

## AN ATTEMPT TO PLANARIZE 2,3,5,6-TETRAARYLTHIENO[3,2-*b*]THIOPHENE BY FeCl<sub>3</sub>-ASSISTED ANNULATION

Nguyen Hien<sup>1</sup> and Nguyen Thi Lieu<sup>2</sup>

<sup>1</sup>*Faculty of Chemistry, Hanoi National University of Education*

<sup>2</sup>*Faculty of Chemistry, Hanoi Metropolitan University*

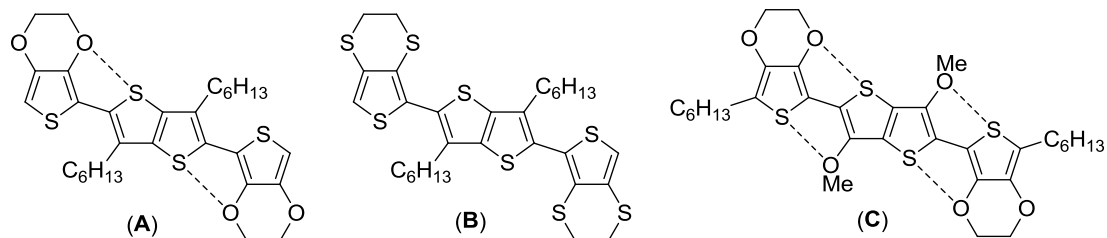
**Abstract.** Thieno[3,2-*b*]thiophene is a typical core structure in a number of conjugated organic opto-electronic materials. In this work, an attempt to planarize 2,3,4,6-tetraarylthieno[3,2-*b*]thiophene based on the FeCl<sub>3</sub> oxidative annulation was described. Thus, two cyclized 2,3,5,6-tetraarylthieno[3,2-*b*]thiophenes **5a** and **5b** were synthesized in moderate yields. NMR and HR-MS analysis indicated the annulation between only one pair of the phenyl substituents.

**Keywords:** Thieno[3,2-*b*]thiophene, Suzuki-Miyaura reaction, FeCl<sub>3</sub> oxidative annulation.

### 1. Introduction

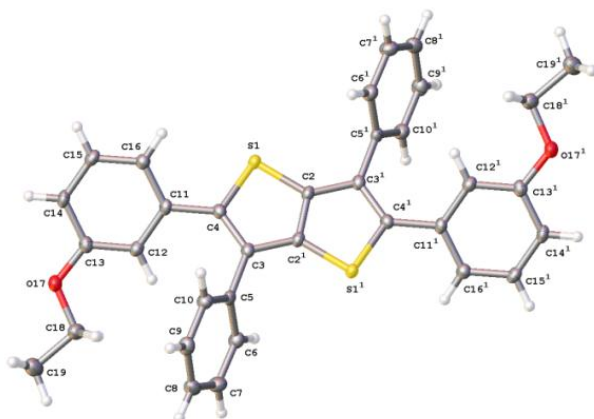
Thieno[3,2-*b*]thiophene (**TT**) has been used as a key monomer or incorporated in functionalized oligomers and polymers developed as *p*-type organic semi-conductors, optoelectronics, and electroluminescence [1]. The inter-molecular sulfur-sulfur interactions allow materials formulating this core structure to increase the electronic transport between adjacent molecules. Skabara and co-workers reported on the synthesis of two novel **TT**-based conjugated molecules **A** and **B** starting from Stille coupling reactions of dibromo\_\*\*TT\*\* and stannylthiophenes (Figure 1) [2]. Electro-chemical and optical investigations provided the repeating band gaps as 2.21 and 3.01 eV for **A**, and 2.45 and 3.14 eV for **B**. While non-covalent S⋯O interactions in **A** resulted in a planar conformation, and hence, a high degree of conjugation length, the twisted conformation was observed for the 3,4-ethylenedithiothiophene analogue **B**. As expected, the hole mobilities for **A** and **B** were reported to be 4.0 and  $1.5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. A similar phenomenon was observed by Frere who investigated the oligomer possessing 3,6-dimethoxythieno[3,2-*b*]thiophene **C** (Figure 1) [3]. On the spot, the S⋯O intra-molecular interactions along with the rigid **TT** unit also led to a planar conformation.

