C–H Activation

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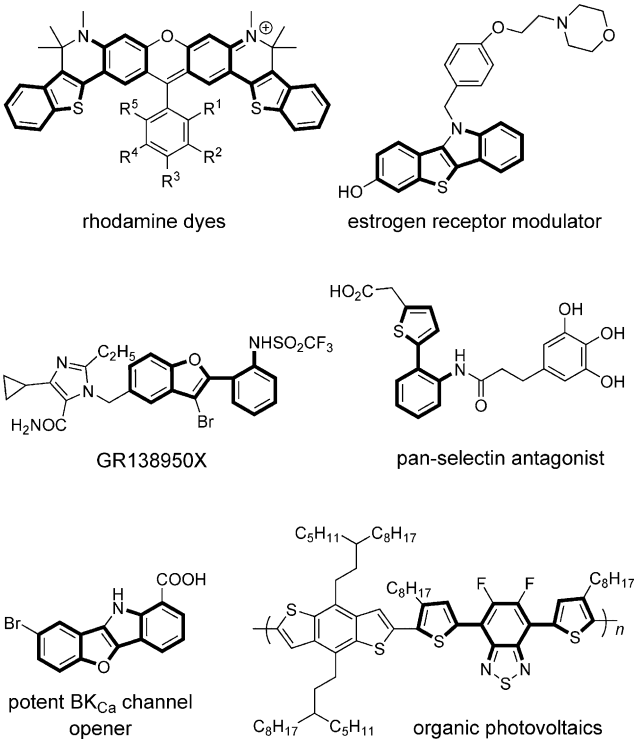
Use of the Wilkinson Catalyst for the *ortho*-C–H Heteroarylation of Aromatic Amines: Facile Access to Highly Extended π-Conjugated Heteroacenes for Organic Semiconductors**

*Yumin Huang, Di Wu, Jingsheng Huang, Qiang Guo, Juan Li, and Jingsong You**

Abstract: *An unprecedented catalytic system composed of the Wilkinson catalyst [$Rh(PPh_3)_3Cl$] and CF_3COOH enabled the highly regioselective cross-coupling of aromatic amines with a variety of heteroarenes through dual C–H bond cleavage. This protocol provided a facile and rapid route from readily available substrates to (2-aminophenyl)heteroaryl compounds, which may be conveniently transformed into highly extended π-conjugated heteroacenes. The experimental studies and calculations showed that thianaphtheno[3,2-b]indoles have large HOMO–LUMO energy gaps and low-lying HOMO levels, and could therefore potentially be high-performance organic semiconductors. Herein we report the first use of a rhodium(I) catalyst for oxidative C–H/C–H coupling reactions. The current innovative catalyst system is much less expensive than $[RhCp^*Cl_2]_2/AgSbF_6$ and could open the door for the application of this approach to other types of C–H activation processes.*

(2-Aminophenyl)heteroaryl motifs are not only prevalent in biologically active molecules, pharmaceuticals, and organic and polymeric functional materials, but are also versatile building blocks for the synthesis of various complex functional molecules (Scheme 1).[1] Although a number of methods have been established for the construction of such structures, they often suffer from tedious multistep synthesis and purification. Undoubtedly, it would be desirable to develop a strategy for the rapid and concise synthesis of these important aryl–heteroaryl frameworks. Recently, as the most promising transformation to construct aryl–heteroaryl scaffolds, transition-metal-catalyzed oxidative C–H/C–H cross-coupling between a simple arene and a heteroarene has attracted considerable attention.[2] Given that aromatic amines are widespread compounds, their dehydrogenative cross-coupling with various heteroarenes would rapidly provide a wide range of (2-aminophenyl)heteroaryl skeletons.

Although transition-metal-catalyzed C–H/C–H oxidative cross-coupling reactions between a simple arene and a heteroarene have experienced rapid growth,[3] two major obstacles, namely, the problematic regioselectivity of such reactions and the requirement of a large excess of the arene (as a solvent or cosolvent) to ensure cross-coupling rather than homocoupling, have imposed a limitation on the scope of application. Clearly, taking advantage of the intrinsic functional group on the aromatic ring as the directing group would overcome the above problems.[4] Despite the existence of a wide range of both natural and designed functional groups, there are very few examples of the transition-metal-catalyzed directed *ortho*-C–H heteroarylation of arenes through twofold C–H activation. Among these examples, the only aromatic compounds used have been N-heteroaryl arenes (Scheme 2 A)[4a,c] and electron-poor arenes, such as benzamides (Scheme 2 B).[4b,d] To our knowledge, no transition-metal-catalyzed dehydrogenative cross-coupling reaction of a heteroarene with an electron-rich arene bearing a directing group has been described.[5] Thus, the development of an innovative catalytic system to meet such a challenge caused by the distinctly different electronic nature of the functional groups is required.



