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Palladium-Catalyzed Selective Aryl Ring C–H Activation of *N*-Acyl-2-aminobiaryls: Efficient Access to Multiaryl-Substituted Naphthalenes

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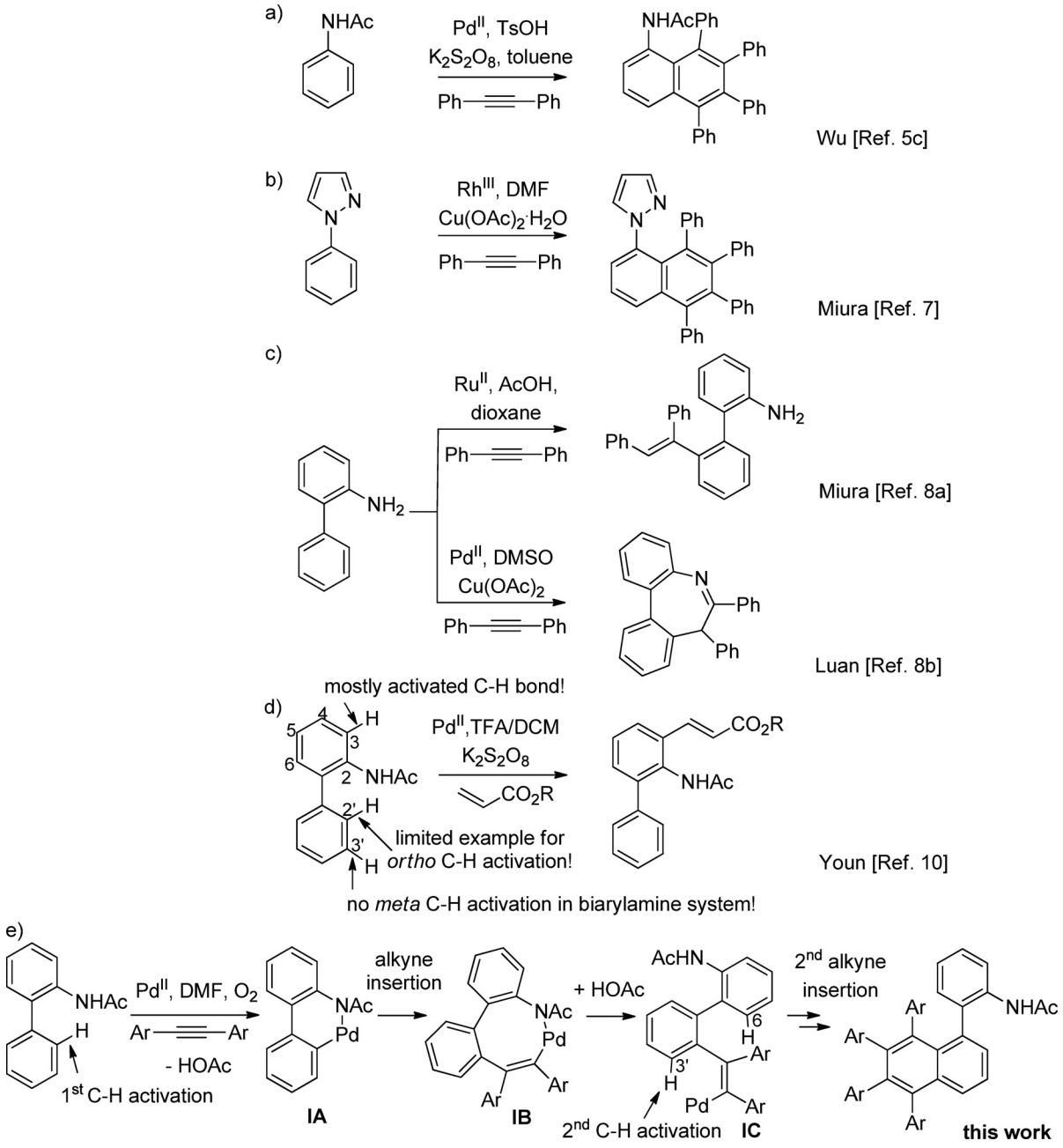
Abstract: Palladium-catalyzed cycloaromatization of *N*-acyl-2-aminobiaryls, through a sequence of *ortho* C–H bond activation/alkyne insertion/*meta* C–H bond activation/alkyne insertion, was developed. An efficient synthesis of multiaryl-substituted naphthalenes, *N*-[2-(5,6,7,8-tetraarylnaphthalen-1-yl)aryl]acetamides, was demonstrated using molecular oxygen as the sole oxidant. Furthermore, through Buchwald's synthetic protocol, two compounds were converted into corresponding fluorescent carbazoles in 30–40% yield by intramolecular C–N bond formation.

