

Fluorescent Naphthyl- and Anthrylazoles from the Catalytic Coupling of Phenylazoles with Internal Alkynes through the Cleavage of Multiple C–H Bonds**

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Polycyclic aromatic and heteroaromatic compounds have attracted considerable attention because of their electrochemical and photochemical properties, and their application as π -conjugated functional materials such as organic semiconductors and luminescent materials.^[1] Polyarylated derivatives with condensed aromatic cores are of particular interest because of their stability, their enhanced ability to transport charge, and their fluorescent properties in the solid-state that are brought about by the aryl groups.^[2–4] Among the interesting examples is 1,3,6,8-tetraphenylpyrene, which was shown to be applicable to organic light-emitting diodes with field-effect transistor characteristics.^[2] Recently, more sterically congested tetraarylpyrenes were synthesized and their solid-state emission properties were examined.^[3]

Multiply arylated compounds are usually prepared by bromination of the parent aromatic compounds with subsequent cross-coupling with arylmetal reagents. Since the cross-coupling reaction is usually hampered by steric bulk, the construction of more densely arylated arenes by this method is problematic.^[5] An alternative strategy includes the Diels–Alder reaction between polyarylated benzynes and cyclopentadienones.^[4] This method enables the synthesis of exhaustively arylated naphthalene and anthracene units, however, the product yields are low because of steric repulsion between the bulky reagents.^[6] Compared to benzyne, diarylacetylenes are more effective and readily available building blocks. Thus, transition-metal-catalyzed aromatic homologation^[7] by the coupling of ArX with two alkyne molecules has been developed as an efficient and easily tunable synthetic protocol for highly substituted arenes possessing extended aromatic cores.^[8] Herein, we report our

new findings that phenylazoles undergo an advanced type of aromatic homologation, by the cleavage of two C–H bonds^[9,10] under rhodium catalysis,^[8g,h] to give (1,2,3,4-tetraaryl-naphthalen-5-yl)azoles; the heterocycle functions as an effective directing group and enhances the fluorescent properties of the products (vide infra). Furthermore, similar treatment of a suitable phenylazole substrate with four equivalents of an alkyne leads to the cleavage of four C–H bonds to afford a polyarylated anthracene (1:4 coupling product) that is highly fluorescent.

In an initial attempt, 1-phenylpyrazole (**1a**) was used as a typical azole substrate for the reaction with diphenylacetylene (**2a**). The examination of different reaction conditions (see the Supporting Information) revealed that $[(\text{Cp}^*\text{RhCl}_2)_2]/\text{C}_5\text{H}_2\text{Ph}_4$ (1,2,3,4-tetraphenylcyclopentadiene) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ are suitable choices for the catalyst and the oxidant, respectively. Thus, under optimal conditions (1 mol % $[(\text{Cp}^*\text{RhCl}_2)_2]$, 4 mol % $\text{C}_5\text{H}_2\text{Ph}_4$, 1 equiv $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in DMF at 80 °C for 6 h under N_2) the 1:2 coupling product, 1-(1,2,3,4-tetraphenyl-naphthalen-5-yl)pyrazole (**3a**), was obtained in 93 % yield ($\text{R}^1 = \text{R}^2 = \text{H}$, $\text{R}^3 = \text{R}^4 = \text{Ph}$ in Equation (1); Table 1, entry 1).