Scheme 1. Examples of significant functional molecules containing the (2-aminophenyl)heteroaryl motif.

[*] Y. Huang, Prof. Dr. D. Wu, J. Huang, Q. Guo, J. Li, Prof. Dr. J. You
Key Laboratory of Green Chemistry and Technology of the Ministry of Education, College of Chemistry and State Key Laboratory of Biotherapy, West China Medical School, Sichuan University
29 Wangjiang Road, Chengdu 610064 (PR China)
E-mail: jsyou@scu.edu.cn

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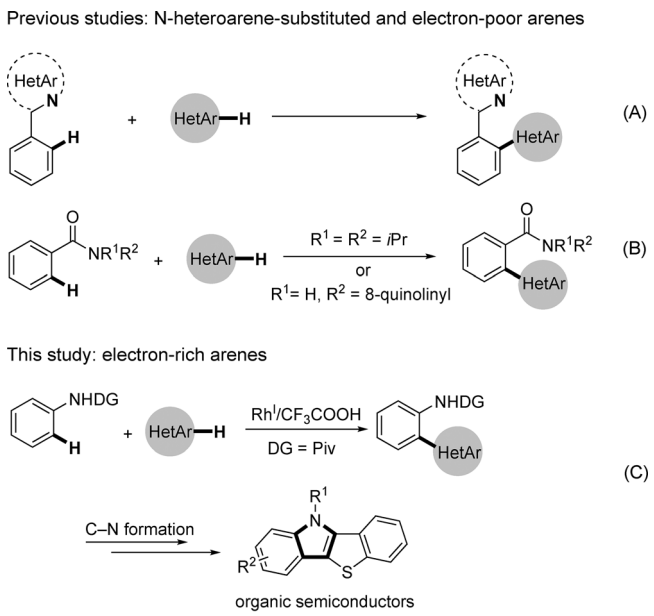
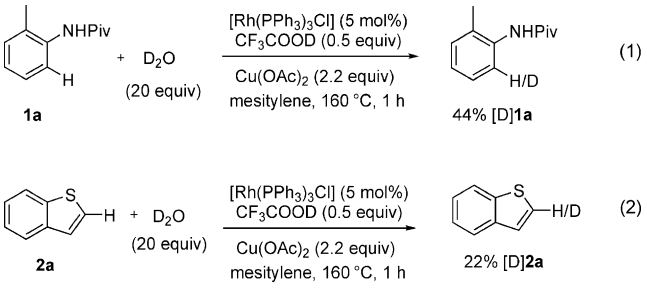


Scheme 2. Transition-metal-catalyzed directed oxidative C–H/C–H cross-coupling between a simple arene and a heteroarene. DG = directing group, HetAr = heteroaryl, Piv = pivaloyl.

Over the past decade, rhodium-catalyzed C–H activation has emerged as a powerful method for carbon–carbon and carbon–heteroatom bond formation. The most frequently used rhodium catalyst for such reactions is [Cp*Rh] (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl), usually in combination with $AgSbF_6$.[6,7] It is known that the Wilkinson catalyst, $[Rh(PPh_3)_3Cl]$, is a versatile catalyst that can promote a broad range of transformations.[8] As part of our ongoing effort to construct aryl–heteroaryl structures,[4c] we herein report an unprecedented catalyst system composed of the Wilkinson catalyst and CF_3COOH that enables the highly regioselective cross-coupling of electron-rich aromatic amines with various heteroarenes through dual C–H bond cleavage (Scheme 2C). From an economic viewpoint, this much less expensive innovative catalyst system than the $[RhCp^*Cl_2]_2/AgSbF_6$ system[9] is quite appealing and could open the door for the application of this approach to other types of C–H activation processes.

