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Rhodium-Catalyzed Selective Oxidative (Spiro)annulation of 2-Arylindoles by Using Benzoquinone as a C2 or C1 Synthon

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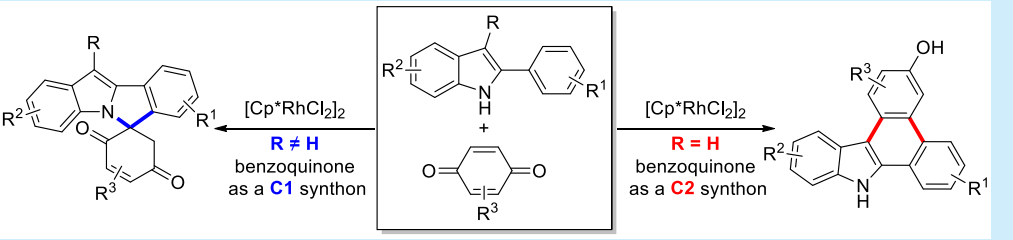
Supporting Information



ABSTRACT: Rhodium-catalyzed substrate-tunable oxidative annulation and spiroannulation reactions of 2-arylindoles with benzoquinone leading to 9*H*-dibenzo[*a*,*c*]carbazol-3-ols and new spirocyclic products are reported. Intriguingly, with 2-aryl-substituted indoles, benzoquinone could act as a C2 synthon to afford dibenzo[*a*,*c*]carbazoles. On the contrary, when 2-aryl-3-substituted indoles were used, benzoquinone switched to act as a C1 synthon to furnish spirocyclic compounds. In addition, further transformations of the obtained products demonstrate the synthetic utility of the present protocol.

Fused carbazole derivatives have attracted much attention because they are privileged scaffolds in numerous naturally occurring alkaloids,[1] bioactive organic molecules,[2] and novel organic electroluminescent materials.[3] As a result, a number of synthetic routes toward fused carbazole derivatives have been documented.[4] For example, dibenzo[*a*,*c*]carbazoles can be prepared through a palladium-catalyzed intramolecular annulation of 2-(2-bromoaryl)-3-arylindoles,[5] a dual C−H functionalization of indoles with cyclic diaryliodoniums,[6] a cascade reaction of 2-arylindoles with diaryliodoniums,[7] or an intermolecular cyclization of 2-(2-halophenyl)-indoles with iodobenzenes.[8] Whereas these existing routes are usually efficient and reliable, the development of new methods for the synthesis of dibenzo[*a*,*c*]carbazoles starting from easy-to-obtain substrates is still in high demand.

Recently, a transition-metal-catalyzed heteroatom-containing moiety-directed C−H functionalization/intramolecular cyclization cascade turned out to be one of the most powerful strategies for the construction of complex polycyclic scaffolds.[9] In this regard, the NH indole moiety has emerged as a versatile functionalizable directing group for the synthesis of various indole-containing polycyclic compounds. For example, NH indole-directed oxidative annulations of 2-arylindoles with different coupling partners, such as diazo compounds,[10] sulfoxonium ylides,[11] ketenes,[12] carbon monoxide,[13] alkynes,[14] or alkenes,[15] could be successfully utilized for the selective synthesis of benzocarbazole, isoindoloindolone, indoloisoquinoline, or isoindoloindole derivatives (Scheme 1). On the contrary, Rh(III)- or Ir(III)-catalyzed C−H functionalization reactions using benzoquinone as a coupling partner have been used in the direct construction of several hard-to-prepare cyclic skeletons reported by Xu, Wang, and Ison's groups.[16] However, to our knowledge, a Rh(III)-catalyzed NH indole-directed oxidative (spiro)annulation with benzoquinone has

Scheme 1. Transition Metal-Catalyzed Oxidative Annulation Reactions of 2-Arylindoles

