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SYNTHESIS OF SOME MONO AND DIALKYNYL DERIVATIVES CONTAINING THIENO[3,2-*b*]THIOPHENE RING VIA SONOGASHIRA ALKYNYLATION REACTION

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ABSTRACT

*The Sonogashira cross-coupling reactions were used to synthesize 5 new monoalkynyl derivatives (**10a-e**) and 2 dialkynyl derivatives (**12a-b**) containing thieno[3,2-b]thiophene from monoaryl thieno[3,2-b]thiophen in moderate yield. The procedure was optimized and triphenylphosphine (0.2 eq.), palladium diacetate (0.1 eq), copper (I) iodide (0.2 eq.), THF, iPr_2NH were found to be the best in these cases. The structures of the (**10a-e**) and (**12a-b**) compounds were elucidated by ^1H and ^{13}C NMR and mass spectral analysis.*

Keywords: alkynylthiophene, cross-coupling reaction, monoarylthiophene, Sonogashira reaction, thieno[3,2-*b*]thiophene.

TÓM TẮT

Tổng hợp một vài dẫn xuất monoankinyl và điankinyl có chứa vòng thieno[3,2-b]thiophen bằng phản ứng ghép chéo Sonogashira

*Phản ứng ghép chéo Sonogashira được dùng để tổng hợp được 5 dẫn xuất mới monoankin (**10a-e**) và 2 dẫn xuất điankin (**12a-b**) có chứa dị vòng thieno[3,2-b]thiophen với hiệu suất trung bình. Điều kiện phản ứng được nghiên cứu tối ưu hóa là triphenylphosphin (0.2 eq.), paladi điaxetat (0.1 eq), đồng (I) iodide (0.2 eq.), THF, iPr_2NH là điều kiện tốt cho phản ứng này. Cấu trúc của các hợp chất mới được nghiên cứu bằng phổ ^1H, ^{13}C NMR và phổ khối lượng.*

Từ khóa: ankinylthiophen, phản ứng ghép chéo, monoarylthiophen, phản ứngnSonogashira, thieno[3,2-*b*]thiophen.

1. Introduction

The small band gap of organic semiconducting polymers has been a challenge for scientists. To overcome this problem, extension of the π system by increasing the conjugated length of the molecule is one of the most efficient approaches. Thieno[3,2-*b*]thiophene is a stable and electron-rich π-conjugated core with four carbon atoms that is a

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useful building block for the construction of organic semiconductors with different conjugation lengths by extending the conjugation length. Shi *et al.* reported Sn-TIPS as a new high performance semiconductor; Figure 1 (left) [1].

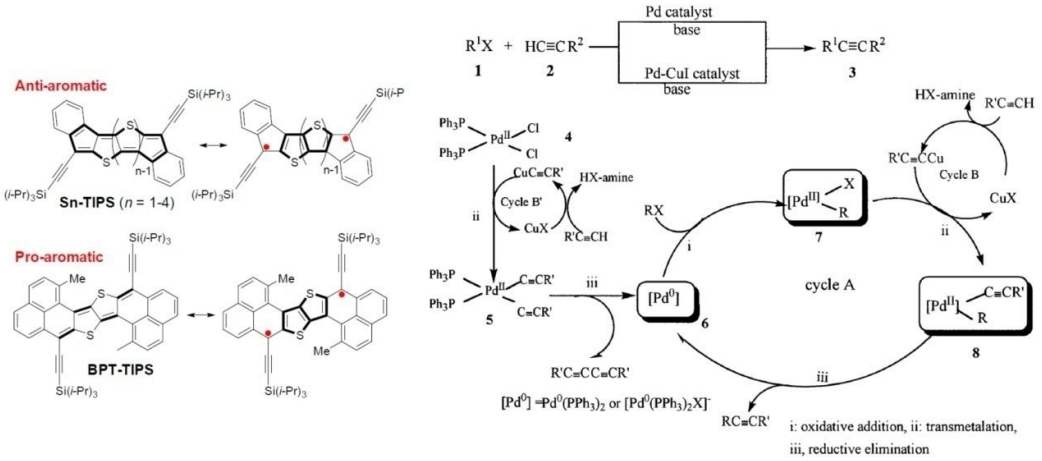


Figure 1. *Structures of anti-aromatic bisindeno-thienoacenes* ***Sn-TIPS*** *(n = 1-4) and proaromatic bisphenaleno-thieno[3,2-b]thiophene* ***BPT-TIPS****[1] andPd-catalyzed cross-coupling reactions of* sp^2*-C halides with terminal acetylenes and Outline of the reaction scheme for Pd–Cu catalyzed cross-coupling of* sp^2*-C halides with terminal acetylenes [2].*

