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Synthesis of Fluorescent Indazoles by Palladium-Catalyzed Benzannulation of Pyrazoles with Alkynes

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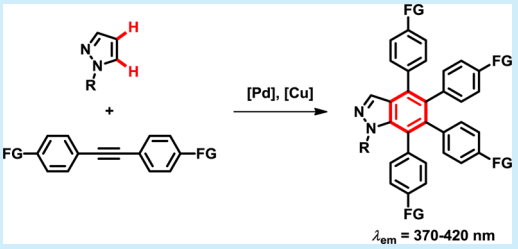
Supporting Information

ABSTRACT: The synthesis of indazoles from pyrazoles and internal alkynes is described. Instead of complex benzenoid compounds, readily available pyrazoles were used for the preparation of indazoles by reaction of the C−H bonds of the heterocyclic ring. Oxidative benzannulation was also applied to imidazoles, providing benzimidazoles. This convergent strategy enabled alteration of the photochemical properties of benzo-fused diazoles by varying the substituents at the benzene ring, thus leading to the development of tetraarylindazoles as new fluorophores.



Indazole is one of the most important heterocycles in medicinal chemistry, leading to the development of many marketed drugs and promising drug candidates having the indazole nucleus.[1] In contrast to the popularity of indazole as a bioisostere for indole and benzimidazole in drug discovery, indazole has been utilized much less frequently than other benzannulated heterocycles in materials chemistry.[2] However, with the availability of new synthetic methods for preparing electronically and sterically varied indazole chromophores, the development of new indazole-based functional materials has been facilitated.[3] The same synthetic strategies used for the identification of biologically active indazole compounds can be applied to the preparation of fluorescent probes and organic light emitting diode (OLED) materials, such as functional group transformation and transition-metal-catalyzed cross-coupling reactions.[4] However, the scope of indazoles that can be accessed by these routes is dependent on the availability of indazole reactants, thus leaving a large part of chemical space conceivable with indazole unexplored.[5]

Recently, it was found that direct C−H functionalization reactions are useful for constructing the indazole core via ring closure (Figure 1A).[6,7] In these cyclative approaches, the pyrazole ring was actually formed by C−H functionalization, requiring prefunctionalized benzene rings that are not readily accessible. However, in order to fine-tune the properties of the indazole core by manipulating the substituents at the benzene ring, it is desirable to develop a convergent approach that can generate functionalized benzene rings from readily available pyrazoles at a later stage of the indazole synthesis. Despite the remarkable expansion of the C−H functionalization reactions in the synthesis of heterocycles, there are surprisingly few reports about the construction of indazoles by manipulating the C−H bonds of pyrazoles.[8] Although it is established that the C−H bonds of pyrazoles are susceptible to transition-metal-catalyzed C−H functionalization, simultaneous functionalization of two C−H bonds of pyrazoles as a method to rapidly build fused pyrazoles remains underexplored.[9−11]

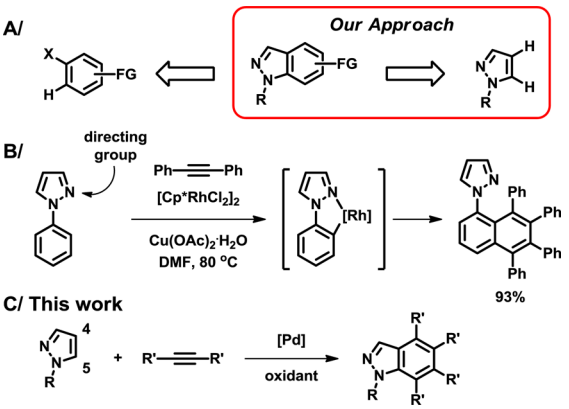


Figure 1. (A) Conventional method versus our approach for the synthesis of indazoles. (B) Pyrazole as a directing group in the annulation of arenes. (C) Benzannulation of pyrazoles with alkynes for the synthesis of functionalized indazoles.

