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One-Pot Unsymmetrical {[4 + 2] and [4 + 2]} Double Annulations of *o*/*o*′-C−H Bonds of Arenes: Access to Unusual Pyranoisoquinolines

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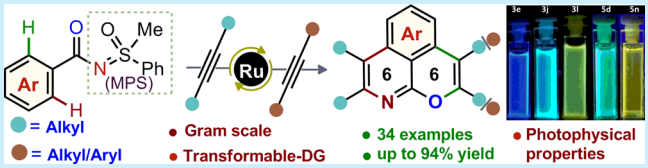
Supporting Information

ABSTRACT: With the aid of a transformable sulfoximine directing group, unprecedented one-pot unsymmetrical double annulations {[4 + 2] and [4 + 2]} of hetero(arenes) with alkynes are revealed under Ru(II) catalysis. Functionalization of both *ortho*-C−H bonds of (hetero)arene is reflected in the building of unusual 6,6-fused pyranoisoquinoline skeletons. Construction of four [(C−C)−(C−N) and (C−C)−(C−O)] bonds occurs in one step under single catalytic conditions. The challenging unsymmetrical double annulations of both *o*-C−H bonds of arenes with two distinct alkynes is effectively demonstrated. Control experiments and deuterium scrambling findings are shown.



The transition-metal-catalyzed directing group (DG)-assisted oxidative annulation of ubiquitous arene C−H bonds has been found remarkable in building novel polycyclic heteroarenes that are commonly present in bioactive molecules and natural products, exhibiting broad application in pharmaceuticals and advanced materials.[1] Although monoannulation strategies have largely been useful, the stepwise sequential annulation of multiple C−H bonds has been shown to be feasible for fabricating π-extended fused heterocycles (Scheme 1A).[2−4] With these advances, creation of a one-pot sequential/domino double annulation of arene motifs with alkynes was recently accomplished, although with a narrow scope.[5] By contrast, double annulations of arene's *o*-C−H bonds with alkynes have yet to be widely achieved, as the molecular rigidity and conformation strain hamper this reaction.[5,6] Moreover, uncontrolled reactivity, lack of selectivity, and the catalyst dependent functionalization of a particular DG-aided *o*-C−H bond raises concern.[7] Despite these significant challenges, the Rh(III)-catalyzed oxidative domino double annulation of C−H bonds of benzoylacetonitrile,[8] enamino ester,[9] *N*-hydroxybenzamidines,[10] or polyaromatic aldehyde[11] with alkynes has independently been studied (Figure 1B). Thus, double annulation of both *o*-C−H bonds of arene moieties with two alkynes was successful under Rh catalysis, primarily forming C−C with either C−O/C−N bonds and are confined to 6,6-bifused heteroarenes (Figure 1B).[8−11]

We herein developed a Ru-catalyzed transformable methylphenyl sulfoximine (MPS)−DG-assisted unsymmetrical double annulation of both *o*-C−H bonds of (hetero)arene carboxyamide with unactivated alkynes, which is unprecedented. This process constructs pyranoisoquinoline {6,6-bifused structures with O and N involving two distinct [4 + 2] annulations} (Figure 1C).

To probe the feasibility of the hypothesis (Figure 1C), the domino [4 + 2] and [4 + 2] double annulation of *N*-[4-methylbenzoyl]methylphenyl sulfoximine (**1a**) with 4-octyne