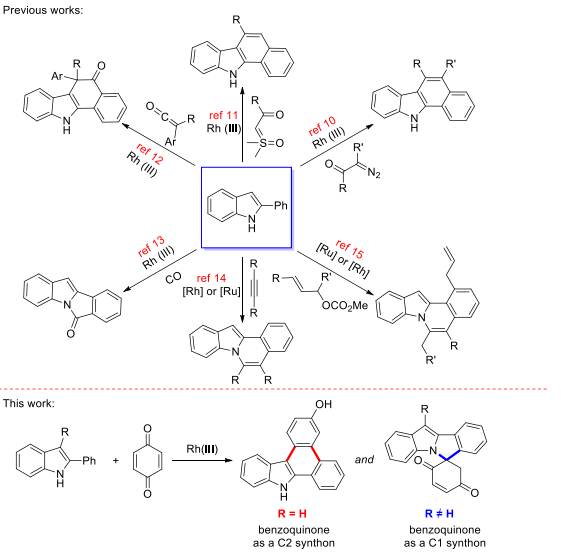


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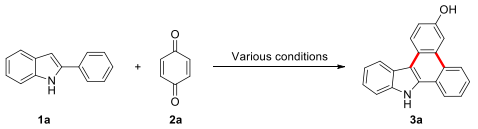
Table 1. Optimization of Reaction Conditions for the Synthesis of 3a[a]



entry	catalyst	additive	base	solvent	yield (%)[b]
1	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$		PhCl	30
2	$[Cp^*RhCl_2]_2$	AgOAc		PhCl	29
3	$[Cp^*RhCl_2]_2$	NaOAc		PhCl	30
4	$[Cp^*RhCl_2]_2$	CsOAc		PhCl	36
5	$[Cp^*RhCl_2]_2$	CsOAc	Et_3N	PhCl	70
6	$[Cp^*RhCl_2]_2$	CsOAc	Et_2NH	PhCl	37
7	$[Cp^*RhCl_2]_2$	CsOAc	DIPA	PhCl	47
8	$[Cp^*RhCl_2]_2$	CsOAc	Na_2CO_3	PhCl	46
9	$[Cp^*RhCl_2]_2$	CsOAc	K_2CO_3	PhCl	42
10	$[Cp^*RhCl_2]_2$	CsOAc	K_3PO_4	PhCl	25
11	$[Cp^*RhCl_2]_2$	CsOAc	Et_3N	toluene	43
12	$[Cp^*RhCl_2]_2$	CsOAc	Et_3N	*o*-xylene	37
13	$[Cp^*RhCl_2]_2$	CsOAc	Et_3N	dioxane	44
14	$[Cp^*IrCl_2]_2$	CsOAc	Et_3N	PhCl	9
15	$Cp^*Co(CO)I_2$	CsOAc	Et_3N	PhCl	0
16	$[RuCl_2(p\text{-cymene})]_2$	CsOAc	Et_3N	PhCl	0
17	$Pd(OAc)_2$	CsOAc	Et_3N	PhCl	0
18		CsOAc	Et_3N	PhCl	0
19	$[Cp^*RhCl_2]_2$		Et_3N	PhCl	0
20[c]	$[Cp^*RhCl_2]_2$	CsOAc	Et_3N	PhCl	58
21[d]	$[Cp^*RhCl_2]_2$	CsOAc	Et_3N	PhCl	53
22[e]	**$[Cp^*RhCl_2]_2$**	**CsOAc**	**Et_3N**	**PhCl**	**72**

[a]Reactions were run with **1a** (0.4 mmol), **2a** (1.2 mmol), catalyst (0.02 mmol), additive (0.8 mmol), base (1.2 mmol), solvent (10 mL), 140 °C, 22 h. [b]Isolated yield. [c]$[Cp^*RhCl_2]_2$ (0.01 mmol). [d]120 °C. [e]**2a** (0.8 mmol), 10 h.

not been reported. As part of our interest in the Rh(III)-catalyzed oxidative annulations,[17] we herein report a tunable oxidative (spiro)annulation of 2-arylindoles with benzoquinone, leading to two different types of indole-containing fused or spirocyclic products (Scheme 1). Interestingly, benzoquinone acted as either an efficient C2 synthon or a C1 synthon in this Rh(III)-catalyzed oxidative annulation reaction with 2-substituted or 2,3-disubstituted indoles as the substrates.

