

A Facile Approach to Site-Selective Direct Alkenylation of Thieno[3,2-*b*]Thiophene by a [Pd]-[Cu]-[Ag] Trimetallic Catalytic System

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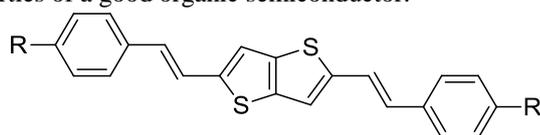
ABSTRACT

In this paper, the synthesis of 2-alkenylthieno[3,2-*b*]thiophene by direct [Pd]-[Cu]-[Ag] catalyzed C-H activation of thieno[3,2-*b*]thiophene with various alkenes was described. The structures of products **3a-f** as well as the site-selectivity of the Heck-type cross-coupling reaction were clarified by NMR and MS analyses.

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Introduction

Thieno[3,2-*b*]thiophene (**TT**) is a stable and electron-rich π -conjugated motif that is a useful building block for the construction of organic semiconductors of different conjugation lengths [1-9]. According to computational studies, **TT** is a p-type semiconductor, considering its high electron injection barrier [10-12]. In the recent decades, the catalytic modification of aromatic heterocycles is an important transformation, and methods for the functionalization of **TT** in particular, have recently received significant attention in the field of organic material science [1-9]. Rod-type oligomers of **TT** in which the **TT** unit is end-capped with styrene moieties having various groups at the para positions were synthesized basing on the Wittig, the Horner-Wadsworth-Emmons, or the palladium-catalyzed Stille reactions (Fig. 1) [13-15]. On the basis of optical measurements, the band gaps of these alkenylated **TTs** ranged from 2.7 to 2.93 eV with charge mobilities of up to $2.6 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ that are required as properties of a good organic semiconductor.



R = H, C₄H₉, C₆H₁₃, C₈H₁₇, *St*-Bu

Figure 1. Co-oligomers containing **TT** used for conjugated organic materials.

Over the last four decades, the Heck reaction of aryl or vinyl halide and an alkene has become one of the most popular C-C bond forming processes in organic synthesis [16-19]. This traditional palladium-catalyzed cross-coupling has, however, several drawbacks concerning the atom-economy and environmental impacts. A pioneering study of direct oxidative Heck reaction between un-halogenated arenes and activated alkenes was reported by Fujiwara and Moritani [20-22]. In 2005, Gaunt and co-workers succeeded in finding conditions for palladium-catalyzed alkenylation of indoles by solvent-

controlled regioselective CH functionalization [23]. In 2013, a facile indole-to-carbazole π -extension via direct alkenylation of indole and subsequent concerted Diels-Alder cycloaddition and oxidation by a [Pd]-[Cu]-[Ag] trimetallic system was described by Itami's group [24].

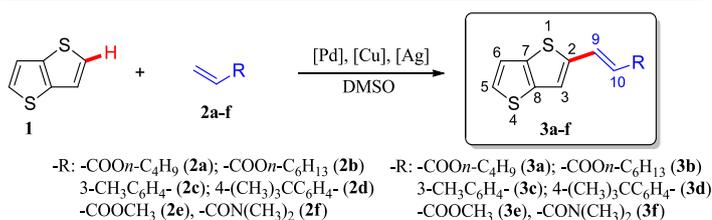
To fine tune the band gap of organic semiconducting polymers, extension of the π system by increasing the conjugated length of the molecule is one of the most efficient strategy. It helps bringing about decreased band gap that is often associated with an increased charge carrier mobility. In terms of atom- and step-economy and a green procedure as well, palladium-assisted C-H activation appears to be straightforward for direct functionalization. Taking these advantages into consideration, we report herein a convenient procedure that allows transforming **TT** selectively to 2-monoalkenyl-**TT** derivatives via [Pd]-[Cu]-[Ag]-catalyzed C-H functionalization.

Experimental section

The title compound thieno[3,2-*b*]thiophene **1** was prepared according to published procedures [25]. Catalysts, solvents and other chemicals were purchased from Sigma-Aldrich or Merck and were used as received otherwise indicated. THF were dried over sodium wire and redistilled in the presence of benzophenone as indicator just before used.