By the same manner, McCulloch *et al.* synthesized liquid-crystalline semiconducting polymer (PBTTT) containing thieno[3,2-*b*]thiophene moieties with a very high charge-carrier mobility [3]. Another example, dinaphtho[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DNTT) and alkylated benzothieno[3,2-*b*][1]benzothiophene (C13BTBT) were proved to be an effective to make a very high thin film mobility of 3.1 cm^2/Vs and 17.2 cm^2/Vs, respectively, in VD-OFETs [4,5].

One of the best tools to build the conjugation system is the Sonogashira reaction, which is a powerful method to make C_{sp}–C_{sp2} bond [2, 6, 7]. Reaction and mechanism were performed in Figure 1 (right) including three bases steps: i-oxidative addition; ii-transmetalation, iii-reductive elimination. In this paper we were interested in using Sonogashira in making C_{sp}-C_{sp2} bond based C-Br bond and -C≡C-H one between monoalkylthiophene and alkynes.

2. Experimental

2.1. Experimental section

Solvents and other chemicals were purchased from Sigma-Aldrich, Merck were used as received, unless indicated. The ^1H NMR and ^{13}C NMR spectra were recorded on the Bruker Avance 500 NMR spectrometer in $CDCl_3$. Chemical-shift data for each signal was

reported in ppm units. Mass spectra were obtained from Mass Spectrometry Facility of The Vietnam Academy of Science and Technology on LC-MSD-Trap-SL spectrometer.

2.2. Synthetic procedure

General procedure:

To the argon degassed solution of THF (6 mL) and iPr_2NH (6 mL) was added 2,3,6-tribromo-5-(1,2-dihydroacenaphthylen-6-yl)thieno[3,2-b]thiophene or 2,3,6-tribromo-5-(naphthalen-1-yl)thieno[3,2-b]thiophene (0.25 mmol, 1 eq.), Ph_3P (13.1 mg, 0.05 mmol, 0.2 eq., 262 g/mol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.1 eq., 224 g/mol), CuI (10 mg, 0.05 mmol, 0.2 eq., 190 g/mol). The resulting solution was refluxed to dissolve all substrates and reagents. The reaction solution was added slowly alkynes (1.2 eq.) then refluxed at 75 °C for 2-3 h. The progress of reaction was monitored by TLC (eluent: n-hexane). The mixture was concentrated *in vacuo*. The products were purified with column chromatography.

*Synthesis of 3,6-dibromo-2-(1,2-dihydroacenaphthylen-6-yl)-5-(2-phenylethynyl)thieno [3,2-b]thiophene (**10a**)*

Following the general procedure, using 2,3,6-tribromo-5-(1,2-dihydroacenaphthylen -6-yl)thieno[3,2-b]thiophene (**9a**, 132 mg, 0.25 mmol, 1 eq., 529 g/mol), Ph_3P (13.1 mg, 0.05 mmol, 0.2 eq., 262 g/mol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.1 eq., 224 g/mol), CuI (10 mg, 0.05 mmol, 0.2 eq., 190 g/mol) and 1-ethynylbenzene (30.6 mg, 0.30 mmol, 1.2 eq., 102 g/mol) gave **10a** as a pale yellow powder (58 mg, 550 g/mol, 42%), mp. 188 °C. IR (cm^{-1}, KBr): 3100, 2924, 2874, 1717, 1601, 1456. ^1H NMR ($CDCl_3$, 500 MHz) δ (ppm): 7.60 (d, J = 8.0 Hz, 2H), 7.59 (m, 1H), 7.55 (d, J = 7.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.38 (m, 1H), 7.35 (t, J = 7.0 Hz, 2H), 3.45 (s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 148.6, 146.4, 140.6, 139.3, 139.2, 137.9, 131.6, 131.3, 129.9, 129.0, 128.8, 128.5, 125.1, 122.3, 121.3, 121.0, 120.6, 118.8, 108.7, 102.9, 98.8, 30.5, 30.3.

