OL Organic Letters

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Synthesis of Redox-Active Phenanthrene-Fused Heteroarenes by Palladium-Catalyzed C−H Annulation

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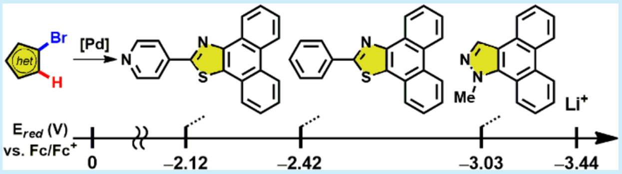
Cite This: https://dx.doi.org/10.1021/acs.orglett.9b04545 Read Online

ABSTRACT: Pd-catalyzed C−H annulation reactions of halo- and aryl-heteroarenes were developed using readily available *o*-bromobiaryls and *o*-dibromoaryls, respectively. A variety of five-membered heteroarenes rapidly provided the corresponding phenanthrene-fused heteroarenes, which led to the identification of phenanthro-pyrazole and thiazole as new, stable −2 V redox couples. The flexible syntheses and tunability of the redox potentials of these azole-fused phenanthrenes over a wide range are expected to facilitate their application as redox-active organic functional materials.



The design and synthesis of new redox-active cores are critical undertakings in the development of organic functional materials as electron transfer mediators.[1] Electrochemical redox mediators have been extensively utilized in various electrochemical energy storage systems in recent years. This includes their use as negative- and positive-potential charge carriers in redox-flow batteries,[2] redox shuttle additives for lithium-ion batteries,[3] mobile molecular catalysts for lithium−oxygen batteries,[4] and solid-state organic electrode materials for aqueous zinc-ion batteries.[5] The organic materials provide distinctive tunability, and thus, the desired physicochemical and electrochemical properties can be achieved by structural modification. However, to optimize the electrochemical performance, the radical species generated by electron transfer must be stable and undergo the reversible reaction rapidly, which has been one of the most challenging characteristics to attain.[6]

Polycyclic aromatic hydrocarbons (PAHs) are promising scaffolds for redox-active materials as they can delocalize unpaired electrons in π-conjugated systems. As a redox-active core, PAHs offer extremely negative potentials that are even comparable to those of alkali ions, such as Li^+, Na^+, and K^+ (−3.44, −3.11, and −3.33 V vs Fc/Fc^+, respectively, converted from the standard hydrogen electrode).[7−9] In addition, the incorporation of a heteroaromatic ring provides the unique opportunity to implement another redox-active core, while retaining the fast electron transfer rate enabled by the PAH framework.[10] For example, Little and co-workers demonstrated that the fused planar framework increased the electron transfer rate and improved the stability of the corresponding radical cations of phenanthroimidazoles, leading to the development of reversible oxidative electron transfer mediators.[11] In these applications, the redox potentials of phenanthroimidazoles were tuned by modification of substituents through condensation reactions. However, condensation reactions that can be successfully applied to phenanthroimidazoles cannot be readily applied to other heteroaromatic systems.[12,13]

To provide a diverse library of phenanthroheteroarenes, the C−H functionalization of heterocycles has been recognized as one of the most straightforward approaches.[14,15] Many difunctionalized biaryl building blocks have been developed for the C−H annulation of heteroarenes, including cyclic diaryliodoniums,[16] dibenzosiloles,[17] dibenzogermoles,[17] and diiodobiaryls[18] (Figure 1A). However, most of these building blocks are prohibitively expensive with limited availability and

