FULL PAPER

Pd-Catalyzed β-Selective C–H Arylation of Thiophenes with Triarylantimony Difluorides

Yuki Kitamura,[a] Yuki Murata,[a] Ayaka Oguri,[a] Mio Matsumura,[a] Naoki Kakusawa,[b] Hiroshi Naka,*[c] and Shuji Yasuike*[a]

Dedication

[a] Y. Kitamura, Dr. Y. Murata, A. Oguri, Dr. M. Matsumura, Prof. Dr. S. Yasuike https://orcid.org/0000-0001-9232-5205
School of Pharmaceutical Sciences
Aichi Gakuin University
1-100 Kusumoto-cho, Chikusa-ku, Nagoya 464-8650, (Japan)
E-mail: s-yasuik@dpc.agu.ac.jp
[b] Dr. N. Kakusawa
Faculty of Pharmaceutical Sciences
Hokuriku University
Ho-3 Kanagawa-machi, Kanazawa 920-1181, (Japan)
[c] Dr. H. Naka https://orcid.org/0000-0002-1198-6835
Research Center for Materials Science
Nagoya University
Chikusa, Nagoya 464-8602, (Japan)
E-mail: h_naka@nagoya-u.jp

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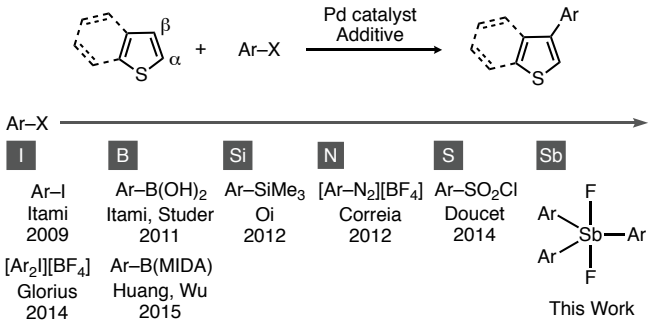
Abstract: Regioselective C–H arylation using pentavalent organoantimony compounds as a new class of arylating reagents is described. The reaction of thiophenes with triarylantimony difluorides in the presence of 5 mol% of $Pd(OAc)_2$ and 2 equiv $CuCl_2$ at 80 ºC under aerobic conditions afforded the β-arylated thiophene derivatives in moderate-to-high yields. The reaction is sensitive to the electronic nature of the triarylantimony difluorides: those bearing an electron-donating group on the phenyl ring showed higher reactivity than those have an electron-withdrawing group.

Introduction

Aryl-substituted thiophenes and benzo[*b*]thiophenes have attracted increasing attentions in medicinal chemistry[1] and materials science.[2,3] For instance, 2-amino-3,4-diaryl-thiophenes show p53-MDM2 binding inhibitory activity;[4] 3-(2,4-dichlorophenyl)thiophene derivatives act as potential PI3K inhibitors;[5] 3-aryl-benzothiophenes bearing a triazole group exhibit 5-LO inhibitor activity.[6] The Pd-catalyzed direct C–H arylation has become one of the most powerful tools for the synthesis of arylated thiophenes.[7,8] The C–H arylation of thiophenes typically proceeds at the most acidic α-position under basic conditions.[7,9] In contrast, C–H arylation at the β-position without any directing group has been more challenging (Scheme 1).[10] In 2009, Itami et al. developed the first β-selective C–H arylation of thiophenes with aryl iodides using a $PdCl_2/P[OCH(CF_3)_2]_3/Ag_2CO_3$ catalytic system.[11] Since then, improved β-selective arylation methods have been constantly reported based on the discovery of alternative arylating agents for aryl iodides. Itami and Studer et al. developed β-selective coupling of thiophenes with aryl boronic acids using Pd–bipyridyl catalysts and 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO, an oxidant).[12] Wu and Huang et al. showed that benzothiophene reacts with aryl MIDA boronates and benzoquinone (BQ) in the presence of Pd–alkoxy catalysts under acidic conditions (MIDA = *N*-methyliminodiacetic acid).[13] Oi et al. reported arylation of thiophenes with arylsilanes using a $PdCl_2(MeCN)_2$ catalyst in the presence of stoichiometric $CuCl_2$.[14] Doucet et al. developed coupling of thiophenes with aryl sulfonyl chlorides in the presence of Li_2CO_3.[15] Glorius et al. proved that arylation of thiophenes with aryl iodoniums undergoes using Pd-C heterogeneous catalyst.[16] Correia et al. reported $Pd(OAc)_2$-catalyzed arylation of benzothiophenes with aryldiazonium tetrafluoroborates.[17] Whereas these methods could be used complementarily, however, each reaction has several drawbacks in substrate scope, efficiency, and regioselectivity.



