TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC SƯ PHẠM TP HỒ CHÍ MINH

Tập 18, Số 9 (2021): 1559-1564

HO CHI MINH CITY UNIVERSITY OF EDUCATION
JOURNAL OF SCIENCE

Vol. 18, No. 9 (2021): 1559-1564

ISSN:
2734-9918

Website: *http://journal.hcmue.edu.vn*

Research Article

MONOARYLATION OF DIPHENYLDITHIENYLETHENE BY LIGAND-FREE PALLADIUM CATALYZED C-H ACTIVATION

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Received: May 25, 2021; Revised: June 20, 2021; Accepted: September 01, 2021

ABSTRACT

This work reports on a green and convenient methodology for the arylation of diphenyldithienylethene by direct ligand-free palladium-catalyzed C–H bond functionalization. Based on this approach, a new diphenyldithienylethene-based compound with aryl substituent ***DTE-3-CHO-1*** *was successfully synthesized from thiophene via four steps. These compounds were structurally identified by NMR and HR-MS spectral analyses.*

Keywords**:** aggregation-induced emission; diphenyldithienylethene; direct palladium-catalyzed arylation; fluorescence

1. Introduction

Over the past decades, luminescent organic materials have been developed and applied to many research fields including photoelectronic devices, fluorescent sensors, bioimaging trackers, and photoluminescence therapy. In particular, aggregation-induced emissions (AIE) have gained increasing attention on account of their fundamental importance and highly promising potential applications. Many compounds are showing the AIE effects such as tetraarylethenes, multi-substituted alkenylated benzenes, heteroatom-bridged pentacyclic compounds (1,1-disubstituted tetraphenylgermole, *p*-aryltetraphenylphospoles, 1,1-diphenyltetraphenylsiloles, tetrabromothiophene, *N*-phenyltetraphenylpyrrole, tellurophenes, 1,1-disubstitutedtetraphenylstannoles), and boron diketonates (Mei et al., 2015). Among them, tetraphenylethene has been widely developed due to its facile synthesis and straightforward post-functinalization for multi-purposed applications (Hong et al., 2011). The synthesis of tetraarylethenes was based on titan-assisted McMurry coupling of

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Cite this article as: Le Tin Thanh, Nguyen Thi Phuong Nhi, Nguyen Hien, Le Thi Hong Hai, Le Thanh Thanh, & Dang Thanh Tung (2021). Monoarylation of diphenyldithienylethene by ligand-free palladium catalyzed C-H activation. *Ho Chi Minh City University of Education Journal of Science, 18*(9), 1559-1564.

ketones. Normally, this approach gave low yields with many accompanying isomer products. Recently, there have been two efficient methodologies to construct multiarylated ethenes with high yields based either on palladium-catalyzed *syn*-direct diarylation of arylethynyl *N*-methyliminodiacetyl boronates (Lin et al., 2019) or palladium-catalyzed consequential multi-Suzuki reaction of di-, tri- and tetraboronated ethenes (Zhang et al., 2020).

Post-monofunctionalized TPEs have applications in various research fields because of their interesting physical properties (Li et al., 2013). For example, 2-formylthienyl-TPE showed bright green color mechanoluminescence upon pressing or grinding under daylight at room temperature (Rananaware et al., 2015). 2-PyrylTPE was observed to quench light emissions in solution by π-π stacking of luminophores and to exhibit the AIE characteristics in the condensed phase by the restriction of intramolecular rotation (RIR) (Zhao et al., 2011). TPE carboxylic acid has been studied for its application in photobleaching and bioimaging activity towards bacteria including several species of gram-negative and gram-positive (Shi et al., 2019; Liu et al., 2017). Almost all of the post-monofunctionlized TPEs were synthesized after two steps, which are bromination and the classical palladium catalyzed coupling reactions or the metal halide exchanged reaction (Zhang et al., 2014).

To give a convenient approach for post-monofunctionalisation of diphenyldithienylethenes (DTE) that have dual fluorescent and aggregation induced emission effects, we have studied a synthetic protocol to synthesize monoarylated DTE by a direct ligand-free palladium-catalyzed arylation of DTE with 3-bromobenzaldehyde.

2. Materials and methods

2.1. Instrumentation

NMR spectroscopic data were acquired on a Bruker Avance III at 500 MHz for ^{1}H–NMR and 125 MHz for ^{13}C–NMR. HR–MS spectra were recorded on a Bruker MICROTOF-Q 10,187.

2.2. Material

Reagents and solvents were obtained from commercial suppliers and were used without further purification. Column chromatography was carried out using Merck Kieselgel 60 silica gel (particle size: 32-63 Å). Analytical TLC was performed using Merck precoated silica gel 60 F-254 sheets. All the CH activation reactions were carried out under a nitrogen atmosphere.