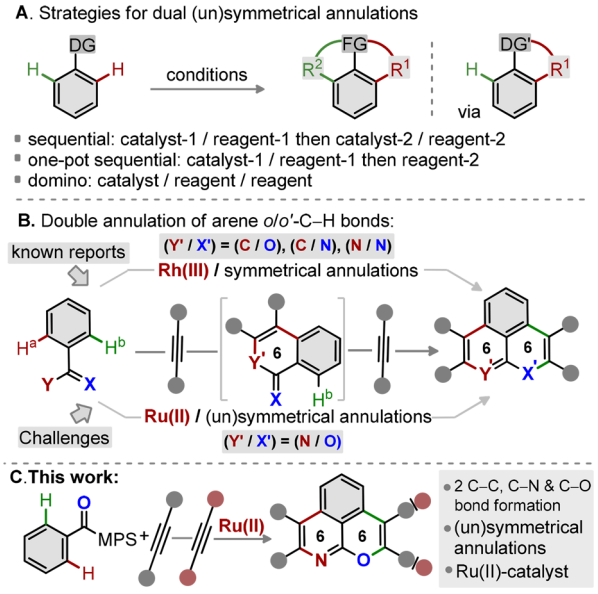


Figure 1. Multiple annulation of (hetero)arenes.

(**2a**) was explored under Ru catalysis (Table 1). Gratifyingly, the expected pyranoisoquinoline **3a** (with the inclusion of two alkyne motifs on the periphery) was formed, albeit in 8% yield, under the catalytic conditions of $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol %) and $AgSbF_6$ (20 mol %) in DCE at 120 °C for 24 h (entry 1). Because bases significantly promote the Ru-mediated C−H activation, various acetate bases were then carefully tested (entries 2−6); NaOAc, KOAc, and $Mn(OAc)_2{\cdot}3H_2O$ were poor (entries 2−4), whereas AgOAc was moderate (entry 5), and finally, $Cu(OAc)_2{\cdot}H_2O$ was found to be the best, providing 50%

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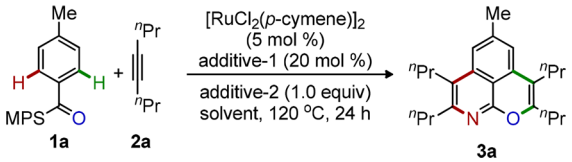
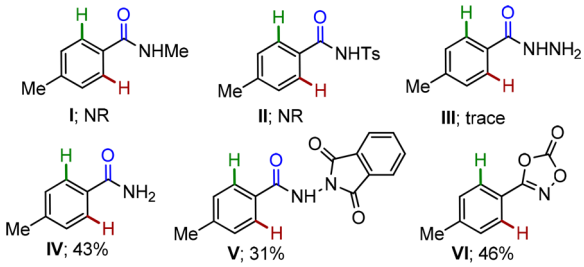
Table 1. Optimization of Reaction Conditions[a]



entry	additive 1 (20 mol %)	additive 2 (1.0 equiv)	solvent	yield of **3a** (%)[b]
1	$AgSbF_6$		$ClCH_2CH_2Cl$	08
2	$AgSbF_6$	NaOAc	$ClCH_2CH_2Cl$	trace
3	$AgSbF_6$	KOAc	$ClCH_2CH_2Cl$	13
4	$AgSbF_6$	$Mn(OAc)_2{\cdot}3H_2O$	$ClCH_2CH_2Cl$	trace
5	$AgSbF_6$	AgOAc	$ClCH_2CH_2Cl$	36
6	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	$ClCH_2CH_2Cl$	50
7	$NaPF_6$	$Cu(OAc)_2{\cdot}H_2O$	$ClCH_2CH_2Cl$	39
8	KPF_6	$Cu(OAc)_2{\cdot}H_2O$	$ClCH_2CH_2Cl$	42
9	$AgBF_4$	$Cu(OAc)_2{\cdot}H_2O$	$ClCH_2CH_2Cl$	38
10	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	toluene	27
11	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	MeCN	trace
12	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	55
13[c]	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	71
14[d]	**$AgSbF_6$**	**$Cu(OAc)_2{\cdot}H_2O$**	**1,4-dioxane**	**83**



[a]Conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol %), additive 1 (20 mol %), additive 2 (0.3 mmol), solvent (2.0 mL) at 120 °C. [b]Isolated yield. [c]$[RuCl_2(p\text{-cymene})]_2$ (10 mol %), $AgSbF_6$ (40 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (1.0 equiv). [d]$[RuCl_2(p\text{-cymene})]_2$ (10 mol %), $AgSbF_6$ (40 mol %), $Cu(OAc)_2{\cdot}H_2O$ (1.5 equiv), and **2a** (1.2 mmol) were used.