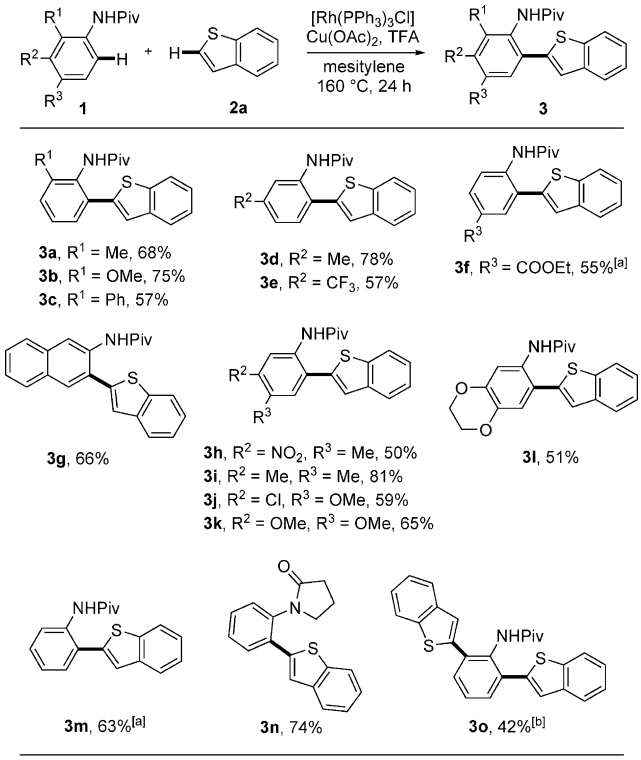
We started our investigation by examining the cross-coupling between *N*-2-tolylpivalamide (**1a**) and benzothiophene (**2a**) as a model reaction (see Table S1 in the Supporting Information). The extensively used $[\{RhCp^*Cl_2\}_2]/AgSbF_6$ system did not afford the coupled product **3a**; however, **3a** was formed in 40% yield in the absence of $AgSbF_6$ (see Table S1). Other additives were then examined, and CF_3COOH was found to be the most efficient. We assumed that CF_3COOH could facilitate the formation of a highly electrophilic cationic Rh^{III} species that is more reactive toward *ortho*-C–H bond activation.[10] Among the Rh sources investigated, the catalytic system composed of $[Rh(PPh_3)_3Cl]$ and CF_3COOH proved to be the best choice. Finally, the best result was observed when the reaction was performed in the presence of $[Rh(PPh_3)_3Cl]$ (5 mol%), $Cu(OAc)_2$ (2.2 equiv), and CF_3COOH (0.5 equiv) in mesitylene at 160°C for 24 h (see Table S1).

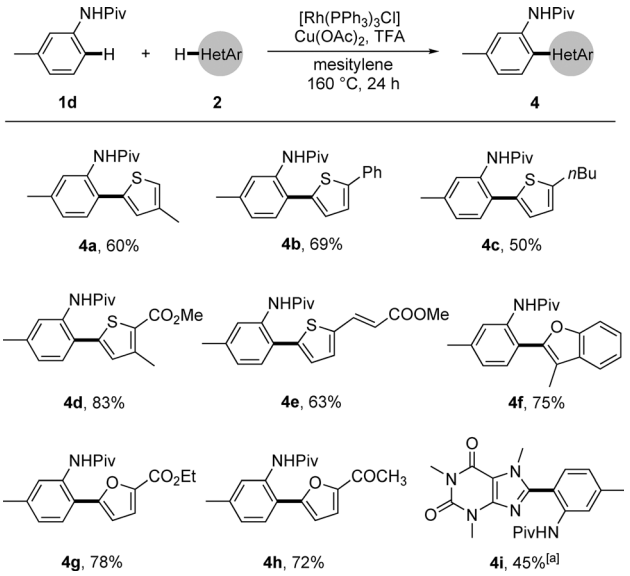
To clarify whether C–H bond activation of the arene precedes C–H bond activation of the heteroarene or vice versa, H/D exchange experiments were carried out for each coupling partner, **1a** and **2a** [Eqs. (1) and (2)]. When *N*-2-tolylpivalamide (**1a**) was treated with D_2O for 1 h, 44% of the starting material was deuterated to give [D]**1a**, whereas the H/D exchange ratio of benzothiophene (**2a**) was 22%. These results suggested that the cross-coupling reaction might begin with the *ortho*-C–H activation of **1a**. Thus, we speculated that a plausible mechanism could involve: 1) the oxidation of Rh^I to Rh^{III} by the Cu^{II} salt, 2) the *ortho*-C–H activation of **1a** to generate the six-membered rhodacycle, 3) the subsequent formation of the key aryl–rhodium(III)–heteroaryl species with **2a**, and 4) reductive elimination to produce the coupled product **3a**.[4c,11]