Scheme 1. Arylating reagents (Ar–X) for Pd-catalyzed β-selective C–H arylation of thiophenes.

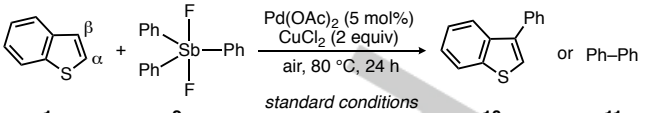
Thus, the development of a new arylating method has been continuously demanded. In particular, there is no universal

method for the installation of electron-rich aryl groups (*e.g.* $CH_3OC_6H_4$) to β-positions of thiophenes with high efficiency. Herein, we report that the Pd-catalyzed β-selective direct C–H arylation of thiophene could be effectively promoted with triarylantimony difluorides (Ar_3SbF_2).[18] The scope of this method is reasonably broad and covers arylating reagents bearing electron-rich substituents. For the first time, Pd-catalyzed C–H arylation of (benzo)thiophenes with a neutral group 15 arylating reagent was achieved.

Results and Discussion

During the course of our studies on the synthesis, structure, reactivity, and biological activity of pentavalent organoantimony(V) compounds, we have recently found that pentavalent organoantimony(V) compounds serve as efficient aryl donors in the Pd-catalyzed Suzuki-[19,20] and Sonogashira-type reactions.[21] These cross-coupling reactions of arylantimony compounds with arylboronic acids or alkynes smoothly proceed in the absence of base reagents and copper cocatalysts. Pentavalent organoantimony(V) compounds could be also used as psedo-arylhalides for Pd-catalyzed C–C(Ar) bond formation in Heck-,[22-24] Stille-,[25] and Hiyama-type reactions.[26] Based on these knowledges, we initially focused on achieving the Pd catalyzed C–H arylation of benzothiphene (**1a**) using organoantimony or bismuth compounds **2a**–**9** (Table 1). The reaction of **1a** (1 equiv) with **2a** or **3**–**5** was performed using $Pd(OAc)_2$ (5 mol%) and $CuCl_2$ (2 equiv) in 1,2-dichloroethane (DCE) under air at 80 ºC for 24 h by referring to Oi's catalytic system [**1a**/arylsilane/Pd catalyst/$CuCl_2$/DCE, 80 ºC] (entries 1–4).[14] The reaction proceeded smoothly with pentavalent organoantimony compounds such as Ph_3SbF_2 (**2a**), Ph_3SbCl_2 (**3**), and $Ph_3Sb(OAc)_2$ (**4**) whereas trivalent Ph_3Sb (**5**) gave inferior results. Among these reagents, Ph_3SbF_2 (**2a**) was found to be the best phenyl group donor for the reaction in terms of the yield of the coupling product (**10**: 93%) and the regioselectivity of the arylation (β-selectivity, 97%) (entry 1). Organobismuth compounds **6**–**9** gave biphenyl (**11**) as a main product, and the desired coupling product **10** was hardly obtained (entries 5–8). These results showed that the reactivity of triphenylpnictogen reagents was considerably affected by the constitutive metal (Sb, Bi), the valence [(III), (V)], and the substituent (F, Cl, OAc) on the metal. Several commercially available Pd catalysts were also screened (entries 9–13) but $Pd(OAc)_2$ remained the best in term of the yield of **10** (entry 1). The reaction did not proceed in the absence of the Pd catalyst (entry 14). The use of other oxidative additives in place of $CuCl_2$ resulted in lower yields of **10** (entries 15–24 vs 1). Decreasing the loading of $CuCl_2$ from 2 equiv to 1 equiv significantly reduced the yield of **10** (entry 25). The addition of $CuCl_2$ is essential, and the reaction hardly proceeded in its absence (entry 26). A screening of solvents showed that the reaction proceeded smoothly in DCE, whereas other solvents gave disappointing results (entries 1, 27–32). When the reaction was performed under an argon atmosphere, the coupling product was obtained in a slightly lower yield (entry 33). The best result was obtained when benzothiophene **1a** was treated with Ph_3SbF_2 (**2a**, 1 equiv) using $Pd(OAc)_2$ (5 mol%) as the catalyst, and $CuCl_2$ (2 equiv) as the oxidant in DCE at 80 ºC under aerobic conditions. Since Ph_3SbF_2 (**2a**) has three phenyl groups, the reaction of **1a** and **2a** was carried out in a 3:1 ratio (entry 34). However, the yield

