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Direct Arylation as a Synthetic Tool for the Synthesis of Thiophene-Based Organic Electronic Materials

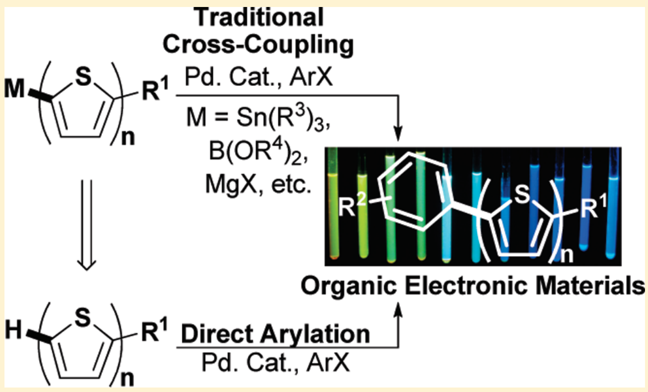
Derek J. Schipper* and Keith Fagnou†

Centre for Catalysis Research & Innovation, Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6N5, Canada

S Supporting Information

ABSTRACT: The efficient synthesis of thiophene based organic electronic materials can be carried out in high yields using simple starting materials by employing palladium-catalyzed direct arylation. The direct arylation method was applied to the (formal) synthesis of ten molecules that have exhibited promise for applications as optoelectronic materials. The syntheses feature the following advantages over traditional cross-coupling techniques: (1) higher yields, (2) fewer synthetic operations, (3) lower catalyst loadings, and (4) does not employ organometallic intermediates. The advantages of direct arylation make it an ideal strategy for the synthesis of thiophene containing organic electronic materials.

KEYWORDS: optical materials



INTRODUCTION

Organic materials have been studied intensively in recent years and are making significant contributions to the fields of light-emitting diodes,[1] field-effect transistors,[2] and photovoltaics,[3] among others. However, as these technologies become commercialized, the active compounds will be required in larger quantities. Therefore, efficient syntheses of these compounds is of paramount importance. State of the art syntheses usually rely on traditional cross-coupling reactions (Suzuki, Stille, Negishi, Kumada, etc.). However, these methods have drawbacks including the use an organometallic reagent which generates a stoichiometric amount of metal waste and is often toxic, difficult to handle, expensive, or require extra synthetic steps. Recently, direct arylation has emerged as a viable alternative to traditional cross coupling, wherein the organometallic component is replaced with a simple arene (Scheme 1).[4,5] Although this method should be widely applicable, there is a paucity of examples of its utilization for the construction of organic materials.[6]

Ohta and co-workers made pioneering contributions over two decades ago reporting the first direct arylation of thiophenes with aryl halides via C−H bond functionalization using palladium catalysis which gave moderate yields at elevated temperatures (150 °C) and moderate yields.[5a] Lemaire et al. have described thiophene arylation under phase transfer conditions which proceeded at 80 °C with improved yields.[5b,c] Doucet has reported thiophene arylation conditions that employ low catalyst loadings at 150 °C.[5l,p,s] Although the mechanism of the C−H bond cleavage step in direct arylation has been debated, several research groups, including our own, have provided evidence for the concerted metalation deprotonation pathway. This mechanistic understanding lead to the development of pivalate as a proton shuttle[7]/internal base[8] additive, which we have found gives superior reactivity under our reported conditions.[5r]

Herein, we report the application of the direct arylation method to the (formal) synthesis of a broad range of thiophene-based molecules which have exhibited promise for applications as optoelectronic materials (Figure 1). These syntheses require less synthetic operations, are high yielding and avoid the use of organometallic reagents.

In the course of a research program dedicated to the development of direct arylation reactions, we became interested in organic electronic materials based on the thiophene moeity because they represent an important class of materials.[9] In addition, thiophenes are ideal subsrates for direct arylation due to the facile palladation through a concerted metalation-deprotonation pathway which renders the reaction generally highly selective for the 2/5 position on thiophenes.[10] We surmised that the application of the direct arylation reaction to the synthesis of known organic electronic molecules would result in shorter syntheses and therefore higher yields while avoiding organometallic intermediates and superfluous waste.

EXPERIMENTAL DETAILS

General Methods. All palladium-catalyzed direct arylations were carried out under argon atmosphere. NMR spectra were recorded in $CDCl_3$ or Pyridine d_5 solutions on a Bruker AVANCE 400 MHz

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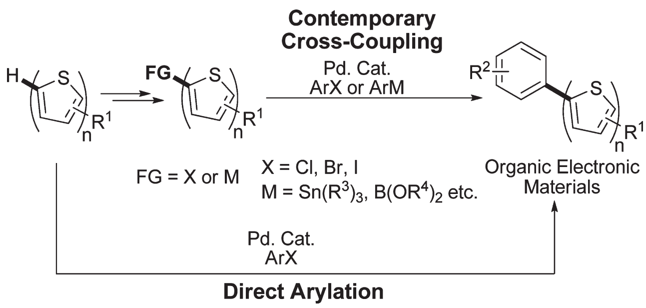
Scheme 1. Synthesis of Thiophene Organic Materials



spectrometer. HPLC grade toluene is dried and purified via MBraun SP Series solvent purification system. *N,N*-Dimethylacetamide was degassed and dried over molecular sieves prior to use. The compounds: (4-bromophenoxy)(*tert*-butyl)dimethylsilane,[11] tris(4-bromophenyl)amine[12] were prepared via literature procedures. All other reagents, reactants and solvents were used as received from commercial sources. Unless noted below, all other compounds have been reported in the literature or are commercially available.