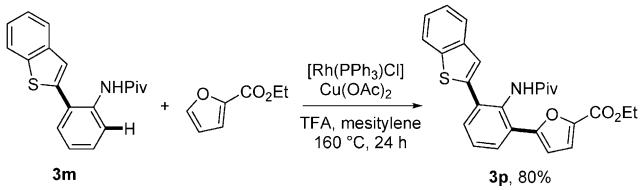
Having optimized the reaction conditions, we investigated the scope of the reaction with respect to the pivalanilide substrate (Scheme 3). Pivalanilides bearing electron-donating, electron-withdrawing, or bulky groups all smoothly underwent the cross-coupling reaction with benzothiophene (products **3a–l**). The catalytic system was tolerant of various functional groups, such as ester, nitro, chloride, and methoxy groups (products **3f**,**h**,**j**, and **k**), and 1-phenylpyrrolidin-2-one could also be converted into the corresponding product **3n** in 74% yield. The transformation exhibited good regioselectivity: The *meta*-substituted and disubstituted pivalanilides studied afforded the products of C–H activation at the less sterically hindered position (products **3d**,**e** and **3g–l**). Unsubstituted pivalanilide selectively underwent *ortho*-heteroarylation to afford the monosubstituted product **3m** in 63% yield and could also give the symmetrical diheteroaryl derivative **3o** in 42% yield when the amount of benzothiophene was increased. The treatment of **3m** with ethyl 2-furancarboxylate further yielded the unsymmetrical diheteroaryl-substituted aromatic amine **3p**.

Subsequently, we turned our attention to the use of other heteroarenes (Scheme 4). Various thiophenes and furans containing both electron-donating and electron-withdrawing groups smoothly underwent the cross-coupling reaction with *N*-*m*-tolylpivalamide (products **4a–h**). When 3-methylthiophene was employed as the substrate, the cross-coupling occurred regioselectively at the less sterically hindered C5





Scheme 4. Scope of the reaction with respect to the heteroarene substrate. Reaction conditions: **1d** (0.25 mmol), **2** (0.75 mmol), [Rh(PPh_3)$_3$Cl] (5 mol%), $Cu(OAc)_2$ (2.2 equiv), TFA (0.5 equiv), mesitylene (0.6 mL), 160°C, 24 h, N_2 atmosphere. The yields given are for the isolated product. [a] The reaction was carried out with **1d** (0.75 mmol) and caffeine (0.25 mmol).

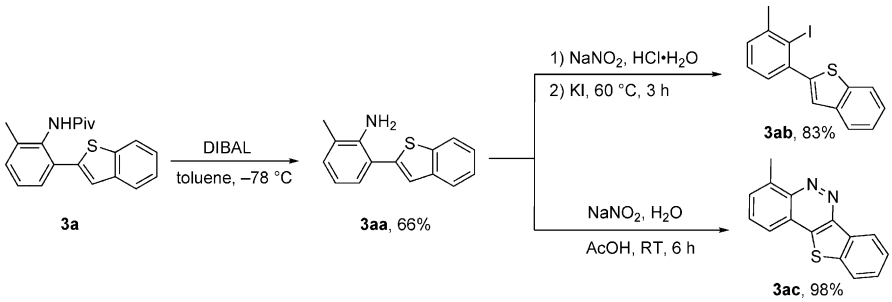


Scheme 3. Scope of the reaction with respect to the pivalanilide substrate. Reaction conditions: pivalanilide **1** (0.25 mmol), **2a** (0.75 mmol), [Rh(PPh_3)$_3$Cl] (5 mol%), $Cu(OAc)_2$ (2.2 equiv), TFA (0.5 equiv), mesitylene (0.6 mL), 160°C, 24 h, N_2 atmosphere. The yields given are for the isolated product. [a] The reaction was carried out with **1** (0.75 mmol) and **2a** (0.25 mmol). [b] The reaction was carried out with **1** (0.25 mmol), **2a** (1.5 mmol), [Rh(PPh_3)$_3$Cl] (7.5 mol%), $Cu(OAc)_2$ (4.4 equiv), and TFA (1 equiv) in mesitylene (1.2 mL) at 160°C for 24 h under a N_2 atmosphere. TFA = trifluoroacetic acid.