Initially, a mixture of 2-phenyl-1*H*-indole **1a** (0.4 mmol) and benzoquinone **2a** (1.2 mmol) in PhCl was treated with $[Cp^*RhCl_2]_2$ (5 mol %) and $Cu(OAc)_2$ (0.8 mmol) at 140 °C for 22 h. It was observed that the desired Rh(III)-catalyzed oxidative annulation reaction with **2a** proceeded smoothly to provide 9*H*-dibenzo[*a*,*c*]carbazol-3-ol (**3a**) in 30% yield (Table 1, entry 1). To improve the efficiency, AgOAc, NaOAc, or CsOAc was tried as an additive (entries 2−4). Among them, CsOAc provided the best result (36%). Notably, using Et_3N (3.0 equiv) as the coadditive remarkably improved the reaction efficiency (entry 5). Next, the effect of bases, including Et_2NH, DIPA, Na_2CO_3, K_2CO_3, and K_3PO_4, on this reaction was investigated; it turned out that all of them were less effective than Et_3N (entry 5 vs 6−10). In addition, with the use of toluene, *o*-xylene, or 1,4-dioxane as the solvent, this reaction gave **3a** in a lower yield (entry 5 vs 11−13). Then, we also examined the effect of different catalysts on this reaction, and it was observed that $[Cp^*IrCl_2]_2$ gave **3a** in 9% yield (entry 14), whereas $[Cp^*Co(CO)I_2]$, $[RuCl_2(p\text{-cymene})]_2$, and $Pd(OAc)_2$ failed to provide **3a** (entries 15−17). Furthermore, control experimental results suggested that the formation of **3a** was not observed in the absence of $[Cp^*RhCl_2]_2$ or CsOAc (entries 18 and 19). Decreasing the loading of $[Cp^*RhCl_2]_2$ to 2.5 mol % or lowering the reaction temperature to 120 °C resulted in a lower yield of **3a** (entries 20 and 21). Finally, the treatment of **1a** with **2a** (2.0 equiv) at 140 °C for 10 h could afford **3a** in 72% yield (entry 22).

With the optimized conditions (Table 1, entry 22), we next examined the generality of this novel synthesis of 9*H*-dibenzo[*a*,*c*]carbazol-3-ols (**3**) (Scheme 2). With benzoquinone (**2a**), the substrate scope of various 2-arylindoles (**1**) was first investigated. The experimental results suggested that **1b−g** bearing different types of R substituents (including Me, MeO, F, Cl, Br, and CF_3) at the para position of the 2-phenyl ring of **1** reacted well with **2a** to give **3b−g** in 56−73% yield. In addition, different R^1 groups (such as CH_3, Cl, and Br) attached at the ortho and meta positions of the 2-phenyl ring of **1** were all tolerated with the standard conditions to provide **3h−m** in modest to good yield. To our surprise, the oxidative annulation reaction of *meta*-chloro-substituted indole (**1l**) with **2a** afforded two regioisomers (10:7), whereas with *meta*-methyl- and *meta*-bromo-substituted indoles (**1k**) and (**1m**), the reactions occurred exclusively at the less hindered position to give **3k** and **3m** in 78 and 66% yield. With 2-(naphthalen-1-yl)-1*H*-indole (**1n**), this reaction also proceeded smoothly to afford **3n** in 47% yield. When 2-(furan-2-yl)-1*H*-indole (**1o**) and 2-(thiophen-2-yl)-1*H*-indole (**1p**) were subjected to the reaction conditions, **3o** and **3p** could be obtained, albeit in lower yield. Next, the effect of different R^2 groups on this reaction was investigated, and indoles **1q−u** having either electron-rich methyl or electron-deficient fluoro, chloro, and bromo groups at different positions of the indole's phenyl ring

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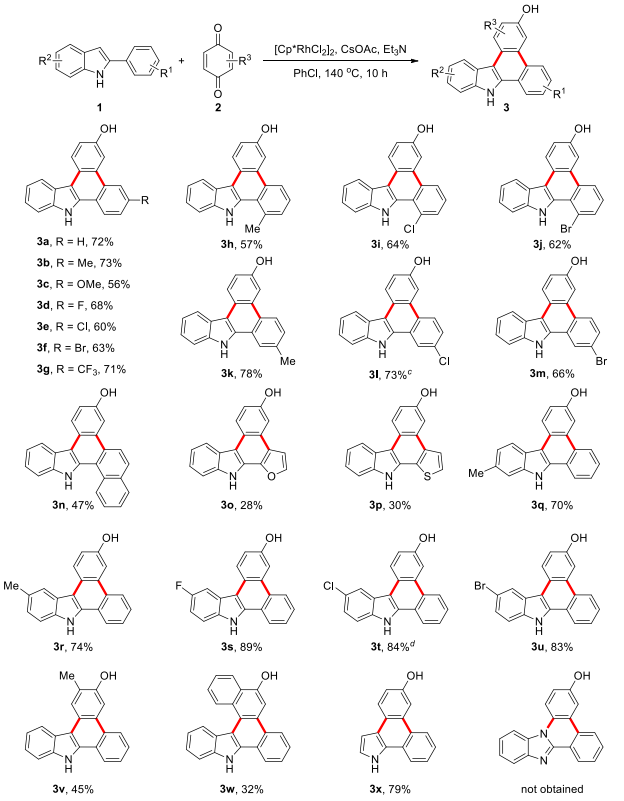
Scheme 2. Synthesis of 9*H*-Dibenzo[*a*,*c*]carbazol-3-ols (3)[a,b]