*Synthesis of 3,6-dibromo-2-(1,2-dihydroacenaphthylen-6-yl)-5-(2-m-tolylethynyl) thieno[3,2-b]thiophene (**10b**)*

Following the general procedure, using 2,3,6-tribromo-5-(1,2-dihydroacenaphthylen -6-yl)thieno[3,2-b]thiophene (**9a**, 132 mg, 0.25 mmol, 1 eq., 529 g/mol), Ph_3P (13.1 mg, 0.05 mmol, 0.2 eq., 262 g/mol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.1 eq., 224 g/mol), CuI (10 mg, 0.05 mmol, 0.2 eq., 190 g/mol) and 1-ethynyl-3-methylbenzene (34.8 mg, 0.30 mmol, 1.2 eq., 116 g/mol) gave **10b** as a yellow powder (63.5 mg, 564 g/mol, 45 %), mp. 182.5 °C. IR (cm^{-1}, KBr): 3043, 2930, 2830, 1640, 1600, 1522, 1424. ^1H NMR($CDCl_3$, 500 MHz) δ (ppm): 7.60 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.0 Hz, 1H), 7.50 (d, J = 7.0 Hz, 1H), 7.48 (t, J = 7.0 Hz, 1H), 7.42 (s, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.0 Hz, 2H), 72.6 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 3.45 (s, 4H), 2.37 (s, 3H); ^{13}C NMR

($CDCl_3$, 125 MHz) δ (ppm): 148.5, 146.4, 140.5, 139.3, 139.1, 138.2, 137.8, 132.1, 131.3, 129.9, 128.7, 128.7, 128.3, 125.1, 122.0, 121.4, 121.0, 119.9, 118.8, 108.6, 102.9, 99.1, 81.3, 30.5, 30.3, 21.2.

*Synthesis of 3,6-dibromo-2-(1,2-dihydroacenaphthylen-6-yl)-5-(2-p-tolylethynyl)thieno [3,2-b]thiophene (**10c**)*

Following the general procedure, using 2,3,6-tribromo-5-(1,2-dihydroacenaphthylen-6-yl)thieno[3,2-b]thiophene (**9a**,132 mg, 0.25 mmol, 1 eq., 529 g/mol), Ph_3P (13.1 mg, 0.05 mmol, 0.2 eq., 262 g/mol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.1 eq., 224 g/mol), CuI (10 mg, 0.05 mmol, 0.2 eq., 190 g/mol) and1-ethynyl-4-methylbenzene (34.8 mg, 0.30 mmol, 1.2 eq., 116 g/mol) gave **10c** as a pale yellow powder (43.7 mg, 564 g/mol, 31%), mp. 181 °C. IR (cm^{-1}, KBr): 3029, 2917, 2853, 1725, 1672, 1595, 1498, 1340; ^1H NMR ($CDCl_3$, 500 MHz)δ (ppm): 7.60 (d, *J* = 8.0 Hz, 1H),7.55 (d, *J* = 8 Hz, 1H),7.49 (d, *J* = 8.0 Hz, 2H),7.49 (m, 1H),7.35 (t, *J* = 7.0 Hz, 2H),7.19 (d, *J* = 8.0 Hz, 2H),3.45 (s, 4H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm):148.5, 146.4, 140.3, 139.3, 138.9, 137.8, 132.3, 131.5, 131.4, 131.3, 129.9, 129.2, 128.7, 125.1, 121.5, 121.0, 119.9, 119.2, 118.8, 108.4, 102.9, 99.1, 81.1, 30.5, 30.3, 29.7, 21.6.