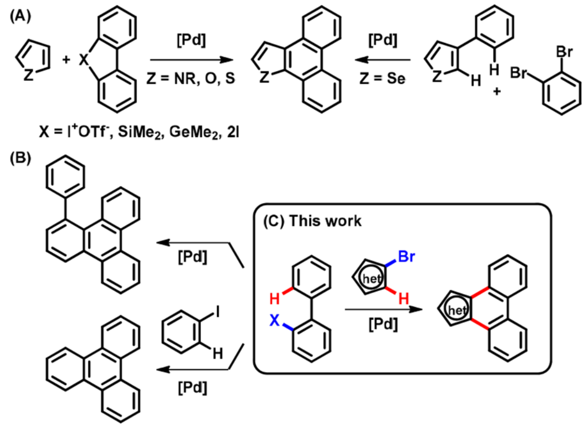


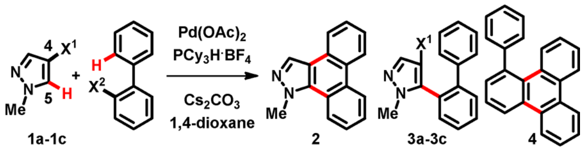
Figure 1. (A) C−H annulation using difunctionalized aryls. (B) C−H annulation using monofunctionalized biaryls. (C) C−H annulation of one- and two-heteroatom-containing heteroarenes for the synthesis of phenanthroheteroarenes.

Received: December 18, 2019

thus not practical for the synthesis of electronically and sterically varied phenanthroheteroarenes. Alternatively, a couple of examples using *o*-dibromobenzene were reported, yet its potential in the synthesis of π-extended heteroarenes has not been fully demonstrated.[19] In addition, readily available, inexpensive *o*-halobiaryls have been used for the annulation of aromatic compounds (Figure 1B).[20,21] However, compared to haloarenes, heteroaromatic counterparts possess relatively activated C−H bonds and electronically varying C−X bonds, making it challenging to develop a general protocol for heterocoupling over dimerization and trimerization.[22] Recognizing the opportunity to develop redox-active materials by exploiting the rigid, π-conjugated phenanthroheteroarenes, we developed a convergent approach using C−H annulation reactions of readily available heteroarenes with *o*-bromobiaryls and *o*-dibromoarenes (Figure 1C). The rapid access to phenanthroheteroarenes facilitated investigation of their electrochemical properties.

On the basis of the recent reports that *o*-halobiphenyls readily undergo dimerization, we envisioned that the choice of halides would be critical for promoting heterocoupling reactions.[21] Pyrazole was selected as a representative heterocycle for optimization studies because it would be feasible to compare the electrochemical properties of pyrazole-fused phenanthrene with those of the other two-nitrogen-containing azole, imidazole-fused counterpart.[11a,23] A series of experiments with 4-halopyrazoles and 2-halobiphenyls showed that the balance between the two halide functions was important for the formation of phenanthropyrazole **2** (Table 1). When 4-chloropyrazole **1a** was employed, the corresponding C5 arylation product **3a** was predominantly formed (entry 1).[24] In contrast, the combination of 4-bromopyrazole **1b** and 2-bromobiphenyl produced the desired annulation product **2** in 82% yield (entry 2), whereas the other mismatched cases afforded decreased yields of **2** and increased yields of the undesired dimer **4** (entries 3−5). When the solvent was switched from 1,4-dioxane to DMF, a considerable amount of the C5 arylation product **3b** was obtained (Scheme 1A; also see Table S1 for optimization studies). The resubjection of **3b** to the reaction in 1,4-dioxane enabled ring closure, suggesting that stepwise, double C−H arylation is one of viable pathways for the synthesis of the phenanthropyrazole.[20] In the absence of 2-bromobiphenyl, trimerization of the pyrazole was operative, in addition to the formation of dimer **1b′** (Scheme 1B). Presumably, the oxidative addition of 4-bromopyrazole **1b** followed by C−H arylation at the C5 position of another pyrazole provided intermediate **1b′**, which served as an *o*-bromobiaryl unit to ultimately generate **5**. This result was similar to trimerization of thiazole and oxazole but was not extended to pyrrole and indole (Scheme S1).[22]