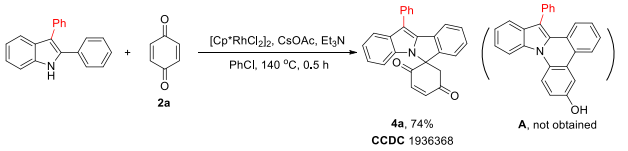


[a]Reaction conditions: **1** (0.4 mmol), **2** (0.8 mmol), $[Cp^*RhCl_2]_2$ (0.02 mmol), CsOAc (0.8 mmol), Et_3N (1.2 mmol), PhCl (10 mL), 140 °C, 10 h. [b]Isolated yields. [c]Two regioisomers (10:7) were obtained, and the major isomer is given. [d]CCDC 1936367.

were compatible with the reaction conditions to afford **3q**−**u** in 70−89% yield. It is noted that the structure of **3t** was unambiguously confirmed by X-ray single-crystal diffraction. Subsequently, the scope of benzoquinones (**2**) was studied, and we found that the reactions of 2-methylbenzoquinone (**2b**) and 1,4-naphthoquinone (**2c**) with **1a** smoothly proceeded to provide **3v** and **3w** in 45 and 32% yield. In contrast, other benzoquinones (**2**), such as 2-chlorobenzoquinone, 2-bromobenzoquinone, 2,5-dimethylbenzoquinone, methyl 3,6-dioxocyclohexa-1,4-dienecarboxylate, and 1,2-benzoquinone, could not react with **1a**. Finally, we also tried the reactions of 2-phenyl-1*H*-pyrrole and 2-phenyl-1*H*-benzo[*d*]imidazole with **2a**, and it was observed that 2-phenyl-1*H*-pyrrole worked well to afford **3x** in 79% yield, whereas 2-phenyl-1*H*-benzo[*d*]imidazole could not participate in this reaction.

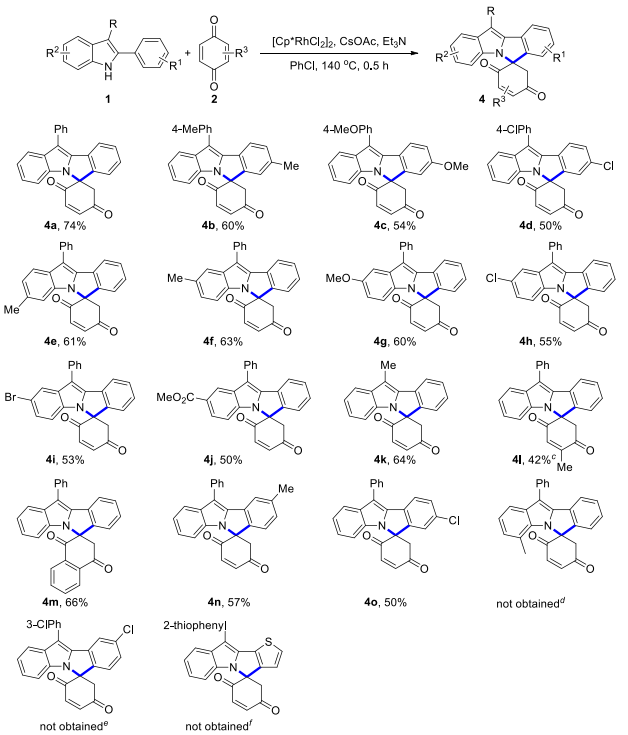
Having established an efficient route to dibenzo[*a*,*c*]carbazoles (**3**) through the Rh(III)-catalyzed oxidative annulation of **1** with **2**, we envisioned that if the C3 position of indoles is occupied by a substituent, then the annulation might switch to take place on the N-1 position of indoles, thus leading to the formation of a new N-1 annulation product, indolo[1,2-*f*]phenanthridine. To verify the hypothesis, 2,3-diphenyl-1*H*-indole was treated with benzoquinone for 0.5 h under the optimized reaction conditions for the synthesis of **3a** (Table 1, entry 22). To our surprise, the envisioned N-1 annulation leading to indolo[1,2-*f*]phenanthridine (**A**) was not observed. However, an unexpected N-spiroannulation reaction with benzoquinone as a C1 synthon smoothly proceeded to give a spiro compound 11′-phenylspiro[cyclohex[3]ene-1,6′-isoindolo[2,1-*a*]indole]-2,5-dione (**4a**) in 74% yield, whose structure was unambiguously confirmed by X-ray single-crystal diffraction (Scheme 3). Literature searching suggested that the