Keywords: alkynes; aromatic homologation; C–H activation; naphthalenes; palladium

Polycyclic aromatic hydrocarbons (PAHs) or linear π-conjugated systems are highly fluorescent materials with versatile applications in dyes, optical sensors, molecular electronics, nonlinear optics, light-emitting diodes, photovoltaic cells, and field-effect transistors.[1] Currently, the preparation of higher-order aromatic hydrocarbons from halogenated or other prefunctionalized and traceless removable directing group-mediated aromatic compounds has become methodologically less appealing because of an increasing demand for greener and atom-economic synthetic approaches.[2] Transition metal-catalyzed C–H bond activation methodology has unique advantages for syntheses of a variety of molecules – including not only bioactive but also functional optoelectronic material compounds since directing group- and chelation-assisted C–H bond activation has provided a concise approach for efficient C–C, C–N, and C–O bond formation in recent decades.[3] Therefore, direct ring construction through the use of metal-catalyzed multiple C–H bond functionalizations with internal alkynes as an inserting unit has provided an opportunity for the synthesis of bioactive or polyaromatic π-conjugated molecules.[4]

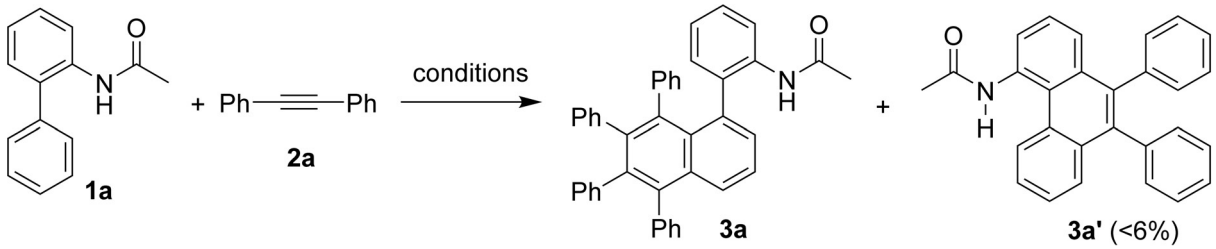
Some advanced studies on Rh- or Pd-catalyzed directing group- and chelation-assisted aromatic homologation strategies for syntheses of PAHs have been reported.[5] Wu and coworkers developed an *N*-acyl-directed consecutive C–H bond activation and insertion of alkynes on anilides, leading to tetraaryl-substituted naphthalenes (Scheme 1a). More recently, Chatani demonstrated the chelation-assisted nickel-catalyzed oxidative annulation through double C–H activation/alkyne insertion of benzamides.[6] Miura and co-workers demonstrated an Rh-catalyzed aromatic homologation of phenylazoles to yield fluorescent naphthalenes (Scheme 1b).[7] Other relevant studies by Miura and Luan showed Ru-catalyzed alkenylation and palladium-catalyzed [5+2] oxidative annulation of *o*-arylanilines with internal alkynes, providing alkenylation products and dibenzo[*b*,*d*]azepines, respectively (Scheme 1c).[8] Although the aromatic homologation of 2-phenylphenol was demonstrated under Rh catalysis, the reaction scope was limited to only one example.[9] Furthermore, a straightforward aromatic ring construction through directing group-assisted C–H bond functionalization in a 2-aminobiaryl system has not yet been reported. C–H bond activation generally favors C-3–H over C-2′–H in an acidic medium, and knowledge on NHAc-directed C–H activation of C-2′–H on a 2-phenyl moiety is limited to only two examples involving nitro