The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer in CDCl₃. Chemical shift was reported in ppm units with tetramethylsilane (TMS) as internal reference. Splitting patterns are designated as s (*singlet*), d (*doublet*), t (*triplet*), quint (*quintet*), sex (*sextet*), and m (*multiplet*). The structures of the synthesized products were elucidated by ¹H and ¹³C NMR in combination with the HMQC and HMBC analyses. HR-MS measurements were performed on a LQT Orbitrap XL using ESI method. MS measurements were acquired on an HPLC-MS Agilent 1100, Agilent Technologies, USA using ESI method. Melting points were measured on a Stuart-Scientific SMP3 apparatus without correction.

2-Alkenylthieno[3,2-*b*]thiophenes **3a-f** were synthesized by C-H activation reaction in 47-75% when a solution of **TT 1** and an alkene **2** in DMSO was treated with Pd(OAc)₂, Cu(OAc)₂, and Ag₂O (Scheme 1).



Scheme 1. Regioselective alkenylation of thieno[3,2-*b*]thiophene **1 with alkenes **2a-f**. Conditions: **1** (1.0 eq.), alkene (3.0 eq.), Pd(OAc)₂ (0.1 eq.), Cu(OAc)₂ (0.2 eq.), Ag₂O (1.0 eq.), DMSO, 100 – 110 °C**

A representative procedure is as follows: A solution of thieno[3,2-*b*]thiophene **1** (28 mg, 0.2 mmol, 1.0 eq.), an alkene **2** (0.6 mmol, 3.0 eq.), Pd(OAc)₂ (4.5 mg, 0.02 mmol, 0.1 eq.), Ag₂O (46.4 mg, 0.2 mmol, 1.0 eq.), and Cu(OAc)₂ (7.28 mg, 0.04 mmol, 0.2 eq.) in DMSO (1.0 mL) was stirred in a closed pressure tube at 100-110 °C for 4 ÷ 8 h. The progress of the reaction was monitored by TLC (*n*-hexane/ethyl acetate). When the starting material was completely consumed as indicated by TLC, the dark brownish mixture was allowed to cool to room temperature, diluted with ethyl acetate and filtered through celite to remove the precipitate. The organic layer was washed with water (three times) and dried over anhydrous Na₂SO₄. After evaporation of the solvent under reduced pressure, the alkenylated thieno[3,2-*b*]thiophenes **3a-f** were isolated by column chromatography on silica gel using suitable eluents. Besides the desired monoalkenyl **TT**, small amounts of dimers of **TT** or ketones were observed due to hydration-oxidation of the C=C alkene. Their presence was proved by ¹H NMR and HR-MS (data not shown).

n-Butyl (*E*)-3-(thieno[3,2-*b*]thiophene-3-yl)acrylate **3a**: Starting from **1** (28 mg, 0.2 mmol) and *n*-butylacrylate (77 mg, 0.6 mmol), **3a** was isolated (40 mg, yield 75%) as a pale yellow liquid (*n*-hexane/ethyl acetate, 99 : 1, v/v). ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.80 (d, 1 H, J = 15.5 Hz), 7.47 (d, 1 H, J = 5.5 Hz), 7.39 (s, 1 H), 7.21 (d, 1 H, J = 5.5 Hz), 6.23 (d, 1 H, J = 15.5 Hz), 4.20 (t, 2 H, J = 6.5 Hz), 1.68 (quint, 2 H, J = 7.5 Hz), 1.43 (sex, 2 H, J = 7.5 Hz), 0.96 (t, 3 H, J = 7.0 Hz). ¹³C NMR (CDCl₃, 125 MHz): δ(ppm) 166.8 (C11), 141.6 (C2), 140.8 (C7), 139.5 (C8), 137.9 (C9), 129.9 (C5), 123.4 (C3), 119.7 (C6), 116.9 (C10), 64.5 (C13), 30.8 (C14), 19.2 (C15), 13.7 (C16) (analyzed with HSQC and HMBC data). HR-MS (ESI-[M+H]) calcd for C₁₃H₁₅O₂S₂ 267.0613, found 267.0653.