2.3. Synthesis

Di(thiophen-2-yl)methanone ***1****:* A mixture of 2-thienoic acid (1.2 g, 0.01 mol, 1 eq), thiophene (0.84 g, 0.01 mol, 1 eq), and phosphorus pentoxide (1.6 g, 0.12 mol, 1.2 eq) in anhydrous toluene (10 mL) was refluxed for 2h. Another portion of phosphorus pentoxide (1.6 g, 0.12 mol, 1.2 eq) was added and the mixture was continued to reflux for another 2h. The precipitate was filtered off and the combined filtrates were washed with water (3 x 50 mL), 1*M* aq. NaOH (3 x 50 mL), dried over Na_2SO_4, concentrated *in vacuo* to give a residue which was chromatographed over silica gel (*n*-hexane: ethyl acetate (5:1)) to give **1** (970 mg, 50 %) as a white solide. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 7.91 (2H, *dd, J* = 4.0 Hz, *J* = 1.0 Hz), *δ* 7.70 (2H, *dd*, *J* = 5.0 Hz, *J* = 1.0 Hz), *δ* 7.19 (2H, *dd, J* = 5.0 Hz, *J* = 4.0 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 178.8, 142.9, 133.4, 133.1, 127.9 (Bottalico et al., 2009).

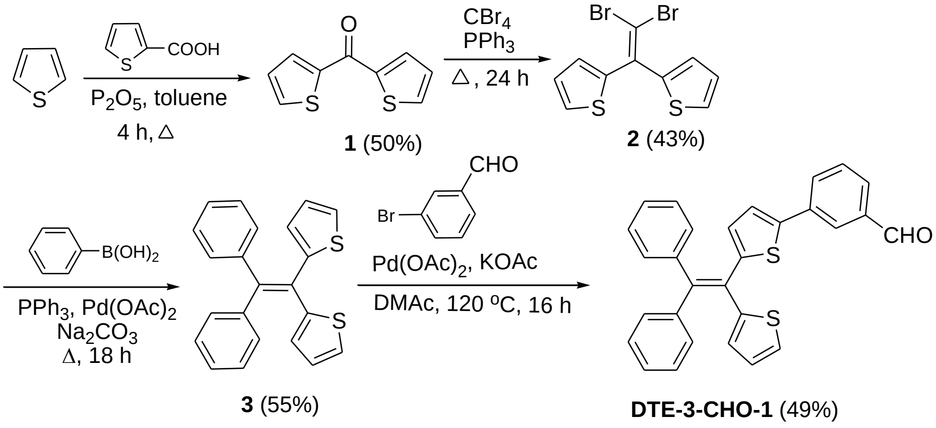
1,1-Bis(thiophen-2-yl)-2,2-dibromoethene ***2:*** **1** (194 mg, 1 mmol, 1.0 eq), CBr_4 (662 mg, 2 mmol, 2.0 eq) and PPh_3 (1.05 g, 4 mmol, 4.0 eq) were dissolved in dry toluene (8.0 mL). The solution was refluxed for 24h. After filtration, the filtrate was washed with water (3 x 50 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Chromatography on silica gel (*n*-hexane) afforded **2** (150 mg, 43 %) as a red oil. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 7.39 (2H, *dd*, *J* = 5.0 Hz, *J* = 1.0 Hz), *δ* 7.10 (2H, *dd*, *J* = 4.0 Hz, *J* = 1.0 Hz), *δ* 7.00 (2H, dd, *J* = 5.0 Hz, *J* = 4.0 Hz) (Chang et al., 2016).

1,1-Bis(thiophen-2-yl)-2,2-diphenylethene ***3:*** A mixture of **2** (70 mg, 0.2 mmol, 1.0 eq), PPh_3 (26 mg, 0.1 mmol, 0.5 eq), Na_2CO_3 (106 mg, 1.0 mmol, 5.0 eq), $Pd(OAc)_2$ (5 mg, 0.022 mmol, 0.1 eq) and phenylboronic acid (122 mg, 1.0 mmol, 5.0 eq) in dioxane : H_2O 4:1 (v:v) (10 mL) was refluxed overnight. After the completion of the reaction, the precipitate was filtered and the filtrate was washed with water (3 x 50 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane) to yield **3** (38 mg, 55 %) as a white solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 7.19-7.13 (12H, *m*), 6.80 (2H, *dd*, *J* = 5.0 Hz, *J* = 4.0 Hz), 6.76 (2H, *dd*, *J* = 4.0 Hz, *J* = 1.0 Hz) (Wang et al. 2018); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 145.6, 143.2, 142.3, 130.6, 129.7, 128.0, 127.0, 126.6, 126.3, 126.1.