*Synthesis of 3,6-dibromo-2-(1,2-dihydroacenaphthylen-6-yl)-5-(2-(2-methoxynaphthalen-6-yl)ethynyl)thieno[3,2-b]thiophene (**10d**)*

Following the general procedure, using 2,3,6-tribromo-5-(1,2-dihydroacenaphthylen-6-yl)thieno[3,2-b]thiophene (**9a**, 132 mg, 0.25 mmol, 1 eq., 529 g/mol), Ph_3P (13.1 mg, 0.05 mmol, 0.2 eq., 262 g/mol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.1 eq., 224 g/mol), CuI (10 mg, 0.05 mmol, 0.2 eq., 190 g/mol) and 2-ethynyl-6-methoxynaphthalene (54.6 mmg, 0.30 mmol, 1.2 eq., 182 g/mol) gave **10d** as a pale yellow powder (24 mg, 630 g/mol, 15%), mp. 185 °C. IR (cm^{-1}, KBr): 3070, 2925, 2862, 1728, 1597, 1452. ^1H NMR ($CDCl_3$, 500 MHz)δ (ppm): 8.05 (s, 1H), 7.74 (t, *J* = 8.5 Hz, 2H),7.60 (t, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 1H),7.50 (t, *J* = 7.0 Hz, 1H),7.36 (t, *J* = 7.5 Hz, 2H),7.19 (dd, *J* = 9.0 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H), 3.46 (s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm):158.7, 148.6, 146.4, 140.4, 139.3, 139.0, 137.9, 134.5, 131.6, 131.3, 129.9, 129.5, 128.7, 128.6, 128.4, 127.0, 125.1, 121.6, 121.0, 120.0, 119.6, 118.5, 117.1, 108.5, 05.9, 102.9, 99.6, 81.4, 55.4, 30.5, 30.3. MS (ESI): calcd. for $[M+H]^+$, $[C_{31}H_{19}Br_2OS_2]^+$, 631, found 631; calcd. for $[M-H]^-$, $[C_{31}H_7Br_2OS_2]^-$, 629, found 629.

*Synthesis of 3,6-dibromo-2-(naphthalen-1-yl)-5-(2-m-tolylethynyl)thieno[3,2-b]thiophene (**10e**)*

Following the general procedure, using 2,3,6-tribromo-5-(naphthalen-1-yl)thieno[3,2-*b*]thiophene (**9b**, 126 mg, 0.25 mmol, 1 eq., 503 g/mol), Ph_3P (13.1 mg,

0.05 mmol, 0.2 eq., 262 g/mol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.1 eq., 224 g/mol), CuI (10 mg, 0.05 mmol, 0.2 eq., 190 g/mol)and 1-ethynyl-3-methylbenzene (30.6 mmg, 0.30 mmol, 1.2 eq., 116 g/mol) gave **10e** as a pale yellow powder (35 mg, 538 g/mol, 27%), mp. 181 °C. IR (cm^{-1}, KBr): 3057, 2930, 2852, 1730, 1590, 1487.^{1}H NMR ($CDCl_3$, 500 MHz)δ (ppm): 7.98 (dd, *J* = 7.5, 1.5 Hz, 1H),7.94 (dd, *J* = 7.5, 2.0 Hz, 1H),7.83 (dd, *J* = 8.0, 1.5 Hz, 1H),7.59 - 7.50 (m,4H),7.43 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H),7.28 (t, *J* = 7.5 Hz, 1H),7.20 (d, *J* = 7.5 Hz, 1H), 2.38 (s, 3H);^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 140.3, 138.87, 133.6, 132.1, 131.7, 130.1, 130.0, 129.8, 129.6, 128.9, 128.7, 128.46, 128.40, 126.9, 126.4, 125.8, 125.0, 122.0, 121.7, 108.5, 103.8, 99.2, 81.2, 21.2; MS (ESI): calcd. for $[M+H]^+$, $[C_{25}H_{15}Br_2S_2]^+$, 539, found 539; calcd. for$[M-H]^-$, $[C_{25}H_{13}Br_2S_2]^-$, 537, found 537.