n-Hexyl (*E*)-3-(thieno[3,2-*b*]thiophene-3-yl)acrylate **3b**: Starting from **1** (28 mg, 0.2 mmol) and *n*-hexylacrylate (94 mg, 0.6 mmol), **3b** was isolated (41 mg, yield 70%) as a yellow liquid (*n*-hexane/ethyl acetate, 99 : 1, v/v). ¹H NMR (CDCl₃, 500 MHz): δ(ppm) 7.80 (d, 1 H, J = 15.5 Hz, H9), 7.47 (d, 1 H, J = 5.0 Hz), 7.39 (s, 1 H), 7.21 (d, 1 H, J = 5.0 Hz), 6.23 (d, 1 H, J = 15.5 Hz, H10), 4.19 (t, 2 H, J = 6.5 Hz), 1.69 (quint, 2 H, J = 7.5 Hz), 1.40 (m, 2 H), 1.31 (m, 2 H), 0.90 (t, 3 H, J = 6.0 Hz). ¹³C NMR (CDCl₃, 125 MHz): δ(ppm) 166.8 (C=O), 141.6, 140.8, 139.5, 137.9, 129.9, 123.4, 119.7, 116.9, 64.8, 30.5, 28.7, 25.7, 22.6, 14.0.

(*E*)-2-(3-Methylstyryl)thieno[3,2-*b*]thiophene **3c**: Starting from **1** (28 mg, 0.2 mmol) and 3-methylstyrene (71 mg, 0.6 mmol), **3c** was isolated (25 mg, yield 50%) as a pale yellow

solid (*n*-hexane); m.p. 164-166 °C. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.35 (d, 1 H, J = 5.0 Hz, H5), 7.29 (br s, 1 H, H15), 7.27 (br s, 1 H, H12), 7.24 (d, 1 H, J = 7.5 Hz, H9), 7.23 (d, 1 H, J = 15.5 Hz, H9), 7.20 (d, 1 H, J = 5.0 Hz, H6), 7.19 (s, 1 H, H3), 7.07 (d, 1 H, J = 7.0 Hz, H16), 6.89 (d, 1 H, J = 16.0 Hz, H10). ¹³C NMR (CDCl₃, 125 MHz): δ(ppm) 145.3 (C11), 139.5 (C7), 138.3 (C2), 137.9 (C8), 136.7 (C13), 128.64 (C10), 128.61 (C14), 128.59 (C16), 127.3 (C5), 127.1 (C15), 123.6 (C12), 122.4 (C9), 119.6 (C6), 118.3 (C3), 21.4 (CH₃) (analyzed with HSQC and HMBC data).

(*E*)-2-(4-*tert*-Butylstyryl)thieno[3,2-*b*]thiophene **3d**: Starting from **1** (28 mg, 0.2 mmol) and 4-*tert*-butylstyrene (96 mg; 0.6 mmol), **3d** was isolated (28 mg, yield 47%) as a pale yellow solid (*n*-hexane); m.p. = 143-145 °C. ¹H NMR (CDCl₃, 500 MHz): δ(ppm) 7.41 (d, 2 H, J = 8.5 Hz, Ph), 7.37 (d, 2 H, J = 8.5 Hz, Ph), 7.34 (d, 1 H, J = 5.0 Hz, **TT**), 7.22 (d, 1 H, J = 16.5 Hz, H9), 7.20 (d, 1 H, J = 5.5 Hz, **TT**), 7.19 (s, 1 H, **TT**), 6.91 (d, 1 H, J = 16.0 Hz, H10), 1.32 (s, 9 H, *t*-Bu). ¹³C NMR (CDCl₃, 125 MHz): δ(ppm) 151.0, 145.5, 139.5, 137.8, 134.0, 128.3, 127.2, 126.2, 125.7, 121.8, 119.6, 118.1, 34.7 (*tert*-C), 31.3 (CH₃). MS (ESI-[M+H]) calcd for C₁₈H₁₉S₂ 299.0, found 299.0.

Methyl (*E*)-3-(thieno[3,2-*b*]thiophene-3-yl)acrylate **3e**: Starting from **1** (28 mg, 0.2 mmol) and methyl acrylate (52 mg, 0.6 mmol), **3e** was isolated (28 mg, yield 62%) as a yellow solid (*n*-hexane/ethyl acetate, 99 : 1, v/v); m.p. 78-80 °C. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.82 (d, 1 H, J = 16.0 Hz, H9), 7.48 (d, 1 H, J = 5.5 Hz, **TT**), 7.41 (s, 1 H, **TT**), 7.23 (d, 1 H, J = 5.0 Hz, **TT**), 6.24 (d, 1 H, J = 15.5 Hz, H10), 3.80 (s, 3 H, -OCH₃). ¹³C NMR (CDCl₃, 125 MHz): δ(ppm) 167.2 (C=O), 141.5, 140.9, 139.5, 138.2, 130.1, 123.6, 119.7, 116.3, 51.7 (OCH₃).