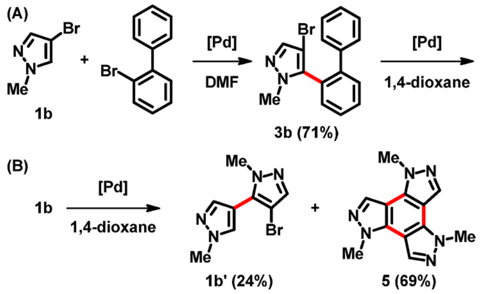
Table 1. Effects of Halides on C−H Annulation of 4-Halopyrazoles[a]



entry	X^1	X^2	1a−c	2	3a−c	4
			yield (%)			
1	Cl (**1a**)	Br	46	0	54 (**3a**)	16
2	Br (**1b**)	Br	2	82 (82)[b]	0 (**3b**)	18
3	I (**1c**)	Br	4	54	0 (**3c**)	0
4	Br (**1b**)	I	71	6	10 (**3b**)	34
5	I (**1c**)	I	0	63	0 (**3c**)	22

[a] Reaction conditions: pyrazole (0.50 mmol), *o*-halobiaryl (0.75 mmol), $Pd(OAc)_2$ (0.025 mmol), $PCy_3H{\cdot}BF_4$ (0.050 mmol), Cs_2CO_3 (1.5 mmol), 1,4-dioxane (0.50 M), 16 h, 140 °C. ^{1}H NMR yield. [b] Isolated yield in parentheses.

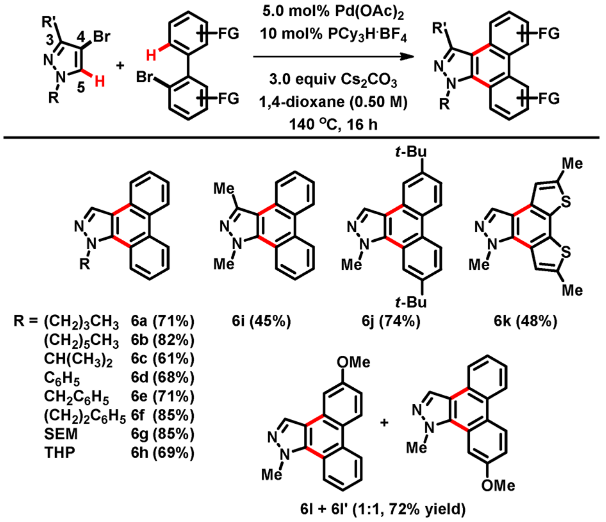
Scheme 1. C−H Annulation of 4-Bromo-1-methylpyrazole[a]



[a] See Table 1 for reaction conditions. (A) DMF was used instead of 1,4-dioxane. (B) *o*-Bromobiaryls were not added.

Bromopyrazoles having various N substituents were used to synthesize phenanthropyrazoles (Scheme 2, **6a−h**). The presence of a methyl group at the C3 position was also tolerated (**6i**). In addition to the biphenyl group, other symmetrical biaryl groups were smoothly attached to the pyrazole ring (**6j** and **6k**). However, the use of an unsymmetrical *o*-biaryl produced a mixture of inseparable regioisomers due to 1,4-migration of the Pd intermediates (**6l** and **6l′**).[25]

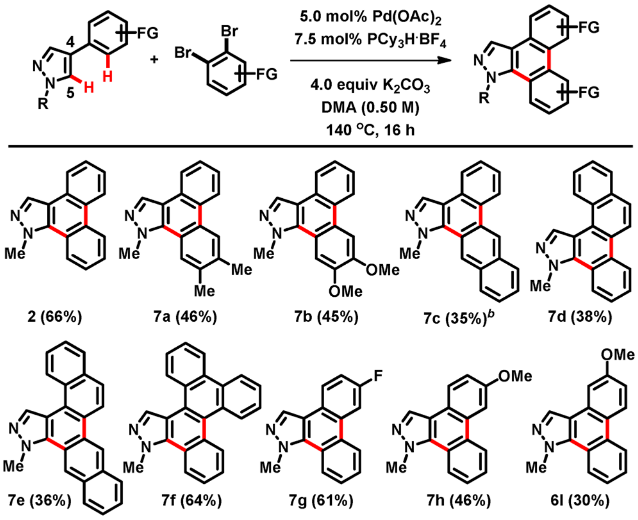
Scheme 2. C−H Annulation of 4-Bromopyrazoles with *o*-Bromobiaryls (method A)[a]



[a] See Table 1 for reaction conditions.

