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# Synthesis of 2,9-dialkylated phenanthro[1,2-*b*:8,7-*b*′]dithiophenes via cross-coupling reactions and sequential Lewis acid-catalyzed regioselective cycloaromatization of epoxide

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ABSTRACT

Phenanthro[1,2-*b*:8,7-*b*′]dithiophene (PDT) was prepared via Suzuki–Miyaura or Negishi cross-coupling of a 2-thienylboron or -zinc compound with 1,4-dibromobenzene, followed by Lewis acid-catalyzed regioselective cycloaromatization of the epoxide. A series of 2,9-dialkylated phenanthro[1,2-*b*:8,7-*b*′]dithiophene (PDT) derivatives could also be synthesized in good yields by Suzuki–Miyaura coupling of the brominated PDT with alkylboranes by introducing linear alkyl substituents.

Organic field-effect transistors (OFETs) have attracted considerable interest as key components in future ubiquitous electronics due to advantages such as flexibility, light weight, and ease of design.[1] One particular acene-type molecule, pentacene,[2] has served as the active semiconducting layer in OFETs owing to the high field-effect mobility ($\mu$) of 5.5 $cm^2 V^{-1} s^{-1}$ that it has shown in a thin-film transistor,[3] and its state-of-the-art value of 40 $cm^2 V^{-1} s^{-1}$ in single crystals.[4] However, pentacene is unstable under atmospheric conditions, and readily photodegrades owing to its relatively high HOMO energy (−5.0 eV), which arises from its extended $\pi$-conjugation.[5] Recently, a phenacene-type molecule, picene, incorporating the same number of benzene rings as pentacene, has become the focus of considerable interest because it becomes superconductive[6] with alkali-metal doping, and also shows high field-effect mobility in a transistor (1.1 $cm^2 V^{-1} s^{-1}$ in a thin-film OFET).[7] Moreover, a picene-based FET is stable in air because picene has a larger energy bandgap ($E_g = 3.3$ eV) and a lower HOMO energy (−5.5 eV) than pentacene.[8] The potential utility of phenacene-type molecules makes the development of more efficient synthetic methods[9] and further improvement in their OFET properties[10–12] matters of some importance.

We have recently reported the synthesis of picenes[13] and fulminene[14] by the palladium-catalyzed Suzuki–Miyaura coupling of (*Z*)-alkenylboronates with polyhalobenzene and sequential intramolecular double cyclization via C—H activation. This protocol is also applicable to the synthesis of phenanthro[1,2-*b*:8,7-*b*′]dithiophene (PDT) by replacing the terminal phenyl rings in picene with thiophene rings, aiming at increased intermolecular $\pi$–$\pi$ interactions due to the large atomic radius of sulfur, which may enhance its performance in OFETs.[15] Results showed that OFET devices fabricated with thin films of PDT formed by thermal deposition exhibited carrier mobility as large as $1.1 \times 10^{-1}$ $cm^2 V^{-1} s^{-1}$, and suggested that fabrication using a solution process might be possible owing to PDT's high solubility in common organic solvents.

However, we found that this synthetic strategy is not suitable for the large-scale synthesis of PDT because in some cases a mixture of stereoisomers of the coupled products is formed through (*E*)/(*Z*) isomerization upon Suzuki–Miyaura coupling, leading to a lower yield of the desired products. To produce derivatives of PDT for use as organic semiconductors, a more efficient synthetic method is highly desirable. Here we report a new synthetic route to the PDT core structure using cross-coupling reactions. Furthermore, the solubility of PDT might be improved by introducing long alkyl chains, as this may induce a self-assembly process by the 'fastener effect', leading to high crystallinity in thin films. Some examples of this have already been reported in alkyl-substituted picene[16] and alkylated thienoacene.[17,18]

To explore a new synthetic route to PDT, we investigated the palladium-catalyzed Suzuki–Miyaura coupling of commercially