*5-(4-Ethoxyphenyl)thiophene-2-carbaldehyde (**11**).* K_2CO_3 (1.5 equiv, 9 mmol, 1.245 g), $Pd(OAc)_2$ (2 mol %, 0.12 mmol, 26.9 mg), $PCy_3 \cdot HBF_4$ (4 mol %, 0.24 mmol, 88.4 mg), and pivalic acid (30 mol %, 1.8 mmol, 183.8 mg) were weighed to air and placed in a 50 mL round bottomed pressure vessel equipped with a magnetic stir bar. The tube was purged with argon, and toluene (20 mL, 0.3 M), 2-thiophenecarboxaldehyde (2 equiv, 12 mmol, 1.1 mL) and 1-bromo-4-ethoxybenzene (6 mmol, 857 μL) were then added. The reaction mixture was then vigorously stirred at 110 °C for 16 h. The solution was then cooled to rt, diluted with CH_2Cl_2 and H_2O. The aqueous phase was extracted with CH_2Cl_2 (3X). The organics were combined and dried over $MgSO_4$, filtered, and evaporated under reduced pressure. Excess 2-thiophenecarboxaldehyde was then removed using Kugelrohr distillation to give **11** in 99% yield (1.35 g). Spectral data corresponded to that previously described in the literature.[13a] Alternatively, the reaction was carried out in an manner similar to **15** and gave an 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): 1.44 (3H, t, J = 7.0 Hz), 4.08 (2H, q, J = 7.0 Hz), 6.94 (2H, d, J = 8.9 Hz), 7.29 (1H, J = 4.0 Hz), 7.60 (2H, d, J = 8.9 Hz), 7.71 (1H, d, J = 4.0 Hz), 9.86 (1H, s).

*5,5′,5″-(4,4′,4″-Nitrilotris(benzene-4,1-diyl))trithiophene-2-carbaldehyde (**12**).* K_2CO_3 (1.5 equiv, 0.45 mmol, 62.2 mg), $Pd(OAc)_2$ (6 mol %, 0.018 mmol, 4.0 mg), $PCy_3 \cdot HBF_4$ (12 mol %, 0.036 mmol, 13.3 mg), pivalic acid (30 mol %, 0.09 mmol, 9.2 mg) and tris(4-bromophenyl)amine (0.3 mmol, 144.6 mg) were weighed to air and placed in a screw-capped vial equipped with a magnetic stir bar. The vial was purged with argon then toluene (1.3 mL, 0.23 M) and 2-thiophenecarboxaldehyde (6 equiv, 1.8 mmol, 180 μL) were then added. The reaction mixture was then vigorously stirred at 100 °C for 16 h. The solution was then cooled to rt, diluted with CH_2Cl_2 and H_2O. The aqueous phase was extracted with CH_2Cl_2 (3×). The organics were combined and dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to afford **12** in 89% yield (153.7 mg). Spectral data corresponded to that previously described in the literature.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): 7.19 (6H, d, J = 8.7 Hz), 7.36 (3H, d, J = 4.0 Hz), 7.61 (6H, d, J = 8.7 Hz), 7.74 (3H, d, J = 4.0 Hz), 9.89 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, $CHCl_3$): 123.6, 124.6, 127.6, 128.4, 137.6, 142.0, 147.5, 153.6, 182.7.

*(4-(2,2′-Bithiophen-5-yl)phenoxy)(tert-butyl)dimethylsilane (**13**).* K_2CO_3 (1.5 equiv, 0.45 mmol, 62.2 mg), $Pd(OAc)_2$ (2 mol %, 0.006 mmol, 1.4 mg), $PCy_3 \cdot HBF_4$ (4 mol %, 0.012 mmol, 4.4 mg), pivalic acid (30 mol %, 0.09 mmol, 9.2 mg) and 2,2′-bithiophene (5 equiv to avoid diarylation, 1.5 mmol, 249.4 mg) were weighed to air and placed in a screw-capped vial equipped with a magnetic stir bar. The vial was purged with argon then toluene (1 mL, 0.3 M) and (4-bromophenoxy)(*tert*-butyl)dimethylsilane (0.3 mmol, 73 μL) were then added. The reaction mixture was then vigorously stirred at 100 °C for 16 h. The solution was then cooled to rt, diluted with CH_2Cl_2 and H_2O. The aqueous phase was extracted with CH_2Cl_2 (3X). The organics were combined and dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to afford **13** in 52% yield (57.7 mg). Spectral data corresponded to that previously described in the literature.[15] ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): 0.22 (s, 6H), 1.00 (s, 9H), 6.85 (2H, d, J = 8.7 Hz), 7.02 (1H, dd, J = 5.1, 3.6 Hz), 7.10 (1H, d, J = 3.8 Hz), 7.12 (1H, d, J = 3.8 Hz), 7.17 (1H, dd, J = 3.6, 1.1 Hz), 7.20 (1H, dd, J = 5.1, 1.1 Hz) 7.46 (2H, d, J = 8.7 Hz).

*5-(4-(Diphenylamino)phenyl)thiophene-2-carbaldehyde (**15**).* K_2CO_3 (1.5 equiv, 0.75 mmol, 103.7 mg), $Pd(OAc)_2$ (2 mol %, 0.01 mmol, 2.2 mg), $PCy_3 \cdot HBF_4$ (4 mol %, 0.02 mmol, 7.4 mg), pivalic acid (30 mol %, 0.15 mmol, 15.3 mg) and 4-bromo-*N,N*-diphenylaniline (0.5 mmol, 162.1 mg) were weighed to air and placed in a screw-capped vial equipped with a magnetic stir bar. The vial was purged with argon then toluene (1.7 mL, 0.3 M) and 2-thiophenecarboxaldehyde (2 equiv., 1 mmol, 92 μL) were then added. The reaction mixture was then vigorously stirred at 100 °C for 16 h. The solution was then cooled to rt, diluted with CH_2Cl_2 and H_2O. The aqueous phase was extracted with CH_2Cl_2 (3×). The organics were combined and dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to afford **15** in 91% yield (162.4 mg). Spectral data corresponded to that previously described in the literature.[16] ^{1}H NMR (400 MHz, $CDCl_3$,