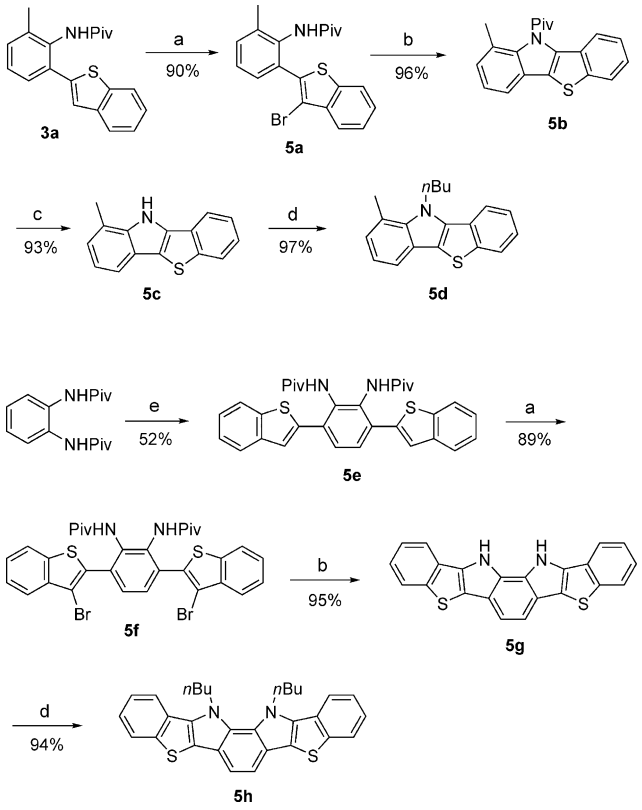
position to give **4a**. Furthermore, caffeine also reacted with *N*-*m*-tolylpivalamide at the acidic C2 position to provide **4i**.

To further illuminate the synthetic utility of this protocol, we investigated a variety of transformations of the resultant (*ortho*-aminophenyl)heteroaryl derivatives. First, the pivaloyl group of **3a** could be readily removed by treatment with DIBAL to give a free amino group (Scheme 5).[12] The free amino group could be further transformed into various functional groups, such as an iodide group.[13] The amino moiety is also a useful synthetic handle for the construction of an extended π-system. For example, an important type of benzothieno[3,2-*c*]cinnoline, **3ac**, was synthesized by diazotization of the amino group and internal cyclization at the C3 position of the benzothiophene moiety.[14]

Large acenes, such as pentacene, have the disadvantage of poor air stability as organic semiconductors in electronic devices owing to their high-lying HOMO energy levels.[15] Recently, highly extended π-conjugated heteroacenes have attracted considerable attention as a result of their greater air stability with respect to that of oligoacenes.[16] We next focused our attention on the synthesis of thianaphtheno[3,2-*b*]indole π-scaffolds (Scheme 6).[1f,l–n] *N*-Butyl-9-methylthianaphtheno[3,2-*b*]indole (**5d**, BMTNI) was synthesized by the sequential bromination of **3a**, intramolecular amination under CuI/*N*,*N*-dimethylglycine catalysis, deprotection by treatment with NaOH/ethanol, and N-alkylation in 78% total yield. Highly condensed *N*,*N*′-dibutylthianaphtheno[2′,3′:4,5]pyrrolo[3,2-*g*]thianaphtheno[3,2-*b*]indole (**5h**, DTNPTNI) with seven fused aromatic rings was constructed by sequential diheteroarylation of an *o*-diaminobenzene derivative, bromination, cyclization, and N-alkyla-



Scheme 5. Transformations of **3a**. DIBAL = diisobutylaluminum hydride.



Scheme 6. Synthesis of **5d** and **5h**: a) NBS, $CHCl_3$/AcOH (1:1), 0°C→RT; b) CuI, *N*,*N*-dimethylglycine hydrochloride, K_3PO_4, DMF, 140°C; c) NaOH, EtOH, 130°C; d) NaH, *n*BuBr, DMF, 0°C→RT; e) benzothiophene, $[Rh(PPh_3)_3Cl]$, $Cu(OAc)_2$, TFA, mesitylene, 160°C. DMF = *N*,*N*-dimethylformamide, NBS = *N*-bromosuccinimide.