As a complement to the annulation with *o*-bromobiaryls, *o*-dibromoarenes could be used to diversify the polycyclic ring system (Scheme 3).[19] By using a catalytic system similar to that developed for the reaction of the 4-bromopyrazoles, the 4-phenylpyrazole was subjected to C−H annulation with *o*-dibromobenzene to afford **2**, albeit in a moderate conversion

Scheme 3. C−H Annulation of 4-Arylpyrazoles with o-Dibromoaryls (method B)[a]



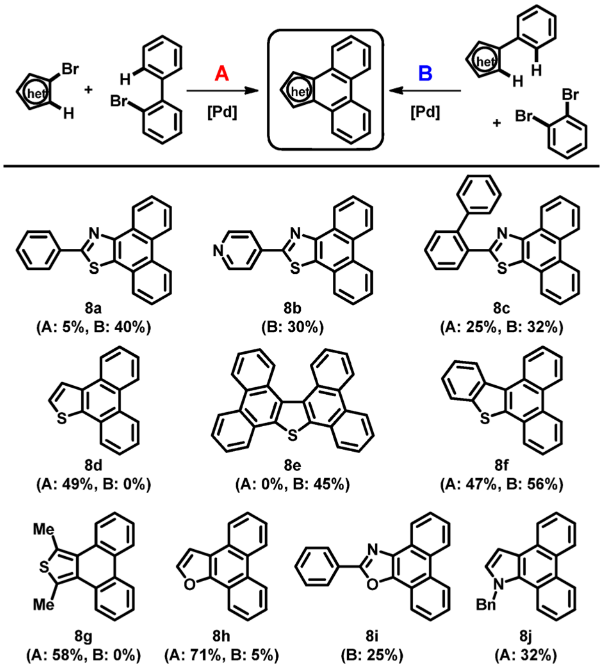
[a]Reaction conditions: pyrazole (0.75 mmol), o-dibromoarene (0.50 mmol), Pd(OAc)$_2$ (0.025 mmol), PCy$_3$H·BF$_4$ (0.0375 mmol), K$_2$CO$_3$ (2.0 mmol), DMA (0.50 M), 16 h, 140 °C. [b]A reduced amount of pyrazole was used (0.50 mmol).

(Table S2). It was envisioned that using π-extended or substituted dibromoarenes could lead to further expansion and substitution of the heterocyclic framework. o-Dibromoarenes having dimethyl and dimethoxy groups and o-dibromonaphthalene were employed to give **7a−c**, respectively. Suzuki coupling of bromopyrazoles enabled various aryl groups to be preinstalled at the pyrazole core, which smoothly underwent annulation (**7d−h**). When an m-methoxy group was present at the C4 aryl ring, **6l** was obtained by C−H arylation at the less sterically hindered position. In this way, the heterocyclic ring was extended with different π-conjugated networks, generating unsymmetrically substituted heterocycle derivatives in a selective and systematic manner.

Methods A and B developed for the annulative C−H activation of pyrazoles were both generally applicable for the π-extension of other five-membered heteroaromatic rings (Scheme 4 and Table S5). Notably, the developed approach allowed the general synthesis of 2-aryl phenanthrothiazoles that were not previously readily accessible (**8a−c**).[15b,c,26] When 4-bromothiazole having two reactive C−H bonds at the heterocyclic core was used, C−H arylation took place at both positions (**8c**, method A). Furthermore, phenanthrothiophenes were synthesized from readily available thiophene derivatives and dibromobenzene, as a complement to the annulation of bromothiophenes and 9-stannafluorenes that are not readily available (**8d−g**).[27] In addition, oxygen-containing heterocycles as well as a pyrrole underwent annulation to afford **8h−j**. The annulation was also applied to halopyridines, where 2- and 4-bromopyridines resulted in low yields and 3-bromopyridine formed both regioisomers (Scheme S2). These inexpensive halo(hetero)arenes can be readily purchased and assembled in a modular fashion, greatly expanding the scope of accessible polycyclic heteroaromatic compounds.

