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Article

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Regioselective Synthesis of 2-Alkenylindoles and 2-Alkenylindole-3-carboxylates through the Cascade Reactions of *N*-Nitrosoanilines with Propargyl Alcohols

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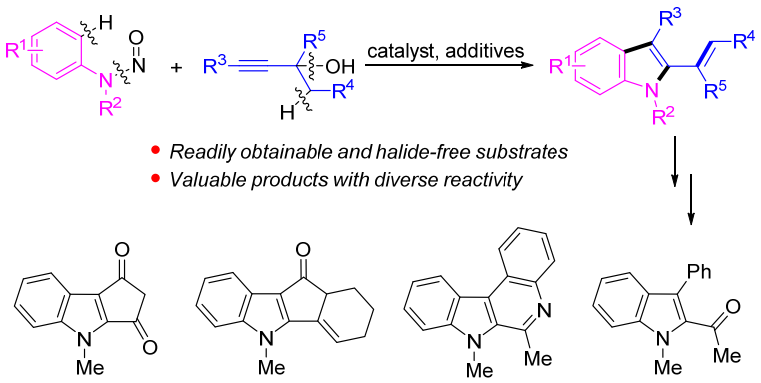


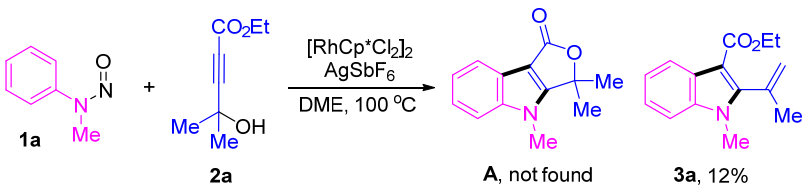
Abstract: In this paper, a novel and efficient synthesis of 2-alkenylindoles and 2-alkenylindole-3-carboxylates *via* the cascade reactions of *N*-nitrosoanilines with propargyl alcohols is presented. Mechanistically, the formation of the title compounds is trigged by a Rh(III)-catalyzed C(sp^2)–H alkenylation of *N*-nitrosoaniline with propargyl alcohol followed by the simultaneous intramolecular amination/cyclization, NO extrusion and dehydration. With this method, a variety of diversely substituted 2-alkenylindole derivatives were prepared in good efficiency and exclusive site-selectivity. To the best of our knowledge, this is the first example in which the indoyl and the alkenyl units are formed sequentially in one pot from halide-free substrates through a redox neutral C–H bond activation. In addition, the utility of the 2-alkenylindole products thus obtained was remarkably showcased by their facile transformations into the synthetically and biologically significant compounds such as 2-acylindole, benzocarbazole, indoloquinoline, pyridoindolone, cyclopentaindolone and indenoindolone.

INTRODUCTION

In recent years, direct functionalizations of the inert aromatic C(sp^2)−H bonds catalyzed by transition-metal (TM) catalysts have attracted much attention due to their excellent step-economy and atom-efficiency.[1] Meanwhile, it is noted that in order to realize the desired inert C−H bond activations (CHAs), a directing group (DG) is usually needed to enhance the reactivity and to control the regioselectivity *via* its interaction with the TM catalyst. In many cases, however, the DG is left behind in the product as an undesired moiety, and additional transformations have to be carried out to remove it. To address this issue, using traceless DGs allowing for themselves' simutaneuous removal or transformation is an ideal and attractive strategy. In this aspect, the easily obtainable *N*-nitrosoanilines[2-3] are attracting intensive interests owing to the following reasons. First, the nitroso group has a high affinity to interact with metals,[4] and thus can be used as a powerful DG in metal-catalyzed CHA reactions.[5] Second, the *N*-nitroso moiety can also act as an internal oxidant through the cleavage of the oxidizing N−N bond, and this unique feature often results in significant increases in substrate reactivity, substantial reduction of waste formation, and facile release of the NO moiety during the corresponding CHA processes. Inspired by those pioneering studies and as a continuation of our recent interests in the development of novel and efficient synthesis of heterocyclic compounds *via* CHA reactions,[6] we have studied the reaction of *N*-nitrosoaniline with 4-hydroxy-2-alkynoate[7] with the aim to develop a novel synthetic route toward the naturally occurring and biologically valuable indole fused furan(on)e derivative (Scheme 1).[8] Herein, we report our detailed results obtained in this aspect.

RESULTS AND DISCUSSION

Our study was initated by treating *N*-methyl-*N*-nitrosoaniline (**1a**) with ethyl 4-hydroxy-4-methyl-pent-2-ynoate (**2a**) in the presence of $[RhCp^*Cl_2]_2$ and $AgSbF_6$ in DME at 100 °C under nitrogen for 10 h. From this reaction, to our surprise, the desired 3,3,4-trimethyl-3,4-dihydro-1*H*-furo[3,4-*b*]indol-1-one (**A**) was not found.[7] On the other hand, ethyl 1-methyl-2-(prop-1-en-2-yl)-1*H*-indole-3-carboxylate (**3a**) was isolated in 12% yield (Scheme 1).



Scheme 1. Formation of **3a** from the Reaction of **1a** with **2a**

Although the expected **A** was not obtained from this reaction, we soon realized that the formation of **3a** is also highly rewarding. First, 2-alkenylindole derivatives not only possess potent biological activities as representatively shown by Fluvastatin as a cholesterol lowering drug and hepatitis C virus replication inhibitor (Figure 1),[9-10] but also serve as versatile intermediates in the synthesis of indole-related fine chemicals.[11-15] While a number of methods for the preparation of 2-alkenylindoles such as coupling of 2-iodoindoles with tributyl(vinyl)stannane,[16] Pd-catalyzed reactions of 2-(2,2-dibromovinyl) anilines with acrylates,[17] Pd-catalyzed heteroannulation of 2-(2-propynyl)tosylanilide with alkene,[18] Pd-catalyzed cascade reactions of 2-haloanilines with enol ether of enones[19] or propargyl alcohols,[20] rearrangement of 2-(2-aminobenzyl)furans,[21] metal-catalyzed addition of indole C2−H bond to alkynes,[22] C−H alkenylation of indoles,[23] and cascade reactions of acetanilide with enyne[24] have been developed so far, some of these literature methods still suffer from tedious pre-activation of starting materials, production of halide byproducts, poor regioselectivity and low atom-economy. As a result, there is still an urgent demand for the development of more sustainable, regioselective and robust methods for the preparation of 2-alkenylindoles. Second, the indole-3-carboxylate scaffold is highly valuable in medicinal chemistry as exemplified by a number of marketed drugs such as Arbidol (used as an inhibitor of virus entry and membrane fusion), Dolasetron (used in the treatment of nausea, vomiting, and acute gastroenteritis), Tropisetron (used as an analgesic in fibromyalgia) (Figure 1).[9-10,25] Therefore, the formation of **3a** as an indole derivative containing both the 2-alkenyl and the 3-carboxylate units from the reaction of the easily obtainable **1a** with **2a** deserves a systematic study with the prospect to be developed as a new synthetic protocol for the synthesis of 2-alkenylindole-3-carboxylate derivatives.

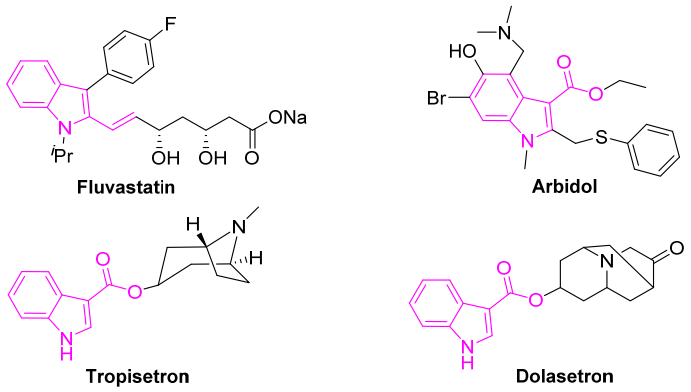
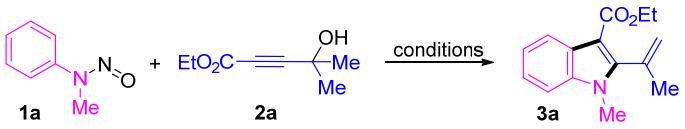


Figure 1. Some Biologically Significant 2-Alkenylindole and Indole-3-carboxylate Derivatives