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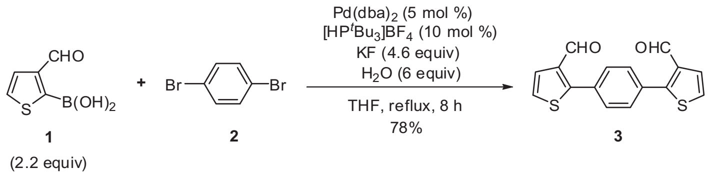
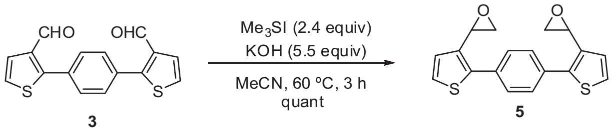


**Scheme 1.**

available 3-formyl-2-thiopheneboronic acid (**1**) with 1,4-dibromobenzene (**2**) affording the corresponding coupled product **3** in 78% yield (Scheme 1).[19]

We screened various reaction conditions to develop an efficient synthetic route to **3**. The results are summarized in Table 1. To our surprise, we found that chemoselective C—H zincation across 3-formylthiophene (**4**) occurred at the 2-position (adjacent to the formyl group) of the thiophene ring, using TMPZnCl·LiCl.[20] Negishi coupling of the in situ generated 2-thienylzinc reagent with 1,4-dibromobenzene (**2**) using a catalyst system of $Pd(dba)_2$ (dba = dibenzylideneacetone) with a phosphonium salt, $[HP^tBu_3]BF_4$ used as a precursor of the phosphine ligand proceeded at reflux to furnish **3** in 65% yield (entry 1).[21] However, other palladium precursors and phosphine-based ligands including biarylphosphine (Sphos)[22] and $PdCl_2(dppf){\cdot}C_6H_6$[23] (dppf = 1,1′-bis(diphenylphosphino) ferrocene) were found to be inferior (entries 2–4). PEPPSI-IPr ((PEPPSI = pyridine-enhanced precatalyst preparation stabilization and initiation, IPr = 1,3-diisopropylimidazol-2-ylidene),[24] recently introduced by Organ, displayed a modest catalytic activity to afford **3** in 52% yield as determined by NMR (entry 5). With palladacycle precatalysts[25] utilized in the $sp^2$–$sp^2$ Negishi couplings, compound **3** was obtained in lower yields (entries 6–10).