of **3a** (entry 6). We thus believe the redox-active acetate base helps the C−H activation as well regeneration of the active Ru(II) catalyst. Other additives, including $NaPF_6$, KPF_6, and $AgBF_4$, were moderate (entries 7−9). The reaction in toluene or MeCN was ineffective (entries 10 and 11); this double annulation in 1,4-dioxane produced **3a** in 55% yield (entry 12). The use of 10 mol % of Ru catalyst under identical conditions led to 71% **3a** (entry 13). The annulation among **1a** and two molecules of **2a** was smoothly commenced under the optimized reaction conditions of $[Ru(p\text{-cymene})Cl_2]_2$ (10 mol %), $AgSbF_6$ (40 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (1.5 equiv) in 1,4-dioxane at 120 °C for 24 h (entry 14). Notably, four bonds [C−C and C−N along with C−C and C−O] are constructed through the replacement of two *o*-C−H bonds of arene in a single operation.[12] The DG-assisted annulation of arenes is routinely studied; however, the nonexistence of direct double annulation of amide-enabled arenes to 6,6-fused pyranoisoquinoline warrants further investigation. Consequently, the role of amide-DG in this one-pot double annulation of *o*-C−H bonds of arene was examined under the optimized conditions (entry 14, Table 1).[2,3] Despite our repeated attempts, the NH-Me (**I**) or NH-tosyl (**II**) amide and hydrazide (**III**) DG bearing benzamides failed to undergo these domino [4 + 2] double annulations with **2a**. However, simple amide (**IV**) or amides with an internal oxidizable moiety (**V** and **VI**) reacted with **2a** to yield a moderate amount of **3a**. Thus, MPS−DG surfaces are vital, as this moiety ensures the occurrence of synthetically challenging one-pot [4 + 2] double annulations of arenes with alkynes to directly construct 6,6-fused pyranoisoquinoline.

The reaction generality of this newly conceived Ru-catalyzed domino [4 + 2] oxidative double annulations of *N*-aroyl sulfoximines (**1**) with unactivated alkyne was probed under the optimized catalytic conditions shown in entry 14, Table 1. The results are detailed in Scheme 1. The reaction of **1** having either electron-donating (e.g., Me, ^{t}Bu, OMe, OPh), electron-withdrawing (Ph, CO_2Me), or labile halo groups (e.g., F, Cl, Br) in the *para* position of arene with 4-octyne (**2a**) produced the respective pyrano[4,3,2-*ij*]isoquinolines (**3a−j**) in moderate to good yields. X-ray crystallographic studies elucidate the structure of **3a** (Scheme 1).[13] The gram-scale synthesis of **3a** (1.47 g) proves the robustness of the annulation; isolation of methylphenyl sulfoxide (precursor for MPS) makes MPS transformable.[5e−g] The modifiable functional groups (Cl, Br, F, and CO_2Me) were tolerated. Diannulation of 2-naphthalene (**1k**) and carbazole-3 (**1l**) carboxylic acid derivatives with **2a** independently delivered **3k**/**3k′** (60%) and **3l** (70%), respectively; the first annulation selectively occurs at the sterically less hindered C−H site. Carbazole and anthracene structural entities largely contribute to the tuning of the photophysical properties of the molecules; the respective carbazole and anthracene-molded pyranoisoquinoline scaffolds (**3m**, **n**) were accessed in decent yields.[14] The *m*-Me/*m*,*p*-disubstituted amides **1o**/**1p** successfully underwent annulation with **2a**, affording **3o**/**3p**, respectively, albeit in moderate yield; importantly, the steric bulkiness did not obstruct the second annulation. Other internal alkynes, 3-hexyne (**2b**) and 5-decyne (**2c**), were efficient, producing **3q** (94%) and **3r** (88%). Obviously, *ortho*-substitution on arene hampered the domino annulation; the reaction was thus ended with monoannulation (**4q**). An important synthetic deliberation of this strategy is showcased through the fabrication of linear 5,5′-bipyrano[4,3,2-*ij*]isoquinoline (**3s**) and "V-shaped" 5,5′-oxidipyrano[4,3,2-ij]isoquinoline (**3t**) complex skeletons from **1r** and **1s**, respectively. The functionalization of four *o*-C−H bonds of arenes with four alkynes and the formation of eight bonds (4 C−C, 2 C−N, and 2 C−O) in a single operation is significant.