Thus, various conditions were screened to improve the reaction efficiency. First, solvents including DME, DCE, CH_3CN, dioxane, DMSO, toluene and acetone were screened. Among them, DCE was found to be the most efficient (Table 1, entries 1-7). Next, the effect of AgOAc, HOAc, $Cu(OAc)_2$, KF or CsOAc as additive was explored, and they were found to be less effective than $AgSbF_6$ (entries 8-12). In further screening, we found that a combination of $AgSbF_6$ with $Cu(OAc)_2$ as the additive was beneficial for this reaction, and the yield of **3a** increased to 46% in the presence of 0.2 equiv of $AgSbF_6$ and 1 equiv of $Cu(OAc)_2$ (entries 13-17). Next, $Pd(OAc)_2$, $[CoCp^*COI_2]_2$ or $RhCp^*(OAc)_2$ was tried to replace $[RhCp^*Cl_2]_2$ as the catalyst. It turned out while $RhCp^*(OAc)_2$ could give **3a** in a similar yield as that with $[RhCp^*Cl_2]_2$ (entry 20), $Pd(OAc)_2$ and $[CoCp^*COI_2]_2$ were ineffective (entries 18 and 19). Futher study showed that higher reaction temperature resulted in reduced yield (entry 21). Finally, control experiments indicated that either the catalyst or the additive was indispensible for the formation of **3a** (entries 22 and 23).

Table 1. Optimization Studies for the Formation of **3a**[a]



Entry	Catalyst	Additives	Solvent	Yield (%)[b]
1	$[RhCp^*Cl_2]_2$	$AgSbF_6$(1)	DME	12
2	$[RhCp^*Cl_2]_2$	1	DCE	18

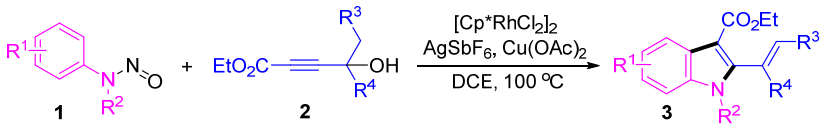
3	$[RhCp^*Cl_2]_2$	1	MeCN	<5
4	$[RhCp^*Cl_2]_2$	1	dioxane	<5
5	$[RhCp^*Cl_2]_2$	1	DMSO	<5
6	$[RhCp^*Cl_2]_2$	1	toluene	6
7	$[RhCp^*Cl_2]_2$	1	acetone	8
8	$[RhCp^*Cl_2]_2$	AgOAc(2)	DCE	6
9	$[RhCp^*Cl_2]_2$	HOAc(3)	DCE	<5
10	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$(4)	DCE	7
11	$[RhCp^*Cl_2]_2$	KF	DCE	<5
12	$[RhCp^*Cl_2]_2$	CsOAc	DCE	<5
13	$[RhCp^*Cl_2]_2$	1+2	DCE	15
14	$[RhCp^*Cl_2]_2$	1+3	DCE	14
15	$[RhCp^*Cl_2]_2$	1+4	DCE	21
16	$[RhCp^*Cl_2]_2$	1+4[c]	DCE	35
17	**$[RhCp^*Cl_2]_2$**	**1+4[d]**	**DCE**	**46**
18	$Pd(OAc)_2$	1+4[d]	DCE	-
19	$[CoCp^*COI_2]_2$	1+4[d]	DCE	-
20	$RhCp^*(OAc)_2$	1+4[d]	DCE	44
21	$[RhCp^*Cl_2]_2$	1+4[d]	DCE	40[e]
22	-	1+4[d]	DCE	-
23	$RhCp^*(OAc)_2$	-	DCE	-

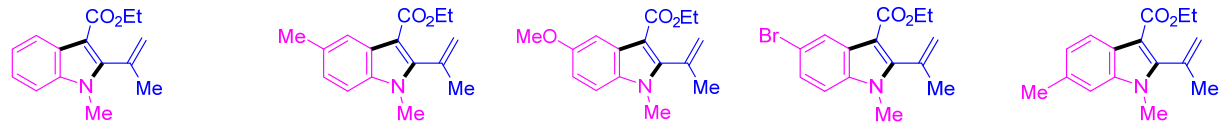
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (0.025 mmol), additive (0.1 mmol), solvent (5 mL), N_2, 100 °C, 12 h. [b] Isolated yields. [c] 0.25 mmol. [d] 0.5 mmol. [e] 120 °C

With the optimum reaction conditions established, the substrate scope for this 2-alkenylindole-3-carboxylates forming reaction was investigated. First, a number of diversely substituted *N*-methyl-*N*-nitrosoanilines **1** were screened by using **2a** as a model substrate (Table 2). Notably, the electronic nature of the phenyl unit in **1** did not show an obvious effect as indicated in the formation of **3c** and **3d**. Interestingly, *meta*-methyl-*N*-nitrosoaniline gave **3e** in a regioselective manner. Furthermore, **1** with either an alkyl or an aryl group other than a methyl unit attached on the amino unit reacted with **2a** readily to give **3f-3i**. Next, the suitability of a range of **2** was studied. It was observed that ethyl 4-hydroxy-4,5,5-trimethylhex-2-ynoate (**2b**), ethyl 4-benzyl-4-hydroxy-5-phenylpent-2-ynoate (**2c**), ethyl 4-hydroxy-4-phenylpent-2-ynoate (**2d**) reacted with **1a** smoothly to give **3j-3l**. Interestingly,

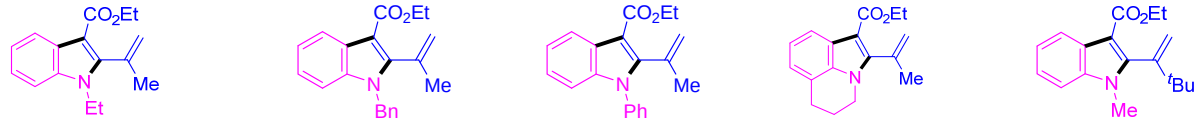
3-(1-hydroxycyclopentyl)propiolate (**2e**) and 3-(1-hydroxycyclohexyl)propiolate (**2f**) were also viable substrates, affording 2-cycloalkenylindole-3-carboxylates **3m** and **3n** in moderate yields.

Table 2. Substrate Scope for the Synthesis of **3**[a,b]

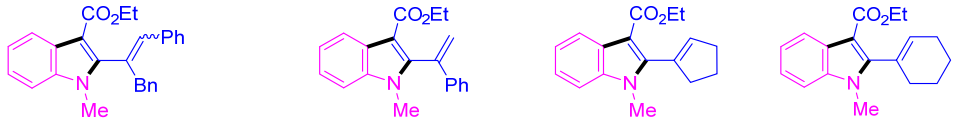




3a, 46% **3b**, 42% **3c**, 44% **3d**, 40% **3e**, 38%



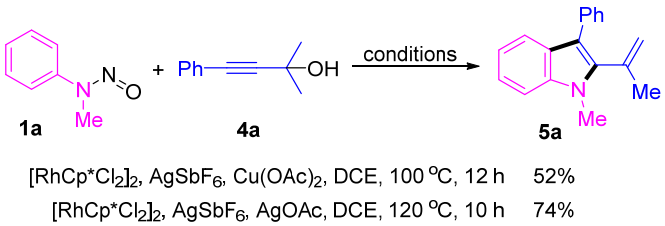
3f, 32% **3g**, 34% **3h**, 35% **3i**, 35% **3j**, 20%



3k, 44% **3l**, 47% **3m**, 45% **3n**, 46%

[a] Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), $[RhCp^*Cl_2]_2$ (0.025 mmol), $AgSbF_6$ (0.1 mmol), $Cu(OAc)_2$ (0.5 mmol), DCE (5 mL), 100 °C, N_2, 12 h. [b] Isolated yields.