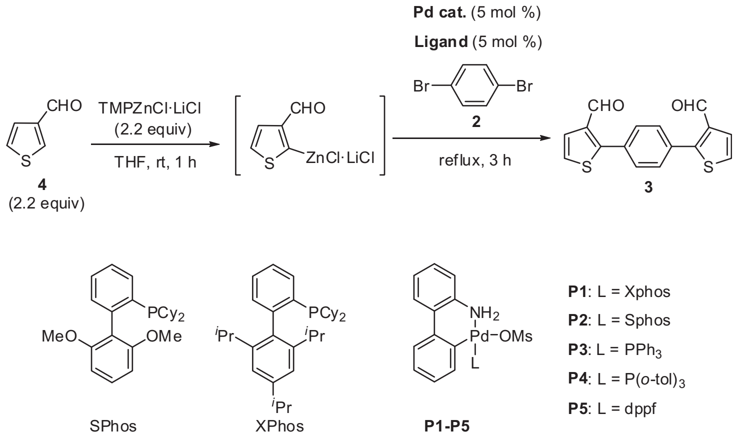


**Scheme 2.**

Following this, sequential epoxidation of **3** gave the desired product **5** quantitatively (Scheme 2).[26,27] We next screened the reaction conditions of acid-mediated[28] and -catalyzed[29] Friedel–Crafts-type cycloaromatization of **5** and the results are summarized in Table 2. Attempted reactions with $MeSO_3H$ and $BF_3{\cdot}OEt_2$ did not proceed, even with the addition of excess reagent. With a stoichiometric amount of $Sc(OTf)_3$, PDT (**6**) was obtained in 32% yield (entry 1). However, the catalytic variant of $Sc(OTf)_3$ was not effective (entry 2). We then explored catalytic reactions with other Lewis acids $M(OTf)_n$, but yields of **6** were insufficient (entries 3–6). To our delight, 10 mol % of $InCl_3$ was found to give better results and afforded **6** in 46% yield (entry 7). Increasing the amount of $InCl_3$ to 20 mol % improved the yield to 50% (entry 8). Varying the concentrations, we found that lower concentrations gave

**Table 1**

Optimization of Negishi cross-coupling of **2** with **4**



| Entry | Pd cat. | Ligand | Yield[a] (%) |
|---|---|---|---|
| 1[b] | $Pd(dba)_2$ | $[HP^tBu_3]BF_4$ | 65 |
| 2[b] | $Pd(OAc)_2$ | SPhos | 46 |
| 3[b] | $Pd(dba)_2$ | P(*o*-tol)$_3$ | 9 |
| 4 | $PdCl_2(dppf){\cdot}C_6H_6$ | — | 55 |
| 5 | PEPPSI·IPr | — | 52 |
| 6 | **P1** | — | 41 |
| 7 | **P2** | — | 36 |
| 8 | **P3** | — | 15 |
| 9 | **P4** | — | 3 |
| 10 | **P5** | — | 4 |

[a] NMR yields based on **2**.

[b] 10 mol % of phosphine ligand was used.

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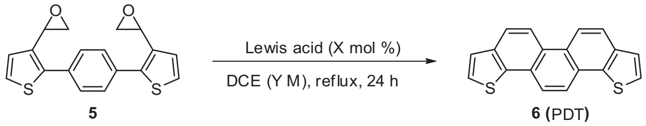
**Table 2**
Screening Lewis acids for electrophilic double cycloaromatization of **5**[a]



| Entry | Lewis acid | (X mol %) | (Y M) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | $Sc(OTf)_3$ | 240 | 0.05 | 32 |
| 2 | $Sc(OTf)_3$ | 10 | 0.05 | <1 |
| 3 | $Bi(OTf)_3$ | 10 | 0.05 | 22 |
| 4 | $Hf(OTf)_4$ | 10 | 0.05 | 0 |
| 5 | $Cu(OTf)_2$ | 10 | 0.05 | <1 |
| 6 | $In(OTf)_3$ | 10 | 0.05 | 26 |
| 7 | $InCl_3$ | 10 | 0.05 | 46 |
| 8 | $InCl_3$ | 20 | 0.05 | 50 |
| 9[c] | $InCl_3$ | 20 | 0.025 | 58 (58) |
| 10[c] | $InCl_3$ | 20 | 0.005 | 64 |

[a] DCE = 1,2-dichloroethane.

[b] NMR yields. An isolated yield is shown in parenthesis.

[c] Reaction time was 12 h.

higher yields of up to 64% (entries 9 vs 10), presumably due to the suppression of an undesired intermolecular side reaction. Considering the longer reaction time and the greater solvent consumption, we adopted the reaction conditions in entry 9 as optimum. With conditions optimized, we could achieve the gram-scale synthesis of PDT (**6**).[30]

In regard to the regioselectivity of cyclization reaction, we have only observed the formation of traces of the corresponding anthra[1,2-*b*:5,6-*b*′]dithiophene (ADT) (**6**′),[31] which is a structural isomer of **6**. We speculate that the selective formation of **6** can be attributed to an electronic effect. As shown in Scheme 3, a primitive DFT calculation disclosed a higher electron density localized on the indicated (red dot) carbon atom on the second side of intermediate **7** to undergo electrophilic cyclization, which favors one of the two possible Friedel–Crafts-type cycloaromatizations on that side.[32] Detailed calculations to gain deeper insight into this regioselectivity are in progress.