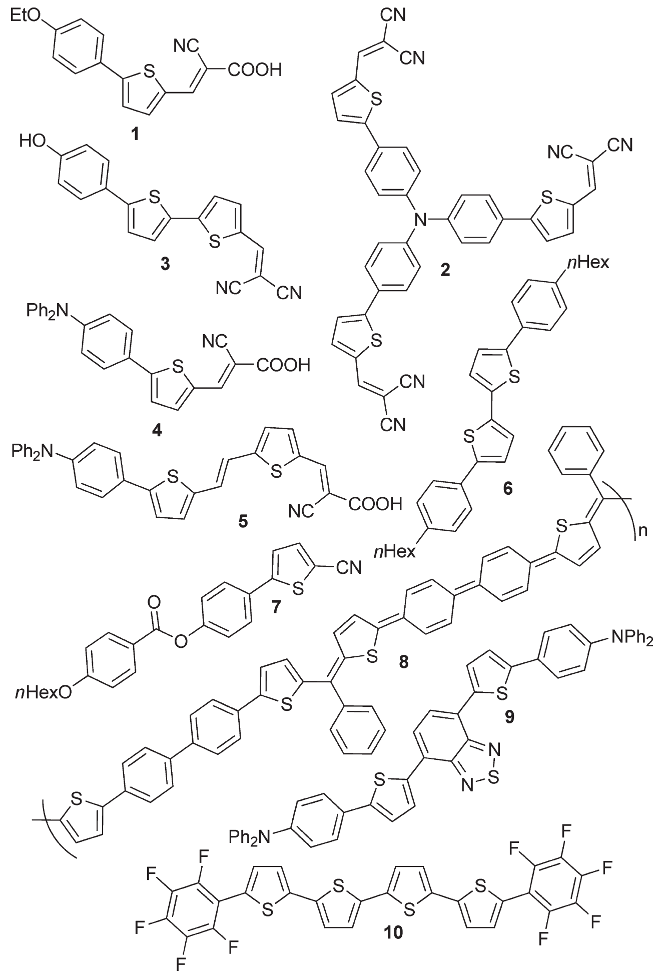


Figure 1. Thiophene-based organic materials.

293K, TMS): 7.03−7.16 (8H, m), 7.26−7.32 (5H, m), 7.51 (2H, d, J = 8.8 Hz), 7.70 (1H, d, J = 4.0 Hz), 9.85 (1H, s).

*5,5′-Bis(4-hexylphenyl)-2,2′-bithiophene (**6**).* K_2CO_3 (2.5 equiv, 0.75 mmol, 103.7 mg), $Pd(OAc)_2$ (2 mol %, 0.006 mmol, 1.3 mg), $PCy_3 \cdot HBF_4$ (4 mol %, 0.012 mmol, 4.4 mg), pivalic acid (30 mol %, 0.09 mmol, 9.2 mg) and 2,2′-bithiophene (0.3 mmol, 50 mg) were weighed to air and placed in a screw-capped vial equipped with a magnetic stir bar. The vial was purged with argon then *N,N*-dimethylacetamide (1 mL, 0.3 M) and 1-bromo-4-hexylbenzene (2 equiv, 0.6 mmol, 124 μL) were then added. The reaction mixture was then vigorously stirred at 100 °C for 16 h. The solution was then cooled to rt, diluted with CH_2Cl_2 and H_2O. The aqueous phase was extracted with CH_2Cl_2 (3X). The organics were combined and dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to afford **6** in 87% yield (127.2 mg). Spectral data corresponded to that previously described in the literature.[17a] ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): 0.89 (6H, t, J = 6.8 Hz), 1.27−1.39 (12H, m), 1.57−1.67 (4H, m), 2.62 (4H, t, J = 7.7 Hz), 7.14 (2H, d, J = 3.8 Hz), 7.17−7.21 (6H, m), 7.51 (4H, d, J = 8.2 Hz).

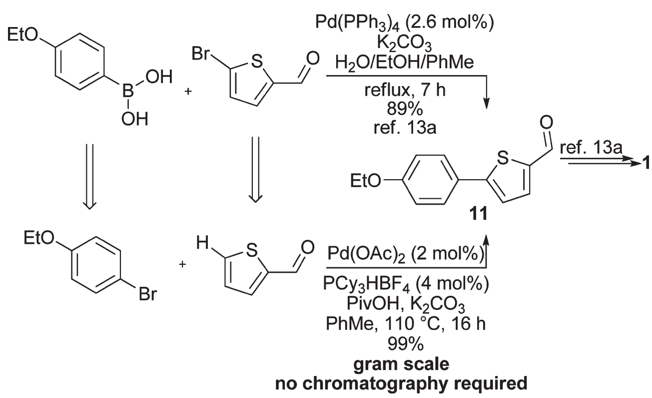
*5-(4-Methoxyphenyl)thiophene-2-carbonitrile (**17**).* K_2CO_3 (1.5 equiv, 0.75 mmol, 103.7 mg), $Pd(OAc)_2$ (2 mol %, 0.01 mmol, 2.2 mg), $PCy_3 \cdot HBF_4$ (4 mol %, 0.02 mmol, 7.4 mg) and pivalic acid (30 mol %, 0.15 mmol, 15.3 mg) were weighed to air and placed in a screw-capped vial equipped with a magnetic stir bar. The vial was purged with argon and toluene (1.7 mL, 0.3 M), 2-thiophenecarbonitrile (2 equiv, 1 mmol, 93 μL) and 4-bromoanisole (1 equiv, 0.5 mmol, 62 μL) were then added. The reaction mixture was then vigorously stirred at 100 °C for 16 h. The solution was then cooled to rt, diluted with CH_2Cl_2 and H_2O. The aqueous phase was extracted with CH_2Cl_2 (3X). The organics were combined and dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to afford **17** in 97% yield (104.9 mg). Spectral data corresponded to that previously described in the literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): 3.85 (3H, s), 6.95 (2H, d, J = 8.9 Hz), 7.16 (1H, d, J = 3.9 Hz), 7.53 (2H, d, J = 8.9 Hz), 7.56 (1H, d, J = 3.9 Hz).

