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$PdCl_2$-Catalyzed Domino Reactions of 2-Alkynylbenzaldehydes with Indoles: Synthesis of Fluorescent 5*H*-Benzo[*b*]carbazol-6-yl Ketones

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The selective synthesis of polycyclic aromatic compounds is of continuing interest in the field of organic chemistry, because these compounds play important roles in both the chemical and pharmaceutical industries. For example, some polycyclic heteroaromatic compounds have been applied as π-conjugated functional materials, such as organic semiconductors and luminescent materials, due to their special electrochemical and photochemical properties.[1–3] Recently, the Lewis acid catalyzed [4+2] cycloaddition of 2-ethynylbenzaldehyde derivatives to unsaturated compounds (alkynes, alkenes, and enols) has become one of the powerful methods for constructing polycyclic aromatic cores (Scheme 1).[4–8] In 2002, Asao and Yamamoto reported a novel method for synthesizing naphthyl ketones the by $AuCl_3$-catalyzed [4+2] benzannulation of 2-alkynylbenzaldehydes with alkynes.[4] Dyker and co-workers subsequently used the method to construct polycyclic heteroaromatic compounds. In all of these studies, the initial formation of the isobenzopyrylium complex **A** was invoked as a key intermediate that led to the observed polycyclic aromatic compounds upon [4+2] cycloaddition with the corresponding unsaturated partners.[7,9] The isobenzopyrylium complex **A** was trapped by Dyker and co-workers by using benzimidazole as the nucleophile.[7] In spite of this, no isobenzopyrilium products **5** or cycloaddition products **6** have been trapped, but indenes **4** were isolated in the presence of indole or *N*-methylindole. Although a possible process for the formation of indenes **4** from **5** was also proposed, involving the Nazarov reaction, no direct experimental evidence supported it.[7] Therefore, expanding the scope of the cycloaddition reaction with respect to indole nucleophiles would represent an important advance. Here we report the first cycloaddition of 2-alkynylbenzaldehydes to indoles to form 5*H*-benzo[*b*]-carbazol-6-yl ketones **6**, catalyzed by $PdCl_2$ (Scheme 1). We found that applying indoles **2** as a reaction partner at room temperature led to products **5**,[9] which could then be transformed into the corresponding 5*H*-benzo[*b*]carbazol-6-yl ketones **6** by elevating the reaction temperature, under the same catalyst system.

We began our investigation by examining the effect of the conditions on the reaction of 2-(phenylethynyl)benzaldehyde (**1A**) with indole (**2a**) and the results are summarized in Table 1. We found that the reaction temperature plays a crucial role in the selectivity (Table 1, entries 1–6). Whereas treatment of substrate **1A** with indole (**2a**) in the presence of $PdCl_2$ at room temperature afforded 3-(3-phenyl-1*H*-isochromen-1-yl)-1*H*-indole (**5Aa**) exclusively, in 85% yield (Table 1, entry 1), another product, 5*H*-benzo[b]carbazol-6-yl(phenyl)methanone (**6Aa**), was obtained at increased temperatures (Table 1, entries 2–6). To our delight, only product **6Aa** was isolated if the temperature was over 120°C. Encouraged by these results, the effect of different solvents was subsequently examined (Table 1, entries 7–12). The results showed that a mixture of *N*-methylpyrrolidone (NMP) and DMSO (v/v=1:4) gave the best results (Table 1, entry 12). We were pleased to find that the yield of **6Aa** was enhanced to some extent when 15 mol% of $PdCl_2$ was used (Table 1, entry 13), but the yield of **5Aa** was only slightly affected under the same conditions (Table 1, entry 14). Finally, a series of other catalysts, including $Pd(OAc)_2$, $PtCl_2$, $Cu(OTf)_2$, AgOTf, and $ZnCl_2$, were evaluated (Tf=triflate; Table 1, entries 15–19). Although these catalysts have activity in the reaction, they were all inferior to $PdCl_2$.