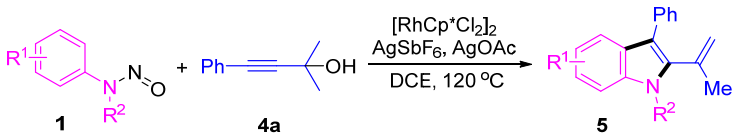
So far, a novel synthesis of 2-alkenylindole-3-carboxylates **3** have been successfully established. Bearing in mind the importance of general 2-alkenylindole derivatives as described above,[9-15] we continued our study by exploring the suitability of general propargyl alcohols in place of 4-hydroxy-2-alkynoates as substrates for this cascade reaction. Thus, **1a** was let to react with 2-methyl-4-phenylbut-3-yn-2-ol (**4a**) under the optimum conditions as described above. To our delight, from this reaction, the desired 2-alkenylindole derivative **5a** was obtained in 52% yield. More promisingly, further efforts in optimizing the reaction conditions in terms of different additives and reaction temperatures showed that **5a** could be obtained in a yield of 74% when the reaction of **1a** with **4a** was run under the catalysis of $[RhCp^*Cl_2]_2$ and assisted by a combination of $AgSbF_6$ (0.2 equiv) with AgOAc (0.5 equiv) as the additive at 120 °C for 10 h (Scheme 2).[26]

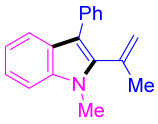


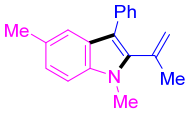
Scheme 2. Formation of **5a** via the Reaction of **1a** with **4a**

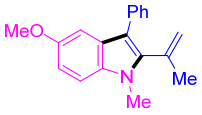
Next, the substrate scope for this 2-alkenylindole forming reaction was investigated. First, a number of diversely substituted **1** were screened by using **4a** as a model substrate. Promisingly, all of them took part in this reaction smoothly to give the corresponding products **5a-5p** in moderate to good yields. Notably, various substituents such as methyl, methoxy, fluoro, chloro, bromo, cyano and trifluoromethyl attached on the phenyl ring of **1** were compatible with the reaction conditions, enabling facile incorporation of functional groups onto the indole skeleton and making further structural elaborations possible (Table 3). It is also important to stress that **1** bearing either an electron-donating group (EDG) or an electron-withdrawing group (EWG) on the *para*-position of the phenyl ring afforded the corresponding products in almost equally good yields (**5b**, **5c** vs **5g**, **5h**). Furthermore, this reaction showed an excellent regioselectivity in that *meta*-methyl, fluoro or bromo substituted *N*-nitrosoanilines underwent this cascade reaction at the less sterically encumbered site to give **5i**, **5j**, or **5k** as the sole product. In addition, its meticulous sensitivity to steric hindrance was also demonstrated by the observation that substrates bearing an *ortho*-substituent showed remarkably reduced efficiency (**5l-5n**). Notably, this reaction was also compatible with disubstituted *N*-nitrosoanilines to give **5o** and **5p**. Second, **1** with either an ethyl, benzyl or phenyl group unit attached on the amino moiety were reacted with **4a** to give **5q-5u** in slightly decreased yields compared with those of their *N*-methyl counterparts, presumably due to the increased steric hindrance. Interestingly, fused tricyclic indole framework, which is widely present in naturally occurring products,[27] could be easily constructed using this method as shown in the formation of **5v**.

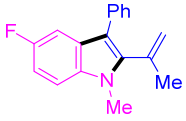
Table 3. Substrate Scope for the Synthesis of **5** (I) [a,b]

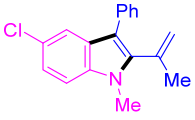


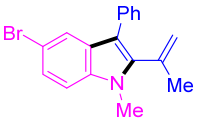

5a, 74%

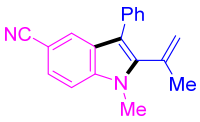

5b, 75%

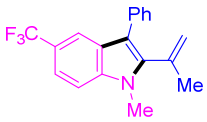

5c, 68%

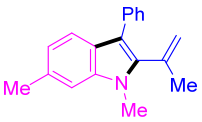

5d, 74 %

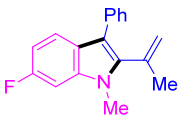

5e, 67%

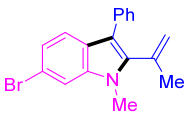

5f, 72%

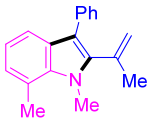

5g, 67%

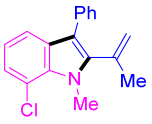

5h, 70%

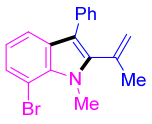

5i, 55%

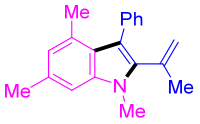

5j, 75%

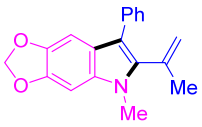

5k, 76%

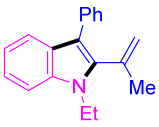

5l, 28%

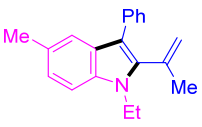

5m, 17%

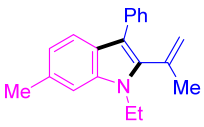

5n, 25%

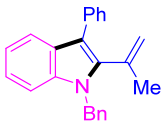

5o, 60%

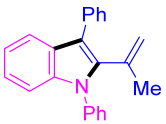

5p, 55%

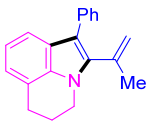

5q, 50%


5r, 52%


5s, 49%


5t, 47%


5u, 54%

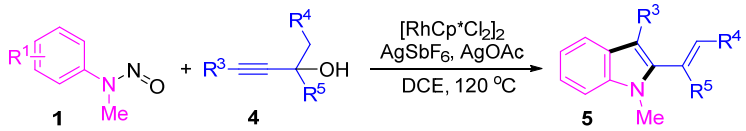

5v, 44%

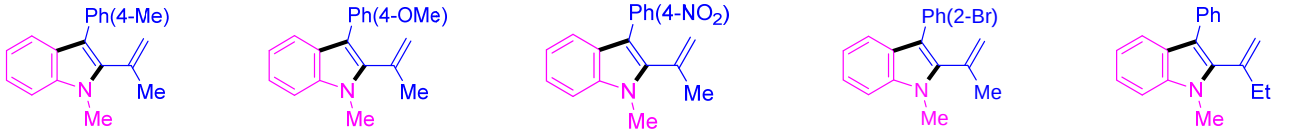
[a] Reaction conditions: **1** (0.5 mmol), **4a** (1.0 mmol), $[RhCp^*Cl_2]_2$ (0.025 mmol), $AgSbF_6$ (0.1 mmol), AgOAc (0.25 mmol), DCE (5 mL), 120 °C, N_2, 10 h. [b] Isolated yields.

Next, the suitability of different propargyl alcohols **4** was tested (Table 4). First, **4** with a 4-methyl, 4-methoxyl, 4-nitro or 2-bromo unit attached on the 4-phenyl ring reacted with **1** smoothly to give **5w**-**5z** in good yields, showing that the electronic nature and the position of the substituents did not have an obvious effect on the efficiency. When 3-methyl-1-phenylpent-1-yn-3-ol was used, a mixture of two isomers **5aa** and **5bb** were obtained in yields of 45% and 20%, respectively. Next, from the reaction of 3,4,4-trimethyl-1-phenylpent-1-yn-3-ol, **5cc** was isolated in a lower yield of 39%. Interestingly, 1-(phenylethynyl)cyclopentan-1-ol and 1-(phenylethynyl)cyclohexan-1-ol could also take part in this reaction to give 2-cycloalkenylindoles **5dd**-**5hh** in yields ranging from 59%-76%. Finally, we found that

2-methyloct-3-yn-2-ol as an alkyl unit substituted propargyl alcohol substrate could also take part in this reaction to give **5ii**, **5jj** and **5kk** in reasonably good yields.