*4,4′-Di(thiophen-2-yl)biphenyl (**19**).* K_2CO_3 (1.5 equiv, 3 mmol, 414.6 mg), $Pd(OAc)_2$ (6 mol %, 0.12 mmol, 26.9 mg), $PCy_3 \cdot HBF_4$ (12 mol %, 0.24 mmol, 88.4 mg), pivalic acid (30 mol %, 0.6 mmol, 61.3 mg) and 4,4′-dibromobiphenyl (1 equiv, 2 mmol, 624.0 mg) were weighed to air and placed in a round bottomed pressure vessel equipped with a magnetic stir bar. The tube was purged with argon, and toluene (6.7 mL, 0.3 M) and thiophene (6 equiv, 12 mmol, 960 μL) were then added. The reaction mixture was then vigorously stirred at 110 °C for 48 h. The solution was then cooled to rt and diluted with CH_2Cl_2 and 2 M HCl. The aqueous phase was extracted with CH_2Cl_2 (3×). The organics were combined and dried over $MgSO_4$, filtered while hot, and evaporated under reduced pressure. The crude product was purified by recrystallization from toluene afford **19** in 66% yield (421.5 mg). Spectral data corresponded to that previously described in the literature.[19c] ^{1}H NMR (400 MHz, Pyridine d_5, 293 K, Pyridine-H): 7.05 (2H, dd, J = 5.1, 3.6 Hz), 7.36 (2H, dd, J = 5.1, 1.1 Hz), 7.44 (2H, dd, J = 3.6 Hz, 1.1 Hz), 7.64 (4H, d, J = 8.6 Hz), 7.71 (4H, d, J = 8.5 Hz).

*N,N-Diphenyl-4-(thiophen-2-yl)aniline (**20**).* K_2CO_3 (1.5 equiv, 0.75 mmol, 103.7 mg), $Pd(OAc)_2$ (2 mol %, 0.01 mmol, 2.2 mg), $PCy_3 \cdot HBF_4$ (4 mol %, 0.02 mmol, 7.4 mg), pivalic acid (30 mol %, 0.15 mmol, 15.3 mg) and 4-bromo-*N,N*-diphenylaniline (0.5 mmol, 162.1 mg) were weighed to air and placed in a screw-capped vial equipped with a magnetic stir bar. The vial was purged with argon and toluene (1.7 mL, 0.3 M) and thiophene (5 equiv, 2.5 mmol, 180 μL) were then added. The reaction mixture was then vigorously stirred at 100 °C for 16 h. The solution was then cooled to rt, diluted with CH_2Cl_2 and H_2O. The aqueous phase was extracted with CH_2Cl_2 (3X). The organics were combined and dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to afford **20** in 86% yield (141.1 mg). Spectral data corresponded to that previously described in the literature.[20] ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): 6.99−7.14 (9H, m), 7.20−7.29 (6H, m), 7.47 (2H, d, J = 8.5 Hz).

*2-(Perfluorophenyl)thiophene (**21**).* K_2CO_3 (1.5 equiv, 3 mmol, 414.6 mg), $Pd(OAc)_2$ (2 mol %, 0.04 mmol, 9.0 mg), $PCy_3 \cdot HBF_4$ (4 mol %, 0.08 mmol, 29.5 mg) and pivalic acid (30 mol %, 0.6 mmol, 61.3 mg) were weighed to air and placed in a round bottomed pressure vessel equipped with a magnetic stir bar. The tube was purged with argon, and toluene (6.7 mL, 0.3 M) pentafluorobenzene (2 equiv, 4 mmol, 444 μL) and 2-bromothiophene (1 equiv, 2 mmol, 194 μL) were then added. The reaction mixture was then vigorously stirred at 100 °C for 16 h. The solution was then cooled to rt and diluted with CH_2Cl_2 and filtered over Celite. The filtrate was evaporated under reduced pressure and the residue was purified by silica gel column chromatography to afford **21** in 86% yield (430 mg). Spectral data corresponded to that previously described in the literature.[21] ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): 7.17−7.21 (1H, m), 7.51−7.54 (1H, m), 7.55 (1H, dd, J = 5.2, 1.1 Hz)