Since the 2-position of the thiophene ring is reported to be readily functionalized, borylation,[33] bromination,[34] and stannylation,[35] as well as various linear alkyl groups, were introduced onto the PDT core (Scheme 4). First, bromination of PDT **6** with a slight excess of butyllithium followed by addition of bromine afforded **8** in 89% yield. Starting from the synthesized **8**, 2,9-dialkylated PDTs **9a**–**9f** were obtained in 69–80% yields by Suzuki–Miyaura coupling reactions[36] with an excess of alkylboranes, derived from the hydroborylation of various terminal alkenes with 9-BBN dimer.[37,38]

In summary, we have developed a more efficient and readily scalable synthetic method for the preparation of the parent PDT molecule by sequential Suzuki–Miyaura or Negishi coupling, epoxidation, and $InCl_3$-catalyzed cyclization. We have successfully used this route to prepare a new class of 2,9-dialkylated PDT derivatives. These diverse synthetic strategies to introduce various alkyl groups onto the common core at the final stage should be applicable to the production of other functionalized PDT molecules. Further study to elucidate the effects of the introduced alkyl chains on the FET characteristics of **9c**–**9f** is currently underway in our laboratories.

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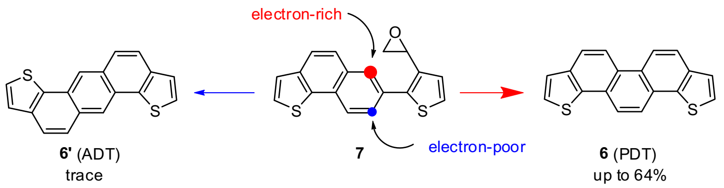
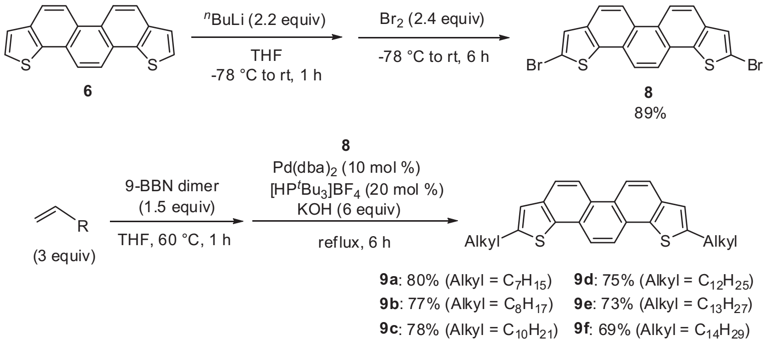
## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.05.035. These data include MOL files and InChiKeys of the most important compounds described in this article.