An attempt to planarize 2,3,5,6-tetraarylthieno[3,2-*b*]thiophene by FeCl<sub>3</sub>-Assisted annulation



**Figure 1.** Thieno[3,2-*b*]thiophene-based organic materials

Recently, we have reported on the synthesis of a library of mono-, di- and tetraarylthieno[3,2-*b*]thiophene by the palladium-catalyzed Suzuki-Miyaura reactions of tetrabromothieno[3,2-*b*]thiophene [4]. According to X-Ray analyses, the substituted thieno[3,2-*b*]thiophenes experienced conformations in which the aryl substituents were twisted from the skeleton of the thieno[3,2-*b*]thiophene core (Figure 2) [5].



**Figure 2.** X-Ray spectrum of 2,5-di(4-ethoxyphenyl)-3,6-diphenylthieno[3,2-*b*]thiophene [5]

To improve the electronic properties of conjugated organic materials, expansion of the p-framework by incorporating aromatic units into aco-planar structure is an effective approach. In this work, we focused on the cyclization of the substituents of 2,3,5,6-tetraarylthieno[3,2-*b*]thiophenes by FeCl<sub>3</sub> oxidative annulation to increase their co-planarity [7].

## 2. Content

### 2.1. Experiments

#### 2.1.1. Chemicals

Unless otherwise stated, chemical reagents and solvents for reactions were purchased from Sigma-Aldrich or Merck and used without further purification. THF were dried by refluxing over sodium wire in the presence of benzophenone as indicator and distilled just before used. Dichloromethane and nitromethane were dried over molecular sieve 3A (Merck) in 24 hours before used. All the reactions were carried out under an atmosphere of argon in oven-dried

glassware with magnetic stirring. Column chromatography was performed with Merck silica gel 60 (0.040 - 0.063  $\mu\text{m}$  grade).

### 2.1.2. Instrumentation

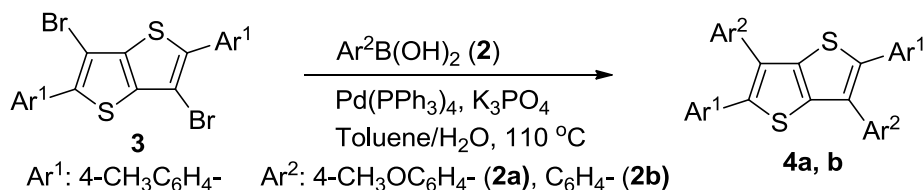
Melting points were measured on a Stuart-Scientific SMP3 apparatus without correction. NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer in  $\text{CDCl}_3$ . Chemical-shift data for each signal were reported in ppm units with tetramethylsilane (TMS) as internal reference, where  $\delta_{\text{TMS}}$  is zero. Splitting patterns were designated as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), and *m* (multiplet). HR-MS spectra were acquired on a LQT Orbitrap XL using ESI technique.

### 2.1.3. Synthesis

The title compound 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene **1** was prepared from thiophene following the reported procedure [6]. 2,5-Di(*p*-tolyl)-3,6-dibromothieno[3,2-*b*]thiophene **3** was obtained by the Suzuki-Miyaura reaction of **1** with *p*-tolylboronic acids [4].

#### \* Synthesis of 2,5-diAr<sup>1</sup>-3,6-diAr<sup>2</sup>thieno[3,2-*b*]thiophene **4a,b**

2,5-DiAr<sup>1</sup>-3,6-diAr<sup>2</sup>thieno[3,2-*b*]thiophene **4a,b** were also synthesized by the Suzuki reactions of **3** with various boronic acids (Scheme 1).



**Scheme 1.** Synthesis of **4a,b**. Conditions: **3** (1.0 eq),  $\text{Ar}^2\text{B(OH)}_2$  (2.6eq),  $\text{Pd}(\text{Ph}_3\text{P})_4$  (0.1 eq),  $\text{K}_3\text{PO}_4$  (4.0 eq), toluene/ $\text{H}_2\text{O}$  (4 : 1), 110 °C, 24 – 36 h.