Scheme 2. Formal Synthesis of 1

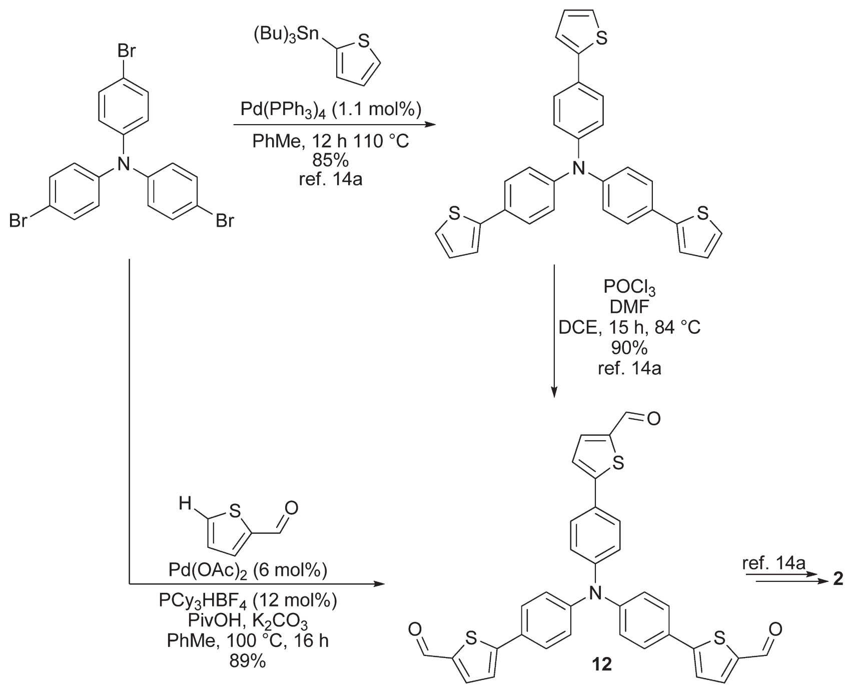


■ RESULTS AND DISCUSSION

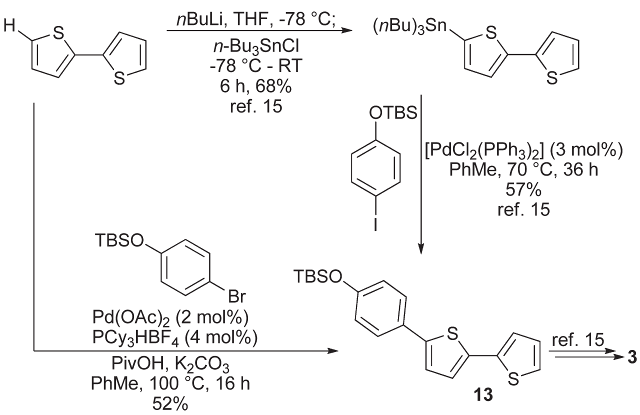
Park and co-workers have reported compound **1** for application in organic dye sensitized solar cells.[13] In a previous report, **1** was synthesized from key intermediate **11** which was produced in 89% yield from a suzuki coupling of 4-ethoxyphenylboronic acid and 5-bromo-2-thiophenecarboxaldehyde (Scheme 2). Using direct arylation, the boronic acid and aryl bromide could be replaced with an aryl bromide and a simple arene respectively. This would provide a more direct route using simpler and cheaper starting materials. Gratifyingly, the direct arylation proceeds using catalytic $Pd(OAc)_2/PCy_3$ with 30 mol % pivalic acid and K_2CO_3 in PhMe at 110 °C for 16 h to give key intermediate **11**. To demonstrate synthetic utility this reaction was carried out on gram scale to afford **11** in quantitative yield highlighting the excellent selectivity of the reaction. Another advantage of this synthesis is that it does not require chromatographic purification, which becomes less practical as the scale of the reaction is increased.

The effectiveness of star-shaped molecule **2** as a donor material in heterojunction solar cells has been shown by Roncali, Leriche and co-workers.[14] The star-shaped molecule **2** was prepared from key intermediate **12** which was assembled via a Stille coupling between 2-(tributylstannyl)thiophene and tris(4-bromophenyl)amine followed be a Vilsmeier−Haack formylation in 77% overall yield (Scheme 3). However, application of a

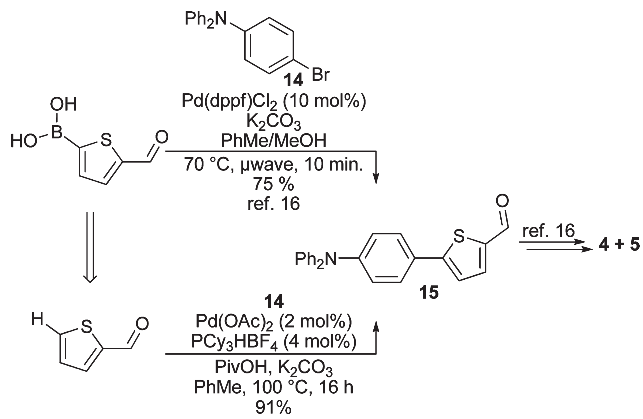
Scheme 3. Formal Synthesis of 2



Scheme 4. Formal Synthesis of 3



Scheme 5. Formal Synthesis of 4 and 5



direct arylation protocol gives **12** in one step and 89% yield using the same aryl bromide and 2-thiophenecarboxaldehyde in place of 2-(tributylstannyl)thiophene.

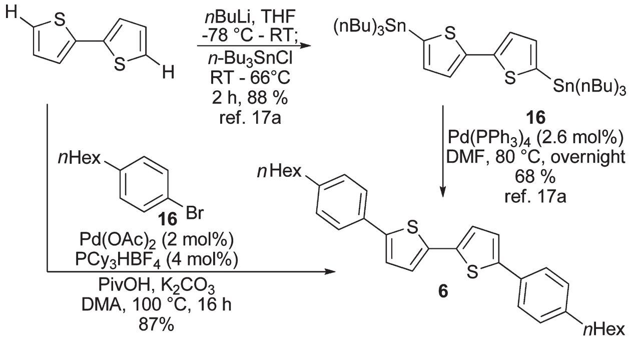
The Swager group has reported the use of compound **3** as a fluorescent marker for In Vivo optical imaging.[15] The synthesis of **3** proceeds with the deprotonation of 2,2′-bithiophene followed by quench with $ClSn(nBu)_3$ to install the requisite stannane for the subsequent Stille coupling which proceeds to give key intermediate **13** in 39% overall yield (Scheme 4). Alternatively, **13** can be prepared in one step from 2,2′-bithiophene using direct arylation under similar conditions as described above in 52% yield while avoiding organotin intermediates.