(*E*)-*N,N*-Dimethyl-3-(thieno[3,2-*b*]thiophene-2-yl)acrylamide **3f**: Starting from **1** (28 mg, 0.2 mmol) and *N,N*-dimethyl acrylamide (60 mg, 0.6 mmol), **3f** was isolated (21 mg, yield 45%) as a brownish yellow solid (CHCl₃/CH₃OH, 99 : 1, v/v); m.p. 129-131 °C. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.83 (d, 1 H, J = 15.0 Hz, H9), 7.45 (d, 1 H, J = 5.5 Hz, **TT**), 7.37 (s, 1 H, **TT**), 7.22 (d, 1 H, J = 5.0 Hz, **TT**), 6.68 (d, 1 H, J = 15.0 Hz, H10), 3.17 (s, 3 H, NCH₃), 3.07 (s, 3 H, NCH₃). ¹³C NMR (CDCl₃, 125 MHz): δ(ppm) 166.2 (C=O), 142.5, 139.8, 139.5, 136.1, 129.4, 122.8, 119.6, 115.9, 37.4, and 35.9 (NCH₃). HR-MS (ESI-[M+H]) calcd for C₁₁H₁₂NOS₂ 238.0, found 237.9.

Results and discussion

Synthesis

We began our investigation of the reaction between **TT 1** and *n*-butyl acrylate **2a** following Gaunt's condition [23]. The alkenylation was conducted in the presence of Pd(OAc)₂ as the catalyst and Cu(OAc)₂ as the oxidant (entry 1, Table 1).

Unfortunately, under this present condition, no conversion was recognized. The use of the Lewis acid AgOCOCF₃ as an additive in combination with Pd(OAc)₂ and Cu(OAc)₂ has been described in the conversion of indole to carbazole by Itami *et al.* [24]. Therefore, this Lewis acid was chosen in our next attempt to directly alkenylate **1** (entries 2-7, Table 1). Indeed, the alkenylation occurred smoothly and regioselectively at the C-2 position in up to 45% yield (entries 2 and 6, Table 1). Decreasing the amounts of each component of the catalytic mixture (Pd(OAc)₂ to 0.05 eq., Cu(OAc)₂ to 0.1 eq., or AgOCOCF₃ to 2.0 eq.) resulted in lowered yields of **3a** (entry 3, 4, and 5, Table 1).

Due to the fact that AgOCOCF₃ was expensive but must be used in excess (4.0 eq.),

We then made a trial with Ag₂O as the additive (*entries 8-14*, Table 1). To our delightfulness, when the reactions were carried out at 100 °C in about 4 - 8 hours, higher reaction yields were achieved (*entry 10, 11 and 14*, Table 1). Increasing the reaction temperature over 120 °C or prolonging the

reaction time to 24 hours didn't improve the reaction yields (*entries 11 and 14*, Table 1). The use of other additives, such as AgNO₃, Ag₂CO₃, or AgOAc proved to be much less efficient (*data not shown*).

Table 1. Optimization of the oxidant and additive in the direct alkenylation reaction

Entry	Pd(II) (eq.)	Cu(II) (eq.)	AgOCOCF ₃ (eq.)	T/time (°C/h)	Yield* (%)	Entry	Pd(II) (eq.)	Cu(II) (eq.)	Ag ₂ O (eq.)	T/time (°C/h)	Yield* (%)
1	0.1	0.2	0	100/14	-	8	0.1	0.2	4	100/14	-
2	0.1	0.2	4	100/14	45	9	0.1	0.2	0.5	80/20	20
3	0.05	0.2	4	100/14	15	10	0.1	0.2	1	100/8	70
4	0.1	0.1	4	100/14	18	11	0.5	0.2	1	100/24	60
5	0.1	0.2	2	100/14	25	12	0.1	0.1	1	100/14	45
6	0.1	0.2	4	100/24	46	13	0.5	0.1	1	100/14	32
7	0.1	0.2	4	80/30	41	14	0.1	0.2	1	120/8	60

Note: **TT 1** and *n*-butyl acrylate were used with 1.0 eq. and 10 eq., respectively. All reactions were conducted in DMSO. * Isolated yields after column chromatography.