Table 1. Pd-catalyzed reaction of organoantimony and bismuth compounds **2a-9** with benzothiophene **1**.[a]

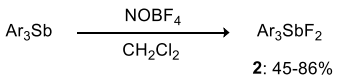


1a **2a** **10** **11**

Entry	Changes from standard conditions	Yield (%)[b] **10** (β:α)[c]	**11**
1	none	93 (97:3)	3
	Arylating reagent instead of Ph_3SbF_2 (**2a**)		
2	Ph_3SbCl_2 (**3**)	62 (91:9)	4
3	$Ph_3Sb(OAc)_2$ (**4**)	80 (94:6)	5
4	Ph_3Sb (**5**)	11	---
5	Ph_3BiF_2 (**6**)	---	81
6	Ph_3BiCl_2 (**7**)	6	54
7	$Ph_3Bi(OAc)_2$ (**8**)	---	39
8	Ph_3Bi (**9**)	---	52
	Palladium catalyst instead of $Pd(OAc)_2$		
9	$PdCl_2$	51 (91:9)	5
10	$PdCl_2(MeCN)_2$	77 (98:2)	5
11	$PdCl_2(PPh_3)_2$	9	---
12	$Pd_2(dba)_3$	71 (93:7)	4
13	$Pd(PPh_3)_4$	3	---
14	Without $Pd(OAc)_2$	---	---
	Additive instead of $CuCl_2$ (2 equiv)		
15	CuF_2 (2 equiv)	4	---
16	$CuBr_2$ (2 equiv)	7	---
17	$Cu(OAc)_2$ (2 equiv)	8	---
18	CuO (2 equiv)	9	---
19	AgOAc (2 equiv)	69 (94:6)	28
20	$AgNO_3$ (2 equiv)	---	27
21	AgO (2 equiv)	---	---
22	Oxone (2 equiv)	8	---
23	TEMPO (2 equiv)	3	---
24	BQ (2 equiv)	---	---
25	$CuCl_2$ (1 equiv)	55 (95:5)	---
26	Without $CuCl_2$	9	---
	Solvent instead of DCE		
27	Dioxane	44 (92:8)	---
28	Toluene	38 (93:7)	---
29	EtOH	4	---
30	DMSO	---	---
31	DMF	---	---
32	NMP	---	---
33	Under argon instead of air	81 (93:7)	5
34	**1a** (1.5 mmol), **2a** (0.5 mmol)[d]	30	---

[a] Conditions: **1a** (0.5 mmol), **2a-9** (0.5 mmol), additive (1.0 mmol), Pd cat. (0.025 mmol Pd). [b] GC yield using dibenzyl as internal standard. The yield 100% corresponds to the formation of 0.5 mmol of **10** and 0.75 mmol of **11**. [c] Regioselectivity was determined by GC analysis. β and α represent 3-phenyl and 2-phenylbenzothiophene, respectively. [d] 100% yield corresponds to the formation of 1.5 mmol of **10**.

was low (30%), which indicated that only one of the three phenyl groups on antimony is involved in the C–H arylation. To investigate the efficiency and generality of the above described C–H arylation, the reaction of various thiophenes (**1**) (0.5 or 1.0 mmol) with Ar_3SbF_2 (**2**) (0.5 mmol) was investigated under the optimized conditions (Table 2). The key arylating reagents, Ar_3SbF_2 (**2a**–**h**), could be easily prepared by the oxidative fluorination of triarylstibanes (Ar_3Sb) using our method (Scheme 2).[18] Reactions of Ar_3Sb with $NOBF_4$ (2 equiv) in CH_2Cl_2 at room temperature afforded **2a**–**h** in 45–86% yields. The C–H arylation of benzothiophene (**1a**) with a variety of Ar_3SbF_2 (**2**) proceeded at the β-position. The yield of the coupling product depends on the electronic nature of substituents on the phenyl rings: Ar_3SbF_2 bearing electron-donating groups and halogens on the phenyl ring furnished the coupling products (**12**–**15**) in good to high yields, whereas Ar_3SbF_2 having electron-withdrawing functionalities such as ethoxycarbonyl and trifluoromethyl groups gave the coupling

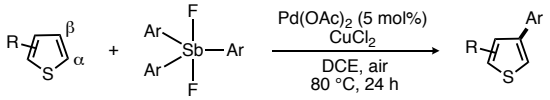


Scheme 2. Synthesis of triarylantimony difluorides **2**.