Inspired by the successful unsymmetrical double annulation of (hetero)arenes with two molecules of single alkyne (Scheme 1), we next executed an identical challenging exploration with different alkynes. Formation of several byproducts from incomplete/nonselective annulation in each step is a potential challenge.[6,7] To address these issues, a two-step synthetic strategy involving (i) MPS-promoted *o*-C−H monoannulation with dialkyl alkyne followed by (ii) C(8)−H activation and annulation of isoquinolone, obtained from Step-I, with structurally diverse alkynes, was planned (Scheme 2). Gratifyingly, the corresponding isoquinolone scaffolds **4a** (57%), **4b** (58%), and **4j** (58%) were constructed from the respective monoannulation of **1a**, **1b**, and **1j** with **2a** when the reaction was conducted under Ru catalysis in the presence of AcOH in DCE (Conditions A, Scheme 2).[3e] Presumably, acetic acid helps protodemetalation and selectively delivers isoquinolone. Next, independent annulation among isoquinolones **4a**/**4b**/**4j** and 1,2-diaryl/alkyl alkynes led to the respective peripheral decorated 6,6-fused pyranoisoquinolines (Scheme 2). The 1,2-

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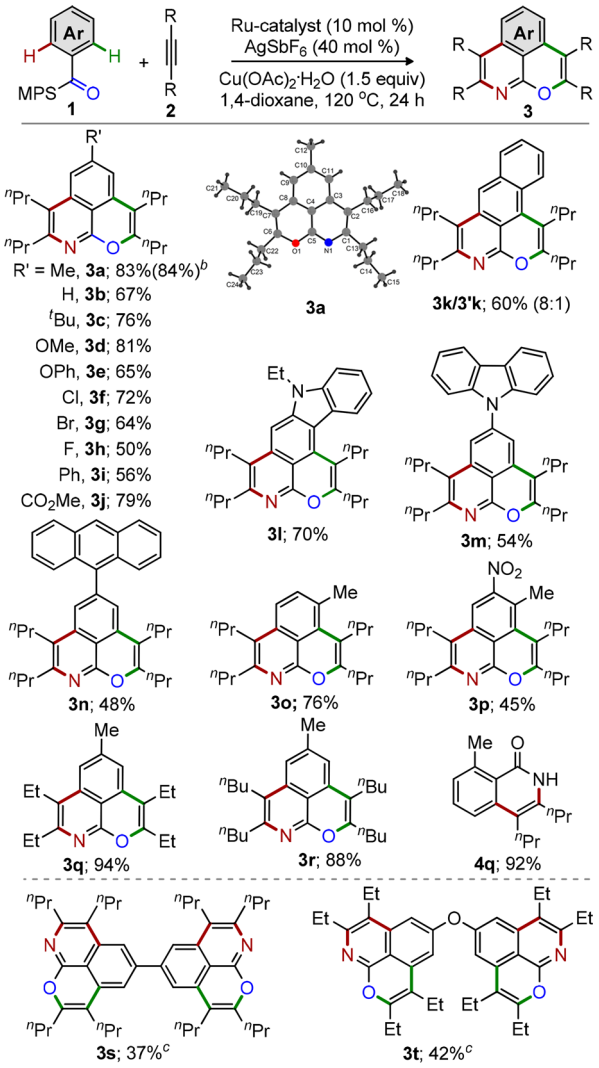
Scheme 1. Synthesis of 6,6-Fused Pyranoisoquinoline[a]