With the standard conditions in hand, we turned our attention to the scope and limitations of the transformations for selectively synthesizing indoles **5** and ketones **6** (Table 2 and Table 3). As shown in Table 2, when the reaction was

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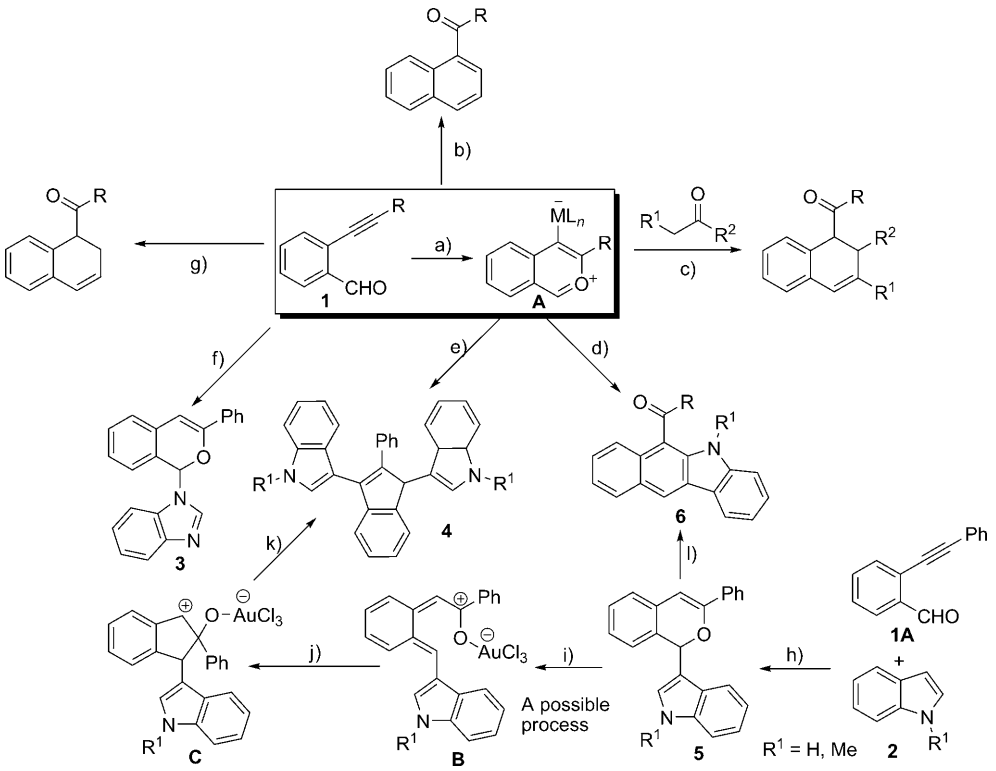
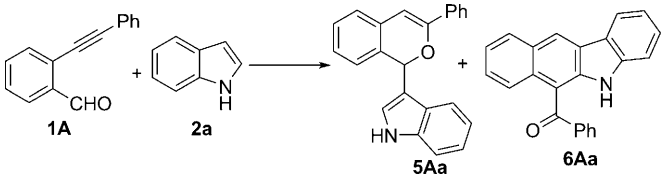


Scheme 1. Lewis acid catalyzed [4+2] cycloaddition reactions; a) $[ML_n]$; b) $AuCl_3$ or $Cu(OTf)_2$, alkyne;[4] c) $AuBr_3$, ketone;[6] d) reaction discussed in this paper and may occur by a Diels–Alder, or other, domino reaction process; e) $AuCl_3$, **2**;[7] f) $AuCl_3$, 1*H*-benzimidazole;[7] g) $Cu(OTf)_2$, alkene;[5] h) $AuCl_3$; i) $AuCl_3$;[7] j) the Nazarov process; k) **2**; l) $PdCl_2$, reaction discussed in this work.

