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RESEARCH ARTICLE

Synthesis and Structural Analysis of 3,6-Diarylthieno[3,2-*b*]thiophenes by Site-selective Pd-catalyzed C-H Functionalization

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Abstract: Thieno[3,2-*b*]thiophene represents a typical core structure in a large number of organic optoelectronic materials and molecular magnetism. One-pot efficient approach to modify the electronic structure of thieno[3,2-*b*]thiophene is to introduce suitable substituents into this π-conjugated skeleton. In this paper, we report on a facile route to precisely functionalize thieno[3,2-*b*]thiophene by the direct Pd-catalyzed arylation reaction with boronic acids. Based on this procedure, a number of 3,6-diarylthieno[3,2-*b*]thiophenes were prepared in good yields. NMR methods and X-Ray crystal structure analysis confirmed high regioselectivities at the C-3 and C-6 positions of thieno[3,2-*b*]thiophene skeleton.

Keywords: C-H functionalization, cross-coupling, direct arylation, palladium catalysis, regioselectivity, thieno[3,2-*b*]thiophene.

1. INTRODUCTION

Thieno[3,2-*b*]thiophene (**TT**) is a common building block found in a wide range of important *p*-type organic semiconductors, optoelectronics, and electroluminescences [1a-h] as well as molecular magnetism [1i-l]. The intermolecular sulfur-sulfur interactions of **TT** have been known to improve the electronic transport between the adjacent molecules [2]. Moreover, compared to thiophenes, the rigid **TT** skeleton with two fused thiophene rings limits the rotational disorder between the moieties, leading to a better π-conjugation [3]. This rigid structure could be employed for adjusting band gaps of organic materials and increasing intermolecular interactions in the solid state.

Very recently, Liu and co-workers have developed highly π-extended copolymers with D-π-A structures containing **TT** moiety, such as benzo[1,2-*b*:4,5-*b'*]dithiophene and thieno-[3,4-*c*]pyrrole-4,6-dione (Fig. **1**) [4].

The polymer photovoltaic devices based on these monomers exhibit power conversion efficiencies as high as 7.71% and short-circuit currents of up to 13.70 $mAcm^{-2}$. The results demonstrate that the incorporation of **TT** units as π-bridges is a feasible way to produce highly efficient polymer solar cells.

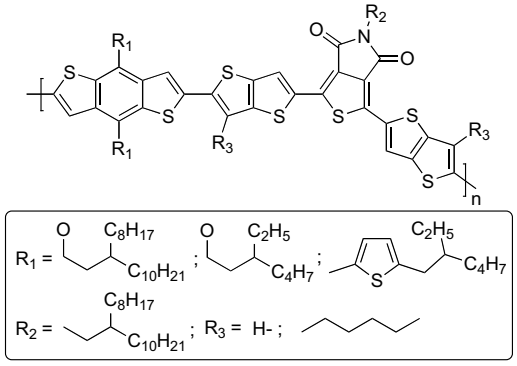

Fig. (1). D-π-A Copolymers containing TT moiety towards highly efficient solar cells.

Expansion of the π-framework *via* the incorporation of planarized aromatic units into conjugated backbones is an efficient approach to tune the physical properties of organic materials [5]. Over the past four decades, the Pd-catalyzed cross-coupling reactions of halogenated heterocycles and organometallic compounds have played an essential role in the synthesis of complex molecules, including drugs, natural products, and organic materials [6]. However, these traditional Pd-catalyzed coupling reactions exhibit several disadvantages in terms of atom-economy such as the requirement of pre-functionalization of the substrates, the employment of expensive organometallic reagents, and waste treatment.

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In this context, the direct C-arylation of aromatic heterocycles by C-H functionalization in the presence of transition metals as catalysts has been proven to be an efficient alternative to the classical cross-coupling reactions [7]. This approach is particularly straighforward in terms of atom-economy aspect and sustainable development of chemical processes. Various direct arylations of heterocycles have been explored where aryltrifluoroborate salts [8], [Ph-I-Ph]BF_4 [9], or aryl halides [10] was employed as coupling partners. Among the reactions of this type, the direct arylation with boronic acids is convenient since the boronic reagents are easily available and stable under normal conditions [11]. To the best of our knowledge, only a few examples of site-selective C-3 Pd-catalyzed arylation of **TT** with moderate yields has been reported in the literatures [11c, 12]. Therefore, extensive studies on one-pot site-selective Pd-catalyzed C-H double-arylation of TT using functionalized boronic acids are nesscessary.