Scheme 1. Directing group- or chelation-assisted C–H bond activation of *N*-substituted anilines and *N*-free or *N*-substituted biaryls.

substitution on C-4 or C-5 in moderate yields (Scheme 1d).[10] The consecutive C–H bond activation and alkyne insertion process is considerably more complex as it may involve dissociative cleavage of the Pd–N bond in the first alkyne-inserted intermediate (**IA**), formation of a relatively less common and unstable eight-membered palladacycle (**IB**), and competing coordination with another resting directing group (NHAc) in intermediate **IC**; this may be followed by second competing C–H bond activation (C-6–H *versus* C-3′–H, Scheme 1e). Our research group has demonstrated palladium-catalyzed C-2′–H activation of *N*-tosyl-2-aminobiaryls followed by the insertion of [60]fullerene and CO to yield fulleroben-zoazepines[11] and phenanthridinones,[12] respectively. The activation of C-2′–H is considerably sensitive to the substitution on the nitrogen of 2-aminobiaryls, which has engendered a demand for developing another new condition for C-2′–H activation by using other *N*-substituted 2-aminobiaryls. In this paper, we report NHAc group-directed double consecutive C–H bond activation/alkyne insertion with *N*-acyl-2-biaryl-

Table 1. Optimization of reaction conditions.[a]



Entry	**1a**:**2a**	Oxidant (equiv.)	Solvent	Temperature [°C]	Additive (mol%)	Yield [%]
1	1:2.4	air	DMF	120	–	52 (88)
2[h]	1:2.4	AgOAc (1)	DMF	120	–	28 (60)
3	1:2.4	$K_2S_2O_8$	DMF	120	–	0
4	1:2.4	$Cu(OAc)_2$ (1)	DMF	120	–	63 (82)
5	1:2.4	BQ (3)	DMF	120	–	0
6[i]	1:2.4	O_2	toluene	120	NaOAc (50)	16 (68)
7[i]	1:2.4	O_2	CB	120	NaOAc (50)	11 (61)
8	1:2.4	O_2	*o*-DCB	120	NaOAc (50)	0
9	1:2.4	O_2	DCE	120	NaOAc (50)	trace
10	1:2.4	O_2	DMSO	120	NaOAc (50)	28
11	1:2.4	O_2	DMF	120	NaOAc (50)	74
12	1:2.4	$Cu(OAc)_2$ (0.2)/O_2	DMF	100	NaOAc (50)	79
13[h]	1:1.2	O_2	DMF	120	NaOAc (50)	44 (78)
14	1:1.8	O_2	DMF	120	NaOAc (50)	67 (82)
15	1:3.0	O_2	DMF	120	NaOAc (50)	67
16	1:2.4	O_2	DMF	120	–	62 (92)
17	1:2.4	O_2	DMF	120	LiOAc (50)	46
18	1:2.4	O_2	DMF	120	KOAc (50)	63
19	1:2.4	O_2	DMF	120	NaOAc (25)	66
20	1:2.4	O_2	DMF	120	NaOAc (100)	58
21[b]	1:2.4	O_2	DMF	120	NaOAc (50)	60
22[c]	1:2.4	O_2	DMF	120	NaOAc (50)	25(80)
23[d]	1:2.4	O_2	DMF	120	NaOAc (50)	64
24[e]	1:2.4	O_2	DMF	120	NaOAc (50)	39
25[f]	1:2.4	$Cu(OAc)_2$ (0.2)	DMF	120	AgOTf (20)	0
26[g]	1:2.4	O_2	DMF	120	NaOAc (50)	0