**2,5-Di(*p*-methoxy)-3,6-di(*p*-tolyl)thieno[3,2-*b*]thiophene **4a**:** To a solution of 2,5-di(*p*-tolyl)-3,6-dibromothieno[3,2-*b*]thiophene **3** (160.0 mg; 0.5 mmol; 1.0 eq) and  $\text{Pd}(\text{Ph}_3\text{P})_4$  (57.7 mg; 0.05 mmol; 0.10 eq) in degassed toluene (4.0 ml) at 60-70 °C were added  $\text{H}_2\text{O}$  (1.0 ml),  $\text{K}_3\text{PO}_4$  (424 mg; 2.0 mmol; 4.0 eq), and *p*-methoxyphenylboronic acid **2a** (182.4 mg; 1.3 mmol; 2.6 eq). The reaction mixture was vigorously-stirred under argon atmosphere at 110 °C until TLC (*n*-hexane) showed the complete consumption of the starting material. The reaction mixture was filtered to remove insoluble particles. The filtrate was washed several times with water, dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure by rotary evaporation. The residue was purified by  $\text{SiO}_2$ -column chromatography to give **4a** (146.3 mg; 55%) as whileneedles, mp = 195-198 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$ (ppm) = 7.39 (d,  $J$  = 8.5 Hz, 2 H), 7.23 (d,  $J$  = 8.0 Hz, 2 H), 7.07 (d,  $J$  = 7.5 Hz, 2 H), 6.89 (d,  $J$  = 9.0Hz, 2 H), 3.83 (s, 3 H), 2.33 (s, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$ (ppm) = 158.9, 138.7, 138.1, 137.3, 131.9, 130.2, 130.0, 129.2, 129.1, 127.6, 114.2, 55.2, 21.2.

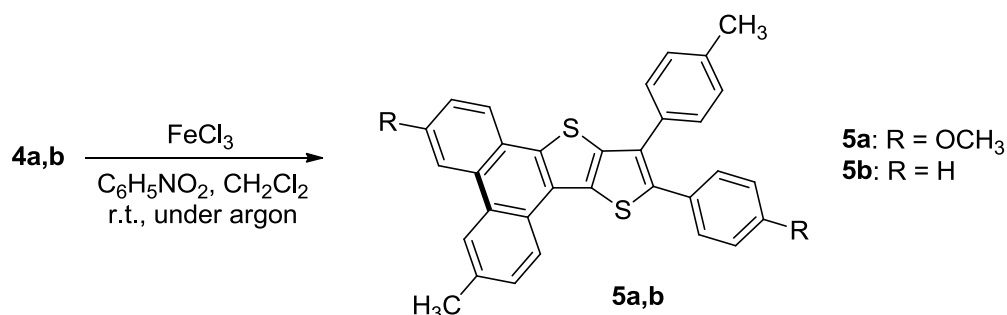
**2,5-Diphenyl-3,6-di(*p*-tolylphenyl)thieno[3,2-*b*]thiophene **4b**** was previously synthesized from **3** by our group [4].

**2,3,5,6-Tetra(thien-2-yl)thieno[3,2-*b*]thiophene **4c**:** Following the general procedures, **4c** was unsuccessfully prepared. Therefore, another condition was tried. Thus, a mixture of **1** (70.0 mg; 0.5 mmol), thien-2-ylboronic acid (384.0 mg; 3.0 mmol; 6.0 eq),  $\text{Pd}(\text{OAc})_2$  (5.6 mg; 0.025 mmol;

An attempt to planarize 2,3,5,6-tetraarylthieno[3,2-*b*]thiophene by FeCl<sub>3</sub>-Assisted annulation

0,05eq), S-Phos (20.5 mg; 0.05 mmol; 0.1 eq) and K<sub>3</sub>PO<sub>4</sub> (848.0 mg; 4 mmol; 8.0 eq) in degassed toluene was refluxed at 110 °C overnight. **4c** was isolated (107.0 mg; 46%) as yellow needles by SiO<sub>2</sub>-column chromatography (*n*-hexane/ethyl acetate 95:5, v/v), mp = 228 - 230 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ(ppm) = 7.38 (d, *J* = 5.5 Hz, 2 H), 7.33 (d, *J* = 5.0 Hz, 2 H), 7.25 (partially overlapped by CDCl<sub>3</sub>), 7.18 (d, *J* = 3.5 Hz, 2 H), 7.10 (t, *J* = 4.5 Hz, 2 H), 7.03 (t, *J* = 4.5 Hz, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ(ppm) = 138.3, 135.3, 135.1, 133.1, 128.1, 127.5, 127.3, 127.2, 126.4, 124.8. HR-MS (ESI-[M+H]<sup>+</sup>) calcd. for C<sub>22</sub>H<sub>12</sub>S<sub>6</sub> 467.9263, found 468.9413.