Hagfeldt and Sun described the application of **4** and **5** as chromophores for dye sensitized solar cells.[16] Both were synthesized through common intermediate **15**, which was prepared in 75% yield via a Suzuki reaction using 10 mol % catalyst (Scheme 5). The direct arylation route to **15** proceeds in 91% yield at 2 mol % catalyst loading and allows 5-formylthiophene-2-boronic acid to be replaced with the cheaper 2-thiophenecarboxaldehyde.

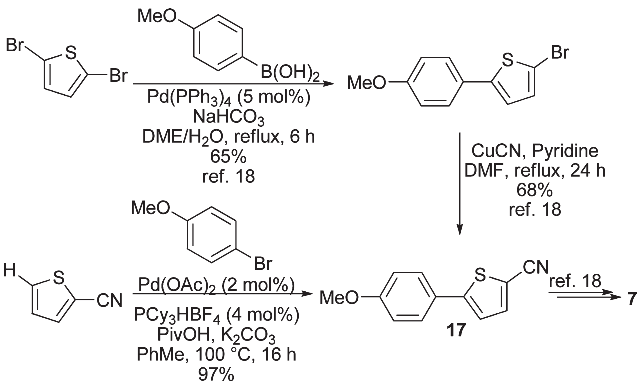
Marks has pioneered the use of **6** in organic field-effect transistors.[17] Bisthiophene **6** was constructed via the funtionalization of 2,2′-bithiophene to the appropriate bisstannane follwed by the Stille coupling with **16** to afford **6** in 60% overall yield (Scheme 6). Conversely, **6** can be made in one step and 87% yield from commercially available starting materials using direct arylation while avoiding organometallic intermediates.

Cheng et al. have reported **7** as a liquid crystalline material.[18] Their synthesis began with a Suzuki coupling with 2,5-dibromothiophene followed by a cyanation reaction using CuCN to give key intermediate **17** in two steps and 44% yield. Using the direct arylation protocol we have synthesized **17** in a single step

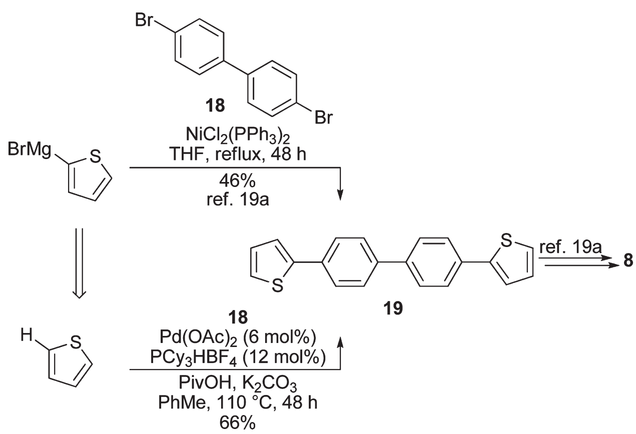
Scheme 6. Synthesis of 6



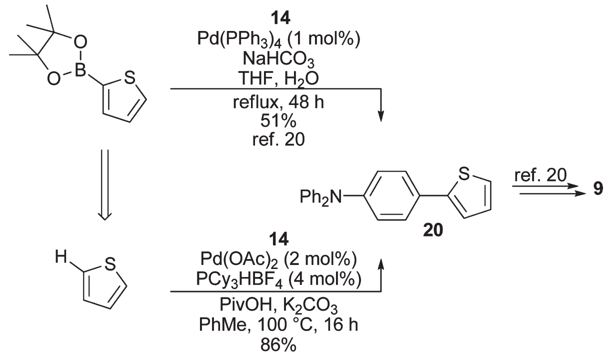
Scheme 7. Formal Synthesis of 7



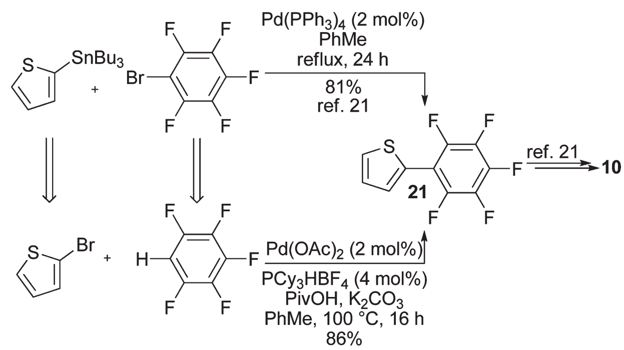
Scheme 8. Formal Synthesis of 8



Scheme 9. Formal Synthesis of 9



Scheme 10. Formal Synthesis of 10



and 97% yield using lower palladium loading and cheaper starting materials (see Scheme 7).

The group of Yang has described **8** as a soluble low band gap conducting polymer.[19a,b] The monomer **19** was assembled via a Kumada coupling in 46% yield (see Scheme 8). By employing direct arylation the Grignard reagent, which must be preformed and can be difficult to handle, can be replaced with an excess of simple thiophene and gives the same product in 66% yield.

Bo, Zhang and co-workers have shown that benzothiadiazole-based molecules such as **9** can be employed in efficient bulk heterojunction solar cells.[20] **9** can be prepared from **20**, which was synthesized via a Suzuki coupling between 2-thiopheneboronic acid pinacol ester and **14** in 51% yield (see Scheme 9). Conversely, **20** can also be prepared in 86% yield by employing the same aryl bromide and using an excess of thiophene in place of 2-thiopheneboronic acid pinacol ester.

Marks has also demonstrated the use perfluorobenzene substituted oligothiophenes such as **10** for use as n-type organic semiconductors.[21] **10** was synthesized from **21** which had been prepared in 81% yield using a Stille coupling between 2-(tributylstannyl)thiophene and bromopentafluorobenzene (see Scheme 10). Using direct arylation organotin compounds can be avoided, giving **21** in 86% yield using 2-bromothiophene and pentafluorobenzene. This example demonstrates that in cases where both arenes have been demonstrated to undergo direct arylation, such as with thiophenes[5] and pentflourobenzene,[22] it is possible to switch the bromine substitution such that bromothiophenes and a simple arenes are utilized as coupling partners.