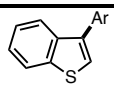
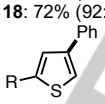
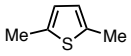
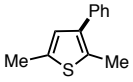
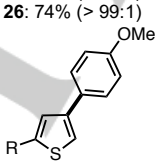
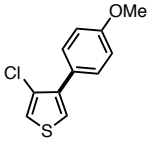
products **16** and **17** in low yields. Sterically hindered *ortho*-substituted Ar_3SbF_2 compound also gave the corresponding product **18** without any difficulty.

Various thiophenes (**1**) were then treated with Ph_3SbF_2 (**2a**) under the optimized conditions. As for volatile thiophenes, 2 equiv amounts of the thiophenes were used relative to Ph_3SbF_2. 2-Substituted thiophenes bearing alkyl, phenyl, or halogen substituents gave the 4-phenylated products (**19**–**22**) in moderate to good yields. 2,5-Dimethylthiophene also afforded β-phenylated product (**23**) in moderate yield. Furthermore, 3-substituted thiophenes were treated with **2a** to give the corresponding products (**24**–**26**) in satisfactory yields. The reaction of **2a** with 2- and 3-acetylthiophenes, and 2-iodothiophene, and thiophene gave a complex mixture under these conditions (data not shown). The antimony reagent **2b** having an electron rich aryl ring ($CH_3OC_6H_4$) reacted with **1a** more rapidly than the phenyl analogue **2a**. Whereas the efficient installation of electron-rich aryl ring through C–H arylation has been considered difficult, the current method gave 3-(4-methoxyphenyl)benzothiophene **12** in 81% yield, which is higher than those reported for aryl group donors such as silane (64%), sulfonyl chloride (62%), and diazonium salt (75%).[14,15,17] This protocol employing **2b** opened a general access to β-(4-alchoxyphenyl)thiophenes **27**–**29**. In all cases, the arylation of thiophenes with **2b** completed in shorter reaction time than **2a** and provided products (**27**–**29**) in higher yields than the phenyl analogues **20**, **22**, and **26**, respectively. These results illustrate the effectiveness of the arylantimony reagent as an aryl group donor in challenging cross-coupling reactions. Doucet et al. reported β-selective arylation of selenophenes with aryl sulfonyl chlorides.[27] Therefore, we examined the reaction of Ph_3SbF_2 **2a** with benzoselenophene under optimum conditions for thiophenes. However, this reaction did not proceed, and Ph_3SbF_2 and benzoselenophene were recovered in 90% and 92% yields, respectively.

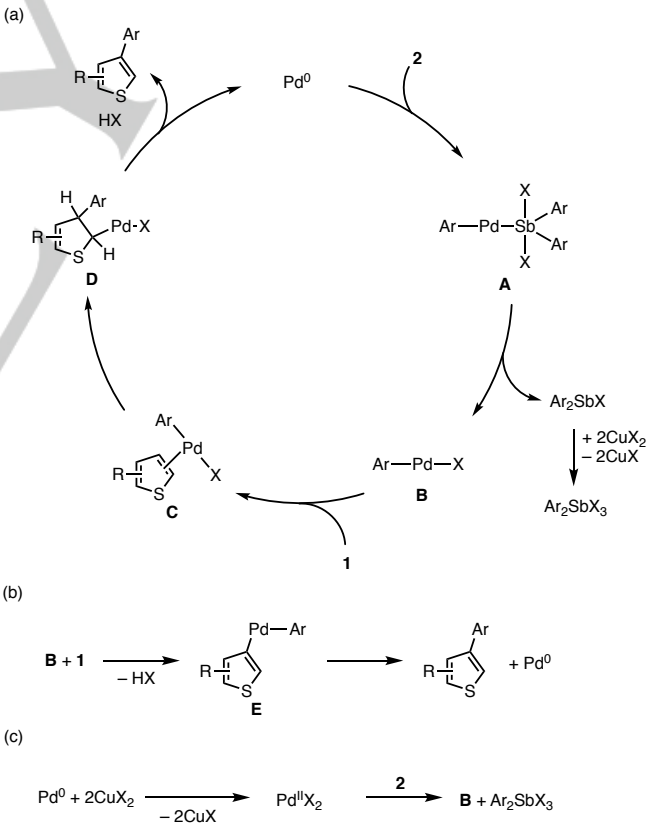
Table 2. Substrate scope: reaction of triarylantimony difluorides with thiophene derivatives.[a,b]



1a–i **2a–h** **12–29**

1	2	Products, yield (β:α)[c]
		