[a] *Reaction conditions*: All reactions were carried out using substrate **1a** (0.3 mmol), **1b** (0.72 mmol), and $Pd(OAc)_2$ (10 mol%) in 2 mL of anhydrous solvents for 24 h unless otherwise noted. Yields [%] were determined through the ^{1}H NMR spectroscopic method using mesitylene as an internal standard. Yields in parentheses are based on converted **1a**.
[b] Ac-Gly-OH was used as a ligand.
[c] 2,2′-bipyridine was used as a ligand.
[d] DMF (3 mL).
[e] DMF (4 mL).
[f] $RuCl_2$(*p*-cymene)/AgOTf.
[g] Instead of **1a**, unprotected 2-aminobiphenyl was used as the reactant.
[h] A by-product **3a′** was isolated in <6% yield.
[i] Trace amount of a by-product, 6-phenylphenanthridine, was isolated.

amines under palladium catalysis, using greener and abundantly available molecular oxygen as an oxidant.

Initially, we expected to observe oxidative coupling of *N*-acyl-2-aminobiphenyl (**1a**) with a diphenylacetylene (**2a**) to yield an azepine. Instead, we observed dual C–H bond cleavage at C-2′ and C-3′ *via* oxidative coupling of two diphenylacetylenes with palladium acetate as a catalyst and air as an oxidant to afford *N*-[2-(5,6,7,8-tetraphenylnaphthalen-1-yl) phenyl]acetamide (**3a**) in *N*,*N*-dimethylformamide (DMF) at 120 °C for 24 h (Table 1, entry 1). Next, we optimized parameters for the formation of *N*-[2-(5,6,7,8-tetraphenylnaphthalen-1-yl)phenyl]acetamide as described herein. Other oxidizing agents, such as AgOAc, $K_2S_2O_8$, and *p*-benzoquinone (BQ), except for $Cu(OAc)_2$, resulted in poor yields (entries 2–5). Other tested aromatic and chlorinated solvents such as toluene, chlorobenzene (CB), *ortho*-dichlorobenzene (*o*-DCB),