Table 2. Optimization of the ratio of alkene 2 and the solvent in the alkenylation reaction

Entry	2a (eq.)	Solvent	Yield* (%)	Entry	2a (eq.)	Solvent	Yield* (%)
1	10	DMSO	41	5	3	DMSO/toluene (9/1; v/v)	33
2	5	DMSO	53	6	3	DMSO/toluene (5/5; v/v)	20
3	3	DMSO	75	7	3	DMSO/toluene (1/9; v/v)	11
4	2	DMSO	65	8	3	Toluene	trace

Note: **TT 1** was used with 1.0 eq. in all reactions. *n*-Butyl acrylate **2a** was used in the optimization. The amounts of Pd(OAc)₂, Cu(OAc)₂, and Ag₂O are used as shown in the optimized condition – entry 10, Table 1. * Isolated yields after column chromatography.

Further screening showed that the optimized ratio of the alkene was 3.0 eq.. It is also noted that the use of DMSO as solvent is critical for high-yield formation of **3a-f**. Bad conversion was observed when the alkenylation was conducted in toluene or in a DMSO-toluene mixed solvent system (*entry 5-8*, Table 2).

Under this optimized condition, both electron-rich alkenes (**2c,d**) and electron-deficient alkenes (**2a,b,e,f**) led to the formation of the desired cross-coupling products by direct activation of the C2-H (see the Structural analysis section). The presence of the three metallic compounds, [Pd], [Cu], and [Ag], in the catalytic system is crucial to furnish the alkenylated **TTs**. Among the different alkenes employed, electron-deficient acrylates **2a,b,e**, and **f** reacted with **1** efficiently to produce the desired C-2-alkenylated products **3a,b,e**, and **f** in 47–75% yield. On the contrary, the reactions of the two styrene derivatives, **2c** and **2d**, were relatively sluggish, yielding **3c** and **3d** in moderate yields (47-50%) even after longer reaction times. These styrenes were prone to undergo unidentified hydration-oxidation under the mentioned reaction conditions. Besides, the *cis-trans* isomerization of the styryl-substituted **TT** was observed in CDCl₃ solution due to the slightly acidic medium of this solvent under storage.

During our progress, Morita *et al.* also reported on the alkenylation reaction of three fused heterocycles, including **TT**, by CH functionalization [26]. In their procedure, a mixture of **TT 1** (1.0 eq.), an alkene (2.0 eq.), Pd(OAc)₂ (0.1 eq.), and AgOAc (2 eq.) in the halogenated solvent 2,2,2-trifluoroethanol (TFE) was stirred under nitrogen atmosphere to afford several 2-alkenylated **TTs** after 24 hours. In our procedure, the alkenylation of **TT** was easily achieved with various alkenes (3 eq.) in the presence of Pd(OAc)₂ (0.1 eq.),

Cu(OAc)₂ (0.2 eq.), and Ag₂O (1.0 eq.) in a more eco-friendly solvent DMSO. After the reaction, the solvent was conveniently removed by simple aqueous extraction. In addition, the alkenylation discovered by us can be carried out under atmospheric condition in significantly shorter reaction times (from about 4 to 8 hours). In terms of simplicity and the scope of substrates, our trimetallic-catalytic system was proved to be effective, resulting in comparable reaction yields with those of Morita's group.

Structural analysis of 2-alkenylthieno[3,2-*b*]thiophene **3a-f**

Theoretically, either of the two alkenylthieno[3,2-*b*]thiophene isomers (**A**) or (**B**) can be formed as the C2-H or C3-H can be activated, respectively. To determine the alkenylation regioselectivity, HSQC and HMBC spectra of **3a** were recorded and analyzed as shown in Figure 2 and Table 3.

In the ¹H NMR spectrum of **3a**, the signals of the two olefinic protons at the C-9 and C-10, and the remaining proton of the **TT** moiety at the C-3 can be easily recognized. Concretely, the C-9 and C-10 proton signals appear as two doublets centered at 7.80 and 6.23 ppm, respectively. The typically high *J* value (15.5 Hz) of these doublets indicated the *trans* conformation of the newly formed C-C double bond. The **TT** proton resonance is undoubtedly assigned at 7.39 ppm as the only singlet in the aromatic range.

