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VIP Direct Coupling

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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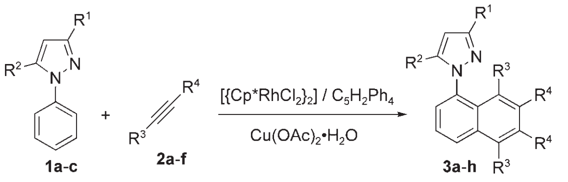
Polycyclic aromatic and heteroaromatic compounds have attracted considerable attention because of their electrochemical and photochemical properties, and their application as π-conjugated functional materials such as organic semiconductors and luminescent materials.[1] Polyarylated derivatives with condensed 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-tetraarylnaphthalen-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 [{Cp*RhCl$_2$}$_2$]/C$_5$H$_2$Ph$_4$ (1,2,3,4-tetraphenylcyclopentadiene) and Cu(OAc)$_2$·H$_2$O are suitable choices for the catalyst and the oxidant, respectively. Thus, under optimal conditions (1 mol% [{Cp*RhCl$_2$}$_2$], 4 mol% C$_5$H$_2$Ph$_4$, 1 equiv Cu(OAc)$_2$·H$_2$O in DMF at 80°C for 6 h under N$_2$) the 1:2 coupling product, 1-(1,2,3,4-tetraphenylnaphthalen-5-yl)pyrazole (**3a**), was obtained in 93% yield ($R^1 = R^2 = H$, $R^3 = R^4 = Ph$ in Equation (1); Table 1, entry 1).



(1)

Table 1 also summarizes the results for the coupling reactions that employed different 1-phenylpyrazoles and internal alkynes with the [{Cp*RhCl$_2$}$_2$]/C$_5$H$_2$Ph$_4$ catalyst system. The reaction of **1a** with diarylacetylenes **2b–d** proceeded efficiently to produce the corresponding 1-(1,2,3,4-tetraarylnaphthalen-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-diphenylnaphthalen-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-diphenylnaphthalen-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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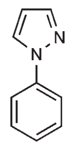
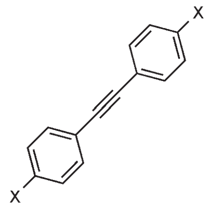
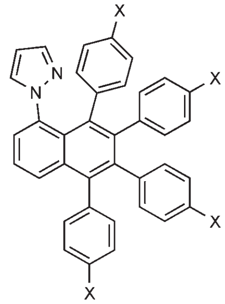
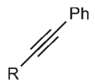
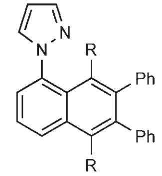
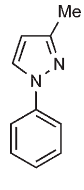
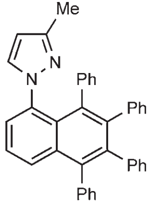
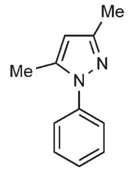
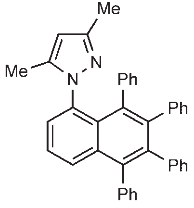
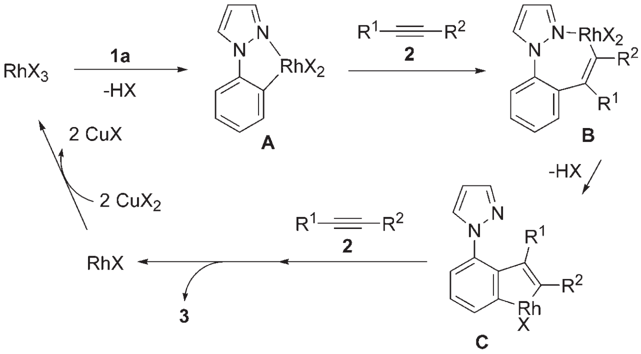
Table 1: Reaction of 1-phenylpyrazoles **1a–c** with alkynes **2a–f**.[a]

Entry	1	2	t [h]	Product, Yield [%][c]
	 **1a**			
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)
				
7	**1b**	**2a**	3	**3g**, 87 (87)
				
8	**1c**	**2a**	1	**3h**, 99 (97)

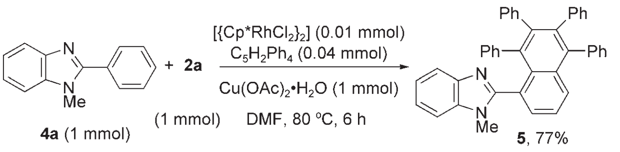
[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), [{Cp*RhCl$_2$}$_2$] (0.01 mmol), $C_5H_2Ph_4$ (0.04 mmol), $Cu(OAc)_2{\cdot}H_2O$ (1 mmol) in DMF (5 mL) at 80°C under N_2. [b] Yield determined by GC analysis and based on the amount of **2** used. Value in parentheses indicates yield after purification. [c] Contaminated with an isomer (**3e**:isomer = 94:6).



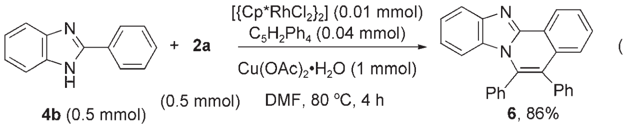
Scheme 1. Plausible mechanism for the reaction of **1a** with **2**.

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]

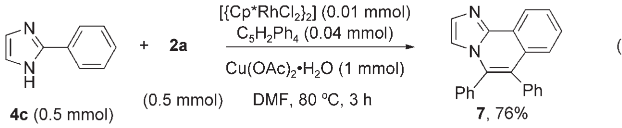
The reaction of 1-methyl-2-phenyl-1*H*-benzimidazole (**4a**) with **2a** gave 2-naphthylbenzimidazole **5** in 77% yield as expected [Eq. (2)]. In contrast, 2-phenyl-1*H*-benzimidazole (**4b**) underwent the reaction with **2a** in a 1:1 manner by the cleavage of C–H and N–H bonds to selectively produce imidazoisoquinoline **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)].



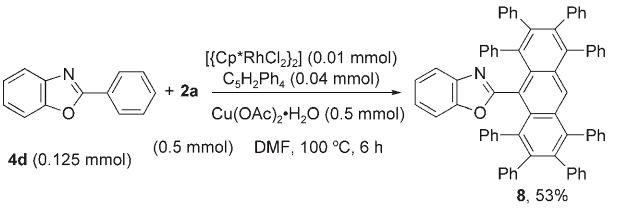
(2)



(3)



(4)



(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-tetraphenylnaphthalene 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

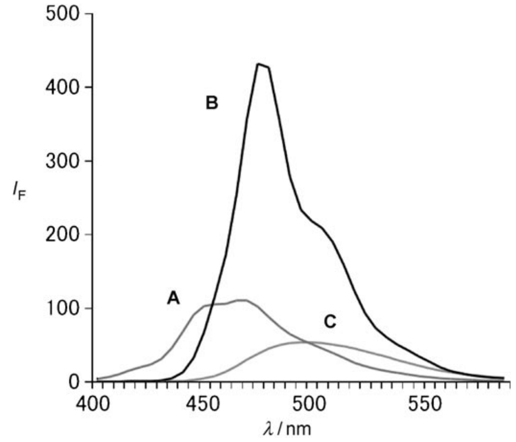


Figure 1. Fluorescence spectra of **3g** (A), **8** (B), and Alq_3 (C) in the solid state when excited at 380 nm.

is important for the flourescent 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 Alq_3 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), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6.2 mg), $C_5H_2Ph_4$ (0.04 mmol, 14.8 mg), $Cu(OAc)_2{\cdot}H_2O$ (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 N_2 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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