1a	**2b** (Ar = 4-$CH_3OC_6H_4$)	**12**: 81% (99:1)[d]
1a	**2c** (Ar = 4-$CH_3C_6H_4$)	**13**: 89% (96:4)
1a	**2d** (Ar = 4-FC_6H_4)	**14**: 79% (95:5)
1a	**2e** (Ar = 4-BrC_6H_4)	**15**: 77% (96:4)
1a	**2f** (Ar = 4-$EtOCOC_6H_4$)	**16**: 42% (95:5)
1a	**2g** (Ar = 4-$CF_3C_6H_4$)	**17**: 39% (90:10)
1a	**2h** (Ar = 2-$CH_3C_6H_4$)	**18**: 72% (92:8)
		
1b (R = Me)	**2a**	**19**: 55% (83:17)
1c (R = *n*Bu)	**2a**	**20**: 68% (> 99:1)
1d (R = Ph)	**2a**	**21**: 74% (95:5)
1e (R = Cl)	**2a**	**22**: 75% (> 99:1)
		
1f	**2a**	**23**: 55%
		
1g (R = Me)	**2a**	**24**: 70% (> 99:1)
1h (R = Ph)	**2a**	**25**: 75% (> 99:1)
1i (R = Cl)	**2a**	**26**: 74% (> 99:1)
		
1c (R = *n*Bu)	**2b**	**27**: 76% (97:3)[d]
1e (R = Cl)	**2b**	**28**: 80% (> 99:1)[d]
		
1i	**2b**	**29**: 88% (> 99:1)[d]

[a] Benzothiophene (0.5 mmol) or monocyclic thiophenes (1.0 mmol), triarylantimony difluorides (0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), $CuCl_2$ (1.0 mmol). [b] Isolated yield based on one aryl group in triarylantimony difluorides (0.5 mmol). 2-Arylthiophenes are included in the yield. [c] The β:α ratio was determined by GC and ^1H NMR analysis. [d] Reaction time of 6 h.



Scheme 3. (a) A proposed catalytic cycle and alternative pathways (b) from an intermediate **B** to Pd^0 and (c) from Pd^0 to **B**. X = F, Cl, or OAc. Neutral ligands coordinated to Pd are omitted for clarity.

At present, the mechanism for this C–H arylation is unclear. We presume that the mechanism would be similar to that of the directed C–H arylation of thiophenes using arylsilanes proposed

by Oi.[14] A possible mechanism for the present coupling reaction is shown in Scheme 3a in consideration of studies by Itami and Studer,[28] Itami and Irle[29] as well as by Larrosa.[30] The initial step of the reaction would be addition of the Ar–Sb bond of Ar_3SbX_2 (X = F, Cl, or OAc) onto the Pd^0 catalyst to form ArPdSb complex **A** which is then transformed to ArPdX complex **B** with liberation of Ar_2SbX. Coordination of thiophene to complex **B** leads to the generation of complex **C** which undergoes arylpalladation of thiophene to give an intermediate **D**. β-Hydride elimination and reductive elimination form the arylthiophene product and HX, and regenerate the Pd^0 species. The Ar_2SbX by-product could serve as a neutral ligand to palladium species **B**–**D**, as proposed by Gushchin et al. in the Heck-type *C*-arylation of alkenes using $Ph_3Sb(OAc)_2$[23] but it could be oxidized to Sb^V species by the Cu^{II} reagent. An alternative pathway is also under consideration (Scheme 3b), where electrophilic aromatic substitution and/or concerted metalation-deprotonation proceed from the above-mentioned intermediate ArPdX **B** and thiophene to form the intermediate **E**, which presumably undergoes reductive elimination to afford the desired product.[14] Whereas we presumed the formation of **B** from Pd^0 *via* complex **A**, we do not exclude the possibility of alternative pathway involving the oxidation of Pd^0 by CuX_2 (2 equiv) to form $Pd^{II}X_2$ and the transmetalation of $Pd^{II}X_2$ and Ar_3SbX_2 (**2**) to give the intermediate **B** and Ar_2SbX_3 (Scheme 3c).

Conclusions

We have demonstrated that triarylantimony difluorides serve as new class of arylating agents for the β-selective C–H arylation of thiophene derivatives. Pentavalent organoantimony compounds with various electron-donating and electron-withdrawing functional groups afforded the corresponding arylthiophene products in satisfactory yields through the palladium-catalyzed C–H arylation under mild conditions. In particular, the arylated products with an electron-donating group are unless otherwise difficult to access as efficiently. This reaction is the first example of a transition metal-catalyzed C–H direct arylation using an organoantimony compound. Furthermore, this is the first report on the use of Ph_3SbF_2 for C(HetAr)–C(Ar) bond formation reaction. Detailed mechanistic studies on the above disclosed C–H arylation and the reaction of triarylantimony difluorides (Ar_3SbF_2) with other coupling partners are in progress.