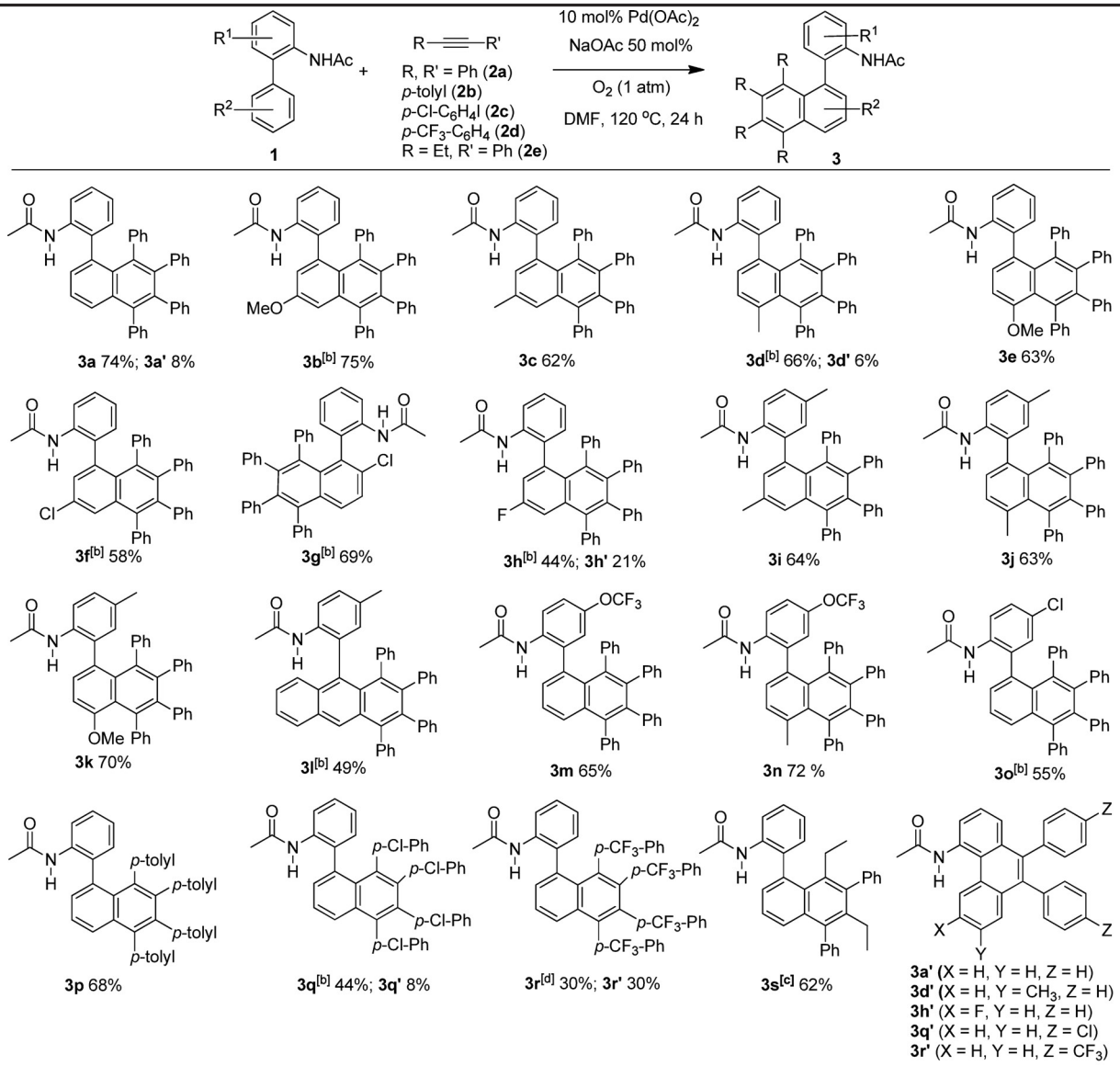
and 1,2-dichloroethane (DCE) did not increase the yields notably (entries 6–9). However, the use of polar aprotic solvents, such as dimethyl sulfoxide (DMSO) and DMF, resulted in a promising increase in yields up to 74% with 50 mol% sodium acetate used as the additive (entries 10 and 11). The use of $Cu(OAc)_2$ (20 mol%)/O_2 as a hybrid oxidant provided a 79% yield at 100 °C (entry 12). Our parameter study of reactant molar ratios, ranging from 1:1.2 to 1:3 for **1a**:**2a**, to achieve full consumption of reactant **1a** revealed that the reaction yield was optimal at a reactant molar ratio of 1:2.4 (entries 11 and 13–15). Notably, among the tested additives including LiOAc and KOAc, the reaction with NaOAc as additive afforded the highest yields (46–66%) for the desired products (entries 16–20). NaOAc played a crucial role in product formation because of its possible potential in stabilizing the relevant Pd(II) intermediates during the reactions. We also examined reactions for observing the additional ligand effect of adding Ac-Gly-OH (entry 21) and 2,2′-bipyridine (entry 22), and no considerable increase in the yields was observed. Furthermore, diluting the solution concentration reduced the yields by a small amount (entries 23 and 24). A control experiment involving the use of $RuCl_2$(*p*-cymene)/AgOTf as a catalyst and another substrate without substitution on the nitrogen of the 2-aminobiphenyl provided no corresponding products (entries 25 and 26). Among the studied conditions, a notable minor by-product, 9,10-diphenyl phenanthrene **3a′**, was isolated in less than 6% yield under certain conditions (entries 2 and 13). Moreover, trace amounts of a by-product, 6-phenylphenanthridine (**3t**),[13] were isolated through oxidative cleavage of diphenylacetylene (entries 6 and 7; see the Supporting Information, Figures S61 and 62 for spectral data). Our examination of the various experimental conditions revealed that the following conditions provided the maximum yield: $Pd(OAc)_2$ (10 mol%) as the catalyst, NaOAc (50 mol%) as the additive, and $Cu(OAc)_2$ (0.2 equiv.)/O_2 as the oxidant at 100 °C (entry 12) or O_2 (1 atm) as the sole oxidant in DMF at 120 °C for 24 h (entry 11).