Table 1. Screening for optimal conditions.[a]



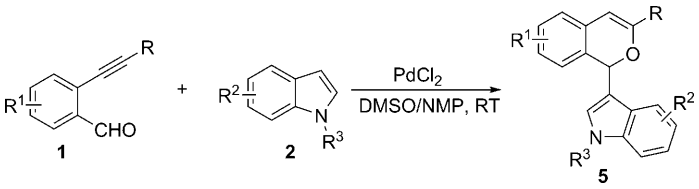
Entry	Catalyst	Solvent [v/v]	T [°C]	t [h]	Yield [%] 5Aa	6Aa
1	$PdCl_2$	DMSO	RT	24	85	0
2	$PdCl_2$	DMSO	50	24	76	<5
3	$PdCl_2$	DMSO	80	24	15	42
4	$PdCl_2$	DMSO	100	24	<5	51
5	$PdCl_2$	DMSO	120	10	0	65
6	$PdCl_2$	DMSO	140	10	0	46
7	$PdCl_2$	CH_3CN	120	16	0	38
8	$PdCl_2$	DMF	120	16	0	19
9	$PdCl_2$	toluene	120	16	0	12
10	$PdCl_2$	NMP	120	10	0	32
11	$PdCl_2$	NMP/DMSO (1:1)	120	10	0	55
12	$PdCl_2$	NMP/DMSO (1:4)	120	10	0	68
13[b]	$PdCl_2$	NMP/DMSO (1:4)	120	10	0	74
14[b]	$PdCl_2$	NMP/DMSO (1:4)	RT	10	86	0
15[b]	$Pd(OAc)_2$	NMP/DMSO (1:4)	120	10	0	25
16[b]	$PtCl_2$	NMP/DMSO (1:4)	120	10	0	45
17[b]	$Cu(OTf)_2$	NMP/DMSO (1:4)	120	10	0	56
18[b]	AgOTf	NMP/DMSO (1:4)	120	10	0	17
19[b]	$ZnCl_2$	NMP/DMSO (1:4)	120	10	0	<5

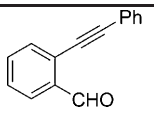
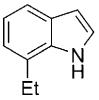
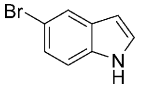
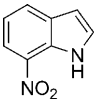
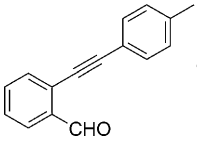
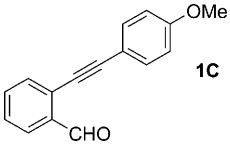
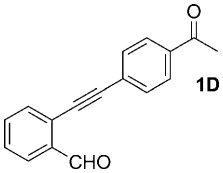
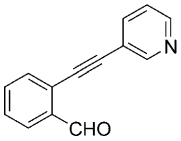
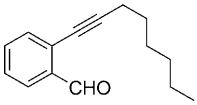
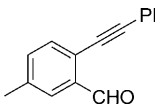
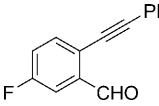
[a] Reaction conditions: **1A** (0.22 mmol), **2a** (0.2 mmol), catalyst (10 mol%), and solvent (2.5 mL). [b] Catalyst (15 mol%).

performed with **1A**, a set of indoles **2b–e** underwent the cycloaddition at room temperature to afford the corresponding indoles **5Ab–Ae** with moderate to good yields, regardless of their steric or electronic nature (Table 2, entries 1–4). Both electron-withdrawing and electron-donating groups on the aryl moiety of the terminal alkyne were well tolerated, though the electron-donating groups (methyl and methoxy) displayed higher activity than the electron-withdrawing group (acetyl) (entries 5–7). The standard conditions were also compatible with 2-{2-(pyridin-3-yl)ethynyl}benzaldehyde (**1E**), a heteroaryl-containing substrate (Table 2, entry 8). However, it was found that alkyl-substituted alkyne **1F** resulted in a decreased yield (Table 2, entry 9). Substrates **1G** and **1H**, containing substituents on the arylaldehyde moiety, were also suitable substrates for the reaction with indole **2a** and $PdCl_2$, at room temperature in 63 and 86% yields, respectively (Table 2, entries 10 and 11).

We next evaluated the one-pot reaction between aldehydes **1** and indoles **2** at 120°C to form compounds **6** (Table 3). It appears from these results that the yields of this reaction are dependent on the substitution pattern of both substrates. For substrate **1A** the reactions with various indoles **2b–f** proceeded smoothly in moderate yields (Table 3, entries 1–5). Moderate yields were still achieved from substrates **1B** and **1C**, which have electron-donating aryl groups on the terminal alkyne (Table 3, entries 6 and 7). However, an electron-deficient aryl group or a heteroaryl group somewhat reduced the yield (Table 3, entries 8 and 9).