Pyrazoles have also been utilized in C−H functionalization reactions with alkynes, serving as a directing group.[12] When alkynes were employed for annulation reactions, functionalization of the adjacent aryl ring predominated, whereas benzannulation of the heterocycle itself, which could generate indazoles, was not favored (Figure 1B).[13,14] In contrast, elegant work by Miura, Satoh, and co-workers showed that benzannulation of indoles provided carbazoles via a Pd-

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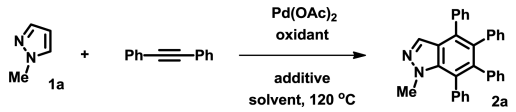
catalyzed 1:2 oxidative coupling with alkynes.[15,16] As most C−H benzannulation methods rely on the use of directing groups, it is notable that a single catalytic system allowed for the functionalization of both C−H bonds of the indole ring without the aid of directing groups.[17] However, indole was the only effective heterocycle, and the method was not extended to other heterocycles. Previously, we developed Pd-catalyzed C−H alkenylation of 4-substituted pyrazoles.[18] Based on that study, we hypothesized that the C−H bonds of simple pyrazoles could be palladated to undergo consecutive carbometalation reactions with alkynes to ultimately provide indazoles (Figure 1C). Although the reactivity of the C4 and C5 positions of pyrazoles are different, we envisioned that readily available pyrazoles could be a general substrate for the preparation of indazoles by double C−H functionalization.

To examine the feasibility of this benzannulation strategy, we first evaluated the catalytic system used for indoles in the reaction of *N*-methylpyrazole (Table 1, entry 1).[16] Although

Table 1. Benzannulation of *N*-Methylpyrazole[a]



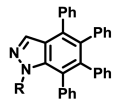
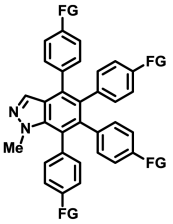
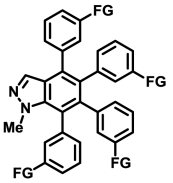
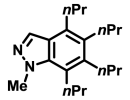
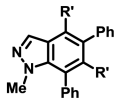
entry	oxidant	additive	solvent	yield (%)
1[b]	Ag_2CO_3	2,6-$Me_2C_6H_3CO_2H$	mesitylene	37
2	Ag_2CO_3		1,4-dioxane	39
3	AgOAc		1,4-dioxane	39
4	$Cu(OAc)_2$		1,4-dioxane	59
5	$Cu(OAc)_2·H_2O$		1,4-dioxane	79
6	$Cu(OAc)_2·H_2O$		DMA	72
7	$Cu(OAc)_2·H_2O$		mesitylene	6
8	$Cu(OAc)_2·H_2O$	Me_3CCO_2H	1,4-dioxane	78
9	$Cu(OAc)_2·H_2O$	$PhCO_2H$	1,4-dioxane	75
10[c]	$Cu(OAc)_2·H_2O$	pyridine	1,4-dioxane	75
11	O_2 (1 atm)		DMA	21

[a]Reaction conditions: pyrazole (0.50 mmol), diphenylacetylene (1.5 mmol), $Pd(OAc)_2$ (0.025 mmol), additive (0.50 mmol), oxidant (1.5 mmol), solvent (1.5 mL), 120 °C. [b]Ag_2CO_3 (1.0 mmol) and 2,6-$Me_2C_6H_3CO_2H$ (0.25 mmol) were used. [c]Pyridine (0.10 mmol) was used.

the yield was moderate, the formation of indazoles could successfully be achieved by C−H functionalization of both the C4 and C5 positions of pyrazoles.[19] In addition, $Cu(OAc)_2·H_2O$ was superior to Ag_2CO_3, AgOAc, and $Cu(OAc)_2$ as the oxidant in 1,4-dioxane (entries 2−5). When the solvent was switched to DMA, no significant decrease of the yield was observed (entry 6). However, the combination of copper acetate monohydrate and mesitylene was not efficient (entry 7). No beneficial effects were observed from carboxylic acids and pyridine (entries 8−10). In terms of the oxidant, oxygen could not replace the copper salt for this transformation (entry 11).[20]

The Pd-catalyzed and Cu-mediated benzannulation reactions provided a wide variety of indazoles from simple pyrazoles in a single step (Table 2). The *N*-alkylpyrazoles, including *n*-butyl-, SEM-, and THP-protected pyrazoles and pyrazolyl propanoate, were transformed to the corresponding indazoles **3**, **4**, **5**, and **6**, respectively (entries 1−4). Although *N*-benzylpyrazole gave a mixture of inseparable products, the reactivity of the one-carbon homologue, phenethyl-substituted pyrazole, was accept-