\* Synthesis of planarized 2,3,5,6-tetraarylthieno[3,2-*b*]thiophene **5a,b**



**Scheme 2.** Synthesis of the one-side cyclized tetraarylthieno[3,2-*b*]thiophene **5a,b**

Conditions: **4** (1.0 eq), FeCl<sub>3</sub> (12.0 eq), C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, r.t., 8 h.

*General procedures:* A solution of FeCl<sub>3</sub> (390.0 mg; 2.4 mmol; 12.0 eq) in anhydrous nitromethane (5 mL) was added dropwise to a solution of **4** (0.2 mmol; 1.0 eq) in degassed anhydrous CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The reaction mixture was stirred at r.t. for 8 hours under argon atmosphere and quenched by an addition of distilled water (100 mL). The organic layer was washed with saturated brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotatory evaporation. The residue was purified by column chromatography (silica gel, *n*-hexane) to give the desired product.

*6-Methoxy-11-(4-methoxyphenyl)-3-methyl-10-(p-tolyl)phenanthro[9,10-*b*]thieno[2,3-*d*]thiophene 5a:* Starting from **4a** (106.5 mg; 0.2 mmol), **5a** (31.8 mg; 30%) was obtained as white needles. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) and <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) are analyzed as shown in Table 2 and Figure 4. HR-MS (ESI-[M+H]<sup>+</sup>) calcd. for C<sub>34</sub>H<sub>26</sub>O<sub>2</sub>S<sub>2</sub> 530.1374, found 531.1464.

*3-Methyl-11-phenyl-10-(p-tolyl)phenanthro[9,10-*b*]thieno[2,3-*d*]thiophene 5b:* Starting from **4b** (94.5 mg; 0.2 mmol), **5b** (42.5 mg; 45%) was obtained as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ(ppm) = 8.76 (d, *J* = 8.5 Hz, 1 H), 8.49 (s, 1 H), 8.39 (d, *J* = 8.0 Hz, 1 H), 7.98 (d, *J* = 8.0 Hz, 1 H), 7.77 (t, *J* = 8.0 Hz, 1 H), 7.69 (t, *J* = 8.0 Hz, 1 H), 7.57 (d, *J* = 8.5 Hz, 2 H), 7.44 (m, 3 H), 7.38 (d, *J* = 8.5 Hz, 1 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 2.62 (s, 3 H), 2.36 (s, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ(ppm) = 140.7, 138.1, 137.7, 136.3, 135.2, 132.4, 131.5, 130.4, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 127.7, 127.6, 127.5, 127.3, 126.7, 125.9, 124.9, 123.8, 123.5, 123.4, 22.1, 21.3. HR-MS (ESI-[M+H]<sup>+</sup>) calcd. for C<sub>32</sub>H<sub>22</sub>S<sub>2</sub> 470.1163, found 471.1322.

## 2.2. Results and discussion

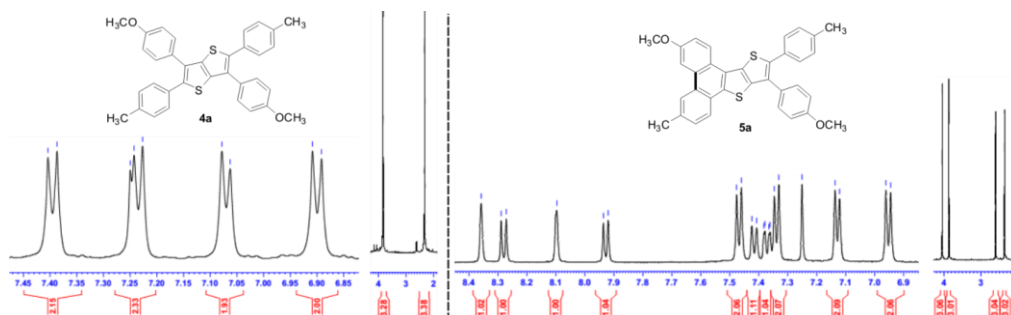
The synthesis of di- and tetraarylthieno[3,2-*b*]thiophenes by the Suzuki-Miyaura cross-coupling reaction proceeded regio-selectively at the C-2 and C-5, and then at the C-3 and C-6 positions as proved by X-Ray analyses [4,5]. Subsequent oxidative cyclization of **4a** and **4b** by FeCl<sub>3</sub> furnished the planarized tetraarylated thieno[3,2-*b*]thiophene **5a** and **5b** with 30% and 45% yields, respectively.