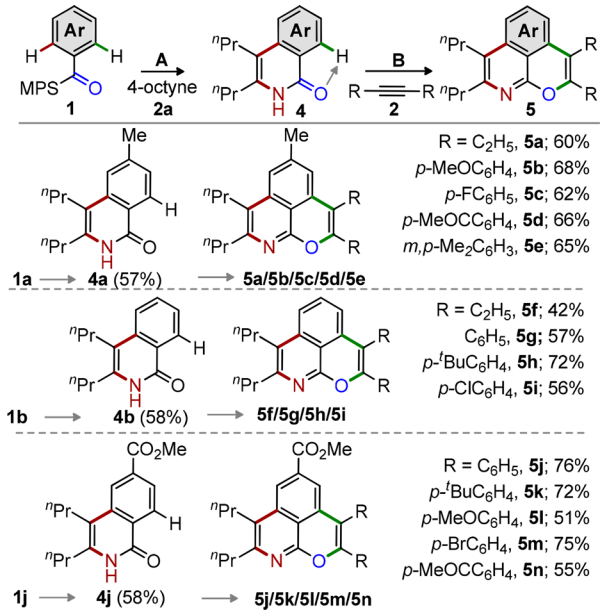


[a]Conditions: **1** (0.5 mmol), **2** (2.0 mmol), Ru catalyst (10 mol %), $AgSbF_6$ (40 mol %), $Cu(OAc)_2·H_2O$ (0.75 mmol), 1,4-dioxane (3.0 mL) at 120 °C for 24 h. [b]Gram scale: **1a** (1.37 g, 5.0 mmol). [c]**1** (0.3 mmol), **2** (2.1 mmol), Ru catalyst (15 mol %), $AgSbF_6$ (60 mol %), $Cu(OAc)_2·H_2O$ (0.9 mmol), 1,4-dioxane (3.0 mL) at 120 °C for 50 h.

diaryl alkynes having electron-donating (^{t}Bu, OMe) and electron-withdrawing (F, Cl, COMe) substitutions on arene successfully participated in this unsymmetrical annulation (Scheme 2).

To gain mechanistic insight into the current transformation, various control experiments were planned and assessed (Figure 2). The deuterium scrambling study of **1b** in the absence (eq 1) or presence (eq 2) of 4-octyne (**2a**) provided 35 and 33% D-incorporation in the arene *o*-positions of precursor **1b**, respectively. Hence, the current C−H activation of arene is reversible (eqs 1 and 2); the participation of alkyne for C−H activation is therefore unviable. However, annulation of N-Me-isoquinolone (**4a-Me**) with **2a** under Ru catalysis was unsuccessful (eq 3); the NH-isoquinolone is therefore essential for the synthesis of pyranoisoquinoline via isoquinolinol-directed annulation with alkyne. Exposing **4a-Me** to the optimized conditions in CD_3CO_2D resulted in 48% D-incorporation of C8, reflecting the O-directed metalation of

Scheme 2. Unsymmetrical Double Annulation of Arenes with Different Alkynes[a]



[a]Conditions A: **1** (0.5 mmol), **2a** (1.0 mmol), Ru catalyst (7.5 mol %), $AgSbF_6$ (30 mol %), AcOH (2.0 mmol), DCE (2.5 mL) at 120 °C for 20 h. Conditions B: **4** (0.3 mmol), **2** (0.45 mmol), Ru catalyst (5.0 mol %), $AgSbF_6$ (20 mol %), $Cu(OAc)_2·H_2O$ (0.3 mmol), 1,4-dioxane (2.0 mL) at 120 °C for 20 h.