Table 4. Substrate Scope for the Synthesis of **5** (II) [a,b]





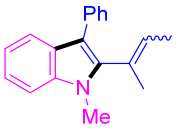
5w, 71%

5x, 65%

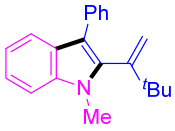
5y, 60%

5z, 70%

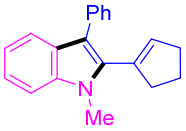
5aa, 45%



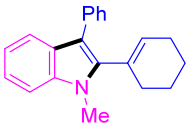
5bb, 20%



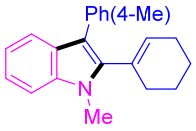
5cc, 39%



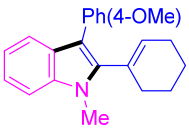
5dd, 59%



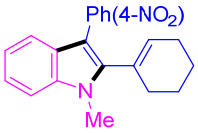
5ee, 61%



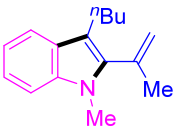
5ff, 60%



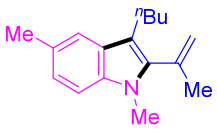
5gg, 76%



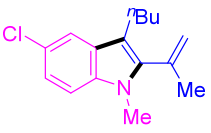
5hh, 72%



5ii, 65%



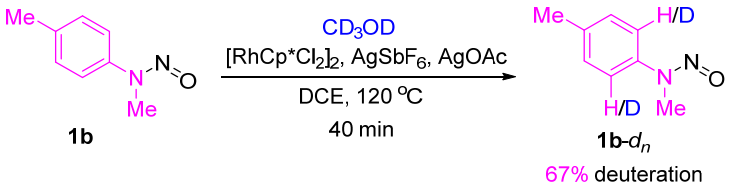
5jj, 69%



5kk, 58%

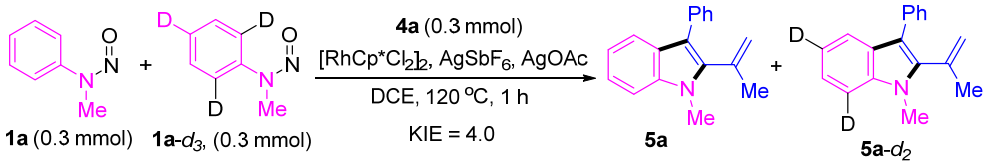
[a] Reaction conditions: **1a** (0.5 mmol), **4** (1.0 mmol), $[RhCp^*Cl_2]_2$ (0.025 mmol), $AgSbF_6$ (0.1 mmol), AgOAc (0.25 mmol), DCE (5 mL), 120 °C, N_2, 10 h. [b] Isolated yields.

To gain some insight into the mechanism of this cascade reaction, several experiments were performed. First, **1b** was treated with CD_3OD under standard reaction conditions as shown in Table 3 for 40 min in the absence of **2**. This led to a significant level of deuterium incorporation (67%) at the *ortho*-position of **1b** (Scheme 3). This result indicates that the Rh(III)-catalyzed *ortho*-C−H bond cleavage of substrate **1b** is reversible.



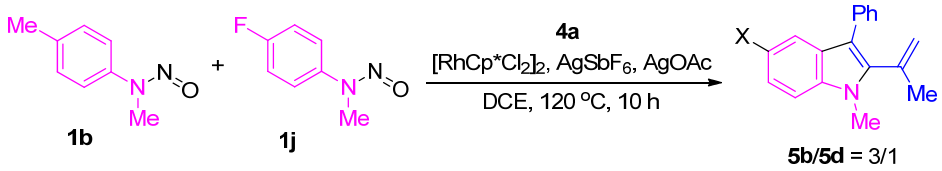
Scheme 3. Reversibility of C−H Bond Activation

Second, the intermolecular kinetic isotopic effect was measured on the basis of competition reactions between **1a** with **4a** and **1a**-d_3 with **4a** at a low degree of conversion. From this study, a kinetic isotope effect value of 4.0 was observed (Scheme 4). This result suggests that the C−H bond cleavage should have been involved in the rate-limiting step.



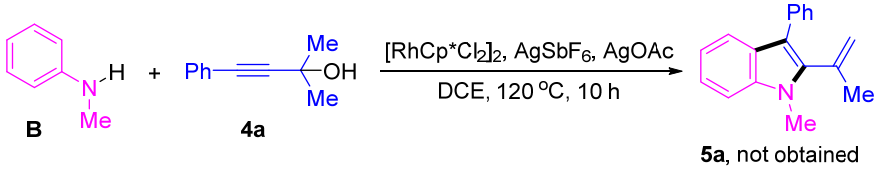
Scheme 4. Intermolecular Kinetic Isotope Effect Study

Third, competition experiments were performed by using *N*-nitrosoanilines bearing EDG and EWG on the phenyl rings (Scheme 5). It was thus found that *p*-methyl substrate (**1b**) reacted with **4a** three times faster than its *p*-F analogue (**1j**). This result suggests that an electrophilic aromatic substitution mechanism might also be involved in this cascade reaction with the Ar−Rh interaction, rather than the acidity of an *ortho*-C−H bond, as the predominant factor dictating the efficiency of the CHA step.



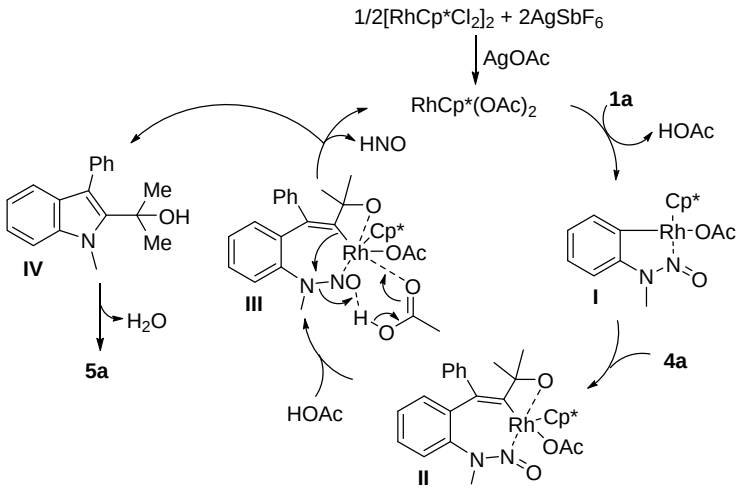
Scheme 5. Competition Study of Substrates with Different Electronic Characteristics

Fourth, *N*-methylaniline (**B**) was treated with **4a** under the optimized reaction conditions used for the preparation of **5a** as shown in Table 3. From this reaction, however, the formation of **5a** was not observed. Meanwhile, **B** remained intact under the reaction conditions (Scheme 6). This result indicates that the presence of a *N*-nitroso unit is indispensable for the Rh(III)-catalyzed CHA reaction as shown above.



Scheme 6. A Control Experiment

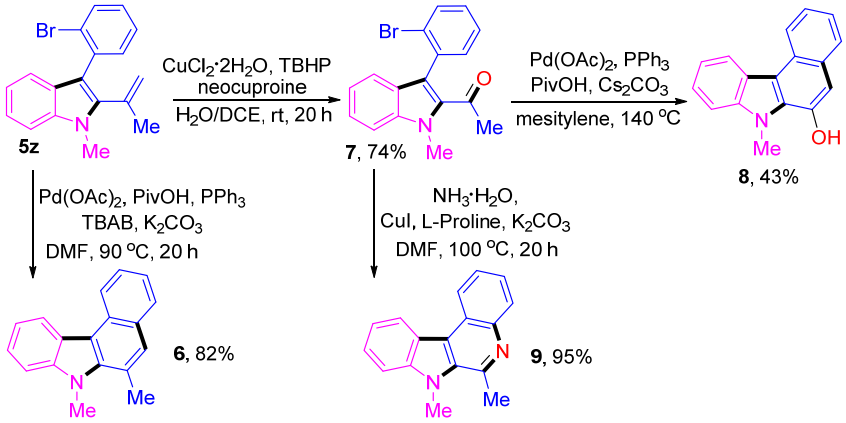
On the basis of our experimental results and literature precedents,[5,20] a plausible mechanism is proposed for the formation of **5a** (Scheme 7). The reaction is likely initiated by the generation of an active cationic Rh(III) species through an anion exchange, which then coordinates to **1a** and undergoes a C−H bond cleavage to furnish the five-membered metallacyclic intermediate **I**. Complexation of **I** with **4a** and the following regioselective insertion of the alkyne triple bond into the C−Rh bond provides a seven-membered rhodacycle **II**. During this process, it is believed that the hydroxyl group in **4a** may provide a binding affinity to Rh(III), which guides the regioselective migratory insertion. Next, an intramolecular substitution occurs with **II** under the assistance of HOAc (as shown by **III**) to form the C−N bond and break the N−N bond to give **IV** along with release of the active catalyst [Cp*Rh(OAc)$_2$]. Next, the in situ formed **IV** undergoes a dehydration to afford the final product **5a**.