Due to the importance of functionalized thieno[3,2-*b*] thiophenes in the development of organic materials, we report herein the synthesis of 3,6-diarylthieno[3,2-*b*]thiophene by the Pd-catalyzed C-H double-arylation of **TT**. The reactions proceeded with very good site-selectivity and yields, proving to be a convenient procedure for the synthesis of arylated **TT**s.

2. EXPERIMENTAL

2.1. General Notes

Unless otherwise stated, chemical reagents and solvents for reactions were purchased from Sigma-Aldrich or Merck and were used without further purification. THF were dried by refluxing over sodium wire in the presence of benzophenone as indicator and distilled just before used. Column chromatography was performed with Merck silica gel 60 (0.040-0.063 μm grade).

2.2. Instrumentation

NMR spectra were recorded on a Bruker Advance 500 NMR spectrometer in $CDCl_3$. Chemical-shift data for each signal were reported in ppm units with tetramethylsilane (TMS) as internal reference, where δ_{TMS} is zero. Splitting patterns are designated as s (*singlet*), d (*doublet*), t (*triplet*), q (*quartet*), and m (*multiplet*). ESI-MS measurements were acquired on an HPLC-MS Agilent 1100, Agilent Technologies, USA. The intensities for the X-ray determination were collected on a D8 QUEST Bruker (Germany) instrument at 100 K with Mo Kα radiation (λ = 0.71073 Å) using a TRIUMPH monochromator. Standard procedures were applied for data reduction and absorption correction. Structure solution and refinements were performed with SHELX. Melting points were measured on a Stuart-Scientific SMP3 apparatus without correction.

2.3. Synthesis

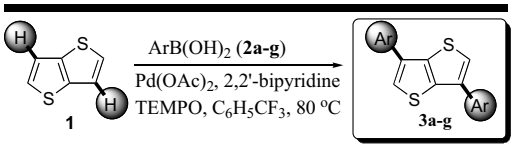
The title compound **TT 1** was prepared from thiophene in 6 steps following the reported procedure [13]. All intermediates show NMR data and physical properties which are in good agreement with literatures.

The C-H activation reactions of **1** (1.0 equiv) with various of boronic acids **2a-g** (4.0 equiv) resulted in site-selective formation of 3,6-diarylthieno[3,2-*b*]thiophenes **3a-g** in 50-74% yields (Scheme **1**). The numeration in the formulas of **3a-g** for NMR analysis is given in Fig. (**2**).

2.4. Procedure for the Pd-catalyzed Direct Arylation of TT

2.4.1. Synthesis of 3a is Chosen as the Representative Procedure

A 5 mL screw-top test tube containing a magnetic stirring bar was dried in an oven at 120°C for 30 min. After cooling, $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), 2,2'-bipyridine (3.1 mg, 0.02 mmol, 10 mol%), and $C_6H_5CF_3$ (0.4 mL) were added under air. The mixture was stirred at room in 30 min. temperature to form the catalytic system. To the resulting solution were added **TT** (28 mg, 0.2 mmol, 1.0 eq.), phenylboronic acid **2a** (97.6 mg, 0.8 mmol, 4.0 eq.), and TEMPO (124.8 mg, 0.8 mmol, 4 eq.). The tube was sealed with a cap. The mixture was heated at 80 °C until TLC (*n*-hexane) showed the complete consumption of the starting material. The redish brown reaction solution was diluted with EtOAc, washed several times with water, dried over Na_2SO_4, and concentrated under reduced pressure by rotary evaporation. The residue was purified by SiO_2-column chromatography (*n*-hexane) to furnish **3a** as a white solid (43.2 mg, 74%). Mp 203-205 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79 (d, 2 H, J = 7.5 Hz, Ph), 7.55 (s, 1 H, **TT**), 7.49 (t, 2 H, J = 7.5 Hz, Ph), 7.37 (t, J = 7.5 Hz, 1 H, Ph); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.2 (C8), 134.9 (C2), 134.7 (C9), 129.0 (C11), 127.8 (C12), 126.6 (C10), 122.3 (C3). MS-ESI: *m/z* cald for $C_{18}H_{13}S_2$ $[M+H]^+$ 293.0, found 292.9.