Table 2. Palladium-catalyzed synthesis of 3-(1*H*-isochromen-1-yl)-1*H*-indoles **5**.[a]

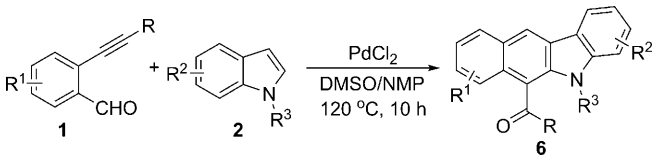


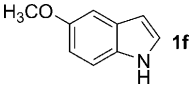
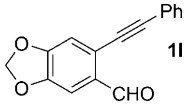
Entry	Substrate **1**	Indole **2**	*T* [h]	Yield [%]
1	 **1A**	 **2b**	24	87 **5Ab**
2	**1A**	 **2c**	24	81 **5Ac**
3	**1A**	 **2d**	36	43 **5Ad**
4	**1A**	 **2e**	24	88 **5Ae**
5	 **1B**	 **2a**	30	85 **5Ba**
6	 **1C**	**2a**	24	72 **5Ca**
7	 **1D**	**2a**	30	59 **5Da**
8	 **1E**	**2a**	36	51 **5Ea**
9	 **1F**	**2a**	36	50 **5Fa**
10	 **1G**	**2a**	36	63 **5Ga**
11	 **1H**	**2a**	36	86 **5Ha**

[a] Reaction conditions: **1** (0.22 mmol), **2** (0.2 mmol), $PdCl_2$ (10 mol%), and NMP/DMSO (v/v = 1:4; 2.5 mL) at room temperature.

We were delighted to find that the standard conditions were reliable with alkyl-substituted alkyne **1F** (Table 3, entry 10).

Table 3. Palladium-catalyzed synthesis of 5*H*-benzo[*b*]carbazol-6-yl ketones (**6**).[a]



Entry	Substrate **1**	Indole **2**	Yield [%]
1	**1A**	**2b**	73 **6Ab**
2	**1A**	**2c**	53 **6Ac**
3	**1A**	**2d**	42 **6Ad**
4	**1A**	**2e**	53 **6Ae**
5	**1A**	 **1f**	63 **6Af**
6	**1B**	**2a**	60 **6Ba**
7	**1C**	**2a**	64 **6Ca**
8	**1D**	**2a**	44 **6Da**
9	**1E**	**2a**	39 **6Ea**
10	**1F**	**2a**	56 **6Fa**
11	**1G**	**2a**	56 **6Ga**
12	**1H**	**2a**	67 **6Ha**
13	 **1I**	**2a**	57 **6Ia**
14	**1I**	**2e**	53 **6Ie**

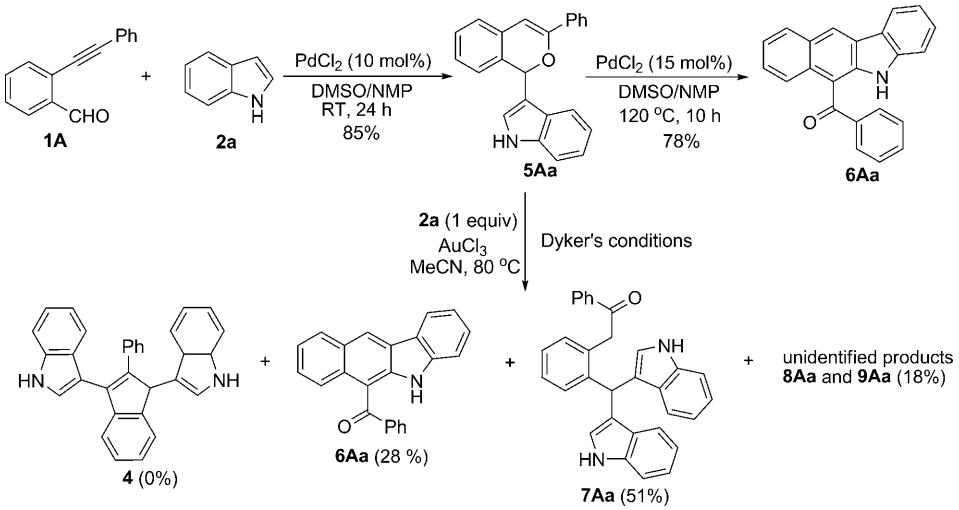
[a] Reaction conditions: **1** (0.22 mmol), **2** (0.2 mmol), $PdCl_2$ (15 mol%), and NMP/DMSO (v/v = 1:4; 2.5 mL) at 120 °C for 10 h.