Experimental Section

General Information

^1H NMR (TMS: *δ*: 0.00 ppm as an internal standard) and ^{13}C NMR ($CDCl_3$: *δ*: 77.00 ppm as an internal standard) spectra were recorded on JEOL JNM-AL400 and JNM-ECZ400S (400 MHz and 100 MHz respectively) spectrometers in $CDCl_3$. GC-MS spectra were recorded on a Agilent 5977E Diff-SST MSD-230V spectrometer. IR spectra were recorded on a SHIMADZU FTIR-8400S spectrometer and are reported in frequency of absorption (cm^{-1}). Only selected IR peaks are reported. Chromatographic separations were carried out using Silica Gel 60N (Kanto Chemical Co., Inc.) under the solvent system stated. Thin-layer chromatography (TLC) was performed using Merck Pre-coated TLC plates (silica gel 60 F_{254}). Most of reagents were used without further purification unless otherwise specified. **1a-i** and each reagents were purchased from wako Fine Chemicals, Japan, ACROS ORGANICS Fine Chemicals, Japan, and TCI Fine Chemicals, Japan. The structures of the products **10**,[16] **12**-**15**,[14] **17**-**24**,[14] **25**-**26**,[16] **27**,[31] **28**,[16] and **29**[15a] were determined by comparing their ^1H NMR spectra with those in the literature. Purity was confirmed by GC and ^1H NMR analysis.

General Procedure for the Preparation of 2[18]

To a stirred solution of Ar_3Sb (0.5 mmol) in dry CH_2Cl_2 (3 mL) at –20 °C or room temperature was added $NOBF_4$ (1.0 mmol). The reaction mixture was stirred at –20 °C or room temperature until TLC indicated complete consumption of the starting material. After dilution with CH_2Cl_2 (20 mL) and water (20 mL), the organic layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (20 mL × 2). The combined extracts were washed with water and brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by column chromatography on SiO_2 (**2a**, **c**-**d**, **g**, and **2h**: Hexane/Et_2O 5:1, **2b**: CH_2Cl_2) to afford triarylantimony difluorides. In the case of **2e**, and **2f** the crude product was purified by recrystallization. All the antimony reagents **2a-h** were prepared according to this general procedures and spectroscopic data were in accordance with those in the literature. [18]

General Procedure for the C–H Arylation

Ar_3SbF_2 (**2**) (0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), $CuCl_2$ (1.0 mmol) and thiophene derivative (**1**) (1.0 mmol or 0.5 mmol) were added to 1,2-dichloroethane (3 mL) in a round-bottom flask. After stirring at 80 ºC for 24 h, the mixture was cooled to room temperature and filtered through a short plug of Celite. The Celite plug was flushed with CH_2Cl_2, and the filtrate was evaporated to dryness under reduced pressure. The crude product was purified on a silica gel column chromatography to give the desired product.

3-Phenylbenzo[*b*]thiophene (10)[16]

Colorless oil (197 mg, 93%); R_f = 0.4 (Hexane); ^1H NMR (400 MHz, $CDCl_3$): *δ* = 7.92 (t, *J* = 4.7 Hz, 2H; Ar-H), 7.59 (d, *J* = 8.3 Hz, 2H; Ar-H), 7.50-7.35 ppm (m, 6H; Ar-H).

3-(*p*-Methoxyphenyl)benzo[*b*]thiophene (12)[14]

Orange oil (194.7 mg, 81%); R_f = 0.5 (Hexane/EtOAc 20:1); ^1H NMR (400 MHz, $CDCl_3$): *δ* = 7.93-7.89 (m, 2H; Ar-H), 7.52 (d, *J* = 9.3 Hz, 2H; Ar-H), 7.41-7.36 (m, 2H; Ar-H), 7.34 (s, 1H; Ar-H), 7.05-7.01 (d, *J* = 8.8 Hz, 2H; Ar-H), 3.88 ppm (s, 3H; OCH_3).

3-(*p*-Tolyl)benzo[*b*]thiophene (13)[14]

White solid (219.8 mg, 89%); R_f = 0.5 (Hexane); ^1H NMR (400 MHz, $CDCl_3$): *δ* = 7.93-7.89 (m, 2H; Ar-H), 7.48 (d, *J* = 7.8 Hz, 2H; Ar-H), 7.41-7.36 (m, 3H; Ar-H), 7.30 (d, *J* = 8.3 Hz, 2H; Ar-H), 2.44 (s, 3H; CH_3).