Initially, we aimed to completely annulate the two pairs of aryl substituents on both wings of the tetraaryl\_\*\*TT\*\* by adjusting the amounts of the oxidative reagents and other reaction conditions. During the optimization of the reaction conditions of **4a**, we found out that the temperature, the reaction time, and especially the amount of the oxidative reagent, FeCl<sub>3</sub>, played an essential role in the cyclization of the adjacent phenyl rings. The best yields were obtained when FeCl<sub>3</sub> was used with 8.0 eq and the reaction was carried out at r.t. for 8 hours (entry 3, Table 1). Increasing the amount of the oxidative reagent or prolonging the reaction time led only to the decomposition of the starting material (entries 4, 5, and 6, Table 1). Lowering the reaction temperature or shortening the reaction time didn't bring about good conversion of the reaction (entries 1 and 2, Table 1). Applying the optimized reaction condition to **4b** afforded the cyclized product **5b** with 45% yield (entry 7, Table 1). Unfortunately, the **4c** was fast and completely decomposed under this condition (entry 8, Table 1). The high electron densities of the thiophene rings could have made **4c** become too sensitive to oxidative reagent.

**Table 1. Optimization of FeCl<sub>3</sub>-assisted oxidative cyclization of 2,3,4,6-tetraarylthieno[3,2-*b*]thiophenes**

Entry	<b>4</b> *	FeCl <sub>3</sub> (eq)	Temp./time (°C/h)	Yield (%)	Entry	<b>4</b> (eq)	FeCl <sub>3</sub> (eq)	Temp./time (°C/h)	Yield (%)
1	4a	6	0/1	5	5	4a	16	r.t./24	-
2	4a	6	r.t./1	8	6	4a	24	r.t./8	-
3	4a	12	r.t./8	30	7	4b	12	r.t./8	45
4	4a	12	r.t./24	12	8	4c	12	r.t./1	-

\* All reactions were carried out in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>NO<sub>2</sub> under argon atmosphere with 1.0 eq of a tetraaryl\_\*\*TT 4



**Figure 3. The <sup>1</sup>H NMR spectra of 4a (left) and 5a (right)**

The structures of all new products were elucidated by NMR and HR-MS spectroscopic methods. As shown in Figure 3, there were remarkable changes in <sup>1</sup>H NMR spectrum of **5a**, the FeCl<sub>3</sub>-assisted cyclized product, compared with that of the starting tetraaryl\_\*\*TT 4a\*\*. In contrast to the simple pattern of the <sup>1</sup>H NMR spectrum of **4a** due to its symmetric structure, the <sup>1</sup>H NMR spectrum of **5b** showed a significantly greater number of resonance signals, indicating that the cyclization occurred on only one side of the tetraaryl\_\*\*TT 4a\*\*. If the annulation were on both wings of the compound, the <sup>1</sup>H NMR spectrum of the product would be as simple as that of **4a**. In addition, the molecular weight of **5a**, found by HR-MS, is 530.1464 which is about 2 a.u. smaller than the calculated molecular weight of **4a** (532.1531). This is also a convincing evidence for the cyclization of one pair of the phenyl substituents of the tetraaryl\_\*\*TT 4a.