Notably, the **TT** proton correlates to four quaternary carbons, namely, the C-9 and the three other carbons belonging to the **TT** skeleton. This correlation proved that the left-over **TT** proton must be at the C-3 position. In other words, the direct alkenylation took place regioselectively at the C-2 position of the fused thiophenes. If the remaining **TT** proton were at the C-2 position, it wouldn't show cross-peaks with as many quaternary carbons as observed.

To further determine the regioselectivity, we tried to recrystallize the obtained alkenylated thieno[3,2-*b*]thiophenes. All attempts to produce qualified crystals for X-Ray analysis were, unfortunately, failed. Hence, an indirect strategy was followed. Thus, 2-iodothieno[3,2-*b*]thiophene was synthesized by iodination of **TT** with NIS in CH₃COOH [27].

The resulting 2-iodothieno[3,2-*b*]thiophene was subjected

to the traditional palladium-catalyzed Heck reaction with 4-*tert*-butylstyrene (Conditions: 2-iodothieno[3,2-*b*]thiophene 1.0 eq., 4-*tert*-butylstyrene 6.0 eq., Pd(OAc)₂ 0.1 eq., PCy₃ 0.2 eq., DMF, 80 °C, under argon, 24 h). As expected, the resulting Heck cross-coupling product showed identical ¹H NMR spectrum with that of the direct alkenylation product **3d**.