Table 2 summarizes the reaction scope study of this double C–H bond activation/alkyne insertion with *N*-acyl-2-aminobiaryls. The reactivity of the studied substrates was highly dependent on the substitution effect produced by both aryl moieties of *N*-acyl-2-aminobiaryls and substituted acetylenes. Notably, substrates **3b–e** containing electron-donating groups (EDGs) on the 2′-aryl moiety underwent dual C–H bond activation and coupling with diphenylacetylene smoothly to provide favorable yields of 62–75%, likely attributed to the enhanced reactivity toward C–H bond activation afforded by EDGs. However, substrates **3f–h** containing an electron-withdrawing group (EWG) did not undergo effective C–H bond activation and coupling with substituted acetylenes and engendered slightly poorer yields (44–69%). Furthermore, the study of the electronic effect between the interplay of both aryl rings revealed the same effect, providing **3i–o** in 49–72% yields. Furthermore, we observed the formation of diphenylphenanthrenes **3a′**, **3d′**, and **3h′** in 8%, 6%, and 21% yields, respectively, through C-2′–H bond activation, diphenylacetylene insertion, C-6–H bond activation, and reductive elimination. Four other typical internal alkynes (**2b–e**) were also examined for the insertion reaction – an internal alkyne with an EDG moiety, di-*p*-tolylacetylene (**2b**), produced **3p** in 68% yield, and those with EWG groups, di-*p*-chlorophenylacetylene (**2c**) and di-*p*-trifluoromethylphenylacetylene (**2d**), resulted in **3q–r** in 44% and 30% yields, respectively. These reactions were concomitant with the formation of diarylphenanthrenes **3q′** and **3r′** in 8% and 30% yields, respectively. In addition, the reaction with unsymmetrical alkyne **2e** formed **3s** solely in 62% yield. The molecular structures of the novel annulated products, represented by substituted naphthalene **3a** and by-product phenanthrene **3r′**, were confirmed through single-crystal X-ray diffraction analysis.[14]

A tentative yet plausible mechanism involving two C–H bond activations and alkyne insertions is presented in Scheme 2. Initially, *ortho* C–H was activated on the 2-aryl moiety to yield intermediate **Ia** after coordination of substrate **1** with palladium(II). Coordination and insertion of alkyne **2** with intermediate **Ia** produced a 7-membered palladacycle intermediate, **Ib**. Dissociation of the Pd(II)–N bond led to two possible second C–H bond activations – activation of the *meta* C-3′–H bond generated a 5-membered palladacycle intermediate, **Ic**, and activation of the C-6–H bond formed a 7-membered palladacycle intermediate, **Ie**. The major product **3** was produced by the second coordination and insertion of the alkyne to intermediate **Ic** followed by reductive elimination from intermediate **Id** or **Id′**, based on a former nickel-catalyzed oxidative annulation *via* C–H activation/alkyne insertion reaction.[6,15] The by-products, phenanthrenes, were produced through further reductive elimination from intermediate **Ie**. The mechanistic investigation of directing group-assisted double C–H activation was conducted through a deuterium-labeling experiment. A kinetic isotope effect (KIE) study revealed a k_H/k_D value of 1.66 in a 20 min reaction (Scheme 3). Because the k_H/k_D value was not extremely high, that both C–H activation steps are the rate-limiting steps is unlikely; therefore, either one of these two steps as the rate-limiting step is more likely. However, determining which step is the rate-limiting one was not feasible in the present study.