Ar = C_6H_5- (**2a**)	**3a**: 74%
3,5-$(CH_3)_2C_6H_3$- (**2b**)	**3b**: 56%
4-$CH_3C_6H_4$- (**2c**)	**3c**: 71%
t-BuC_6H_4- (**2d**)	**3d**: 50%
4-$CF_3C_6H_4$- (**2e**)	**3e**: 64%
2-$CH_3C_6H_4$- (**2f**)	**3f**: 51%
3-$CH_3C_6H_4$ (**2g**)	**3g**: 74%

Scheme (1). Synthesis of 3a-g. Reagents and conditions: **1** (1.0 eq.), $ArB(OH)_2$ (4.0 eq.), $Pd(OAc)_2$ (10 mol%), 2,2'-bipyridine (10 mol%), TEMPO (4.0 eq.), $C_6H_5CF_3$, 80 °C, 2 - 4 hours.

2.4.2. 3,6-Di(3,5-dimethylphenyl)thieno[3,2-b]thiophene (3b)

Pale yellow solid (39 mg, 56%). Mp 178-180°C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.49 (s, 1 H, **TT**), 7.39 (br s, 2 H, Ar), 7.01 (br s, 1 H, Ar), 2.40 (s, 6 H, 2x$\underline{C}H_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.5 (C11), 138.2 (C8), 135.1 (C2), 134.7 (C9), 129.4 (C12), 124.4 (C10), 122.0 (C3), 21.4 ($\underline{C}H_3$). MS-ESI: *m/z* cald for $C_{22}H_{21}S_2$ $[M+H]^+$ 349.1, found 349.0.

2.4.3. 3,6-Di(p-tolyl)thieno[3,2-b]thiophene (3c)

Pale yellow solid (45.5 mg, 71%). Mp 200-202 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (d, 2 H, J = 8.0 Hz, Ar), 7.49 (s, 1 H, **TT**), 7.28 (d, 2 H, J = 7.5 Hz, Ar), 2.41 (s, 3 H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.2 (C8), 137.6 (C12), 134.9 (C2), 131.9 (C9), 129.7 (C11), 126.4 (C10), 121.7 (C3), 21.2 ($\underline{C}H_3$). MS-ESI: *m/z* cald for $C_{20}H_{17}S_2$ $[M+H]^+$ 321.0, found 321.0.

2.4.4. 3,6-Di(4-tert-butylphenyl)thieno[3,2-b]thiophene (3d)

White solid (40.3 mg, 50%). Mp 160-162 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, 1 H, J = 8.5 Hz, Ar), 7.51 (s, 1 H, **TT**), 7.50 (d, 2 H, J = 8.5 Hz, Ar), 1.38 (s, 9 H, 3xC$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.8 (C12), 138.2 (C8), 134.8 (C2), 131.9 (C9), 126.2 (C11), 125.9 (C10), 121.8 (C3), 34.7 (*tert*-C), 31.3 ($\underline{C}H_3$). MS-ESI: *m/z* cald for $C_{26}H_{29}S_2$ $[M+H]^+$ 405.1, found 405.0.

2.4.5. 3,6-Di(4-trifluoromethylphenyl)thieno[3,2-b]thiophene (3e)

White solid (164 mg, 64%). Mp 193-195 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.88 (d, 2 H, J = 8.5 Hz, H10+H14), 7.75 (d, 2 H, J = 8.0 Hz, H11+H13), 7.66 (s, 1 H, **TT**); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.4 (C8), 137.8 (C9), 133.6 (C2), 129.4 (q, J = 32.5 Hz, C12), 126.7 (C10+C14), 126.1 (q, J = 3.75 Hz, C11+C13), 125.6 (q, J = 270 Hz, $\underline{C}F_3$),124.1 (C3). MS-ESI: *m/z* cald for $C_{20}H_{11}F_6S_2$ $[M+H]^+$ 429.4, found 429.8.

2.4.6. 3,6-Di(2-methylphenyl)thieno[3,2-b]thiophene (3f)

White solid (32.6 mg, 51%). Mp 200-202 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (dd, 2 H, J = 8.0 Hz and 1.5 Hz, Ar), 7.32 (dd, 2 H, J = 8.0 Hz and 1.5 Hz, Ar), 7.28 (dd, 1 H, J = 8.0 Hz and 1.5 Hz, Ar), 7.24 (s, 1 H, **TT**), 2.41 (s, 3 H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.7 (C8), 136.3 (C10), 134.8 (C2), 134.7 (C9), 130.7 (C13), 129.4 (C11), 127.9 (C12), 125.9 (C14), 124.4 (C3), 20.6 ($\underline{C}H_3$). MS-ESI: *m/z* cald for $C_{20}H_{17}S_2$ $[M+H]^+$ 321.1, found 321.0.