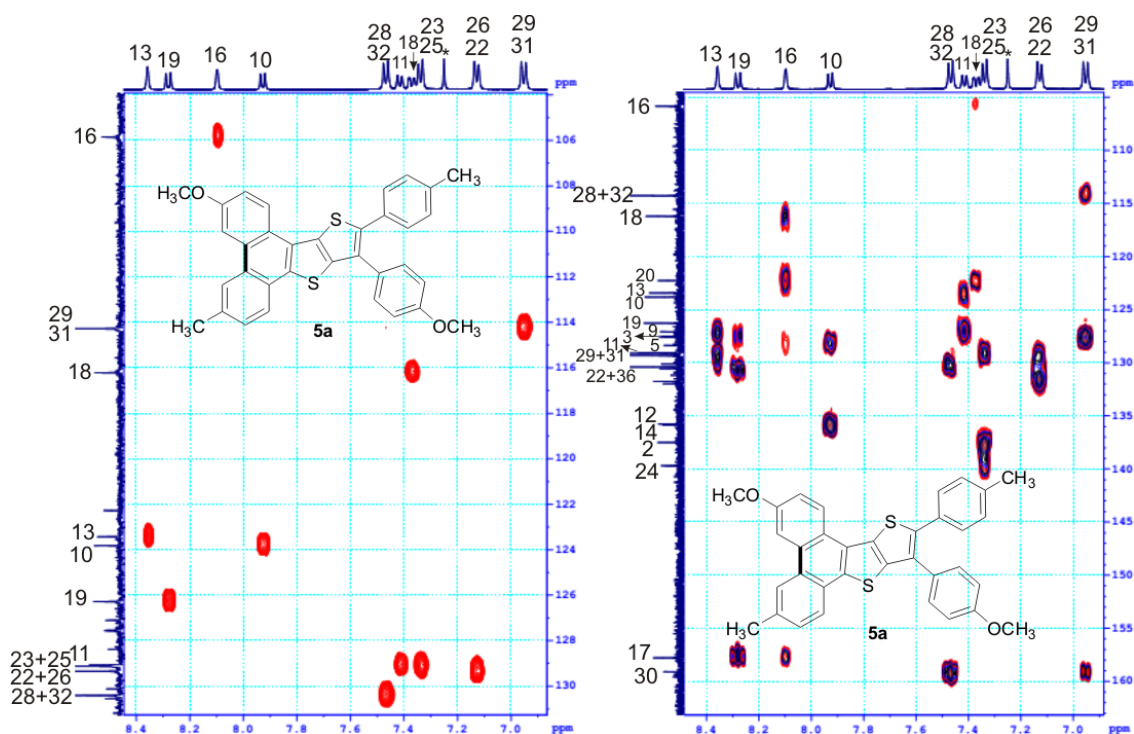


Figure 4. The HSQC (left) and HMBC (right) spectra of **5a**. \* CDCl<sub>3</sub>

On one hand, the resonances of protons and carbons of **5a** were further assigned by 2D NMR (Figure 4 and Table 2). The annulation took place on one side of the tetraaryl\_\*\*TT, leading to two asymmetric parts of the cyclized product **5a**. Protons of the two *un-annulated* benzene rings resonated in the range from 7.48 ppm to 6.95 ppm, which was typical for *normal* substituted benzene derivatives. On the other hand, the resonances of H<sub>10</sub>, H<sub>13</sub>, H<sub>16</sub>, and H<sub>19</sub> of the *annulated* part were shifted to the range above 7.99 ppm due to the enhance anisotropic effect of the extended  $\pi$  system.

*Table 2. HMBC analysis of 5a*

Carbon		Cross-peaks with protons	Carbon		Cross-peaks with protons	Carbon		Cross-peaks with protons
C	$\delta$ (ppm)	H	C	$\delta$ (ppm)	H	C	$\delta$ (ppm)	H
C2	137.5	H23, H25	C13	123.4	H11	C23	129.3	H25
C3	127.5	H29, H31	C14	135.8	H10	C24	129.8	H23, H25
C5	128.4	H10	C15	130.1	H19	C25	129.3	H23
C6	130.5	H19	C16	105.8	H18	C26	130.4	H22
C7	131.9	-	C17	157.8	H16, H19	C27	127.5	H29, H31
C8	131.7	-	C18	116.2	H16	C28	114.3	H29, H31
C9	126.3	H13, H11	C19	126.3	H18	C29	129.1	H31
C10	123.8	H11	C20	122.3	H16, H18	C30	159.1	H28, H29
C11	129.0	H13	C21	139.6	H23, H25	C31	129.1	H29
C12	135.8	H10	C22	130.4	H26	C32	114.3	H29, H31

### 3. Conclusion

In summary, we have described the synthesis of two novel phenanthrene-fused thieno[3,2-*b*]thiophene **5a** and **5b** by partially FeCl<sub>3</sub> oxidative annulation from **4a** and **4b**, respectively. The optimized condition did not work in the case of compound **4c**. The NMR spectra of the one-side cyclized product showed remarkable differences in comparison with those of the tetraaryl\_\*\*TT\*\*. HR-MS analyses further consolidated the NMR data. Experiments to find out a procedure for the synthesis of completely-annulated tetraaryl\_\*\*TTs and the electro-chemical and optical investigations are in progress.