Our preliminary investigation showed that the conversion of compounds **3** to corresponding carbazoles by Pd-catalyzed intramolecular C–N bond formation through the C–H bond activation strategy

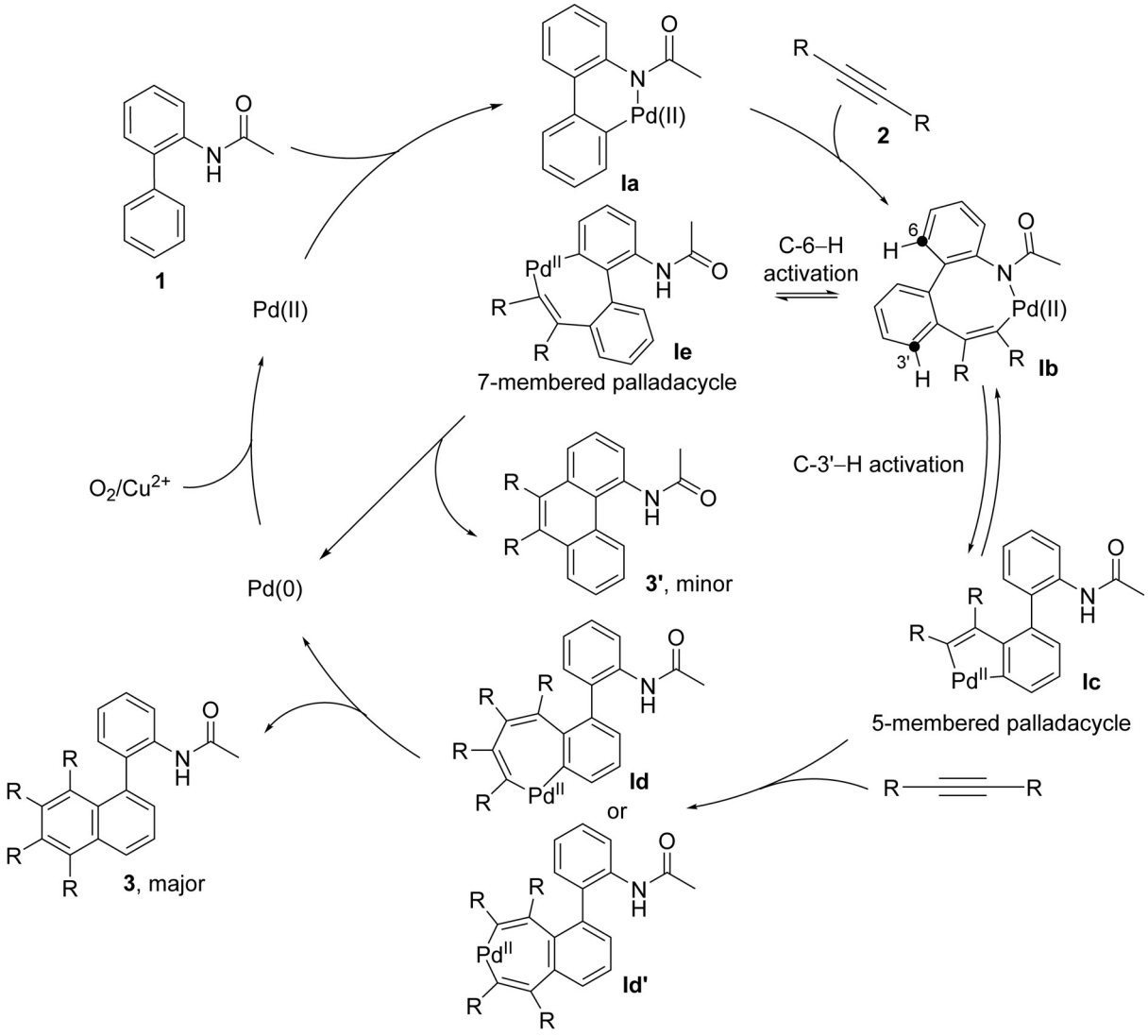
Table 2. Substrate scope study[a]