2.4.7. 3,6-Di(3-methylphenyl)thieno[3,2-b]thiophene (3g)

White solid (142.1 mg, 74%). Mp 127-129^{o}C. The 1D-NMR spectra of **3g** were analyzed in combination with its HSQC and HMBC spectra as shown in Table **2** and Fig. (**4**). MS-ESI: *m/z* cald for $C_{20}H_{17}S_2$ $[M+H]^+$ 321.1, found 321.0.

3. RESULTS AND DISCUSSION

3.1. Synthesis

The reaction of **TT 1** with phenylboronic acid **2a** was investigated as a prototype reaction. In our initial efforts toward the direct coupling of the Csp^2-H bond with phenylboronic acid, a short screening of various oxidants was carried out. Selected results are summarized in Table **1**, entries 1÷5.

We first examined the oxidant $Cu(OAc)_2$ as described by Ranjit and Liu in the case of benzothiazoles and benzoxazoles [11i]. However, we observed no conversion of **1** in the presence of the Pd/Cu co-catalyst (10 and 20 mol%, respectively) and a ligand (30 mol%) with K_3PO_4 (3.0 eq.) as the base (Table **1**, entry 1). Instead, the boronic acid **2a** was homo-coupled to form biphenyl. Our further attempts to explore various reaction solvents, such as DMSO, DMAc, or toluene were unsuccessful (Table **1**, entry 1).

In the mean time, Itami [11c] and Kannaboina [11k] described two noticable Pd-catalyzed C-3 arylation procedures for thiophenes and thiazoles and for 7-azaindoles, respectively, using arylboronics as coupling partners in the presence of various oxidants. These reactions were performed in the presence of $Pd(OAc)_2$ (5÷10 mol%) as the catalyst under mild condition. Encouraged by this study, we applied TEMPO as the oxidant to our arylation of **TT**. To our pleasure, 3,6-diphenylthieno[3,2-*b*]thiophene **3a** was isolated in 74% yield (Table **1**, entry 2) as the desired product. Arylation at other positions of the thieno[3,2-*b*]thiophene skeleton was not identified. In addition, the homo-coupling of phenylboronic acid was significantly minimized. Other oxidants, such as Ag_2O, H_2O_2, or *m*CPBA were found to be ineffective (Table **1**, entries 3÷5).

In order to optimize the reaction conditions, we performed the arylation in the presence of other ligands. Among several ligands examined with $Pd(OAc)_2$, we found that a procedure using 2,2'-bipyridine (bipy) as the ligand provided the highest yield of the coupled product (74%, Table **1**, entry 2). Other nitrogen-containing multidentate ligands, such as 6,6'-dimethyl-2,2'-bipyridine (dmbipy) or phenanthroline (phen) were found to be much less effective (Table **1**, entries 6 and 7).

With α,α,α-trifluorotoluene as the solvent, an improved reaction yield (74%) was achieved (Table **1**, entry 2) [11c,n]. The reaction also proceeded at a lower temperature (80 ^{o}C) and at a significantly shorter reaction time. Replacing α,α,α-trifluorotoluene with other solvents such as DMSO, DMAc, or toluene resulted in lower conversions or no reaction (Table **1**, entries 8 and 9) [11h]. In these cases, the increase of reaction time didn't enhance the reaction efficiency.

To further optimize the reaction conditions, we performed the cross-coupling in various amounts of the catalyst and the oxidant. The reaction also proceeded at lower loadings of the $Pd(OAc)_2$ (5 mol%) catalyst, but with a substantial decrease in the reaction yield (Table **1**, entry 10). We also observed that lowering the amount of TEMPO to 2.0 eq. led to sluggish conversions without affecting the regioselectivity (Table **1,** entry 11) [11c].

