 207 (65).

2,3-Bis(2′′-Fluorophenyl)benzo[*b*]thiophene (13h): White solid, 31 mg (51%). M.p. 95–96 °C. ^{1}H NMR (250 MHz): δ = 6.96 (t, J = 8.7 Hz, 1 H), 7.06–7.30 (m, 4 H), 7.34–7.43 (m, 3 H), 7.49–7.57 (m, 2 H), 7.83–7.93 (m, 2 H) ppm. ^{13}C NMR (62.5 MHz): δ = 115.7, 116.1, 121.9, 122.1, 123.2, 123.3, 123.8, 123.9, 124.0, 124.1, 124.5, 124.8, 129.5, 129.7, 129.8, 130.1, 130.2, 132.3, 139.4, 139.5 ppm. MS (EI): *m*/*z* (%) = 322 (100) $[M]^+$, 302 (30), 257 (15). $C_{14}H_9FS$ (228.15): calcd. C 73.66, H 3.97; found C 73.19, H 4.05.

3-(4′-Fluorophenyl)benzo[*b*]thiophene (12i): Colourless oil, 14 mg (32%). ^{1}H NMR (250 MHz): δ = 7.21–7.29 (m, 2 H), 7.35–7.57 (m, 5 H), 7.67–7.71 (m, 1 H), 8.03–8.07 (m, 1 H) ppm. ^{13}C NMR (62.5 MHz): δ = 115.5, 115.8, 122.1, 122.7, 123.0, 123.4, 124.4, 124.5, 130.2, 130.3, 131.1, 137.8, 140.6, 164.3 ppm. IR: $\tilde{\nu}$ = 2924, 1509, 1217, 820, 806, 736 cm^{-1}. MS (EI): *m*/*z* (%) = 228 (100) $[M]^+$, 208 (3) 183 (70). $C_{14}H_9FS$ (228.15): calcd. C 73.66, H 3.97; found C 73.30, H 4.25.

2,3-Bis(4′-fluorophenyl)benzo[*b*]thiophene (13i): MS (EI): *m*/*z* (%) = 322 (100) $[M]^+$, 302 (15), 257 (10), 207 (15).

3-(1′-Naphthyl)benzo[*b*]thiophene (12j):[23] White solid, 22 mg (44%).

3-(2′-Naphthyl)benzo[*b*]thiophene (12k):[24] White solid, 27 mg (55%).

3-(2′-Thienyl)benzo[*b*]thiophene (12m):[23] White solid, 15 mg (37%).

2,3-Bis(2′-thienyl)benzo[*b*]thiophene (13m): MS (EI): *m*/*z* (%) = 298 (100) $[M]^+$, 253 (45), 240 (5), 195 (5).

Supporting Information (see footnote on the first page of this article): Experimental procedures and characterization data for known compounds.

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[1] a) M. Beller, C. Bolm (Eds.), *Transition Metals for Organic Synthesis*, 2nd ed., Wiley-VCH, Weinheim, **2004**.
[2] A. Kotschy, G. Timári, *Heterocycles from Transition Metal Catalysis*, Springer, Dordrecht, **2005**.
[3] M. Miura, M. Nomura, *Topics in Current Chemistry* (Ed.: N. Miyaura), Springer, Dordrecht, **2002**, vol. 219, pp. 212–240.
[4] G. D. Cuny, *Tetrahedron Lett.* **2003**, *44*, 8149–8152.
[5] M. E. Limmert, R. B. Bedford, *J. Org. Chem.* **2003**, *68*, 8669–8862.
[6] F. Churruca, R. SanMartin, I. Tellitu, E. Domíniquez, *Org. Lett.* **2002**, *4*, 1591–1594.
[7] Z. Novák, P. Nemes, A. Kotschy, *Org. Lett.* **2004**, *6*, 4917–4920.
[8] A. Nagy, Z. Novák, A. Kotschy, *J. Organomet. Chem.* **2005**, *690*, 4453–4461.
[9] A. Funayama, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2005**, *127*, 15354–15355.
[10] Y. Terao, H. Wakui, T. Satoh, M. Miura, M. Nomura, *J. Am. Chem. Soc.* **2001**, *123*, 10407–10408.
[11] H. Wakui, S. Kawasaki, T. Satoh, M. Miura, M. Nomura, *J. Am. Chem. Soc.* **2004**, *126*, 8658–8659.
[12] Y. Terao, H. Wakui, M. Nomoto, T. Satoh, M. Miura, M. Nomura, *J. Org. Chem.* **2003**, *68*, 5236–5243.
[13] A. Yokooji, T. Satoh, M. Miura, M. Nomura, *Tetrahedron* **2004**, *60*, 6757–6763.
[14] Similar selectivity was observed by Miura et al. who were also able to drive the process to selective 2,3-diarylation by changing the ligand: M. Nakano, T. Satoh, M. Miura, *J. Org. Chem.* **2006**, *71*, 8309–8311.
[15] C. Avendao, C. de Diego, J. Elguero, *Magn. Reson. Chem.* **1990**, *28*, 1011–1017.
[16] H. Arnault, *Synthesis* **2002**, 213–216.
[17] D. L. Klayman, R. J. Shine, J. D. Bower, *J. Org. Chem.* **1972**, *37*, 1537–1541.
[18] M. V. Patel, J. J. Rohde, V. Gracias, T. Kolasa, *Tetrahedron Lett.* **2003**, *44*, 6665–6667.
[19] Y. Uozumi, Y. Nakai, *Org. Lett.* **2002**, *4*, 2997–3000.
[20] J. E. Banfield, W. Davies, N. W. Gamble, S. Middleton, *J. Chem. Soc.* **1956**, 4791–4798.
[21] A. Ohta, Y. Akita, T. Ohkuwa, M. Chiba, R. Fukunaga, *Heterocycles* **1990**, *31*, 1951–1958.
[22] B. D. Tilak, *Tetrahedron* **1960**, *9*, 76–95.
[23] D. Robert, L. C. Schuetz, *J. Org. Chem.* **1958**, *23*, 206–208.
[24] H. Blatt, J. J. Brophy, L. J. Colman, W. J. Tairych, *J. Sci. Ind. Res. Sect. B* **1960**, *19*, 395–398.

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