the isoquinolone C8−H bond (eq 3). A set of KIE experiments was performed to understand the rate-determining step (RDS) of this multistep double annulation protocol. The intermolecular competition experiment among **1b-H$_5$**, **1b-D$_5$** (1:1), and **2a** under the optimized conditions exhibited k_H/k_D = 1.38 (eq 4). Similarly, the relative rate of the reaction (k_H/k_D = 1.63) of **4b-H$_4$**, **4b-D$_4$**, and **2a** reveals a secondary KIE in the second annulation to pyranoisoquinoline (eq 4). Finally, the k_H/k_D value for the overall one-step double annulation of **1b-H$_5$** and/or **1b-D$_5$** with **2a** is ∼3.0 (competitive) and ∼1.41 (parallel), clearly advocating that the C−H activations do not happen in the RDS (eq 4).[15] Based on the competition experiments, the electron-rich arenes underwent reaction faster than that of electron-poor arenes. For example, the product ratios **3a**/**3j** (8:1) and **3d**/**3g** (6:1) were obtained from the reaction of **1a**/**1j** (*p*-Me vs *p*-CO_2Me) and **1d**/**1g** (*p*-OMe vs *p*-Br) with **2a**, respectively (eq 5). Likewise, the reaction of an equimolar mixture of **4a** and **4j** with **2a** led to **3a** and **3j** in a 4:1 ratio (eq 6). We therefore presume that the electronic nature of the arenes influences the RDS of this double annulation.

Based on the previous observations and control experiments in Figure 2, probable pathway of MPS-assisted one-pot double annulation of arenes is sketched (Figure 3).

The reaction begins with the coordination of MPS to the active Ru catalyst and activation of the *o*-C−H bond of arenes **1b** to form the respective species **A**. Next, the coordination of alkyne to the cyclometalation complex **A** and insertion makes a seven-membered Ru metallacycle. As MPS−DG is transformable, the $Cu(OAc)_2$/AcOH-promoted concomitant expulsion of methylphenyl sulfoxide delivers isoquinolone architecture **4b′**.[2,3] Next, imide-assisted C(8)−H/C(peri)−H activation forms **C**, and the insertion of alkyne provides seven-membered metallacycle **D**. Finally, Cu-mediated reductive

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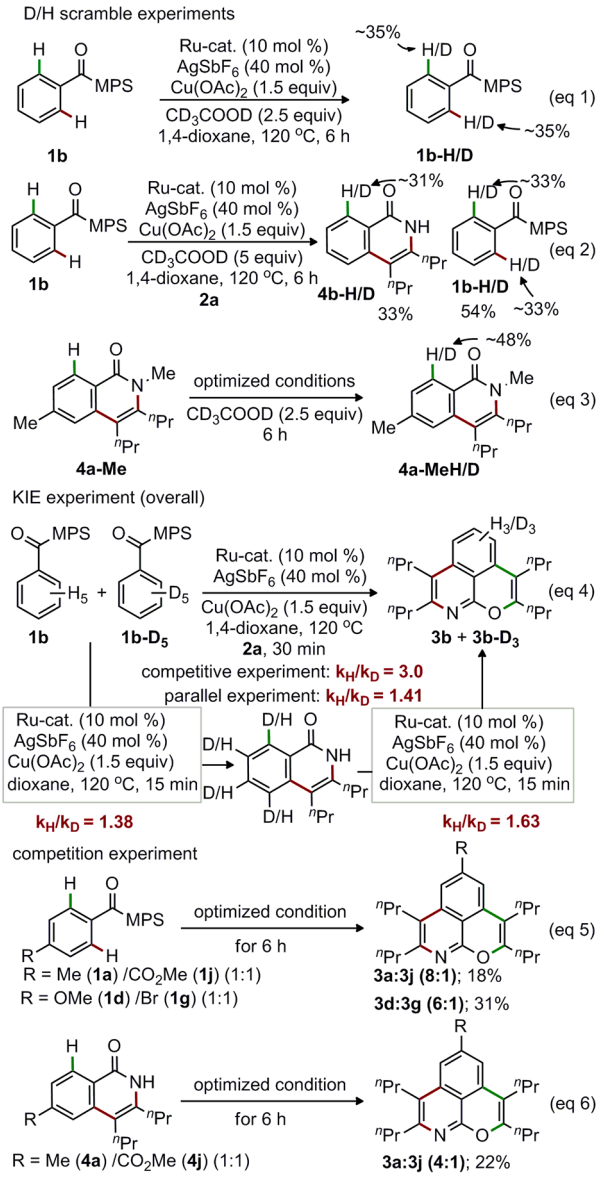

Figure 2. KIE and competition experiment studies.