After a widely screening of various parameters, the optimized conditions for the direct CH arylation of **TT** were established in the employment of $Pd(OAc)_2$ (10 mol%) as the catalyst, bipy (10 mol%) as the ligand, and TEMPO (4.0 eq.) as the oxidant in open air at 80^{o}C (Table **1**, entry 2). Interestingly, the desired coupling product was achieved without using any base or additive. Under the present conditions, 3,6-diphenylthieno[3,2-*b*]thiophene **3a** was identified to be the sole coupling product with good isolated yield (74%). The corresponding C-2 or C-5-phenylation product was not identified. Based on these promising initial results, we further investigated the scope of the reaction substrate with various arylboronic acids.

Infact, our optimized reaction conditions can be applied to a wide variety of arylboronic acids **2b-g** (Scheme **1**). Arylboronic

Table 1. Screening of the reaction condition for the direct arylation of TT with phenylboronic acid.

Entry	Oxidant (eq.)	Ligand (eq.)	Base (eq.)	Solvent	Temp (°C)	Time (h)	Yield[a] (%)
1	$Cu(OAc)_2$, 0.2	b	K_3PO_4, 3.0 eq	c	140	3	*hc*
2	**TEMPO, 4.0**	**bipy (0.1)**	**-**	**$C_6H_5CF_3$**	**80**	**2.5**	**74**
3	Ag_2O, 4.0	bipy (0.1)	d	$C_6H_5CF_3$	120	5	*nr*
4	H_2O_2, 4.0	bipy (0.1)	d	$C_6H_5CF_3$	120	5	*nr*
5	*m*CPBA, 4.0	bipy (0.1)	d	$C_6H_5CF_3$	120	5	*nr*
6	TEMPO, 4.0	dmbipy (0.1)	-	$C_6H_5CF_3$	120	8	*27*
7	TEMPO, 4.0	phen (0.1)	-	$C_6H_5CF_3$	120	8	*18*
8	TEMPO, 4.0	bipy (0.1)	d	c	100	8	*nr*
9	TEMPO, 4.0	phen (0.1)	d	c	120	12	36
10[e]	TEMPO, 4.0	bipy (0.1)	-	$C_6H_5CF_3$	80	2.5	36
11	TEMPO, 2.0	bipy (0.1)	-	$C_6H_5CF_3$	80	8.0	45

Reagents and conditions: **1** (1.0 eq.), **2a**, $Pd(OAc)_2$ (10 mol%), oxidant, base, solvent, 80-140 °C. *Notes*: [a] Isolated yield. *hc*: homo-coupling of **2a**. *nr*: No reaction. [b] 30 mol% of bipy or dmbipy, or phen. [c] DMSO, or DMAc, or toluene. [d] With or without K_3PO_4. [e] $Pd(OAc)_2$ (5 mol%).