We also investigated the effect of substituents on the arylaldehyde moiety and these substituents were tolerated by the reaction (Table 3, entries 11–14). Electron-rich arylaldehyde **1I**, for instance, was treated with indoles **2a** and **2e** successfully in the presence of $PdCl_2$ at 120 °C, affording the target products **6Ia** and **6Ie** in 57 and 53% yields, respectively (Table 3, entries 13 and 14).

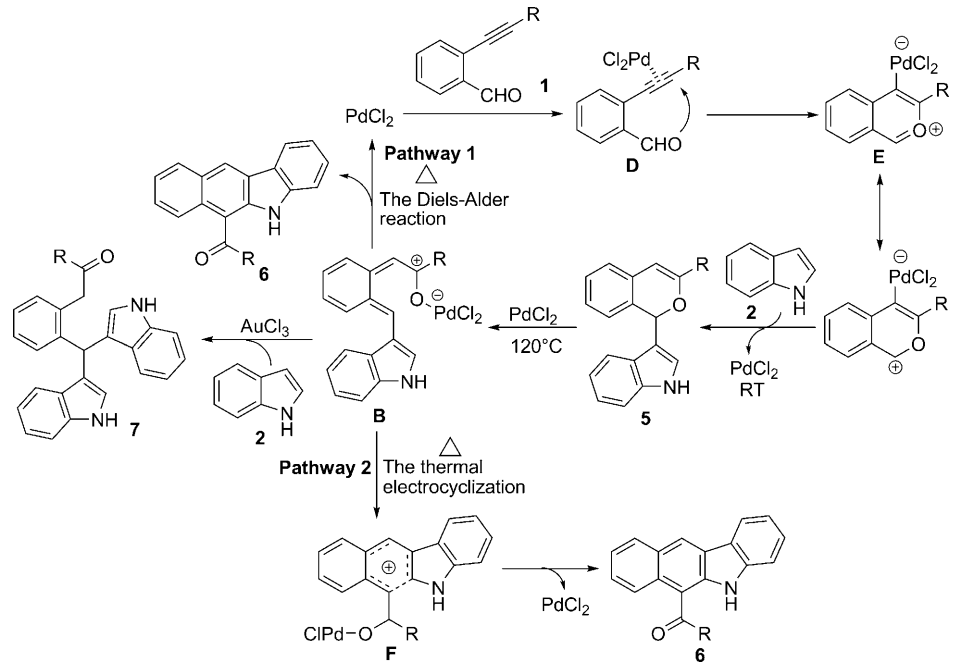
The structures of the products **5** and **6** were unambiguously confirmed by the X-ray single-crystal diffraction analysis of **5Ae**[10] and **6Aa**.[11]

Having trapped product **5**, we performed two further controlled experiments as summarized in Scheme 2. The trapped product **5Aa**, generated from the reaction of 2-(phenylethynyl)benzaldehyde (**1A**) with indole (**2a**) at room temperature, then smoothly underwent the domino rearrangement reaction in the presence of $PdCl_2$ at 120 °C and was transformed into the cycloaddition product **6Aa** in 78% yield. However, reaction of compound **5Aa** under Dyker's conditions produced no product **4**, but did form the cycloaddition product **6Aa**, the ring-opened product **7Aa**, and two unidentified products (**8Aa** and **9Aa**); these results do not support Dyker's proposed process for the formation of indenes **4**.[7]

Possible mechanisms for the present reactions were proposed as outlined in Scheme 3, which were based on the reported mechanism[4–8] and our results. Complexation of the triple bond with $PdCl_2$ takes place readily to afford intermediate **D**, followed by nucleophilic attack of the carbonyl



Scheme 2. Controlled experiments.