Scheme 7. Plausible Mechanism for the Formation of **5a**

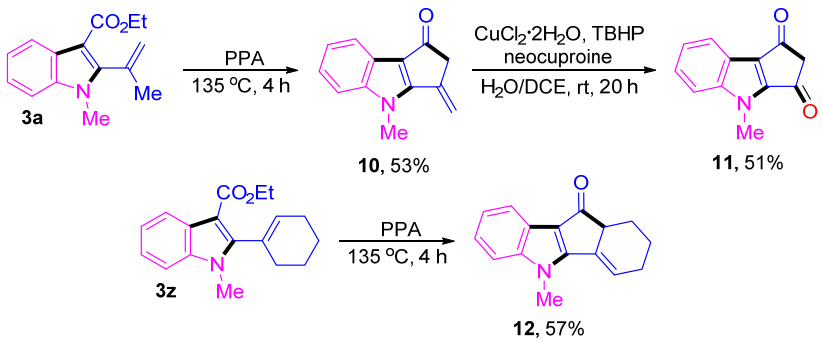
To showcase the versatile usability of the 2-alkenylindole products obtained above, the following transformations were carried out. First, **5z** was found to undergo a Heck type coupling under the promotion of Pd(II) to give benzocarbazole **6** in a yield of 82%.[28] In another example, **5z** readily underwent an alkene oxidative cleavage upon treating with suitable oxidants to afford 2-acyl-3-aryl indole **7** in a yield of 74%. Moreover, **7** could take part in an intramolecular coupling to afford

hydroxylated benzocarbozole **8** under the catalysis of $Pd(OAc)_2$. On the other hand, when **7** was treated with ammonium hydroxide in the presence of CuI and *L*-proline, a benzocarboline derivative **9** was obtained in an excellent yield of 95% (Scheme 8).[29]



Scheme 8. Structural Elaboration of **5z**

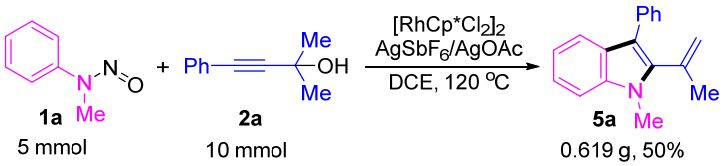
As a further aspect, **3a** was treated with PPA at 135 °C for 4 h. From this reaction, a cyclopenta[*b*]indolone derivative **10** was obtained in a yield of 53%.[30] Through similar procedure, indenoindolone **12**, containing a highly interesting tetracyclic framework, could be prepared from **3z** in yield of 57%.[30] In addition, **10** could readily undergo an alkene oxidative cleavage to give 4-methylcyclopenta[*b*]indole-1,3(2*H*,4*H*)-dione (**11**) with high potential for further structural derivations (Scheme 9).



Scheme 9. Structural Elaboration of **3a** and **3z**

Finally, to additionally demonstrate the power of this newly developed method, the preparation of **5a** was carried out in an enlarged scale of 5 mmol. It turned out that the corresponding reaction proceeded

smoothly to afford **5a** in a yield of 50% (Scheme 10).



Scheme 10. Large Scale Synthesis of **5a**

In summary, we have developed a novel synthesis of 2-alkenylindoles and 2-alkenylindole-3-carboxylates through the cascade reactions of *N*-nitrosoanilines with propargyl alcohols *via* redox-neutral C−H activation, annulation and dehydration. Compared with literature methods, this new protocol has advantages such as simple operational procedure, easily accessible and halide-free substrates, high regio- and chemoselectivity. With all these merits, this new method is expected to find wide applications in related areas.

EXPERIMENTAL SECTION

I. General experimental information

Commercial reagents were used without further purification. *N*-Nitrosoanilines (**1**),[5a] 4-hydroxy-2-alkynoates (**2**),[7a] propargyl alcohols (**4**)[20] except for 4-(2-bromophenyl)-2-methylbut-3-yn-2-ol,[31] and $[RhCp^*Cl_2]_2$[32] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet), br s (broad singlet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. Typical procedure for the synthesis of 3a and spectroscopic data of 3a-3n

To a 15 mL reaction tube equipped with a stir bar were added *N*-methyl-*N*-nitrosobenzamide (**1a**, 68.1 mg, 0.5 mmol), DCE (5 mL), $[RhCp^*Cl_2]_2$ (15.4 mg, 0.025 mmol), $AgSbF_6$ (34.3 mg, 0.1 mmol), $Cu(OAc)_2$ (90.8 mg, 0.5 mmol) and ethyl 4-hydroxy-4-methylpent-2-ynoate (**2a**, 156.2 mg, 1.0 mmol) with stirring. The mixture was stirred under N_2 at 100 °C for 12 h. Then, it was cooled to room temperature. The resulting mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (20:1) as eluent to afford **3a** (56.0 mg, 46%). **3b-3n** were obtained in a similar manner.

Ethyl 1-methyl-2-(prop-1-en-2-yl)-1*H*-indole-3-carboxylate (3a)

Yellow solid (56.0 mg, 46%), mp 86-88 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 7.2 Hz, 3H), 2.16 (s, 3H), 3.69 (s, 3H), 4.37 (q, *J* = 7.2 Hz, 2H), 5.09 (s, 1H), 5.58 (s, 1H), 7.25-7.28 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 6.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.5, 23.3, 30.1, 59.5, 103.9, 109.7, 119.3, 121.8, 121.9, 122.5, 126.5, 136.5, 137.2, 148.5, 165.1. HRMS calcd for $C_{15}H_{17}NO_2Na$: 266.1151 $[M+Na]^+$, found: 266.1151.

Ethyl 1,5-dimethyl-2-(prop-1-en-2-yl)-1*H*-indole-3-carboxylate (3b)

Yellow solid (54.0 mg, 42%), mp 54-55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.40 (t, *J* = 7.2 Hz, 3H), 2.15 (s, 3H), 2.50 (s, 3H), 3.65 (s, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 5.07 (s, 1H), 5.56 (t, *J* = 1.6 Hz, 1H), 7.08-7.12 (m, 2H), 8.03 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.5, 21.8, 23.4, 30.0, 59.4, 103.7, 109.7, 119.2, 121.4, 123.6, 124.3, 132.4, 136.9, 137.3, 148.0, 165.2. HRMS calcd for $C_{16}H_{19}NO_2Na$: 280.1308 $[M+Na]^+$, found: 280.1304.

Ethyl 5-methoxy-1-methyl-2-(prop-1-en-2-yl)-1*H*-indole-3-carboxylate (3c)

Yellow solid (60.0 mg, 44%), mp 97-99 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.40 (t, *J* = 6.6 Hz, 3H),

2.15 (s, 3H), 3.66 (s, 3H), 3.89 (s, 3H), 4.34-4.37 (m, 2H), 5.07 (s, 1H), 5.56 (s, 1H), 6.91 (d, J = 9.0 Hz, 1H), 7.21 (d, J = 9.0 Hz, 1H), 7.70 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.4, 23.4, 30.2, 55.8, 59.4, 103.48, 103.55, 110.5, 112.6, 119.2, 127.4, 131.6, 137.3, 148.5, 155.9, 165.2. HRMS calcd for $C_{16}H_{19}NO_3Na$: 296.1257 $[M+Na]^+$, found: 296.1258.

Ethyl 5-bromo-1-methyl-2-(prop-1-en-2-yl)-1*H*-indole-3-carboxylate (3d)

Yellow solid (65.2 mg, 40%), mp 65-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.41 (t, J = 6.8 Hz, 3H), 2.15 (s, 3H), 3.67 (s, 3H), 4.36 (q, J = 7.2 Hz, 2H), 5.09 (s, 1H), 5.59 (t, J = 1.6 Hz, 1H), 7.17 (d, J = 8.8 Hz, 1H), 7.34 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 8.30 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.4, 23.2, 30.3, 59.7, 103.6, 111.2, 115.5, 119.7, 124.4, 125.4, 128.1, 135.2, 136.7, 149.2, 164.6. HRMS calcd for $C_{15}H_{17}BrNO_2$: 322.0437 $[M+H]^+$, found: 322.0435.

Ethyl 1,6-dimethyl-2-(prop-1-en-2-yl)-1*H*-indole-3-carboxylate (3e)

Yellow solid (49 mg, 38%), mp 82-84 °C. ^{1}H NMR (400 Hz, $CDCl_3$) δ: 1.41 (t, J = 7.2 Hz, 3H), 2.15 (s, 3H), 2.49 (s, 3H), 3.66 (s, 3H), 4.36 (q, J = 7.6 Hz, 2H), 5.07 (s, 1H), 5.56 (t, J = 1.6, 1H), 7.09 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.5, 21.7, 23.4, 30.1, 59.4, 103.3, 109.4, 119.1, 121.4, 124.0, 126.7, 131.4, 134.9, 137.3, 148.4, 165.2. HRMS calcd for $C_{16}H_{19}NO_2Na$: 280.1308 $[M+Na]^+$, found: 280.1300.