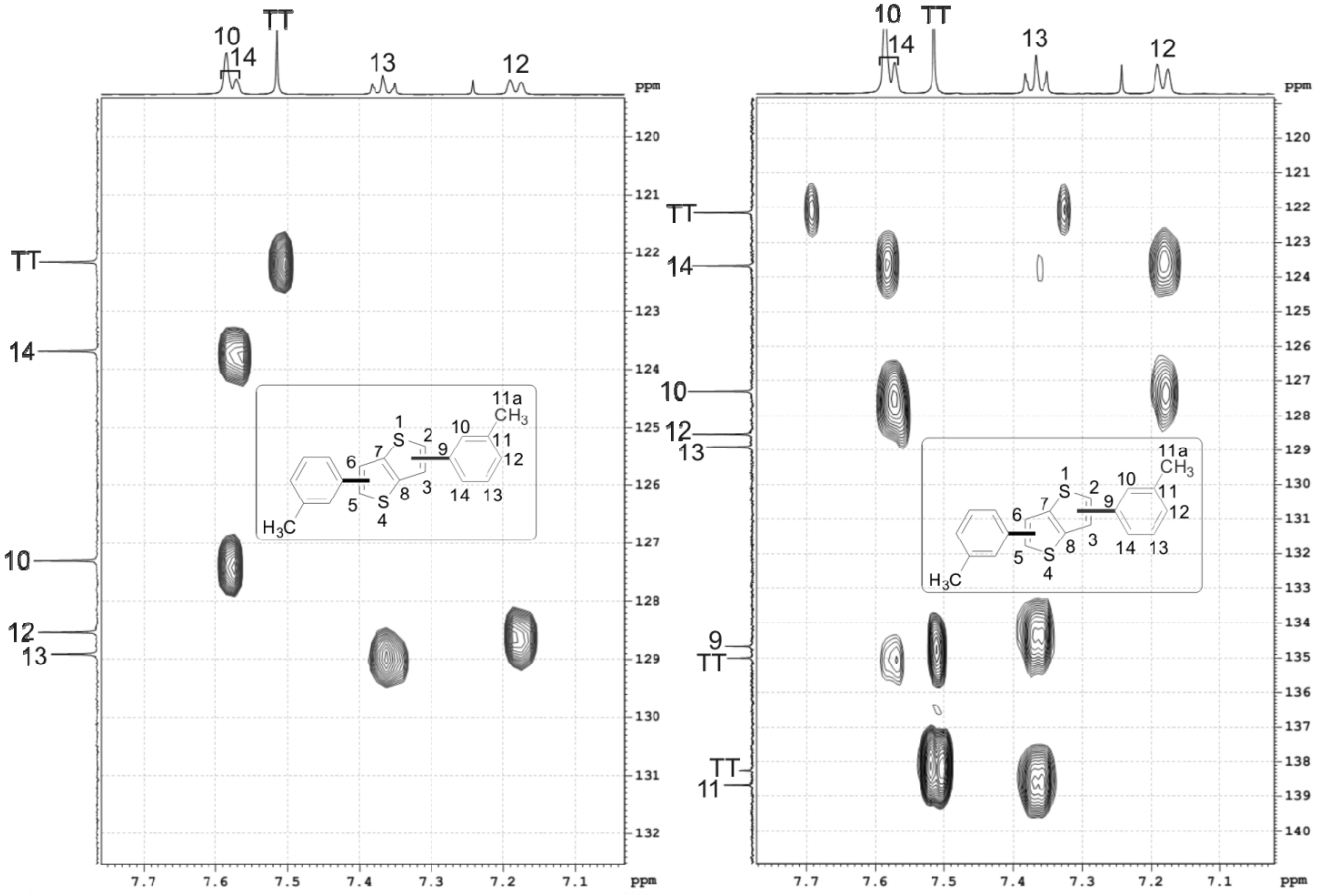


Fig. (2). HSQC (*left*) and HMBC (*right*) spectra of 3g.

acids bearing either electron-withdrawing groups (**2e**) or electron-donating groups (**2a-d**, **2f**, and **2g**) smoothly underwent the direct arylation with high regioselectivity *via* double C-H functionalization at the C-3 and the C-6 positions.

3.2. Structural Analysis

3,6-Di(3-methylphenyl)thieno[3,2-b]thiophene ***3g****:* Compound **3g** has a symmetric structure. Therefore, we observed signals for only half of the molecule. In the ^{1}H NMR spectrum of **3g**, the C-13 proton is undoubtedly assigned at 7.37 ppm as the only triplet in the aromatic range. To differentiate the two couples of the similar protons H3/H10 and H12/H14, the HSQC and HMBC spectra were recorded. The 2D-NMR spectra analysis of **3g** is summarized in Table **2** and Fig. (**2**).

In the HMBC spectrum of **3g**, the methyl carbon C-11a showed two cross-peaks, one with the singlet at 7.59 ppm, and one with the doublet centered at 7.18 ppm (J = 8.0 Hz) which correspond to C-10 and C-12 protons, respectively (*data not shown*). Consequently, the *pseudo* doublet centered at 7.57 ppm (partially overlaped by the singlet of C-10 proton) can be confidentially assigned to the C-14 proton.

Finally, the singlet at 7.52 ppm is assigned to the isolated **TT** proton resonance. This **TT** proton correlates to three quaternary carbons, namely, the C-9 carbon of the aryl moiety and the two other carbons belonging to the **TT** skeleton. These correlations, however, cann't help to reliably locate the remained **TT** proton, or in other words, to determine the regioselectivity of the direct arylation.

Theoretically, either of the two isomers, 2,5-diarylthieno [3,2-*b*]thiophene or 3,6-diarylthieno[3,2-*b*]thiophene, can be formed. To further explore the regioselectivity of the direct arylation reaction, **3b** were recrystalized from $CHCl_3$ to furnish well qualified single crystals. The structure of **3b** as well as the regioselectivity was then unambiguosly clarified by X-Ray crystal structure analysis (Fig. **3**) [14].