**Acknowledgement:** This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.01-2012.26.

## REFERENCES

- [1] Bronstein H., Chen Z., Ashraf S. R., Zhang W., Du J., Geerts Y., Janssen R. A. J., Heeney M., McCulloch I., 2011. *Thieno[3,2-*b*]thiophene-diketopyrrolopyrrole-containing polymers for high-performance organic field-effect transistors and organic photovoltaic devices*. J. Am. Chem. Soc., Vol. 133, p. 3272.
- [2] McEntee G. J., Skabara P. J., Vilela F., Gambino S., Coles S. J., Hursthouse M. B., Harrington R. W., Clegg W., 2010. *Synthesis and electropolymerization of hexadecyl functionalized bithiophene and thieno[3,2-*b*]thiophene end-capped with EDOT and EDTT units*. Chem. Mater., Vol. 22, p. 3000.
- [3] Turbiez M., Hergue N., Leriche P., Frere P., 2009. *Rigid oligomers based on the combination of 3,6-dimethoxythieno[3,2-*b*]thiophene and 3,4-ethylenedioxythiophene*. Tetrahedron Lett., Vol. 50, p. 7148.
- [4] Nguyen H., Nguyen X. D., Tran Q. T., Vo N. B., Nguyen H. T., Vuong T. M. H., Dang T. T., 2014. *Programmed synthesis of tetraarylthieno[3,2-*b*]thiophene by site-selective Suzuki cross-coupling reactions of tetrabromothieno[3,2-*b*]thiophene*. Synlett, Vol. 25, p. 93.
- [5] Nguyen H., Vu M. L., 2014. *Synthesis and structural analysis of arylated thieno[3,2-*b*]thiophene by site-selective Suzuki - Miyaura cross-coupling reaction*. Vietnam Journal of Chemistry, Vol. 52, p. 564.
- [6] Fuller L. S., Iddon B., Smith K. A., 1997. *Synthesis, metallation and bromine→lithium exchange reactions of thieno[3,2-*b*]thiophene and its polybromo derivatives*. J. Chem. Soc., Perkin Trans., Vol. 1, p. 3465.
- [7] Cao Y., Wang X.-Y., Wang J.-Y., Pei J., 2014. *Iron(III) chloride promoted cyclization: A facile approach to polycyclic aromatics for functional materials*. Synlett, Vol. 24, p. 313.