Ethyl 1-ethyl-2-(prop-1-en-2-yl)-1*H*-indole-3-carboxylate (3f)

Yellow liquid (41.1mg, 32%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.42 (t, J = 7.2 Hz, 3H), 1.48 (t, J = 7.2 Hz, 3H), 2.25 (s, 3H), 4.22 (q, J = 7.2 Hz, 2H), 4.44 (t, J = 7.2 Hz, 2H), 5.17 (s, 1H), 5.62 (t, J = 1.2 Hz, 1H), 7.30-7.33 (m, 2H), 7.38-7.40 (m, 1H), 8.26-8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.5, 15.7, 23.6, 38.6, 59.5, 103.7, 110.0, 119.0, 121.8, 121.9, 122.4, 126.7, 135.3, 137.4, 148.1, 165.1. HRMS calcd for $C_{16}H_{19}NO_2Na$: 280.1308 $[M+Na]^+$, found: 280.1303.

Ethyl 1-benzyl-2-(prop-1-en-2-yl)-1*H*-indole-3-carboxylate (3g)

Yellow solid (54.2 mg, 34%), mp 83-84 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.48 (t, *J* = 7.2 Hz, 3H), 2.11 (s, 3H), 4.44 (t, *J* = 7.2 Hz, 2H), 5.11 (s, 1H), 5.42 (s, 2H), 5.54 (s, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 7.22-7.23 (m, 2H), 7.27-7.31 (m, 4H), 8.27 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.5, 23.5, 47.2, 59.6, 104.5, 110.7, 119.4, 121.9, 122.1, 122.8, 126.0, 126.7, 127.5, 128.8, 136.2, 137.18, 137.20, 148.6, 165.1. HRMS calcd for $C_{21}H_{21}NO_2Na$: 342.1465 $[M+Na]^+$, found: 342.1466.

Ethyl 1-phenyl-2-(prop-1-en-2-yl)-1*H*-indole-3-carboxylate (3h)

Yellow solid (53.3 mg, 35%), mp 122-123 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.36 (t, *J* = 7.2 Hz, 3H), 1.92 (s, 3H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.91 (s, 1H), 5.25 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.19-7.24 (m, 3H), 7.39-7.44 (m, 3H), 8.15 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.5, 23.5, 59.7, 105.3, 110.9, 120.9, 121.7, 122.3, 123.0, 126.3, 128.3, 128.5, 129.3, 136.3, 137.1, 137.7, 148.3, 165.2. HRMS calcd for $C_{20}H_{19}NO_2Na$: 328.1308 $[M+Na]^+$, found: 328.1310.

Ethyl 2-(prop-1-en-2-yl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-1-carboxylate (3i)

Yellow solid (47.1 mg, 35%), mp 77-79 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.34 (t, *J* = 7.2 Hz, 3H), 2.10 (s, 3H), 2.11-2.14 (m, 2H), 2.91 (t, *J* = 6.6 Hz, 2H), 3.97 (t, *J* = 5.4 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 5.01 (s, 1H), 5.47 (s, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.5, 22.8, 23.1, 24.8, 42.6, 59.4, 103.7, 118.8, 119.2, 119.7, 122.0, 122.2, 124.9, 133.6, 136.8, 146.8, 165.4. HRMS calcd for $C_{17}H_{19}NO_2Na$: 292.1308 $[M+Na]^+$, found: 292.1315.

Ethyl 2-(3,3-dimethylbut-1-en-2-yl)-1-methyl-1*H*-indole-3-carboxylate (3j)

Yellow liquid (28.5 mg, 20%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.19 (s, 9H), 1.40 (t, *J* = 7.2 Hz, 3H), 3.67 (s, 3H), 4.30-4.38 (m, 2H), 5.17 (s, 1H), 5.71 (s, 1H), 7.26-7.29 (m, 2H), 7.33-7.34 (m, 1H), 8.19-8.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.5, 30.5, 31.0, 37.5, 59.3, 105.3, 109.7, 117.9, 121.9, 122.4, 126.6, 136.5, 147.5, 149.7, 165.3. HRMS calcd for $C_{18}H_{23}NO_2Na$: 308.1621 $[M+Na]^+$, found: 308.1619.

Ethyl 2-(1,3-diphenylprop-1-en-2-yl)-1-methyl-1*H*-indole-3-carboxylate (3k)

Yellow liquid (87.0 mg, 44%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.46 (t, *J* = 7.2 Hz, 3H), 2.81 (s, 3H), 3.93-3.99 (m, 2H), 4.41-4.46 (m, 2H), 6.77-6.78 (m, 2H), 6.82 (s, 1H), 7.03-7.04 (m, 3H), 7.08 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.15-7.19 (m, 3H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.6, 29.4, 46.2, 59.7, 104.6, 110.0, 121.8, 122.0, 122.4, 126.5, 126.9, 127.3, 128.0, 128.5, 129.3, 131.6, 133.1, 136.2, 136.6, 138.5, 145.7, 165.1. HRMS calcd for $C_{27}H_{25}NO_2Na$: 418.1778 $[M+Na]^+$, found: 418.1780.

Ethyl 1-methyl-2-(1-phenylvinyl)-1*H*-indole-3-carboxylate (3l)

Green solid (71.7 mg, 47%), mp 89-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21 (t, *J* = 7.2 Hz, 3H), 3.59 (s, 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 5.43 (s, 1H), 6.21 (s, 1H), 7.26-7.32 (m, 7H), 7.34-7.38 (m, 1H), 8.25-8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 30.5, 59.5, 105.7, 109.8, 118.7, 122.0, 122.1, 122.8, 126.0, 126.7, 128.2, 128.6, 136.7, 138.4, 139.8, 146.0, 165.0. HRMS calcd for $C_{20}H_{19}NO_2Na$: 328.1308 $[M+Na]^+$, found: 328.1310.

Ethyl 2-(cyclopent-1-en-1-yl)-1-methyl-1*H*-indole-3-carboxylate (3m)

Yellow liquid (60.6 mg, 45%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.40 (t, *J* = 7.2 Hz, 3H), 2.09-2.14 (m, 2H), 2.62-2.64 (m, 2H), 2.72-2.74 (m, 2H), 3.63 (s, 3H), 4.34 (q, *J* = 7.2 Hz, 2H), 5.88 (s, 1H), 7.23-7.26 (m, 2H), 7.29-7.31 (m, 1H), 8.17-8.19 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.6, 23.9, 30.4, 33.7, 36.6, 59.4, 104.6, 109.7, 121.7, 121.8, 122.5, 126.7, 134.5, 134.8, 136.8, 144.8, 165.3. HRMS calcd for $C_{17}H_{19}NO_2Na$: 292.1308 $[M+Na]^+$, found: 292.1306.

Ethyl 2-(cyclohex-1-en-1-yl)-1-methyl-1*H*-indole-3-carboxylate (3n)

Yellow solid (65.1 mg, 46%). mp 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 7.2 Hz, 3H), 1.75-1.78 (m, 2H), 1.82-1.86 (m, 2H), 2.27 (br s, 4H), 3.67 (s, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 5.80 (t, *J* = 1.6 Hz, 1H), 7.24-7.29 (m, 2H), 7.31-7.34 (m, 1H), 8.18-8.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ:

14.6, 21.9, 22.8, 25.5, 29.1, 30.1, 59.3, 103.7, 109.7, 121.7, 121.8, 122.3, 126.7, 130.3, 130.7, 136.4, 149.4, 165.4. HRMS calcd for $C_{18}H_{21}NO_2Na$: 306.1465 $[M+Na]^+$, found: 306.1470.

2. Typical procedure for the synthesis of 5a and spectroscopic data of 5a-5kk

To a 15 mL reaction tube equipped with a stir bar were added *N*-methyl-*N*-nitrosobenzamide (**1a**, 68.1 mg, 0.5 mmol), DCE (5 mL), AgOAc (41.7 mg, 0.25 mmol), $[RhCp^*Cl_2]_2$ (15.4 mg, 0.025 mmol), $AgSbF_6$ (34.3 mg, 0.1 mmol) and 2-methyl-4-phenylbut-3-yn-2-ol (**4a**, 160.2 mg, 1.0 mmol) with stirring. The mixture was stirred under N_2 at 120 °C for 10 h. Then, it was cooled to room temperature. The resulting mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (500:1) as eluent to afford **5a** (91.5 mg, 74%). **5b-5kk** were obtained in a similar manner.