**Scheme 3.**



**Scheme 4.**

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27. *Synthesis of **5**.* To a solution of **3** (3.21 g, 10.8 mmol, 1 equiv) in anhydrous acetonitrile (216 mL) in a 300 mL 2-neck round-bottom flask under an argon atmosphere were added trimethylsulfonium iodide (5.29 g, 25.9 mmol, 2.4 equiv) and powdered KOH (3.33 g, 59.4 mmol, 5.5 equiv) at room temperature. The reaction mixture was stirred at 60 °C for 3 h, quenched with water (100 mL), and extracted with chloroform (300 mL × 2). The combined organic layers were washed with brine and dried over $MgSO_4$. Filtration and evaporation afforded product **5** (3.52 g, 10.8 mmol, quant) as a white solid. Mp >270 °C. FT-IR (KBr, $cm^{-1}$): 3076 (s), 2941 (s), 2906 (s), 2854 (s), 1257 (s), 1242 (s), 925 (m), 831 (w), 729 (w), 655 (w). $^1H$ NMR (300 MHz, $CDCl_3$, rt): $\delta$ 3.02 (m, 2H), 3.21 (m, 2H), 4.00 (m, 2H), 6.93 (d, $J$ = 5.4 Hz, 2H), 7.28 (d, $J$ = 5.4 Hz, 2H), 7.61 (s, 4H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): $\delta$ 48.5, 50.2, 50.3, 124.9, 125.9, 129.5, 133.0, 134.4, 134.5, 141.7, 141.8. HRMS ($EI^+$) Calcd for $C_{18}H_{14}O_2S_2$: 326.0435. Found: 326.0414.
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30. *Synthesis of PDT (**6**).* To a solution of epoxide **5** (2.61 g, 8 mmol, 1 equiv) in anhydrous 1,2-dichloroethane (320 mL) in a 500 mL 2-neck round-bottom flask under an argon atmosphere was added anhydrous indium chloride (354 mg, 1.6 mmol, 20 mol %) at room temperature. The reaction mixture was stirred at 100 °C for 12 h, quenched with water (200 mL), and extracted with chloroform (300 mL × 2). The combined organic layers were washed with brine and dried over $MgSO_4$. Filtration and evaporation afforded a pale yellow solid. Column chromatography on silica gel (chloroform/hexane = 2:1) gave product **6** (1.33 g, 4.6 mmol, 58%) as a pale yellow solid. $^1H$ NMR (300 MHz, $CDCl_3$, rt): $\delta$ 7.56 (dd, $J$ = 12.9, 5.4 Hz, 4H), 8.06 (d, $J$ = 9 Hz, 2H), 8.23 (s, 2H), 8.69 (d, $J$ = 9 Hz, 2H).
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38. *Typical procedure for alkylation of **8**:* To a solution of terminal alkene (0.6 mmol, 3 equiv) in anhydrous THF (4 mL) in a 20 mL Schlenk under argon was added 9-BBN dimer (75 mg, 0.3 mmol, 1.5 equiv) at room temperature. The reaction mixture was stirred at 60 °C for 1 h, then cooled to room temperature before adding $Pd(dba)_2$ (11.5 mg, 0.02 mmol, 10 mol %), $[HP^tBu_3]BF_4$ (11.6 mg, 0.04 mmol, 20 mol %), powdered KOH (67.3 mg, 1.2 mmol, 6 equiv), and compound **8** (89.6 mg, 0.2 mmol, 1 equiv). The reaction mixture was stirred at 85 °C for 6 h, quenched with water (10 mL), and extracted with chloroform (30 mL × 2). The combined organic layers were washed with brine and dried over $MgSO_4$. Filtration and evaporation afforded a pale yellow solid. Column chromatography on silica gel (chloroform/hexane = 2:3) gave **9a** in 80% yield, which was further purified by recrystallization from hexane to give analytically pure samples as a white solid. Mp = 175–176 °C. FT-IR (KBr, $cm^{-1}$): 2953 (m), 2926 (w), 2883 (m), 2850 (m), 1463 (m), 1433 (m), 1361 (s), 1292 (m), 817 (w), 723 (w). $^1H$ NMR (600 MHz, $CDCl_3$, rt): $\delta$ 0.90 (t, $J$ = 7.2 Hz, 6H), 1.26–1.40 (m, 12H), 1.42–1.47 (m, 4H), 1.83 (quintet, $J$ = 7.2 Hz, 4H), 3.00 (t, $J$ = 7.2 Hz, 4H), 7.17 (s, 2H), 7.89 (d, $J$ = 9 Hz, 2H), 8.09 (s, 2H), 8.60 (d, $J$ = 9 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): $\delta$ 14.1, 22.7, 29.1, 29.1, 30.9, 31.4, 31.8, 119.9, 121.5, 121.9, 123.3, 126.6, 127.1, 137.7, 138.0, 146.4. Anal. Calcd for $C_{32}H_{38}S_2$: C, 78.96; H, 7.87. Found: C, 78.58; H, 7.78.

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