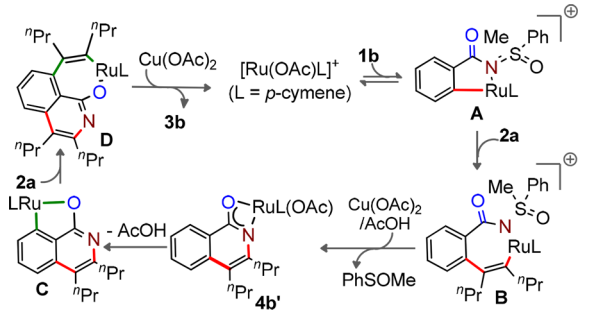

Figure 3. Proposed mechanistic cycle.

elimination from Ru-embedded species delivers the desired pyranoisoquinoline **3b** with the generation of active catalyst for the next cycle.

Most of the synthesized compounds are brightly fluorescent. To understand the photophysical properties of the present pyranoisoquinolines, the steady-state absorption and photoluminescence (PL) measurements for the respective compounds **3e**, **3j**, **3l**, **5d**, and **5n** in acetone were examined (Figure 4).[13] The fluorescence spectra of **3** and **5** show emission maxima

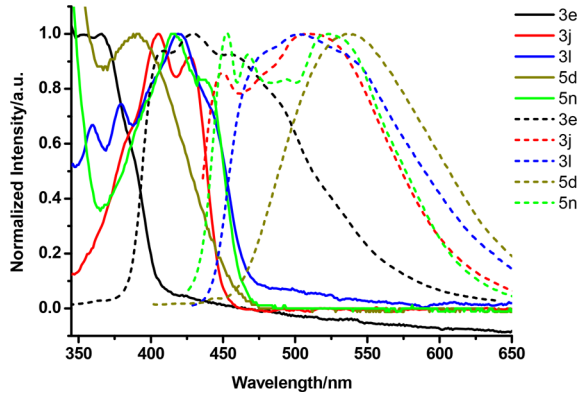

Figure 4. Normalized absorption (solid lines) and PL spectra (dotted lines) of derivatives of **3** (**3e, 3j, 3l**) and **5** (**5d, 5n**) dispersed in acetone medium (1×10^{-5} M).

at 429−536 nm, with broad bandwidths and high intensities. Based on their properties, these compounds will act as a fluorescent probe for biological labeling and organic light-emitting diode applications.

In summary, a one-pot unsymmetrical multiple annulative functionalization method for (hetero)arene *o*-C−H bonds with alkynes is developed with the aid of modifiable MPS under Ru catalysis, which offers a new avenue for the synthesis of conjugated heterocycles. The current protocol gives convenient access to 6,6-fused pyranoisoquinoline from readily available carboxylic acid derivatives and alkynes via the construction of four (C−C and C−N and C−C and C−O) bonds in a single operation involving domino [4 + 2] double annulations. The unsymmetrical double annulations of both *o*-C−H bonds of arenes with two distinct alkynes are also evaluated. Gram-scale synthesis determines the robustness of the catalytic system. Deuterium scrambling studies and control experiments support our understanding of the reaction mechanism. Steady-state absorption and photoluminescence measurements are also provided.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02068.

Detailed experimental procedures, NMR spectra, and X-ray crystallographic data (PDF)
HRMS data (PDF)

Accession Codes

CCDC 1846554 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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