3-(5-(2,2-Diphenyl-1-(thiophen-2-yl)vinyl)thiophen-2-yl)benzaldehyde **DTE-3-CHO-1**: A suspension of **3** (69 mg, 0.2 mmol, 1.0 eq), $Pd(OAc)_2$ (1.0 mg, 0.006 mmol, 0.03 eq), KOAc (58 mg, 0.6 mmol, 3.0 eq) and 3-bromobenzaldehyde (3.0 eq) in DMAc (5.0 mL) was stirred at 120 °C for 16h. All the insolubles were filtered and the combined filtrates were washed with water (3 x 30 mL), dried over Na_2SO_4, and the solvent was evaporated *in vacuo* to give a crude residue which was purified by column chromatography on silica gel (*n*-hexane:ethyl acetate 9:1, v/v) to give the pure monoarylated product **DTE-3-CHO-1** (44 mg, 49%) as a yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$) δ 10.00 (*s*, 1H), 7.96 (*t*, J = 2.0 Hz, 1H), 7.74 – 7.69 (*m*, 2H), 7.48 (*t*, J = 7.5 Hz, 1H), 7.22 – 7.14 (*m*, 11H), 7.11 (*d*, J = 4.0 Hz, 1H), 6.87 – 6.81 (*m*, 2H), 6.73 (*d*, J = 4.0 Hz, 1H). ^{13}C-NMR δ_C (125 MHz, $CDCl_3$) *δ* 192.0, 145.2, 143.1, 143.0, 142.9, 142.8, 136.9, 131.1, 130.9, 130.6, 130.6, 129.9, 129.5, 128.4, 128.2, 128.0, 127.3, 127.1, 126.6, 126.4, 126.3, 123.3. HR-ESI-MS: calcd $[C_{29}H_{21}OS_2]^+$ ($[M+H]^+$) = 449.1034, found = 449.1012.

3. Results and discussion

Diphenyldithienylethene was synthesized by two methodologies. First, dissymmetric 1,1-diphenyl-2,2-(hetero-)arylethene was synthesized by Suzuki and/or Stille coupling reaction of corresponding gem-dibromoethene and boronic or stannyl (hetero-)aryl (Zhang et al., 2014). One year later, diphenyldithienylethene was synthesized by desulfurization of thiiranes (Mlostoń et al., 2016). This method was known as ‘two-fold extrusion reaction’ and needed further two steps for synthesis of starting materials including diaryldiazomethane and dithienyl thioketones or dithienyldiazomethane and diaryl thioketones. In our strategy, we have modified the synthesis of diphenyldithienylethene by reversing both reactants via gem-dibromodithienylethene and phenylboronic acids. Gem-dibromodithienylethene was synthesized after two steps as described in Scheme 1. The Suzuki reaction was employed for the construction of tetrasubstituted ethene **3** which was isolated in 55% yield. The post-monoarylation of diphenyldithienylethene **3** by direct palladium catalyzed reaction was conducted at C2-atom of thiophene ring. The new compound **DTE-3-CHO-1** was synthesized with moderate yields (49%). The structures of **DTE-3-CHO-1** were confirmed by NMR and HR-MS spectroscopies.



***Scheme 1.** Synthetic strategy for* **DTE-3-CHO-1**

4. Conclusions

We reported herein a new synthetic pathway for the preparation of diphenyldithienylethene. The direct palladium catalyzed C-H bond fuctionalization provided a convenient approach for the regioselective monoraylation of diphenyldithienylethene. The structure of the obtained compound was confirmed by NMR and HR-MS spectral data. This method can be easily applied to prepare arylated diphenyldithienylethene with interesting photophysical properties. In addition, the fluorescence and the aggregation induced emission of this compound have shown promising results which will be published soon in due course.

- ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*
- ***Acknowledgment:*** *This research was funded by the Ministry of Education and Training under a grant number B2018-SPS-22.*

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MONO ARYL HÓA DIPHENYLDITHIENYLETHENE THÔNG QUA PHẢN ỨNG HOẠT HÓA TRỰC TIẾP LIÊN KẾT C-H SỬ DỤNG XÚC TÁC PALLADIUM KHÔNG LIGAND

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Ngày nhận bài: 25-5-2021; ngày nhận bài sửa: 20-6-2021; ngày duyệt đăng: 01-9-2021

TÓM TẮT

Bài báo trình bày một phương pháp hiệu quả để thực hiện aryl hoá diphenyldithienylethene thông qua phản ứng hoạt hoá trực tiếp liên kết C-H sử dụng xúc tác palladium không ligand. Hợp chất diphenyldithienylethene ***DTE-3-CHO-1*** *được tổng hợp từ thiophene qua bốn giai đoạn. Giai đoạn chìa khoá của quá trình tổng hợp* ***DTE-3-CHO-1*** *là phản ứng hoạt hoá trực tiếp liên kết C-H được thực hiện giữa diphenyldithienylethene* ***3*** *và 3-bromobenzaldehyde sử dụng xúc tác* $Pd(OAc)_2$*, base KOAc trong dung môi DMAc tại 120 ℃ trong 16h.* ***DTE-3-CHO-1*** *thu được với hiệu suất 49%. Hợp chất* ***DTE-3-CHO-1*** *tổng hợp được hứa hẹn là một hợp chất có các tính chất quang lí hấp dẫn. Cấu trúc của diphenyldithienylethene* ***DTE-3-CHO-1*** *cũng như các hợp chất trung gian trong quá trình tổng hợp được xác định dựa vào phổ NMR và HR-MS. Hợp chất* ***DTE-3-CHO-1*** *là một hợp chất mới.*

Từ khóa: aggregation-induced emission; diphenyldithienylethene; phản ứng aryl hoá trực tiếp xúc tác palladium; fluorescence