The direct arylation method is not without limitations. In the formal synthesis of **1**, **2**, **4**, **5** and **7** two equivalents of the thiophene coupling partner per aryl bromide is required to achieve desirable product yields. However, the use of this excess is mitigated because it is readily available and relatively inexpensive. Additionally, it can be recovered from the reaction mixture by distillation if desired.

It is worth noting that under the conditions reported herein, arylation always occurs selectively at the 2/5 position on thiophene[23] with no byproducts arising from arylation of other positions detectable by spectroscopic methods. However, in cases where there are two possible reactive sites, as in thiophene and 2,2′-bithiophene, after arylation of one position the second position becomes more reactive toward direct arylation[24] which renders diarylation a significant reaction product. This is disadvantageous for the formal synthesis of **3**, **8**, and **9** in which only one arylation is desired. Five equivalents of thiophene coupling partner are required to avoid diarylation and gives **13** and **20** in 52% and 86% yield respectively. Also, six equivalents are required to isolate **19** in 66% yield. Again, the use of excess thiophene is mitigated because it is inexpensive,[25] easily handled and less toxic compared to organometallic coupling partners. However, one potential solution to this problem would be to employ a chlorine atom as an activating/blocking group.[5t] Conversly, if diarylation is desired such as with **6** this reactivity can also be advantageous. The ideal mol ratio of 2:1 aryl bromide to 2,2′-bithiophene can be employed and gives **6** in 87% yield.

CONCLUSION

In conlusion, we have demonstrated the viabilty of direct arylation for the (formal) synthesis of a broad range of thiophene based organic electronic materials. Direct arylation has several advantages to traditional cross-coupling methods currently used for the construction organic electronic materials and should be added to the "synthetic toolbox" of organic materials chemists. Direct arylation should be useful for the rapid and atom economical synthesis of an ever growing quantity of organic electronic materials as well as streamline the synthesis of new thiophene-based organic electronic materials.

ASSOCIATED CONTENT

Supporting Information. Copies of NMR spectra for all coupling products. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION

Corresponding Author
*E-mail: dschi064@uottawa.ca.

Notes
†Prof. Keith Fagnou passed away on November 11, 2009.

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REFERENCES

(1) (a) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610. (b) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897.(c) Mullen, K.; Scherf, U. *Organic Light-Emitting Devices: Synthesis, Properties and Applications*; Wiley-VCH Verlag GMbH & Co. KGaA: Weinheim, Germany, 2006.

(2) (a) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Bredas, J.-L. *Chem. Rev.* **2007**, *107*, 926. (b) Mas-Torrent, M.; Rovira, C. *Chem. Soc. Rev.* **2008**, *37*, 827. (c) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070. (d) Wu, W.; Liu, Y.; Zhu, D. *Chem. Soc. Rev.* **2010**, *39*, 1489.

(3) (a) Ooyama, Y.; Harima, Y. *Eur. J. Org. Chem.* **2009**, 2903. (b) Mishra, A.; Fischer, M. K. R.; Bauerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474. (c) Ning, Z.; Tian, H. *Chem. Commun.* **2009**, 5483.

(4) For reviews see:(a) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (b) Campeau, L.-C.; Stuart, D. R.; Fagnou, K. *Aldrichim. Acta* **2007**, *40*, 35. (c) Li, B.-J.; Yang, S.-D.; Shi, Z.-J. *Synlett* **2008**, 949. (d) McGlacken, G. P.; Bateman, L. M. *Chem. Soc. Rev.* **2009**, *38*, 2447. (e) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792.

(5) For direct arylation of thiophenes see: (a) Ohta, A.; Akita, Y.; Ohkama, T.; Chiba, M.; Fukunaga, R.; Miyafuji, A.; Nakata, T.; Tani, N.; Aoyagi, Y. *Heterocycles* **1990**, *31*, 1951. (b) Gozzi, C.; Lavenot, L.; Ilg, K.; Penalva, V.; Lemaire, M. *Tetrahedron Lett.* **1997**, *38*, 8867. (c) Pivsa-Art, S.; Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 467. (d) Lavenot, L.; Gozzi, C.; Ilg, K.; Penalva, V.; Lemaire, M. *J. Organomet. Chem.* **1998**, *567*, 49. (e) Okazawa, T.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2002**, *124*, 5286. (f) Glover, B.; Harvey, K. A.; Liu, B.; Sharp, M. J.; Tymoschenko, M. F. *Org. Lett.* **2003**, *5*, 301. (g) Yokooji, A.; Satoh, T.; Miura, M.; Nomura, M. *Tetrahedron* **2004**, *60*, 6757. (h) Fournier dit Chabert, J.; Joucla, L.; David, E.; Lemaire, M. *Tetrahedron* **2004**, *60*, 3221. (i) David, E.; Perrin, J.; Pellet-Rostaing, S.; Fournier dit Chabert, J.; Lemaire, M. *J. Org. Chem.* **2005**, *70*, 3569. (j) Kobayashi, K.; Sugie, A.; Takahashi, M.; Masui, K.; Mori, A. *Org. Lett.* **2005**, *7*, 5083. (k) Chiong, H. A.; Daugulis, O. *Org. Lett.* **2007**, *9*, 1449. (l) Battace, A.; Lemhadri, M.; Zair, T.; Doucet, H.; Santelli, M. *Adv. Synth. Catal.* **2007**, *349*, 2507. (m) Yanagisawa, S.; Sudo, T.; Noyori, R.; Itami, K. *J. Am. Chem. Soc.* **2006**, *128*, 11748. (n) Arai, N.; Miyaoku, T.; Teruya, S.; Mori, A. *Tetrahedron Lett.* **2008**, *49*, 1000. (o) Nakano, M.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1851. (p) Požgan, F.; Roger, J.; Doucet, H. *ChemSusChem* **2008**, *1*, 404–407. (q) Roger, J.; Doucet, H. *Org. Biomol. Chem.* **2008**, *6*, 169. (r) Liégault, B.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, K. *J. Org. Chem.* **2009**, *74*, 1826. (s) Roger, J.; Pogan, F.; Doucet, H. *Green Chem.* **2009**, *11*, 425. (t) Liégault, B.; Petrov, I.; Gorelsky, S. I.; Fagnou, K. *J. Org. Chem.* **2010**, *75*, 1047. (u) René, O.; Fagnou, K. *Org. Lett.* **2010**, *12*, 2116. (v) Ueda, K.; Yanagisawa, S.; Yamaguchi, J.; Itami, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 8946.(w) Chen, L.; Roger, J.; Bruneau, C.; Dixneuf, P. H.; Doucet, H. *Chem. Commun.* **2011**, Advance Article, DOI: 10.1039/c0cc04302h.