Synthesis of dialkynyl derivatives containing thieno[3,2-b]thiophene

General procedure: To the argon degassed solution of THF (6 mL) and iPr_2NH (6 mL) was added 2,3,6-tribromo-5-phenylthieno[3,2-*b*]thiophene (**11**, 132 mg, 0.25 mmol, 1 eq., 529 g/mol), Ph_3P (13.1 mg, 0.05 mmol, 0.2 eq., 262 g/mol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.1 eq., 224 g/mol), CuI (10 mg, 0.05 mmol, 0.2 eq., 190 g/mol). The resulting solution was refluxed to dissolve all substrates and reagents. The the reaction solution was added slowly alkynes (2.5 eq.) then refluxed at 75 °C for 2-3 h. The progress of reaction was monitored by TLC (eluent: *n*-hexane). The mixture was concentrated *in vacou*. The products were purified with column chromatography.

*Synthesis of 3-bromo-2-phenyl-5,6-bis(2-phenylethynyl)thieno[3,2-b]thiophene (**12a**)*

Following the general procedure, using 2,3,6-tribromo-5-phenylthieno[3,2-*b*]thiophene (**11**, 113 mg, 0.25 mmol, 1 eq., 453 g/mol), Ph_3P (13.1 mg, 0.05 mmol, 0.2 eq., 262 g/mol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.1 eq., 224 g/mol), CuI (10 mg, 0.05 mmol, 0.2 eq., 190 g/mol) and 1-ethynylbenzene (61.2 mmg, 0.30 mmol, 2.5 eq., 102 g/mol) gave **12a** as a pale yellow powder (25 mg, 495 g/mol, 20%), mp. 150 °C.^{1}H NMR ($CDCl_3$, 500 MHz)δ (ppm): 7.72 (m, 2H), 7.60 (m, 4H), 7.47 (m, 2H), 7.42 (m, 1H), 7.37 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 141.5, 140.1, 136.6, 132.9, 131.8, 131.5, 128.97, 128.93, 128.89, 128.84, 128.77, 128.49, 128.47, 126.8, 122.6, 122.5, 119.9, 99.7, 99.5, 96.5, 81.7.

*Synthesis of 3-bromo-2-phenyl-5,6-bis(2-m-tolylethynyl)thieno[3,2-b]thiophene (**12b**)*

Following the general procedure, using 2,3,6-tribromo-5-phenylthieno[3,2-*b*]thiophene (**11**, 113 mg, 0.25 mmol, 1 eq., 453 g/mol), Ph_3P (13.1 mg, 0.05 mmol, 0.2 eq., 262 g/mol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.1 eq., 224 g/mol), CuI (10 mg, 0.05 mmol, 0.2 eq., 190 g/mol) and 1-ethynyl-3-methylbenzene (61.2 mmg, 0.30 mmol, 2.5 eq.,

116 g/mol) gave **12b** as a pale yellow powder (27.5 mg, 523 g/mol, 21%), mp. 152 °C.^{1}H NMR ($CDCl_3$, 500 MHz)δ (ppm): 7.73 (d, J = 1.5 Hz, 1H), 7.71 (s, 1H), 7.47 (t, J = 7.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.428 (m, 1H), 7.421 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 2.37 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 141.41, 140.0, 138.18, 138.16, 136.6, 132.89, 132.39, 132.13, 129.86, 129.79, 128.98, 128.89, 128.82, 128.77, 128.64, 128.38, 128.36, 126.9, 122.48, 122.39, 120.0, 99.8, 99.7, 96.8, 82.4, 81.5, 21.2;MS (ESI): calcd. for $[M+H]^+$, $[C_{30}H_{20}BrS_2]^+$, 524, found 524; calcd. for $[M-H]^-$, $[C_{30}H_{18}BrS_2]^-$, 522, found 522.

3. Results and Discussion

3.1. Synthesis

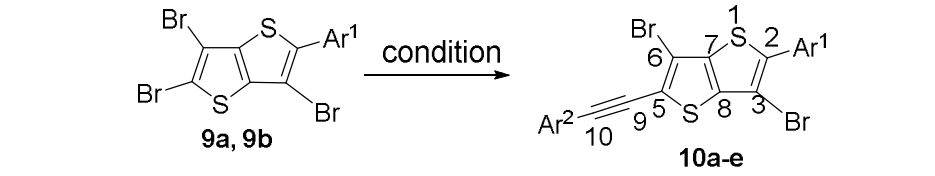
Monoaryl thiophene derivatives **9** were synthesized via Suzuki reaction [8]. As reported in our group [9] whenever increasing the amount of alkynes gave H-insertion products. Therefore optimization of Sonogashira was needed and results were performed in the table 1. The optimization was kept the same for all entries in 6 mL of *i*-Pr_2NH.