1-Methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5a) [20]

Yellow solid (91.5 mg, 74%), mp 105-107 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.86 (s, 3H), 3.65 (s, 3H), 5.08 (s, 1H), 5.45 (t, J = 1.8 Hz, 1H), 7.06 (t, J = 7.2 Hz, 1H), 7.16-7.19 (m , 2H), 7.27 (d, J = 8.4 Hz, 1H), 7.32 (t, J = 7.8 Hz, 2H), 7.47 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.8, 30.4, 109.5, 113.7, 119.5, 120.1, 121.0, 122.0. 125.8, 127.0, 128.3, 129.3, 135.6, 136.6, 137.0, 138.9. HRMS calcd for $C_{18}H_{18}N$: 248.1434 $[M+H]^+$, found: 248.1428.

1,5-Dimethyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5b)

Yellow solid (97.9 mg, 75%), mp 56-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92 (s, 3H), 2.44 (s, 3H), 3.70 (s, 3H), 5.15 (d, J = 1.2 Hz, 1H), 5.51 (t, J = 1.2 Hz, 1H), 7.08 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1 H), 7.23-7.28 (m, 2H), 7.38-7.42 (m, 2H), 7.50 (s, 1H), 7.54 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 23.8, 30.5, 109.2, 113.2, 119.0, 120.8, 123.5, 125.7, 127.1, 128.3, 129.28, 129.34, 135.4, 135.8, 136.7, 139.0. HRMS calcd for $C_{19}H_{20}N$: 262.1590 $[M+H]^+$, found: 262.1574.

5-Methoxy-1-methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5c)

Yellow solid (94.3 mg, 68%), mp 153-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.90 (s, 3H), 3.68 (d, J = 1.2 Hz, 3H), 3.81 (d, J = 2.0 Hz, 3H), 5.14 (s, 1H), 5.50 (d, J = 1.2 Hz, 1H), 6.91 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.18 (d, J = 2.4 Hz, 1H), 7.21-7.28 (m, 2H), 7.38-7.42 (m, 2H), 7.53-7.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.8, 30.6, 56.1, 101.1, 110.4, 112.2, 113.4, 120.9, 125.8, 127.2, 128.4, 129.2, 132.4, 135.8, 136.7, 139.6, 154.8. HRMS calcd for $C_{19}H_{20}NO$: 278.1539 $[M+H]^+$, found: 278.1539.

5-Fluoro-1-methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5d)

Yellow solid (98.2 mg,74%), mp 98-99 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.92 (s, 3H), 3.71 (s, 3H), 5.17 (s, 1H), 5.54 (s, 1H), 6.98 (td, J_1= 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.23-7.28 (m, 2H), 7.35-7.37 (m, 1H), 7.40 (t, J = 7.2 Hz, 2H), 7.50 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.7, 30.6, 104.3 (d, $^{2}J_{C\text{-}F}$ = 23.3 Hz), 110.13 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz), 110.15 (d, $^{2}J_{C\text{-}F}$ = 26.2 Hz), 113.8 (d, $^{4}J_{C\text{-}F}$ = 4.4 Hz), 121.2, 126.0, 127.2 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz), 128.4, 129.0, 133.6, 135.2, 136.4, 140.5, 158.5 (d, $^{1}J_{C\text{-}F}$ = 232.8 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ: -124.4. HRMS calcd for $C_{18}H_{17}FN$: 266.1340 $[M+H]^+$, found:266.1323.

5-Chloro-1-methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5e)

Yellow solid (94.4 mg, 67%), mp 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92 (s, 3H), 3.71 (s, 3H), 5.17 (s, 1H), 5.55 (t, J = 1.6 Hz, 1H), 7.18 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.24-7.30 (m, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.49-7.51 (m, 2H), 7.66 (d, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.7, 30.6, 110.5, 113.4, 118.8, 121.4, 122.1, 125.8, 126.1, 127.9, 128.5, 129.1, 134.9, 135.3, 136.2, 140.1. HRMS calcd for $C_{18}H_{17}ClN$: 282.1044 $[M+H]^+$, found: 282.1038.

5-Bromo-1-methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5f)

Yellow solid (117.4 mg, 72%), mp 105-107 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.84 (s, 3H), 3.63 (s, 3H), 5.09 (s, 1H), 5.47 (s, 1H), 7.12 (d, J = 9.0 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.24 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.33 (t, J = 7.8 Hz, 2H), 7.41 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 1.8 Hz, 1H). ^{13}C NMR (100

MHz, $CDCl_3$) δ: 23.7, 30.6, 111.1, 113.38, 113.42, 121.5, 121.9, 124.7, 126.2, 128.5, 128.6, 129.2, 134.9, 135.7, 136.2, 140.0. HRMS calcd for $C_{18}H_{17}BrN$: 326.0539 $[M+H]^+$, found: 326.0533.

1-Methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole-5-carbonitrile (5g)

Yellow solid (91.2 mg, 67%), mp 183-185 ºC. ^1H NMR (600 MHz, $CDCl_3$) δ: 1.94 (s, 3H), 3.77 (s, 3H), 5.21 (s, 1H), 5.59 (s, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.38 (d, J = 9.0 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.46-7.49 (m, 3H), 8.02 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 23.6, 30.7, 102.9, 110.3, 114.6, 120.9, 122.0, 124.8, 125.1, 126.6, 126.9, 128.6, 129.1, 134.0, 135.6, 138.4, 140.9. HRMS calcd for $C_{19}H_{16}N_2Na$: 295.1206 $[M+Na]^+$, found: 295.1207.

1-Methyl-3-phenyl-2-(prop-1-en-2-yl)-5-(trifluoromethyl)-1*H*-indole (5h)

White solid (110.4 mg, 70%), mp 88-89 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.83 (s, 3H), 3.65 (s, 3H), 5.08 (s, 1H), 5.46 (t, J = 1.6 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.30-7.38 (m, 4H), 7.41-7.44 (m, 2H), 7.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.7, 30.7, 109.8, 114.6, 117.2 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 118.6 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 121.7, 122.4 (q, $^2J_{C\text{-}F}$ = 31.2 Hz), 125.5 (q, $^1J_{C\text{-}F}$ = 269.9 Hz), 126.4, 128.6, 129.3, 134.7, 136.0, 138.2, 140.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -60.1. HRMS calcd for $C_{19}H_{17}F_3N$: 316.1308 $[M+H]^+$, found: 316.1301.

1,6-Dimethyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5i)

White solid (71.9 mg, 55%), mp 101-103 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.04 (s, 3H), 2.63 (s, 3H), 3.79 (s, 3H), 5.26 (s, 1H), 5.62 (t, J = 1.6 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.26 (s, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.66-7.68 (m, 2H), 7.73 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.9, 23.8, 30.4, 109.5, 113.4, 119.1, 120.8, 121.7, 124.7, 125.7, 128.3, 129.2, 131.8, 135.8, 136.7, 137.4, 138.3. HRMS calcd for $C_{19}H_{20}N$: 262.1590 $[M+H]^+$, found: 262.1591.

6-Fluoro-1-methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5j)

White solid (99.5 mg, 75%), mp 124-125 °C. ^1H NMR (600 MHz, $CDCl_3$) δ: 1.86 (s, 3H), 3.72 (s, 3H),

5.14 (s, 1H), 5.51 (s, 1H), 6.76-6.79 (m, 1H), 7.11-7.14 (m, 2H), 7.25-7.28 (m, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.49 (d, J = 6.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 23.7, 30.9, 105.4 (d, $^2J_{C\text{-}F}$ = 19.8 Hz), 105.6 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 112.2, 115.5 (d, $^2J_{C\text{-}F}$ = 17.6 Hz), 121.6, 122.1 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 126.2, 127.7, 130.3, 135.4, 136.1, 139.5, 139.6 (d, $^3J_{C\text{-}F}$ = 11.0 Hz), 157.0 (d, $^1J_{C\text{-}F}$ = 247.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ: -118.5. HRMS calcd for $C_{18}H_{17}FN$: 266.1340 $[M+H]^+$, found: 266.1335.