## CONTENTS

<b>Nguyen Huu Dinh and Hoang Thi Tuyet Lan</b> , Structure of polyaza-heterocycles obtained from reaction of two (3-methylfuroxan-4-yl)phenylhydrazines with formaldehyde	3
<b>Duong Quoc Hoan, Nguyen Thi Thanh Xuan, Truong Minh Luong and Tran Thi Trang</b> , Characterization and bio-activity evaluation of two new acetohydrazides synthesized from curcumin and monocarbonyl curcumin analog	11
<b>Nguyen Thi Tam, Do Thu Huong and Pham Huu Dien</b> , Chemical constituents of the <i>Moringa oleifera</i> Lam. leaves collected in Bac Ninh province	21
<b>Nguyen Quang Tuyen and Dang Ngoc Quang</b> , Optimization of total saponin extraction from Tam that roots using the desirability methodology	26
<b>Nguyen Hien and Nguyen Thi Lieu</b> , An attempt to planarize 2,3,5,6-tetraarylthieno[3,2- <i>b</i> ]thiophene by FeCl <sub>3</sub> -assisted annulation	34
<b>Duong Quoc Hoan and Pham Thi Thuy Dinh</b> , Preparation of some benzo[ <i>d</i> ]thiazole derivatives from vanillin	42
<b>Le Thi Thu Huong, Nguyen Thi My Hanh, Ngo Van Khue, Vu Hai My and Nguyen Nhu Ngoc</b> , A new derivative of butanenitrile from <i>Euphorbia hirta</i> L.	48
<b>Nguyen Van Loi</b> , Study on the chemical composition, biological activity and physico-chemical indicators of the weft-peel oil of Bac Giang oranges extracted by cold-pressing method	53
<b>Nguyen Thi Thanh Chi, Nguyen Thi My Hoa and Truong Thi Cam Mai</b> , Anti-microbial activities of two platinum(II) complexes bearing ethyl eugenoxycetate and synthesis, structure of [PtCl(Ethyl eugenoxycetate-1H)(morpholine)]	60
<b>Nguyen Anh Tien and Nguyen Thi Truc Linh</b> , Structure and magnetization of LaFe <sub>1-x</sub> Co <sub>x</sub> O <sub>3</sub> perovskite nanomaterials synthesized by co-precipitation method	68
<b>Ta Huu Son, Nguyen Van Thu, Le Van Khu and Luong Thi Thu Thuy</b> , Preparation of activated carbons from coffee husks using ZnCl <sub>2</sub> as activating agent	75
<b>Pham Thuy Duong, Hue Minh Thi Nguyen, Nguyen Thanh Tung and Ngo Tuan Cuong</b> , Geometries of Si <sub>n</sub> V <sub>2</sub> <sup>+</sup> clusters (n = 1 - 6) a density functional theory investigation	84
<b>Nguyen Hoang Nam, Tran Thi Hong Van and Nguyen Thi Thanh Huong</b> , Study of supporting electrolytes of KCl-acetate buffer - NH <sub>4</sub> Ac for simultaneous determination of Zn <sup>2+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup> in acid mine drainage in Mao Khe, Quang Ninh by anodic stripping voltammetry at hanging mercury-drop electrode	93
<b>Nguyen Thi Hop and Ta Thi Thao</b> , Simultaneous determination of selected flavour enhancers in beef Pho broth samples by chemometrics-assisted spectrophotometry	104

<b>Bui Thi Thu, Trinh Kim Yen and Dao Van Bay</b> , Efficiency evaluation of stable cyanide complexes conversion and its application	113
<b>Vu Quang Manh, Nguyen Thi Ha, Tran Le Truc Anh, Vu Duc Manh, Nguyen Thanh Hai and Ha Tra My</b> , Ragworm (Nereidae: <i>Tylorrhynchus</i> sp.) in Soil Macrofauna Community structure in Hai Duong province - A Northern Coastal area of Vietnam	123
<b>Tran Thi Thanh Binh, Hoang Ngoc Khac, Nguyen Thi Ha and Vu Quang Manh</b> , Species composition and distribution of polychaete (Polychaeta) in mangrove eco-system, Da Loc commune, Hau Loc district, Thanh Hoa province	132
<b>Nguyen Van Hao, Nguyen Huu Duc and Nguyen Thi Dieu Phuong</b> , Vinalabeo, a new generic name for <i>Vinalabeo tonkinensis</i> (Cyprinidae, Teleostei)	140
<b>Duong Minh Lam, Phung Thi Ngoc Quyen and Tong Thi Mo</b> , Anti-fungal ability of some mangrove endohytic actinomycetes in Vietnam	145
<b>Tran Thi Thuy, Mai Kim Tuyen and Pham Thi Thuy Hang</b> , Fusing two phytase genes by PCR - driven overlap extension	152
<b>Hoang Than Hoai Thu, Dao Van Hoang, Doan Lan Phuong, Hoang Thi Bich and Pham Quoc Long</b> , Aqueous enzymatic extraction of camellia seed oil ( <i>Camellia oleifera</i> ) from Vietnam	162
<b>Nguyen Quang Thao, Nguyen Van Quyen, Nguyen Thao Anh and Nguyen Thanh Dat</b> , Effects of fermentation conditions on ethanol production from corn by <i>Saccharomyces cerevisiae</i> MS42	169
<b>Nguyen Thi Trung Thu and Tran Quang Binh</b> , Determining <i>KCNJ11</i> E23K polymorphism in a group of vietnamese population by restriction fragment length polymorphism method	177
<b>Nguyen Thi Hong Hanh, Bui Thi Nhung, Le Thi Hop and Tran Quang Binh</b> , Relationship between some environmental factors and hyperbetalipoproteinemia in 6 - 11 year-old children in Hanoi	185