Table 1.*Optimization of the oxidant and additive in the direct alkynylation reaction to form****10a***

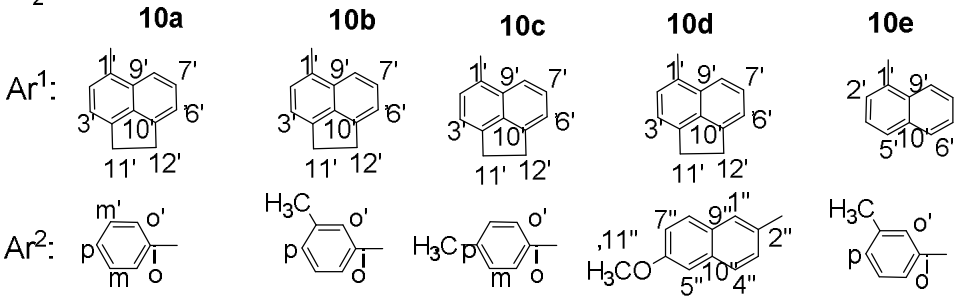
Entry	$Pd(OAc)_2$ (*eq.*)	Cu(I) (*eq.*)	PPh_3 (*eq.*)	Solvent	T/time (^{o}C/h)	Yield (%)
1	0.1	0.2	0.2	Toluene	reflux/3	0, mess
2	0.1	0.2	0.2	DMSO/toluene (5/5; v/v)	reflux/3	15, mess
3	0.1	0.2	0.2	DMSO	reflux/3	33
4	**0.1**	**0.2**	**0.2**	**THF**	reflux/3	**42**
5	0.1	0.2	0.2	DMF	reflux/3	28
6	0.05	0.2	0.2	THF	reflux/3	10
7	0.1	0.3	0.2	THF	reflux/3	15
8	0.1	0.1	0.1	THF	reflux/3	10

First, the solvents were optimized. The reaction in presence of toluene gave a mess. Meanwhile DMSO and DMF gave 33 % and 28 % yield. Luckily, THF was the best and increased the yield up to 42 %. Any changes of Pb (II), Cu(I) and PPh_3 did not give better results. Hence, the others reactions were carried out under entry 4 condition. The monoalkynyl and dialkynyl derivatives were synthesized as shown in Scheme 1 and 2, however, in the process of synthesizing dialkynyl derivatives, the amount of alkynes,

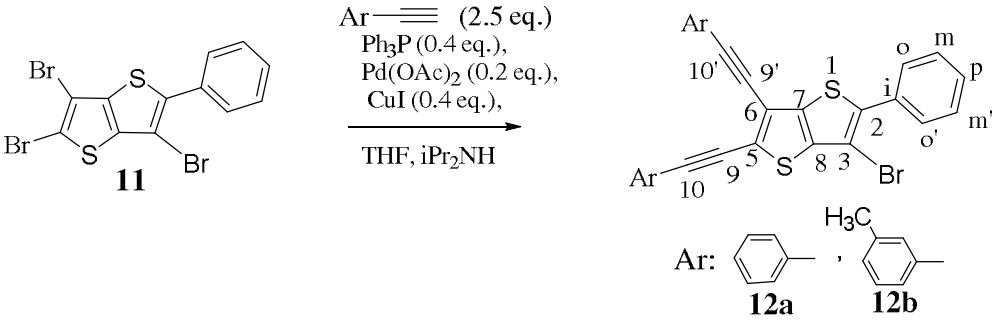
Cu(I), PPh_3 was doubled. The changes of Cu(I) amount gave rise the change of diyne by-products.