Our convergent methods allowed access to a variety of new phenanthrene-fused heteroaromatic compounds. The electrochemical properties of the pyrazole- and thiazole-fused counterparts are largely enigmatic, presumably because of their limited syntheses. We examined the reversibility of the reaction of the pyrazole and thiazole derivatives in redox processes. Cyclic voltammograms (CVs) were obtained for **2**, **8a**, and **8b** in 0.10 M tetrabutylammonium bis(trifluoromethanesulfonyl)imide/N,N-dimethylacetamide (TBATFSI/DMA) under an argon atmosphere (Figure 2 and Table 2). The reduction peak potential (E_{red}) of phenanthropyrazole **2** was −3.03 V versus Fc/Fc$^+$ for one-electron transfer, which is comparable to those of triphenylene, phenanthrene, and biphenyl (−3.04, −3.02, and −3.20 V vs Fc/Fc$^+$, respectively), which are known to have some of the most negative reduction potentials among aromatic compounds (Figure S1).[7] The electrochemical redox ability of **2** appears to improve with the corresponding radical anion of the phenanthrene ring. The bicyclic benzo-fused pyrazole, 1-methylindazole, and pyrazole trimer **5** did not exhibit any redox ability (Figure S2), supporting the idea that the pyrazole ring alone was redox-inactive.

Scheme 4. C−H Annulation for the Synthesis of Phenanthrene-Fused Heteroarenes (methods A and B)[a]



[a]Method A: heteroarene (1.0 mmol), 2-bromobiphenyl (0.50 mmol), Pd(OAc)$_2$ (0.025 mmol), PCy$_3$H·BF$_4$ (0.050 mmol), Cs$_2$CO$_3$ (1.5 mmol), 1,4-dioxane (0.50 M), 16 h, 140 °C. Method B: heteroarene (0.75 mmol), 1,2-dibromobenzene (0.50 mmol), Pd(OAc)$_2$ (0.025 mmol), PCy$_3$H·BF$_4$ (0.0375 mmol), K$_2$CO$_3$ (2.0 mmol), DMA (0.50 M), 16 h, 140 °C. For azoles **8a−c** and **8i**, the amounts of reactants were changed because of a separation issue. See the Supporting Information for details.

When 2-phenyl and 2-(pyridin-4-yl)thiazole were fused with phenanthrene (**8a** and **8b**, respectively), E_{red} emerged at −2.42 V for **8a** and −2.12 V for **8b** (vs Fc/Fc$^+$). Their first redox waves were considerably stable, as demonstrated by the constant peak current ratio ($i_{\mathrm{p,ox}}/i_{\mathrm{p,red}}$) of 0.97, which was maintained for 100 cycles at a rate of 10 mV s^{-1} (Figure 2). For **8b**, which contains a pyridine, the second electron transfer occurred at an $E_{\mathrm{red,2}}$ of −2.76 V versus Fc/Fc$^+$ (Figure S3). In addition, both **8a** and **8b** showed reasonably high diffusion coefficients [6−8 × 10^{-6} cm^2 s^{-1} (Figure S4)] and rate

https://dx.doi.org/10.1021/acs.orglett.9b04545
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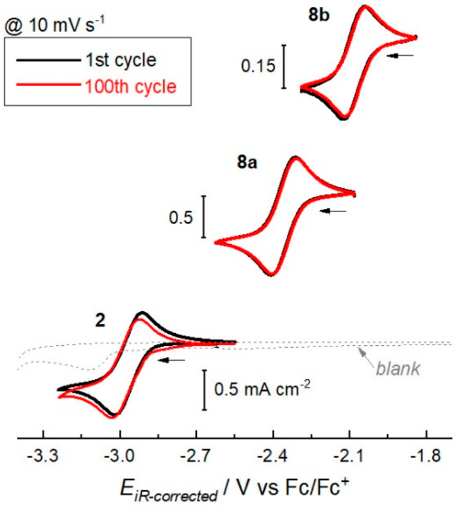
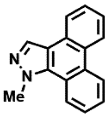
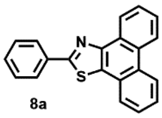
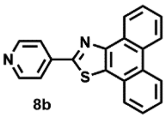
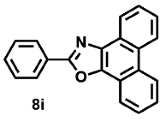