Scheme 3. Rh(III)-Catalyzed Oxidative Spiroannulation of 2,3-Diphenyl-1*H*-indole with 2a



newly formed indole-containing spirocyclic skeleton has not yet been reported. Therefore, the development of an efficient strategy for the preparation of the above-mentioned spiro products with potential bioactivities[18] is in high demand. Thus the scope of this novel oxidative spiroannulation was studied (Scheme 4). Various 2,3-disubstituted-1*H*-indoles (**1**) with a

Scheme 4. Synthesis of *N*-Spiro Compounds (4)[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), CsOAc (0.4 mmol), Et_3N (0.6 mmol), PhCl (4 mL), 140 °C, 0.5 h. [b]Isolated yields. [c]Two regioisomers (2.3:1) were obtained, and the major isomer is given. [d]No reaction occurred. [e]Reaction became messy. [f]Unknown product was obtained, and ^1H NMR spectra was messy.

different R^1 or R^2 group reacted with **2a** to generate **4a**−**j** in modest to good yield. Next, the effect of the R substituent on this spiroannulation was also tested. When 3-methyl-substituted indole was used instead of 3-aryl-substituted indole, this spiroannulation also proceeded smoothly to furnish **4k** in 64% yield. It is noteworthy that indoles having a Br, CHO, or CN group (R) at position 3 could not take part in this reaction. In addition, we also investigated the spiroannu-

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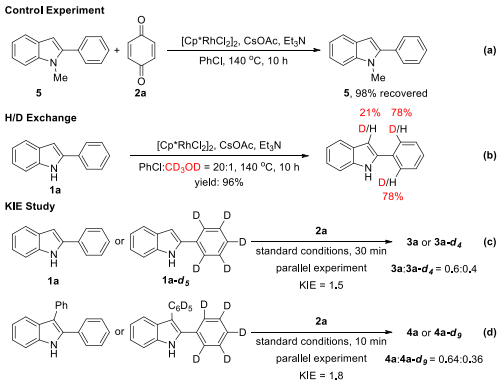
lation of different benzoquinones (**2**) with 2,3-diphenyl-1*H*-indole. With 2-methylbenzoquinone (**2b**), this spiroannulation smoothly proceeded to afford two regioisomers (2.3:1). When 1,4-naphthoquinone (**2c**) was used, **4m** was obtained in 66% yield. Indoles having different aryl groups on the C2 and C3 positions could also undergo this spiroannulation to give **4n** and **4o** in 57 and 50% yield. Finally, it turned out that 7-methyl-2,3-diphenyl-1*H*-indole, 2,3-bis(3-chlorophenyl)-1*H*-indole, and 2,3-di(thiophen-2-yl)-1*H*-indole failed to give the corresponding spiro products (**4**).

To gain some insight into the mechanisms, we performed the following control experiments (Scheme 5). First, when *N*-methyl-substituted indole (**5**) was employed, no reaction was observed, and **5** was recovered in 98% yield, indicating that the indolyl NH unit plays a key role for the aryl C−H activation (Scheme 5a). Second, a H/D exchange of indole (**1a**) was performed in the presence of CD_3OD. From this reaction, **1a** was recovered in 96% yield and H/D exchanges at the ortho position (78% D) of the 2-phenyl ring and at the indolyl C3 position (21% D) were observed by ^1H NMR analysis (Scheme 5b), implying that the C(sp^2)-H activation of the 2-phenyl unit of indole is reversible. Third, two side-by-side reactions using **1a** and **1a**-d_5 were run for 30 min, from which **3a** and **3a**-d_4 were obtained in a ratio of 0.6:0.4 by ^1H NMR analysis and a parallel kinetic isotope effect (KIE) value of 1.5 was observed (Scheme 5c). A similar KIE value (1.8) for the spiroannulation was also obtained (Scheme 5d). These results indicated that the aryl C−H cleavage process might be involved in the turnover-limiting step.