Table 2. Pd-Catalyzed and Cu-Mediated Benzannulation of Pyrazoles[a]

entry	product		yield (%)
1		R = *n*-Bu	3 (76)
2		SEM	4 (80)
3		THP	5 (65)
4		$CH_2CH_2CO_2nBu$	6 (63)
5		CH_2Ph	7 (–)[b]
6		CH_2CH_2Ph	8 (53)
7		FG = Me	2b (62)
8		*t*Bu	2c (60)[c]
9		OMe	2d (75)[c]
10		CO_2Et	2e (66)
11		F	2f (65)
12		Cl	2g (63)[c]
13		FG = Me	2h (71)
14		OMe	2i (62)
15			2j (38)
16		R' = Me	2k (32)
17		Et	2l (34)

[a]Reaction conditions: pyrazole (0.50 mmol), alkyne (1.5 mmol), $Pd(OAc)_2$ (0.025 mmol), $Cu(OAc)_2·H_2O$ (1.5 mmol), 1,4-dioxane (1.5 mL), 120 °C, 16 h. [b]A mixture of inseparable products was obtained. [c]Performed in the presence of LiOAc (0.50 mmol) and DMA (1.5 mL).

able (entries 5 and 6). This difference is attributed to the ease of trapping the Pd catalyst by forming a palladacycle between the nitrogen atom of the pyrazole and the sp^2 carbon center of the tethered *N*-substituent.[13] Diarylalkynes having electronically varying substituents were smoothly prepared by decarboxylative coupling of propiolic acid and used for the benzannulation (entries 7−14).[21] The reactions with *p*-*tert*-butyl-, methoxy-, and chloro-substituted diphenyl alkynes were more efficient in the presence of LiOAc and DMA, which presumably improved the solubility of the reactants (entries 8, 9, and 12). Not only *para*- but also *meta*-substituents were tolerated in this process (entries 13 and 14). Furthermore, this approach was applied to dialkylalkynes; coupling with 4-octyne afforded the corresponding benzannulation product **2j** in moderate yield (entry 15). Unsymmetrical alkynes were also utilized for benzannulation of the pyrazole, where regioisomers **2k** and **2l** were the major isolable products (entries 16 and 17).[19,22] Electron-deficient alkynes, such as dimethyl acetylenedicarboxylate and ethyl phenylpropiolate, were not suitable for this process. The use of trifluoromethylated alkynes consistently generated only the products from the addition of the acetate to the alkynes and subsequent hydrolysis under these conditions.[23,24] Another limitation was that terminal alkynes were not tolerated in this process.

In order to account for the observed regioselectivity in the reaction of unsymmetrical alkynes, a series of deuterium exchange experiments were carried out, indicating that

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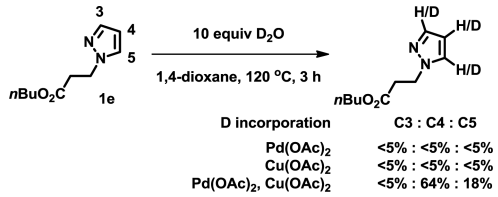
metalation at the C4 position was favored relative to the C3 and C5 positions (Scheme 1). More interestingly, the presence

Scheme 1. Deuteration Experiments



of both $Pd(OAc)_2$ and $Cu(OAc)_2$ was crucial for successful metalation of the pyrazole, indicating that the Cu(II) salt was not a simple oxidant but possibly served as a Lewis acid to promote the metalation step.[22,25]

In an attempt to enhance the regioselectivity, 4-bromopyrazoles **9** were prepared to facilitate oxidative addition at the C4 position.[26] When **9** were subjected to the catalytic system comprising $Pd(OAc)_2$ and $P(tBu)_3H{\cdot}BF_4$, the corresponding indazoles were obtained in good yields (Figure 2). One notable

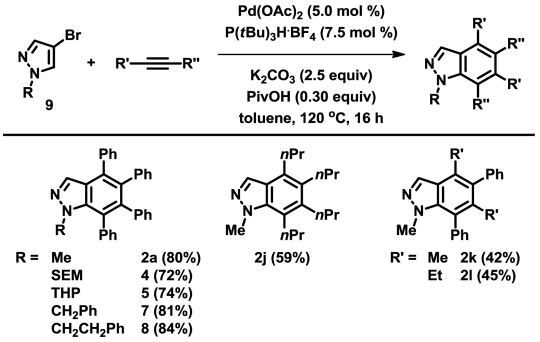


Figure 2. Pd-catalyzed benzannulation of 4-bromopyrazoles.