3-(*p*-Fluorophenyl)benzo[*b*]thiophene (14)[14]

Colorless oil (180.3 mg, 79%); R_f = 0.5 (Hexane); ^1H NMR (400 MHz, $CDCl_3$): *δ* = 7.92 (t, *J* = 4.4 Hz, 1H; Ar-H), 7.85 (t, J = 4.6 Hz, 1H; Ar-H); 7.55 (dd, *J* = 8.8, 5.9 Hz, 2H; Ar-H), 7.41-7.39 (m, 2H; Ar-H), 7.38 (s, 1H; Ar-H), 7.20-7.16 ppm (m, 2H; Ar-H).

3-(*p*-Bromophenyl)benzo[*b*]thiophene (15)[14]

White solid (222.7 mg, 77%); R_f = 0.5 (Hexane); ^1H NMR (400 MHz, $CDCl_3$): *δ* = 7.92 (t, *J* = 4.9, 4.3 Hz, 1H; Ar-H), 7.86 (t, *J* = 4.4, 4.9 Hz, 1H; Ar-H), 7.62 (d, *J* = 8.3 Hz, 2H; Ar-H), 7.46 (d, *J* = 6.8 Hz, 2H; Ar-H), 7.43-7.38 ppm (m, 3H; Ar-H).

3-(*p*-Ethoxycarbonylphenyl)benzo[*b*]thiophene (16)

Yellow oil (118.6 mg, 42%); R_f = 0.4 (Hexane/CH_2Cl_2 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.2 Hz, 2H; Ar-H), 7.95-7.90 (m, 2H; Ar-H), 7.67 (d, *J* = 8.2 Hz, 2H; Ar-H), 7.49 (s, 1H; Ar-H), 7.44-7.40 (m, 2H, Ar-H), 4.43 (q, *J* = 7.3 Hz, 2H; CH_2), 1.43 ppm (t, *J* = 7.3 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 140.7, 140.4, 137.4, 137.0, 130.0, 129.5, 128.5, 124.6, 124.5, 123.0, 122.6, 61.0, 14.3 ppm; IR (film): $\tilde{\nu}$ = 1713 (C=O) cm^{-1}.

3-(*p*-Trifluoromethylphenyl)benzo[*b*]thiophene (17)[14]

Colorless oil (108.5 mg, 39%); R_f = 0.5 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96-7.93 (m, 1H; Ar-H), 7.89-7.87 (m, 1H; Ar-H), 7.76 (d, *J* = 8.8 Hz, 2H; Ar-H), 7.21 (d, *J* = 8.8 Hz, 2H; Ar-H), 7.48 (s, 1H; Ar-H), 7.43-7.41 ppm (m, 2H; Ar-H).

3-(*o*-Tolyl)benzo[*b*]thiophene (18)[14]

Colorless oil (161.5 mg, 72%); R_f = 0.45 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.3 Hz, 1H; Ar-H), 7.44 (d, *J* = 7.3 Hz, 1H; Ar-H), 7.37-7.29 (m, 7H; Ar-H), 2.18 ppm (s, 3H; CH_3).

2-Methyl-4-phenylthiophene (19)[14]

Colorless oil (95.8 mg, 55%); R_f = 0.45 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.3 Hz, 2H; Ar-H), 7.36 (t, *J* = 7.3 Hz, 2H; Ar-H), 7.26 (t, *J* = 10.7 Hz, 2H; Ar-H), 7.20 (d, *J* = 1.4 Hz, 1H; Ar-H), 7.06 (s, 1H; Ar-H), 2.53 ppm (s, 3H; CH_3).

2-*n*-Buthyl-4-phenylthiophene (20)[14]

Orange oil (147.1 mg, 68%); R_f = 0.45 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.3 Hz, 2H; Ar-H), 7.37 (t, *J* = 7.8 Hz, 2H; Ar-H), 7.26 (t, *J* = 6.8, 7.3 Hz, 2H; Ar-H), 7.22 (d, *J* = 1.5 Hz, 1H; Ar-H), 7.07 (s, 1H; Ar-H), 2.85 (t, *J* = 7.3 Hz, 2H; Ar-H), 1.70 (quin, *J* = 7.3 Hz, 2H; Ar-H), 1.43 (sext, *J* = 7.3 Hz, 2H; CH_2), 0.96 ppm (t, *J* = 7.3 Hz, 3H; CH_3).

2,4-Diphenylthiophene (21)[14]

Colorless oil (174.9 mg, 74%); R_f = 0.35 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.60 (m, 4H; Ar-H), 7.59 (d, *J* = 1.5 Hz, 1H; Ar-H), 7.43-7.37 (m, 5H; Ar-H), 7.32-7.28 ppm (m, 2H; Ar-H).