Scheme 3. Possible mechanisms.

oxygen atom on the alkyne (intermediate **D**) to form the Pd complex **E**.[4–8] At room temperature, complex **E** then undergoes a Friedel–Crafts reaction to give product **5**.[7,9] A ring-opening reaction of product **5** yields intermediate **B** in the presence of $PdCl_2$ at 120 °C. Intermediate **B** may then undergo two pathways (1 or 2) to provide the cycloaddition product **6** and regenerate the active Pd species: pathway 1) a [4+2] Diels–Alder reaction or pathway 2) a thermal electrocyclization.[12] Under Dyker's conditions,[7] there is competition between these cyclization reaction pathways and a second Friedel–Crafts reaction, which is caused by the stronger Lewis acidity of $AuCl_3$. Studies into the detailed mechanism are in progress.

As is known, polycyclic aromatic compounds have been widely used in the field of organic materials chemistry due to their interesting electrochemical and fluorescent properties.[1–3] Moreover, metal-complexed conjugated systems are attracting fervent interest due to the possibility of interaction with DNA and their role in fluorescent labeling.[13] In connection with the highly conjugated molecules obtained by our domino reaction, it was assumed that these products, with two heteroatoms, could be chelated with a metal ion, leading to new physical properties. Thus, preliminary experiments using compound **6Aa** as the organic molecular probe have been conducted. As illustrated in Figure 1, we introduced 2.5 equivalents of M^+ (including Co^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, and Ag^+) to a solution of **6Aa** in CH_3CN/H_2O to test the change in the fluorescence emission intensity.[14] These experiments demonstrated that compound **6Aa** could combine with Cr^{3+}, Fe^{3+}, or Cu^{2+} to enhance their fluorescence emission and shift the emission wavelength considerably at room temperature. The enhancement of fluorescence may be attributed to ligand chelation to the metal center, which involves energy transfer from the conjugated ligand to the metal center. Particularly, the combination of **6Aa** with Cr^{3+} resulted in an almost 500% increase in the fluorescent intensity and the peak emission wavelength was shifted from 500 to 575 nm. Moreover, the Fe^{3+} complex may be promising in future DNA research due to its fluorescent properties and benign effect on human health.

In summary, we have demonstrated that, by application of a palladium-catalyzed domino strategy, a variety of functional 5*H*-benzo[*b*]carbazol-6-yl ketones can be readily constructed from a reaction between 2-alkynylbenzaldehydes and indoles. This work is the first to disclose that the isobenzopyrylium complex **A** can, in the presence of $PdCl_2$, be trapped by indole nucleophiles at room temperature to

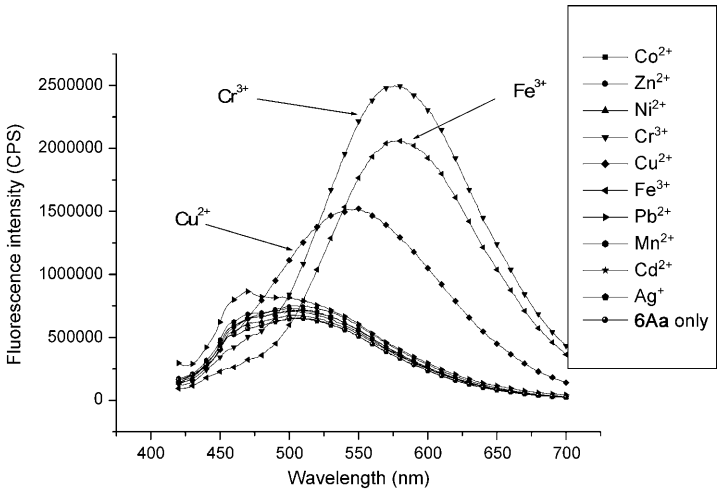


Figure 1. Fluorescence emission spectra of **6Aa** in the presence of different metal ions, Co^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, and Ag^{+} (as their NO_3^- salts) in CH_3CN/H_2O (100:1); $\lambda_{ex}=400$ nm, $[\mathbf{6Aa}]=1\times10^{-4}$ M, $[M^{n+}]=2.5\times10^{-4}$ M.