(6) (a) Wang, Q.; Takita, R.; Kikuzaki, Y.; Ozawa, F. *J. Am. Chem. Soc.* **2010**, *132*, 11420. (b) Masui, K.; Mori, A.; Takamura, K.; Okano, K.; Kinoshita, M.; Ikeda, T. *Org. Lett.* **2004**, *6*, 2011.

(7) Lafrance, M.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 16496.

(8) Lafrance, M.; Lapointe, D.; Fagnou, K. *Tetrahedron* **2008**, *64*, 6015.

(9) Perepichka, I. F.; Perepichka, D. F.; *Handbook of Thiophene-Based Materials*; John Wiley & Sons: Chichester, U.K., 2009.

(10) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 10848.

(11) Vogtle, M. M.; Beck, D. A. S.; Leutert, T.; Ossola, F.; La Vecchia, L. *ARKIVOC* 2008, 210.

(12) Cremer, J.; Bauerle, P. *J. Mater. Chem.* **2006**, *16*, 874.

(13) (a) Park, S. W.; Son, K.-I.; Ko, M. J.; Kim, K.; Park, N.-G. *Synth. Met.* **2009**, *159*, 2571. (b) Lee, K.; Park, S. W.; Ko, M. J.; Kim, K.; Park, N.-G. *Nat. Mater.* **2009**, *8*, 665.

(14) (a) Roquet, S.; Cravino, A.; Leriche, P.; Aleveque, O.; Frere, P.; Roncali, J. *J. Am. Chem. Soc.* **2006**, *128*, 3459. (b) Cravino, A.; Roquet, S.; Leriche, P.; Aleveque, O.; Frere, P.; Roncali, J. *Chem. Commun.* **2006**, 1416. (c) Leriche, P.; Frere, P.; Cravino, A.; Aleveque, O.; Roncali, J. *J. Org. Chem.* **2007**, *72*, 8332.

(15) Nesterov, E. E.; Skoch, J.; Hyman, B. T.; Klunk, W. E.; Bacskai, B. J.; Swager, T. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5452.

(16) Hagberg, D. P.; Marinado, T.; Karlsson, K. M.; Nonomura, K.; Qin, P.; Boschloo, G.; Brinck, T.; Hagfeldt, A.; Sun, L. *J. Org. Chem.* **2007**, *72*, 9550.

(17) (a) Mushrush, M.; Facchetti, A.; Lefenfeld, M.; Katz, H. E.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 9414. (b) Yoon, M.-H.; Facchetti, A.; Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 4678. (c) Yoon, M.-H.; Yan, H.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 10388.

(18) Huang, Y.; Luo, Z.; Cheng, X.; Tschierske, C. *Liq. Cryst.* **2009**, *36*, 61.

(19) (a) Zhang, Q.; Li, Y.; Yang, M. *J. Mater. Sci.* **2004**, *39*, 6089. (b) Yang, M.; Zhang, Q.; Wu, P.; Ye, H.; Liu, X. *Polymer* **2005**, *46*, 6266.

(c) Estrada, L. A.; Montes, V. A.; Zyryanov, G.; Anzenbacher, P., Jr. *J. Phys. Chem. B.* **2007**, *111*, 6983.

(20) Li, W.; Du, C.; Li, F.; Zhou, Y.; Fahlman, M.; Bo, Z.; Zhang, F. *Chem. Mater.* **2009**, *21*, 5327.

(21) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900.

(22) (a) Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 8754. (b) Lafrance, M; Shore, D.; Fagnou, K. *Org. Lett.* **2006**, *8*, 5097. (c) René., O.; Fagnou, K. *Org. Lett.* **2010**, *12*, 2116.

(23) The effects of substituents have not been studies in detail. However competition experiments have been conducted. See: (a) González, J. J.; García, N.; Gómez-Lor, B.; Echavarren, A. M. *J. Org. Chem.* **1997**, *62*, 1286. (b) Campeau, L.-C.; Rousseaux, S.; Fagnou, K. *J. Am. Chem. Soc.* **2005**, *127*, 18020. (c) García-Cuadrado, D.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 1066. (d) Campeau, L.-C.; Parisien, M.; Jean, A.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 581. (e) García-Cuadrado, D.; de Mendoza, P.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2007**, *129*, 6880 See also refs 5j, 7, 8, and 22a.

(24) Lapointe, D.; Gorelsky, S. I.; Fagnou, K. *Unpublished Results.*

(25) Thiophene is \$10/mol, whereas 2-(tributylstannyl)thiophene is \$1702/mol and 2-thienylboronic acid is \$2323/mol (based on current prices from Sigma-Aldrich).