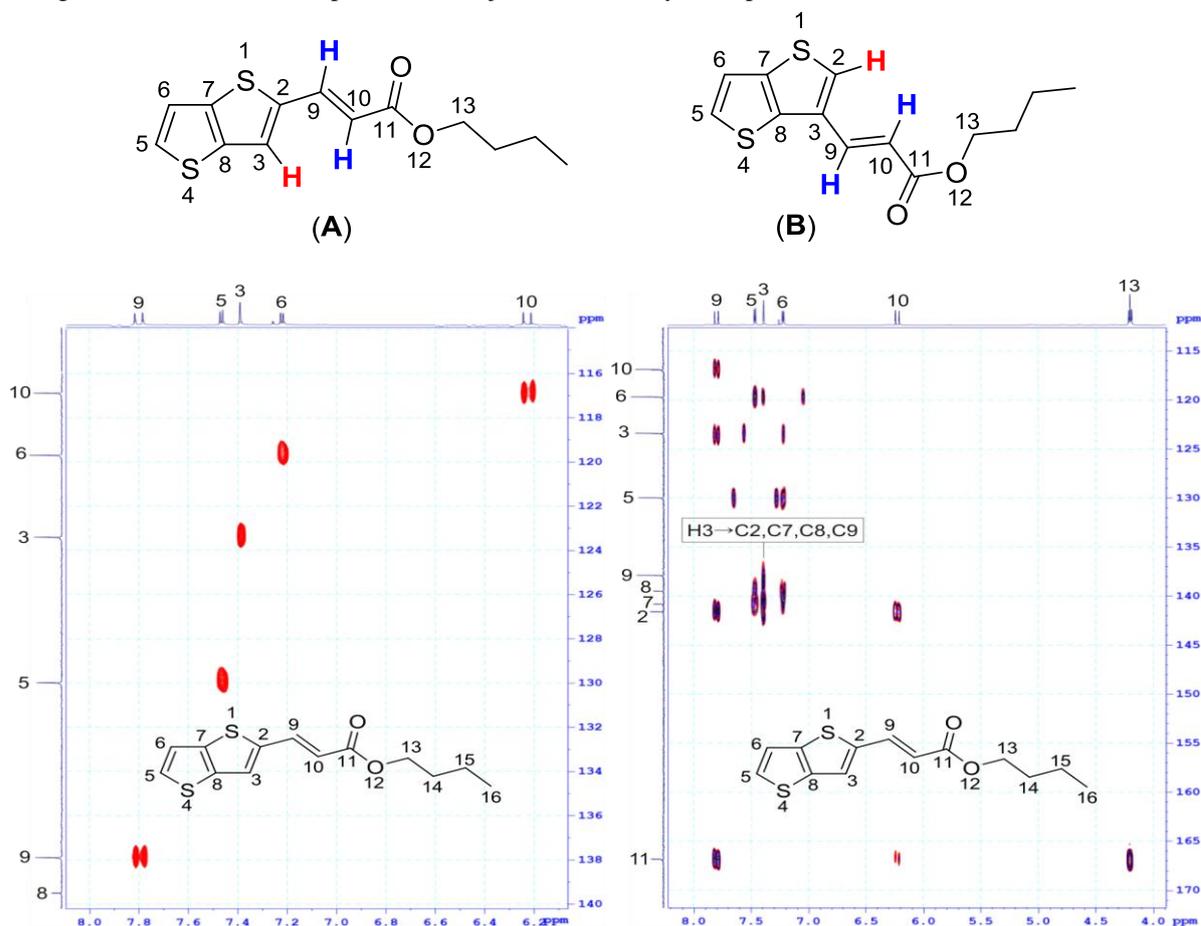


Figure 2. HSQC (left) and HMBC (right) spectra of **3a**

Table 3. HMBC analysis of **3a**

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	141.6	H3, H9, H10	C8	139.5	H3, H6	C14	30.8	H13, H15, H16
C3	123.4	H9	C9	137.9	H3	C15	19.2	H13, H14, H16
C5	129.9	H6	C10	116.9	H9	C16	13.7	H14, H15
C6	119.7	H5	C11	166.8	H9, H10, H13	-	-	-
C7	140.8	H3, H5, H6	C13	64.5	H14, H15	-	-	-

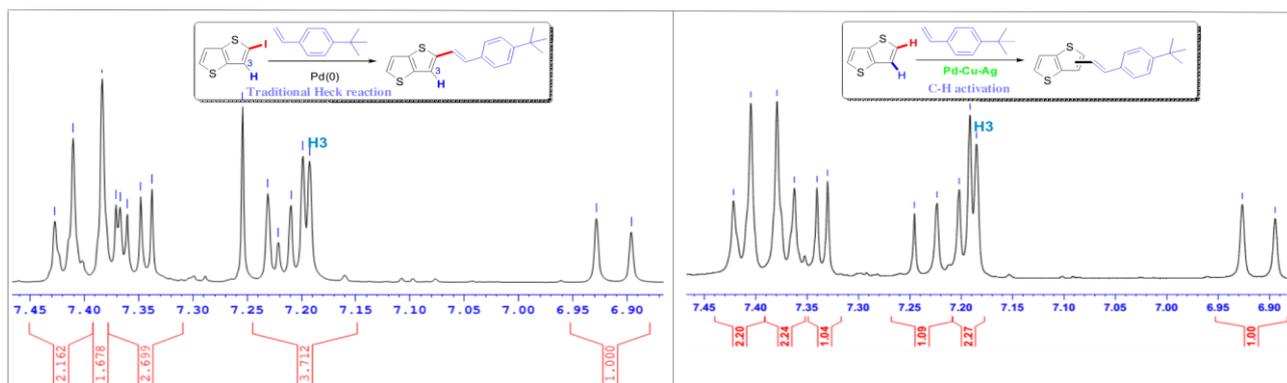


Figure 3. ¹H NMR spectra of the Heck cross-coupling product (left) and **3a** (right)

The regioselectivity reported herein can be explained based on the different electronic property of the two different C-H bonds of **1**. The C-H bonds at the C-2 and C-5 positions are more reactive than those at the C-3 and C-6 positions as the formers are more electron-deficient [23,24].

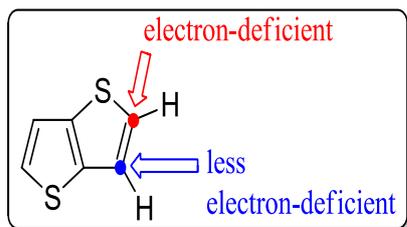


Figure 4. Possible explanation for the site-selectivity of **1 in direct alkenylation reaction**

Conclusion

In summary, the optimization for a Heck-type alkenylation of thieno[3,2-*b*]thiophene was described. Under the optimized condition, desired 2-alkenylthieno[3,2-*b*]thiophenes **3a-f** were conveniently obtained from both electron-rich and electron-deficient alkenes in moderate to good yields by [Pd]-[Cu]-[Ag]-catalyzed CH functionalization. The structural elucidation as well as the alkenylation regioselectivity was solved by means of NMR and MS analyses. Spectroscopic data unambiguously indicated that the CH functionalization took place preferentially at the C-2 position, resulting in the formation of *trans*-alkenes.

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