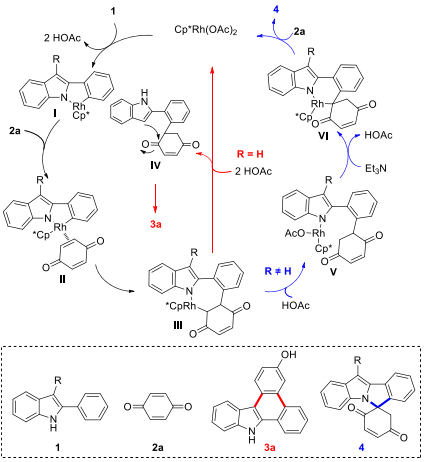
On the basis of the above results and the literature precedent,[16] possible reaction mechanisms are proposed (Scheme 6). First, a Rh(III)-catalyzed dual N−H/C−H bond cleavage of indole (**1**) occurs to afford a rhodacycle **I**. Then, the coordination of benzoquinone (**2a**) to **I** yields **II**, which undergoes a migratory insertion of the coordinated benzoquinone into the Rh−C bond to furnish **III**. With 3-unsubstituted indole (R = H), the protonolysis of **III** with two equivalents of HOAc generates **IV** and regenerates the Rh(III) catalyst. Finally, **IV** undergoes a selective C3 nucleophilic addition, dehydration, and aromatization cascade to provide **3a**. On the contrary, with 2,3-disubstituted indole (R ≠ H), it is proposed that **III** undergoes a selective Rh−C protonolysis with one equivalent of HOAc to afford the key intermediate **V**. Subsequently, with the promotion of Et_3N, a nucleophilic attack of the tertiary α-C atom on the Rh center generates **VI**, which undergoes a C−N reductive elimination to give **4** and a Rh(I) species. The Rh(I) species is oxidized to the active Rh(III) catalyst by benzoquinone in the presence of HOAc.[16a]

To demonstrate the synthetic applications, the further transformations of **3a** and **4a** were carried out (Scheme 7).

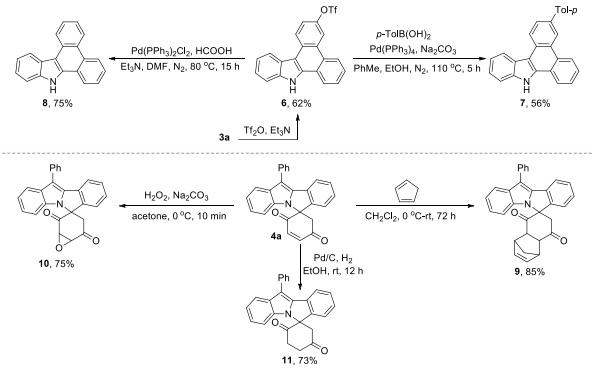
Scheme 5. Mechanistic Studies



Scheme 6. Possible Reaction Mechanisms



Scheme 7. Transformations of Products 3a and 4a



The treatment of **3a** with Tf_2O afforded triflate **6** in 62% yield. Palladium-catalyzed cross-coupling of **6** with boronic acid could afford the 3-(*p*-tolyl)-9*H*-dibenzo[*a*,*c*]carbazole **7**. Moreover, the TfO group of **6** could be removed in the presence of $Pd(PPh_3)_2Cl_2$ and HCOOH to furnish the 9*H*-dibenzo[*a*,*c*]carbazole **8**. On the contrary, the Diels−Alder cycloaddition of **4a** with cyclopentadiene was run, from which the bridged cycle **9** was obtained in 85% yield. Next, with the use of hydrogen peroxide as the oxidant, **4a** could be converted to the epoxide **10**. Finally, the Pd(0)-catalyzed hydrogenation of **4a** with hydrogen could afford **11** in 73% yield.

In summary, we have developed an efficient and practical procedure for the selective preparation of 9*H*-dibenzo[*a*,*c*]-carbazol-3-ols and indole-containing spirocyclic compounds through a Rh(III)-catalyzed substrate-dependent oxidative annulation or spiroannulation reaction of 2-arylindoles with benzoquinone as either a C2 or C1 synthon. In addition, a possible catalytic cycle is also proposed. Further application of benzoquinone to construct fused and spirocyclic skeletons is in progress.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02336.

Experimental procedure, mechanistic studies, X-ray crystal structures of **3t** and **4a**, characterization, and spectral data (PDF)

Accession Codes

CCDC 1936367−1936368 contain 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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