2-Chloro-4-phenylthiophene (22) [14]

Colorless oil (146.0 mg, 75%); R_f = 0.5 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.3 Hz, 2H; Ar-H), 7.39 (t, *J* = 7.3 Hz, 2H; Ar-H), 7.31 (t, *J* = 7.3 Hz, 1H; Ar-H), 7.21 ppm (dd, *J* = 1.9, 7.8 Hz, 2H; Ar-H).

2,5-Dimethyl-3-phenylthiophene (23)[14]

Colorless oil (103.6 mg, 55%); R_f = 0.55 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.35 (t, *J* = 6.3 Hz, 4H; Ar-H), 7.30-7.28 (dd, *J* = 4.3, 2.0 Hz, 1H; Ar-H), 6.70 (s, 1H; Ar-H), 2.44 ppm (s, 6H; CH_3).

3-Methyl-4-phenylthiophene (24)[14]

Colorless oil (121.9 mg, 70%); R_f = 0.55 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.31 (m, 5H; Ar-H), 7.20 (d, *J* = 2.9 Hz, 1H; Ar-H), 7.03 (d, *J* = 3.4 Hz, 1H; Ar-H), 2.28 ppm (s, 3H; CH_3).

3,4-Diphenylthiophene (25)[16]

White plate (177.2 mg, 75%); R_f = 0.4 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 2H; Ar-H), 7.26-7.25 (m, 6H; Ar-H), 7.20-7.18 ppm (m, 4H; Ar-H).

3-Chloro-4-phenylthiophene (26)[16]

Yellow solid (144.1 mg, 74%); R_f = 0.5 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (dd, *J* = 7.3, 1.5 Hz, 2H; Ar-H), 7.43 (t, *J* = 7.3 Hz, 2H; Ar-H), 7.37 (t, *J* = 7.2 Hz, 1H; Ar-H) 7.30 (d, *J* = 3.4 Hz, 1H; Ar-H), 7.25 ppm (d, *J* = 3.9 Hz, 1H; Ar-H).

2-Chloro-4-(4-methoxyphenyl)thiophene (27)[31]

Colorless oil (179.8 mg, 80%); R_f = 0.5 (Hexane/CH_2Cl_2 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.7 Hz, 2H; Ar-H), 7.16 (d, *J* = 1.8 Hz, 1H; Ar-H), 7.08 (d, *J* = 1.8 Hz, 1H; Ar-H), 6.92 (d, *J* = 8.7 Hz, 2H; Ar-H), 3.84 (s, 3H; CH_3).

2-*n*-Buthyl-4-(4-methoxyphenyl)thiophene (28)[16]

Colorless oil (187.2 mg, 76%); R_f = 0.5 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.7 Hz, 2H; Ar-H), 7.11 (d, *J* = 1,3 Hz, 1H; Ar-H), 7.02 (d, *J* = 1.3 Hz, 1H; Ar-H), 6.91 (d, *J* = 9.2 Hz, 2H; Ar-H), 3.82 (s, 3H; CH_3), 2.83 (t, *J* = 7.3 Hz, 2H; CH_2), 1.69 (quin, *J* = 7.6 Hz, 2H; CH_2), 1.42 (sext, *J* = 7.4 Hz, 2H; CH_2), 0.95 (t, *J* = 7.3 Hz, 3H; CH_3).

3-Chloro-4-(4-methoxyphenyl)thiophene (29)[15a]

White solid (179.6 mg, 80%); R_f = 0.5 (Hexane/CH_2Cl_2 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.7 Hz, 2H; Ar-H), 7.08 (s, 2H; Ar-H), 6.96 (d, *J* = 9.2 Hz, 2H; Ar-H), 3.85 (s, 3H; CH_3).

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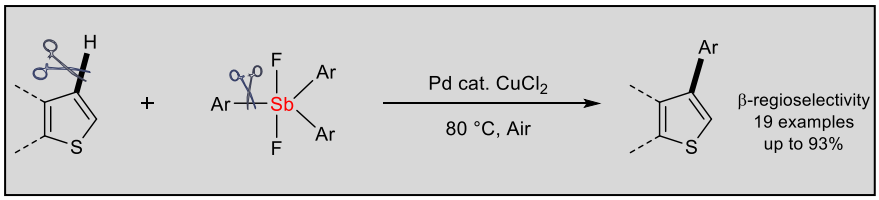

Regioselective C–H arylation using pentavalent organoantimony compounds as a new class of arylating reagents is described. Triarylantimony difluorides with various electron-donating and electron-withdrawing functional groups afforded the corresponding arylthiophene products in satisfactory yields through the palladium-catalyzed C–H arylation under mild conditions.