Figure 2. CV profiles of **2**, **8a**, and **8b** for the first (black) and 100th (red) cycles after scanning over a wide potential range. The dashed curve indicates the blank electrolyte solution (0.10 M TBATFSI/DMA) as the background signal. The arrows indicate the scanning direction. The *y* scale indicates the current density (milliamperes per square centimeter). The working, counter, and reference electrodes were glassy carbon, a platinum wire, and a leak-free Ag/AgCl electrode, respectively. The scan rate was 10 mV s^{-1}, and all CVs were acquired in an argon-filled glovebox.

Table 2. Summary of Electrochemical Characteristics of Phenanthrene-Fused Heteroarenes[a]

heteroarene	E_{red} (V)	ΔE_p (mV)	$i_{p,ox}/i_{p,red}$	D_{red} ($cm^2 \cdot s^{-1}$)	k^0 ($cm \cdot s^{-1}$)
 2	−3.03 (−3.04)	128 (128)	0.86 (1.01)	4.88×10^{-6}	7.69×10^{-4}
 8a	−2.42 (−2.42)	116 (115)	0.97 (0.97)	6.02×10^{-6}	1.08×10^{-3}
 8b	−2.12 (−2.12)	87 (90)	0.98 (0.97)	8.01×10^{-6}	8.29×10^{-4}
 8i	−2.64 (−2.63)	112 (110)	0.85 (0.92)	–	–

[a] Each redox molecule (10 mM) was tested in 0.10 M TBATFSI/DMA at a scan rate of 10 mV s^{-1}. ΔE_p, D_{red}, and k^0 indicate the peak-to-peak separation, the diffusion coefficient for redox molecules, and the standard heterogeneous rate constant, respectively. The data in parentheses indicate the value at the 100th cycle.

constants [0.8−1.0 × 10^{-3} cm s^{-1} (Table 2 and the Supporting Information)].

The redox-active cores of **8a** and **8b** were 2-phenyl benzothiazole and 2-(pyridine-4-yl) benzothiazole, respectively. The phenanthrene ring was idle in this potential range, whereas this π-conjugated structure aided in prompt electron transfer, demonstrating a ΔE_p smaller than those for the parent benzothiazoles (Figure S5 and Table S6). It is worth noting that both phenanthro-pyrazole and thiazole did not show any (quasi)reversible redox event in the positive potential range (Figure S6) unlike the phenanthroimidazole (0.88 V vs Ag/$AgNO_3$)[11a] because of the different electronic character of the heterocycles. In contrast, phenanthroxazole **8d** showed a decrease in the cathodic current over 100 cycles (Table 2 and Figure S7). Thiophene **8g** also displayed unstable CV curves (Figure S8), indicating the occurrence of an electrochemical reaction followed by an undesired chemical reaction (EC process). These results indicate that the type and arrangement of heteroatoms dramatically impact the redox properties and stability of the five-membered heterocyclic family.

In conclusion, Pd-catalyzed C−H annulation reactions of heteroarenes were developed for the synthesis of redox-active phenanthroheteroarenes using readily available (di)-bromoarenes. A wide range of five-membered heteroarenes, such as pyrazole, thiazole, oxazole, thiophene, furan, and pyrrole, were transformed to the corresponding phenanthrene-fused heteroarenes. The position of the substituents and the number of aromatic rings were systematically controlled to provide various polycyclic heteroaromatic compounds. Notably, this comprehensive approach enabled the preparation of phenanthro-pyrazoles and thiazoles, which were found to undergo reversible reduction reactions. The stability of the redox processes of the rigid, planar π-conjugated structures of phenanthrene was demonstrated, in combination with a multitude of electronic effects of the five-membered heteroarenes. This is expected to facilitate the application of these scaffolds in redox-active organic materials, including organic electrode materials and redox-flow batteries, affording high energy density.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04545.

Full experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the Samsung Research Funding & Incubation Center of Samsung Electronics under Project SRFC-MA1702-05. The authors thank Prof. Haesik Yang at Pusan National University for helpful discussions.

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