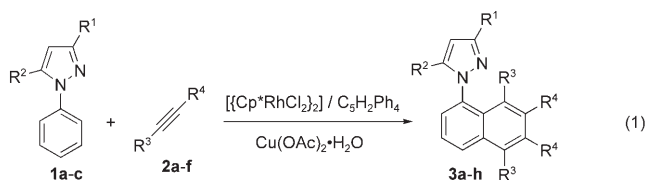


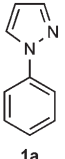
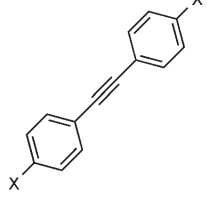
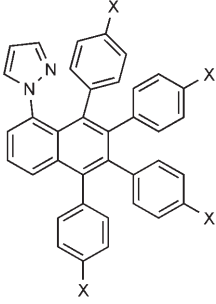
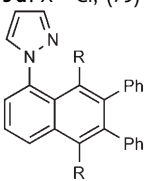
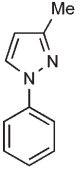
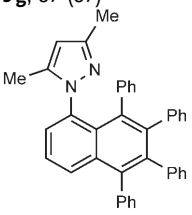
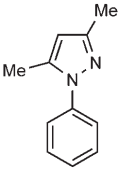
Table 1 also summarizes the results for the coupling reactions that employed different 1-phenylpyrazoles and internal alkynes with the $[(\text{Cp}^*\text{RhCl}_2)_2]/\text{C}_5\text{H}_2\text{Ph}_4$ catalyst system. The reaction of **1a** with diarylacetylenes **2b-d** proceeded efficiently to produce the corresponding 1-(1,2,3,4-tetraaryl-naphthalen-5-yl)pyrazoles **3b-d** in good yields (Table 1, entries 2–4). 1-Phenyl-1-hexyne (**2e**) also reacted with **1a** to give 1-(1,4-dibutyl-2,3-diphenyl-naphthalen-5-yl)pyrazole (**3e**) predominantly, along with a small amount of an unidentified isomer (Table 1, entry 5). From the reaction of 1-phenyl-1-propyne (**2f**) with **1a**, 1-(1,4-dimethyl-2,3-diphenyl-naphthalen-5-yl)pyrazole (**3f**) was obtained in a moderate yield (Table 1, entry 6). 1-Phenyl-3-methylpyrazole (**1b**) and 1-phenyl-3,5-dimethylpyrazole (**1c**) underwent the coupling with **2a** in a similar manner to that of **1a** to produce the corresponding 1-naphthylpyrazoles **3g** and **3h** in good yields (Table 1, entries 7 and 8).

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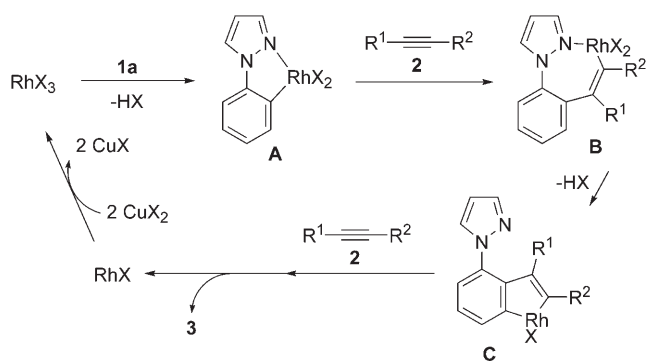
Table 1: Reaction of 1-phenylpyrazoles **1a–c** with alkynes **2a–f**.^[a]

Entry	1	2	t [h]	Product, Yield [%] ^[c]
				
1	1a	2a : X = H	6	3a : X = H, 93 (93)
2		2b : X = Me	6	3b : X = Me, 80 (79)
3		2c : X = OMe	8	3c : X = OMe, (76)
4		2d : X = Cl	6	3d : X = Cl, (79)
				
5		2e : R = Bu	6	3e : R = Bu, 97 (72) ^[c]
6		2f : R = Me	6	3f : R = Me, 36 (20)
		2a	3	3g , 87 (87)
7	1b			
		2a	1	3h , 99 (97)
8	1c			

[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), $[(\text{Cp}^*\text{RhCl}_2)_2]$ (0.01 mmol), $\text{C}_6\text{H}_5\text{Ph}_4$ (0.04 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (1 mmol) in DMF (5 mL) at 80 °C under N_2 . [b] Yield determined by GC analysis and based on the amount of **2** used. Value in parentheses indicates yield after purification. [c] Contaminated with an isomer (**3e**: isomer = 94:6).

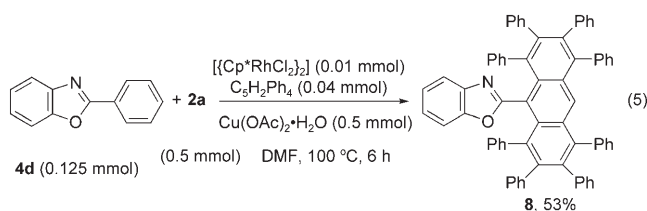
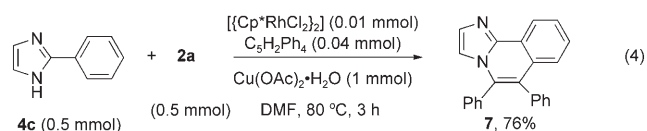
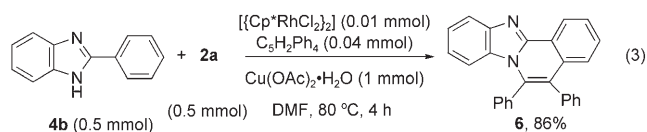
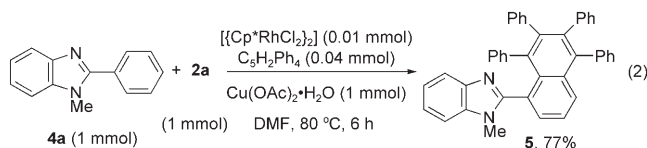
A plausible mechanism for the reaction of **1a** with alkyne **2**, through directed metalation involving rhodacycle intermediates **A–C**,^[11] is illustrated in Scheme 1 (neutral ligands are omitted). In the first step, coordination of the nitrogen atom in the 2-position of **1a** to a Rh^{III} species appears to be the key for the regioselective C–H bond cleavage.^[12] Notably, the direction of the insertion of **2e** and **2f** into the Rh–Ar bonds is consistent with that in the reaction of benzoic acids.^[8g]