Condition: Alkynes (1.2 eq.), Ph_3P (0.2 eq.), $Pd(OAc)_2$ (0.1 eq.), CuI (0.2 eq.), THF, iPr_2NH



Scheme 1. *Synthesis of the target compounds*



Scheme 2. *Alkylation via the Sonogashira reaction*

3.2. Structure determination

Mass spectroscopic spectra of compounds **10d**, **10e**and **12b** indicated that molecular weight of **10d**630 g/mol and molecular formula $C_{31}H_{18}Br_2OS_2$; **10e**: 538 g/mol associated with molecular formula $C_{25}H_{14}Br_2S_2$; **12b**: 523 g/mol (average molecular weight) and molecular formula $C_{30}H_{29}BrS_2$. Pseudo molecular ion peaks of compounds **10d**, **10e** were complicated since they had 2 bromine atoms so we just took one of them to assign.

All compounds were recorded ^{1}H NMR and ^{13}C NMR spectra. Compounds **10a**, **10b**, **10c**, and **10d**contain a 1,2-dihydroacenaphthylen-6-yl group, therefore, their ^{1}H NMR showed a singlet peak at δ 3.4 ppm and H7' was as a triplet peak at δ 7.49 ppm (t, *J* = 7 Hz, 1H) indicating the thieno[3,2-*b*]thiophene moiety was retained under the reaction

condition. In addition, the ^{1}H NMR of compound **10a** had another triplet peaks at δ7.35 ppm (t, *J*= 7.0 Hz, 2H) assigned for Hm/Hm'. Similarly, Hm on the compound **10b** was also a triplet at δ 7.26 ppm (*J* = 7.5 Hz, 1H). On the other hand, Ho/Ho' and Hm/Hm' gave rise to two doublet peaks at δ 7.48 ppm (*J* = 8.0 Hz, 2 H) and δ7.19 ppm (d, *J* = 8.0 Hz) on the ^{1}H NMR spectrum of compound **10c**. On the ^{1}H NMR spectrum of compound **10d** showed enough 11 aromatic protons; **10e**'s showed 10 aromatic protons that met the expected structures. Compounds **12a** and **12b** have got three aromatic rings therefore their ^{1}H NMR spectra showed 16 and 15 protons. Apart from these observations, the ^{1}H NMR spectra of **10b**, **10c**, **10d**, **10e** and **12b** compounds appeared a singlet assigned to the methyl group, at δ 2.37; 2.37; 3.91; 2.38; and 2.37 ppm, respectively.

^{13}C NMR spectra indicated good agreement with their ^{1}H NMR spectra. For example, first, ^{13}C NMR spectra of compounds **10a**, **10b**, **10c**, and **10d** had two peaks at δ 30.55 ppm and 30.39 ppm for carbons of $-CH_2$-CH_2- group on the a 1,2-dihydroacenaphthylen-6-yl moiety. Secondly, the ^{13}C NMR spectra of compounds **10b**, **10c**, **10d**, **10e** and **12b** also gave peak in the strong field at 21.2 ppm (CH_3-Ar), 21.6 ppm (CH_3-Ar), 55.4 ppm (H_3CO-Ar), 21.2 ppm (CH_3-Ar) and 21.2 ppm (CH_3-Ar). Next the ^{13}C NMR spectra showed all peaks of C9 and C10 of the triple bond. Interestingly, C9 and C10 were randomly appeared at the same chemical shift at about 81-83 ppm; compounds **12a** and **12b** had got 2 pairs of triple bond C9 and C10 so theirs showed 2 peaks in the range 81-83 ppm too. Finally, their also gave all peaks associated with aromatic carbons atoms on structures. For instance, compound **10a**, **10b**, **10c**, **10d**, **10e**, **10a** and **12b** had 20, 22, 20, 26, 22, 18 and 22 carbon atoms. Based on these explanations, the MS, ^{1}H NMR and ^{13}C NMR had well supported for addressed structures. Unfortunately, we haven't got acceptable crystals for X-ray, so the experimental evidence for the second alkynyl groups in the **12a** and **12b** were not confirmed yet. This work is being done in our lab.

4. Conclusion

Five monoalkynyl and two dialkynyl derivatives of thieno[3,2-*b*]thiophene were synthesized via Sonogashira cross coupling reaction. However, the second alkynyl group substitution was not confirmed. Changes of CuI played an important role in giving off diyne products.

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