example was the formation of the *N*-benzyl derivative **7** that was not accessible with the $Pd(OAc)_2$ and $Cu(OAc)_2{\cdot}H_2O$ catalytic system. Furthermore, the protocol based on the Pd(0)/Pd(II) catalytic cycle was slightly more efficient than the oxidative benzannulation for the synthesis of indazoles **2j**, **2k**, and **2l**.

Given to the smooth conversion of pyrazoles to the corresponding benzannulated heterocycles, this method was applied to the other two-nitrogen-containing 5-membered heterocycle, namely imidazole (Figure 3). Despite the considerably low reactivity of the C4 position of imidazoles compared with the C5 of imidazoles, benzimidazoles **11a−c** were produced directly from the imidazoles through these two C−H bonds.[27]

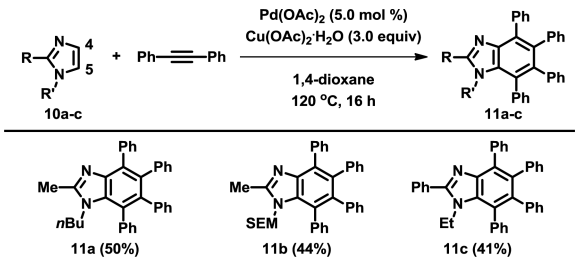


Figure 3. Pd-catalyzed and Cu-mediated benzannulation of imidazoles.

This convergent strategy led to the preparation of a library of electronically diverse π-conjugated indazoles and benzimidazoles, facilitating optimization of the electronic properties. In particular, the solutions of tetraarylindazoles prepared in this study exhibited notable fluorescence under UV irradiation. The solid-state fluorescence of the electronically different tetraarylindazoles **2a** and **2c−g** was measured, where the methoxy variant **2d** emitted deep blue photoluminescence with a maximum emission peak at 416 nm with a full-width at half-maximum of 67 nm (Figure 4).[22] This result indicates that the

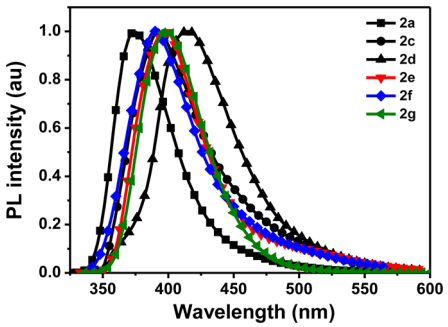


Figure 4. Solid-state PL emission spectra of tetraarylindazoles.

photochemical properties of tetraarylindazoles can be modulated by the benzene substituents of the indazoles for application in OLEDs as blue dopants. The development of blue fluorescent organic molecules with high color purity and sufficient lifetime has been an important goal for commercial applications of OLEDs.[28] In this context, tetraarylindazoles offer a new opportunity to develop high-performing blue fluorescent dopants for OLEDs.

In conclusion, we developed a new pyrazole annulation reaction for preparation of indazoles. A catalytic amount of $Pd(OAc)_2$ along with a stoichiometric oxidant, $Cu(OAc)_2{\cdot}H_2O$, enabled the construction of indazoles possessing different substituents on the benzene ring. Alternatively, 4-bromopyrazoles could be employed for the formation of the same products with similar efficiency. Furthermore, this protocol proved to be general and could be applied to the other diazole, imidazole, to afford the corresponding benzannulated form, benzimidazole. Complementary to many cyclization methods that form heterocyclic rings from functionalized arenes, this new strategy based on the direct conversion of simple diazoles is useful for providing benzo-fused heteroarenes having multiple substituents on the benzene ring. Modification of the *para* substituents of the tetraaryl groups around the indazole core allowed manipulation of the emission wavelength, demonstrating the potential of tetraarylindazoles as a new fluorophore.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00410.

Full experimental details and characterization data (PDF)

Crystallographic data for **2a** (CIF)

Crystallographic data for **2k** (CIF)

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Notes

The authors declare no competing financial interest.

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