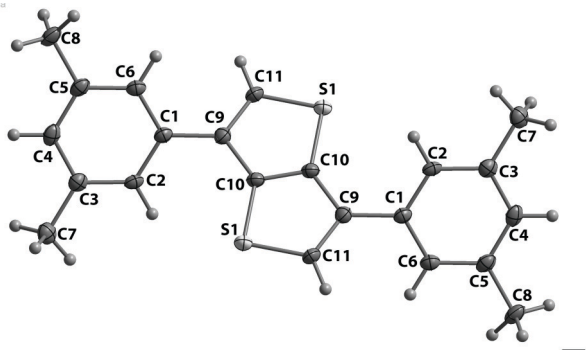
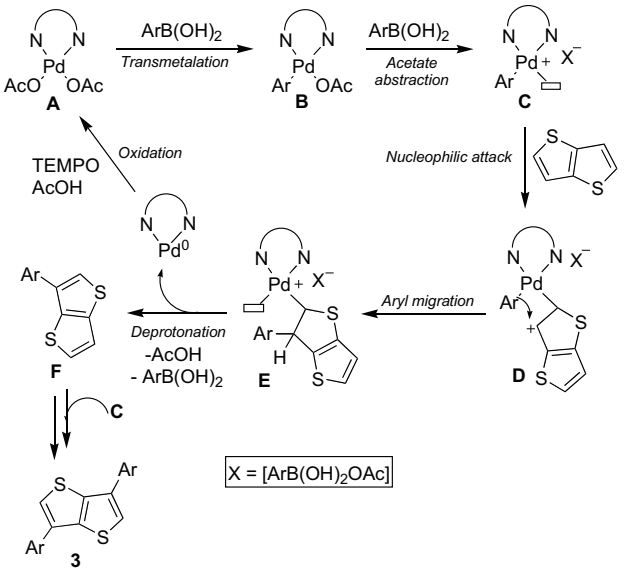


Fig. (3). X-Ray crystal structure of 3b.

Based on related studies, we would like to propose a plausible meachanism for the Pd-catalyzed site-selective double arylation of **TT** (Scheme **2**) [11c]. First, the arylation reaction undergoes an electrophilic addition of the palladium cationic complex to the C-2 position of the **TT** ring. In this step, a resonance-stablized carbocation intermediate **D** is formed which is subsequently attacked by the nucleophilic aryl moiety originated from the boronic acid. Then, the intermediate **E** formed in the carbopalladation step was rearomatized to form the monoarylated **TT** (**F**) by deprotonation and elimination of a [Pd(0)] species that is oxidized to the catalytically active [Pd(II)] (**A**) by TEMPO. The second similar arylation of **F** led to the formation of the 3,6-diarylthieno[3,2-*b*]thiophene **3**. The regioselectivity of this direct C-H double-arylation at the C-3 and C-6 positions of **1** is supported by the excess amounts of the boronic acid [11c].



Scheme (2). Proposed reaction mechanism pathway for the double arylation of thieno[3,2-*b*]thiophene.

CONCLUSION

In conclusion, we have described an efficient method for the site-selective palladium-catalyzed double-arylation reaction of thieno[3,2-*b*]thiophene with various boronic acids. Based on this protocol, a number of symmetric 3,6-diarylthieno[3,2-*b*]thiophenes were synthesized in good

Table 2. HMBC data analysis of 3g.

Carbon		Cross-peaks with Protons	Carbon		Cross-peaks with Protons	Carbon		Cross-peaks with Protons
C	**δ (ppm)**	**H**	**C**	**δ (ppm)**	**H**	**C**	**δ (ppm)**	**H**
C2	135.0	H14, H10	C9	134.7	H3, H13	C12	128.5	H10, H14, H11a
C3	122.1	-	C10	127.3	H14, H12, H11a	C13	128.9	-
C8	138.3	H3	C11	138.7	H13	C14	123.7	H10, H12
						C11a	21.6	H10, H12

yields with C-3 and C-6 regioselectivities. The regioselectivity at the C-3 and C-6 positions was confidentially proven by NMR spectra and X-Ray crystal structure analysis. Concerning the highly efficient approach under mild reaction conditions as well as the importance in functionalization of **TT**s, this research would be interesting and useful for potential applications in material chemistry.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publisher's website along with the published article.

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[14] The crystal structure of **3b** was deposed at the Cambridge Crystallographic Data Center. The data have been assigned to the deposition number CCDC 1519730. They can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.