[a] *Reaction conditions*: All reactions were carried out using substrate **1** (0.30 mmol), substrate **2** (0.72 mmol), additive NaOAc (50 mol%), catalyst $Pd(OAc)_2$ (10 mol%), and O_2 (1 atm) in 2 mL freshly distilled DMF at 120 °C for 24 h.
[b] $Cu(OAc)_2$ (20 mol%)/O_2 (1 atm) at 100 °C.
[c] 5 equiv. of the unsymmetrical alkyne and $Cu(OAc)_2$ (1 equiv.)/O_2 (1 atm) at 80 °C were used.
[d] $Cu(OAc)_2$ (1 equiv.)/O_2 (1 atm) at 80 °C.

was relatively difficult because of the poor reactivity afforded by steric and electronic effects of the naphthalene moiety, with an approximate yield of 30–40% under Buchwald's protocol.[15] The fluorescence spectra of carbazoles **4a** and **4p** and their precursors, naphthalenes **3a** and **3p**, showed emission wavelengths at 411, 410, 399, and 395 nm with quantum yields of 9.4%, 8.0%, 8.8%, and 7.6%, respectively, in a chloroform solution (Supporting Information, Figure S60).

In summary, we have demonstrated a novel aromatic homologation of *N*-acyl-2-aminobiaryls through *ortho* and *meta* C–H bond activations followed by two respective alkyne insertions. The corresponding C–H bond activation of *N*-acyl-2-aminobiaryl appeared to be solvent-controlled, and this reaction used molecular oxygen or copper(II)/oxygen as oxidants to complete a catalytic cycle. A further mechanistic study and development using the described strategy to explore new optoelectronic materials is underway in our laboratory.



Scheme 2. Proposed catalytic cycle.

Experimental Section

General Procedure for the Palladium-Catalyzed Synthesis of *N*-[2-(5,6,7,8-Tetraarylnaphthalen-1-yl)aryl]acetamides

To a dry reaction tube, NaOAc (0.15 mmol) was added and the reaction tube was heated using a flame gun under vacuum. After the tube hads cooled down to room temperature, *N*-acyl-2-aminobiaryl **1** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol), substituted acetylene (0.72 mmol), and a stirring bar were added and the tube was sealed with a septum. Subsequently, freshly distilled DMF (2 mL) was added and the tube was purged with O_2 for 15 min. The tube was closed shortly thereafter using a cap, placed in an oil bath, and the mixture vigorously stirred at 120 °C for 24 h. Upon completion of the reaction, the reaction mixture was cooled down to room temperature and diluted with ethyl acetate followed by filtration through a thin pad of celite. The filtrate was concentrated under vacuum and the crude residue was purified through flash silica gel column chromatography (hexanes/EtOAc) to afford compound **3**.

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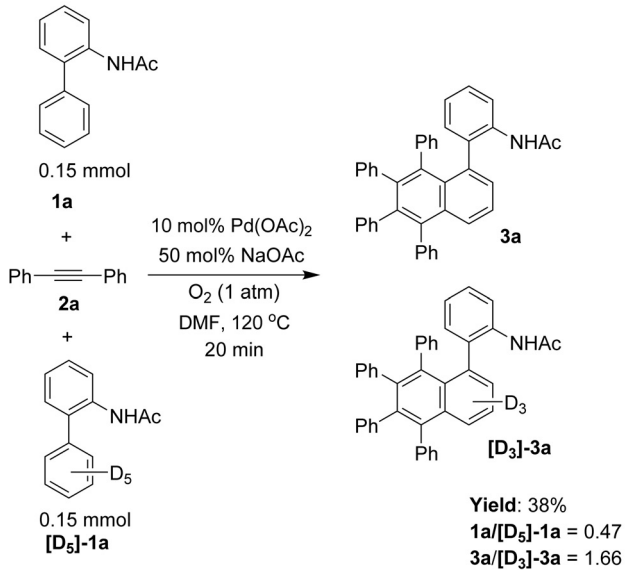

Scheme 3. Deuterium-labeling experiments.

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UPDATES

Palladium-Catalyzed Selective Aryl Ring C–H Activation of *N*-Acyl-2-aminobiaryls: Efficient Access to Multiaryl-Substituted Naphthalenes

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