The reaction of 1-methyl-2-phenyl-1*H*-benzimidazole (**4a**) with **2a** gave 2-naphthylbenzimidazole **5** in 77% yield as expected [Eq. (2)]. In contrast, 2-phenyl-1*H*-benzimidazole (**4b**) underwent the reaction with **2a** in a 1:1 manner by



Scheme 1. Plausible mechanism for the reaction of **1a** with **2**.

the cleavage of C–H and N–H bonds to selectively produce imidazoisquinoline **6** [Eq. (3)]. Using 2-phenyl-1*H*-imidazole (**4c**) gave a similar result to form **7** in 76% yield [Eq. (4)]. Interestingly, the less sterically demanding 2-phenylbenzoxazole (**4d**) reacted with **2a** in a 1:4 ratio to deliver 2-(1,2,3,4,5,6,7,8-octaphenylanthracen-9-yl)benzoxazole (**8**) through the activation of four C–H bonds [Eq. (5)].



Most 1-naphthylpyrazoles **3** obtained above showed solid-state fluorescence in a range of 450–495 nm (see the Supporting Information). Notably, **3g** exhibited a relatively strong emission compared to a typical emitter, such as tris(8-hydroxyquinolino)aluminum (Alq_3), by a factor of 1.8 (λ_{emis} 467 nm, A versus C in Figure 1). In contrast, the parent 1,2,3,4-tetraphenylanthracene did not show fluorescence at all, indicating that substitution of the naphthalene core with a pyrazoyl group at the 5-position as well as four phenyl groups

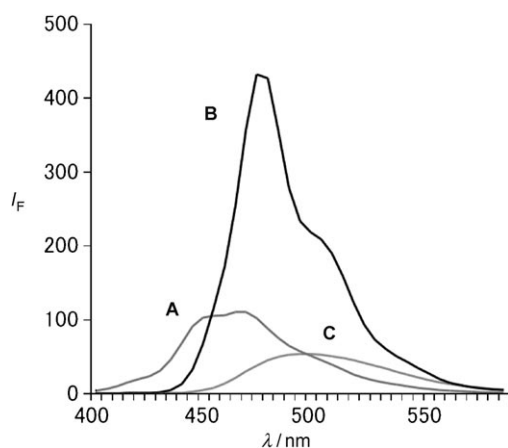


Figure 1. Fluorescence spectra of **3g** (A), **8** (B), and Alq₃ (C) in the solid state when excited at 380 nm.

is important for the fluorescent properties. Interestingly, anthrylbenzoxazole **8** was found to exhibit more intense luminescence (λ_{emis} 477 nm), and the intensity was at least four times stronger than that of Alq₃ in the preliminary estimation (B versus C). Remarkably, the quantum efficiency (Φ) of the solid-state fluorescence of **8** was measured at an absolute value of $66 \pm 2\%$.

In summary, we have demonstrated that polyarylated naphthyl- and anthrylazole derivatives can be constructed efficiently by the direct coupling of phenylazoles with internal alkynes in the presence of a rhodium catalyst and a copper oxidant. The reaction involves the cleavage of multiple C–H bonds, and some of the resulting products exhibit intense fluorescence in the solid state.

Experimental Section

General procedure for Rh-catalyzed reaction of 1-phenylpyrazoles with alkynes: 1-phenylpyrazoles **1** (1 mmol), internal alkyne **2** (1 mmol), [Cp*RhCl₂]₂ (0.01 mmol, 6.2 mg), C₅H₅Ph₄ (0.04 mmol, 14.8 mg), Cu(OAc)₂·H₂O (1 mmol, 199 mg), dibenzyl (ca. 50 mg) as internal standard, and DMF (5 mL) were added to a 20 mL two-necked flask. The resulting mixture was stirred under N₂ at 80°C for 1–8 h. GC and GC-MS analyses of the mixture confirmed formation of **3**. The product was isolated after chromatography on silica gel using hexane/ethyl acetate. Characterization data of products are summarized in the Supporting Information.

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