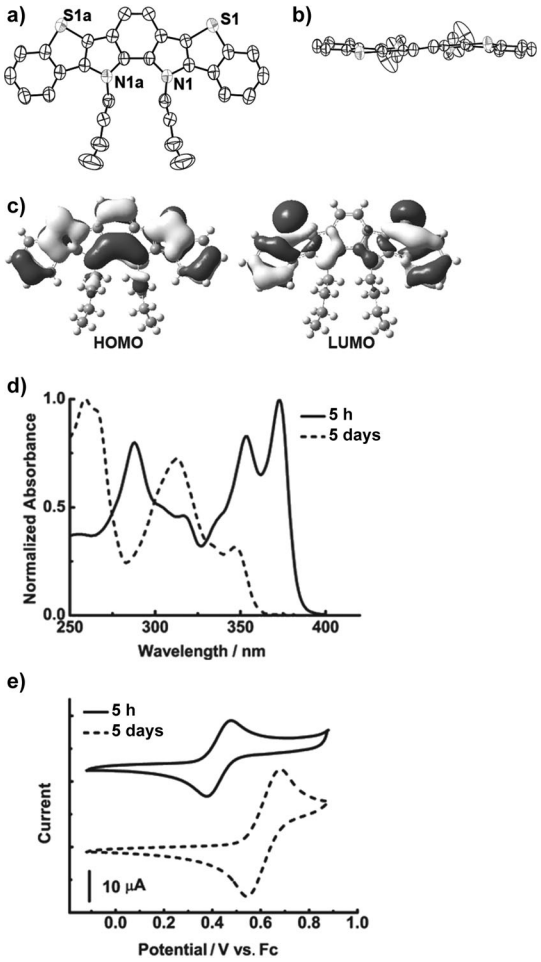


Figure 1. a) Top view and b) side view of **5h** as ORTEP drawings with thermal ellipsoids at 50% probability. H atoms were omitted for clarity. c) HOMO (left) and LUMO (right) orbitals of **5h** as determined by DFT calculations (B3LYP/6-31G) on the basis of the molecular geometry in the single crystal. d) UV/Vis absorption spectra of **5d** and **5h** in CH_2Cl_2. e) Cyclic voltammograms of **5d** and **5h** in CH_2Cl_2.

tion. The N-protecting groups were cleaved spontaneously during the copper-catalyzed intramolecular amination.

We investigated the molecular configuration and photophysical properties of the two thianaphtheno[3,2-*b*]indoles **5d** and **5h**. X-ray structural analysis of **5h** showed good planarity of the fused aromatic core (Figure 1a,b),[17] which may allow closer molecular packing for efficient charge/hole transport in the material. HOMO and LUMO orbitals spreading all over the whole seven fused aromatic rings indicated highly extended conjugation of **5h** (Figure 1c). The optical HOMO–LUMO energy gaps estimated from the absorption edges were large (ca. 3.42 and 3.16 eV for **5d** and **5h**, respectively), and the HOMO levels defined by cyclic voltammetry (−5.35 and −5.16 eV vs. vacuum for **5d** and **5h**, respectively) were low-lying (Figure 1d,e and Table 1) and comparable with those of dinaphtho[2,3-*b*:2′,3′-*f*]thieno-[3,2-*b*]thiophene (DNTT).[16] Such features have been suggested to facilitate device stability for high-performance organic semiconductors.[16]

In conclusion, an innovative catalyst system composed of the Wilkinson catalyst $[Rh(PPh_3)_3Cl]$ and CF_3COOH enabled the cross-coupling of electron-rich aromatic amines with heteroarenes through twofold C−H activation to rapidly afford (2-aminophenyl)heteroaryl motifs. The current protocol features high functionality tolerance, complete regioselectivity, relatively broad generality, and the use of coupling partners in low molar ratios, thus rendering this transformation synthetically useful. This strategy offered a facile route to highly extended π-conjugated heteroacenes. BMTNI and DTNPTNI exhibit large HOMO–LUMO energy gaps and low-lying HOMO levels, which indicate their potential as high-performance organic semiconductors. This facile and rapid method may also be useful for polymerization. Further studies to identify new applications for this reaction are under way.

Table 1: Energy levels of **5d** and **5h**.

Compound	E_g^{opt} [eV][a]	E_{onset}^{ox} [V][b]	HOMO [eV][c]	LUMO [eV][d]
5d	3.42	0.55	−5.35	−1.93
5h	3.16	0.36	−5.16	−2.00

[a] $E_g^{opt} = 1240/\lambda_{onset}$. [b] Estimated from the oxidation onset of the CV (in CH_2Cl_2). [c] HOMO = $-(4.8+E_{onset}^{ox})$. [d] LUMO = (HOMO + E_g^{opt}).

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[17] CCDC 1008477 (**5h**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