afford 3-(1*H*-isochromen-1-yl)-1*H*-indoles **5**, which can then be converted into 5*H*-benzo[*b*]carbazol-6-yl ketones **6** by elevating the reaction temperature . Most importantly, the preliminary fluorescence emission experiments on product **6Aa** showed that this type of compound might exhibit intense fluorescence and can interact with metal ions, such as Cr^{3+}, Fe^{3+}, and Cu^{2+}, to enhance the fluorescence emission intensity, which provides a new route for the design and discovery of new fluorescent materials for biochemical study. Further fluorescence emission experiments on the Cr^{3+}, Fe^{3+}, and Cu^{2+} complexes with the other compounds **6** are underway in our laboratory.

Experimental Section

Typical experimental procedure for the synthesis of 3-(1*H*-isochromen-1-yl)-1*H*-indoles 5: A mixture of 2-alkynylbenzaldehyde **1** (0.22 mmol), indole **2** (0.2 mmol), and $PdCl_2$ (10 mol%) in NMP/DMSO (v/v=1:4; 2.5 mL) was stirred at room temperature, for the indicated time, or until complete consumption of the starting material had occurred, as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was filtered through a crude column with ethyl acetate as the eluent, followed by evaporation of the solvent in a vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate 4:1) to afford the desired product **5**.

Typical experimental procedure for the synthesis of 5*H*-benzo[*b*]carbazol-6-yl ketones 6: A mixture of 2-alkynylbenzaldehyde **1** (0.22 mmol), indole **2** (0.2 mmol), and $PdCl_2$ (15 mol%) in NMP/DMSO (v/v=1:4; 2.5 mL) was stirred at 120 °C, for the indicated time, or until complete consumption of the starting material had occurred, as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was filtered through a crude column with ethyl acetate as eluent, followed by evaporation of the solvent in a vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate 5:1) to afford the desired product **6**.

Acknowledgements

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Keywords: alkynes · domino reactions · indoles · ketones · palladium

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[10] X-ray crystallographic analysis of **5Ae**: $C_{24}H_{19}NO$, $M=337.4$, triclinic, space group $P2_1/n$, $a=5.7855(11)$, $b=9.3534(19)$, $c=16.804(3)$ Å, $\beta=82.4(4)°$, $V=897.2(3)$ Å^3, $Z=2$, max. $2\theta=52.00$, 4884 measured reflections, 471 parameters, $\mu=0.076$ mm^{-1}, $R1=0.0487$ for 3448 observed reflections $[I>2\sigma(I)]$, $wR2=0.1007$ for all reflections. The intensity data was collected on a Bruker SMART APEXII CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $T=293$ K). The structure was solved by direct methods (SHELXS-97)[12] and refined by full-matrix least-squares methods with all measured reflections (SHELXL-97)[14] for all non-hydrogen atoms with anisotropic thermal parameters.

[11] X-ray crystallographic analysis of **6Aa**: $C_{23}H_{15}NO$, $M=321.36$, orthorhombic, space group $P2_1/n$, $a=5.7905(7)$, $b=13.1822(15)$, $c=20.613(2)$ Å, $\beta=90°$, $V=1573.4(3)$ Å^3, $Z=4$, max. $2\theta=54.98$, 9494 measured reflections, 231 parameters, $\mu=0.083$ mm^{-1}, $R1=0.0417$ for 2097 observed reflections $[I>2\sigma(I)]$, $wR2=0.1071$ for all reflections. The intensity data was collected on a Bruker SMART APEXII CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $T=293$ K). The structure was solved by direct methods (SHELXS-97)[12] and refined by full-matrix least-squares methods with all measured reflections (SHELXL-97)[14] for all non-hydrogen atoms with anisotropic thermal parameters.

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