6-Bromo-1-methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5k)

Yellow solid (124.0 mg, 76%), mp 79-81 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.01 (s, 3H), 3.76 (s, 3H), 5.26 (s, 1H), 5.63 (t, J = 1.2 Hz, 1H), 7.32 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.59-7.61 (m, 3H), 7.65 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 23.7, 30.6, 112.6, 113.9, 115.4, 120.8, 121.4, 123.2, 125.9, 126.2, 128.5, 129.2, 135.1, 136.2, 137.9, 139.4. HRMS calcd for $C_{18}H_{16}BrNNa$: 348.0358 $[M+Na]^+$, found: 348.0360.

1,7-Dimethyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5l)

White solid (36.6 mg, 28%), mp 125-127 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.93 (s, 3H), 2.81 (s, 3H), 3.97 (s, 3H), 5.13 (s, 1H), 5.50 (s, 1H), 6.94 (d, J = 6.6 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.2 Hz, 2H), 7.49-7.51 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 24.1, 33.7, 114.0, 117.5, 120.1, 121.3, 121.4, 125.0, 125.8, 128.0, 128.2, 129.5, 135.7, 136.1, 136.6, 140.1. HRMS calcd for $C_{19}H_{20}N$: 262.1590 $[M+H]^+$, found: 262.1577.

7-Chloro-1-methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5m)

Yellow solid (24.0 mg, 17%), mp 96-98 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.94 (s, 3H), 4.07 (s, 3H), 5.15 (s, 1H), 5.52 (s, 1H), 6.98 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 7.2 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.47 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.9, 33.6, 114.3, 117.1, 118.2, 120.5, 122.0, 123.7, 126.2, 128.3, 129.5, 130.2, 132.5, 134.9, 136.0, 141.2. HRMS calcd for $C_{18}H_{17}ClN$: 282.1044 $[M+H]^+$, found 282.1025

7-Bromo-1-methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5n)

Yellow solid (40.8 mg, 25%), mp 124-126 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.94 (s, 3H), 4.08 (s, 3H), 5.15 (s, 1H), 5.52 (s, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.37-7.40 (m, 3H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.9, 33.8, 104.1, 114.3, 118.8, 121.0, 122.0, 126.2, 127.2, 128.3, 129.5, 130.4, 133.7, 134.8, 136.0, 141.4. HRMS calcd for $C_{18}H_{17}BrN$: 326.0539 $[M+H]^+$, found: 326.0540.

1,4,6-Trimethyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5o)

Yellow liquid (82.6 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.78 (s, 3H), 2.09 (s, 3H), 2.46 (s, 3H), 3.66 (s, 3H), 4.99 (s, 1H), 5.34 (s, 1H), 6.68 (s, 1H), 6.99 (s, 1H), 7.28-7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 21.8, 24.1, 30.6, 107.2, 114.9, 120.4, 123.2, 123.8, 126.3, 127.3, 130.8, 131.5, 131.6, 136.4, 137.1, 137.5, 139.0. HRMS calcd for $C_{20}H_{22}N$: 276.1747 $[M+H]^+$, found: 276.1736.

5-Methyl-7-phenyl-6-(prop-1-en-2-yl)-5*H*-[1,3]dioxolo[4,5-*f*]indole (5p)

Yellow solid (80.1 mg, 55%), mp 195-197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.90 (s, 3H), 3.66 (s, 3H), 5.16 (s, 1H), 5.54 (s, 1H), 5.94 (s, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 7.22-7.26 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.6, 30.9, 100.7, 101.3, 104.3, 110.6, 112.5, 121.4, 125.8, 127.7, 129.7, 135.0, 135.4, 136.5, 138.6, 140.3, 140.7. HRMS calcd for $C_{19}H_{17}NO_2Na$: 314.1151$[M+Na]^+$, found: 314.1149.

1-Ethyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5q)

Yellow liquid (65.3 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.43 (t, *J* = 7.2 Hz, 3H), 1.98 (s, 3H), 4.27 (q, *J* = 7.2 Hz, 2H), 5.26 (s, 1H), 5.58 (s, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.27-7.33 (m, 2H), 7.42-7.47 (m, 3H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.7, 24.0, 38.5, 109.7, 113.7, 119.6, 119.9, 120.8, 121.8, 125.7, 127.2, 128.3, 129.2, 135.6, 135.8, 137.0, 138.3. HRMS calcd for $C_{19}H_{20}N$: 262.1590 $[M+H]^+$, found: 262.1592.

1-Ethyl-5-methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5r)

Yellow solid (71.5 mg, 52%), mp 84-85 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.35 (t, *J* = 7.2 Hz, 3H), 1.91 (s, 3H), 2.43 (s, 3H), 4.19 (q, *J* = 7.2 Hz, 2H), 5.18 (s, 1H), 5.50 (s, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.24-7.27(m, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.50 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.7, 21.5, 24.0, 38.5, 109.4, 113.3, 119.1, 120.5, 123.3, 125.6, 127.5, 128.3, 129.3, 134.2, 135.8, 137.0, 138.5. HRMS calcd for $C_{20}H_{22}N$: 276.1747$[M+H]^+$, found: 276.1751.

1-Ethyl-6-methyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5s)

Yellow solid (67.5 mg, 49%), mp 89-90 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.29 (t, *J* = 7.2 Hz, 3H), 1.84 (s, 3H), 2.43 (s, 3H), 4.11 (q, *J* = 7.2 Hz, 2H), 5.11 (s, 1H), 5.43 (s, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 7.09 (s, 1H), 7.15-7.18 (m, 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 15.7, 21.9, 24.1, 38.3, 109.7, 113.5, 119.3, 120.6, 121.7, 125.1, 125.6, 128.2, 129.1, 131.6, 135.8, 136.2, 137.1, 137.7. HRMS calcd for $C_{20}H_{22}N$: 276.1747 $[M+H]^+$, found: 276.1746.

1-Benzyl-3-phenyl-2-(prop-1-en-2-yl)-1*H*-indole (5t)

Yellow syrup (76.0 mg, 47%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.80 (s, 3H), 5.15 (s, 1H), 5.41 (s, 2H), 5.45 (s, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.12-7.18 (m, 2H), 7.20-7.29 (m, 5H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.9, 47.3, 110.4, 114.3, 119.5, 120.3, 120.9, 122.1, 125.9, 126.1, 127.1, 127.3, 128.3, 128.7, 129.2, 135.5, 136.7, 136.8, 138.3, 138.9. HRMS calcd for $C_{24}H_{21}NNa$: 346.1566 $[M+Na]^+$, found: 346.1570.

1,3-Diphenyl-2-(prop-1-en-2-yl)-1*H*-indole (5u)

Yellow solid (83.5 mg, 54%), mp 104-106 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.71 (s, 3H), 4.98 (s, 1H), 5.22 (s, 1H), 7.16-7.19 (m, 2H), 7.23 (d, *J* = 6.0 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.39-7.44 (m, 5H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ: 23.3, 110.4, 115.9, 119.5, 120.7, 121.7, 122.6, 126.1, 127.5, 127.8, 128.3, 129.2, 129.8, 135.3, 135.8, 137.6, 138.5, 138.9. HRMS calcd for $C_{23}H_{20}N$: 310.1590 $[M+H]^+$, found: 310.1585.

1-Phenyl-2-(prop-1-en-2-yl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (5v)

Yellow solid (60.1 mg, 44%), mp 112-113 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.93 (s, 3H), 2.21-2.25 (m, 2H), 3.00 (t, J = 6.0 Hz, 2H), 4.11 (t, J = 6.0 Hz, 2H), 5.16 (q, J = 0.6 Hz, 1H), 5.47 (t, J = 1.2 Hz, 1H), 6.94 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.02-7.05 (m, 1H), 7.22-7.25 (m, 1H), 7.37-7.40 (m, 2H), 7.55 (d, J = 8.4 Hz, 1H), 7.57-7.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.1, 23.4, 25.2, 42.9, 113.4, 116.9, 119.0, 119.9, 120.2, 122.0, 124.9, 125.6, 128.3, 129.1, 134.1, 136.1, 136.5, 137.3. HRMS calcd for $C_{20}H_{20}N$: 274.1590 $[M+H]^+$, found: 274.1591.

1-Methyl-2-(prop-1-en-2-yl)-3-(*p*-tolyl)-1*H*-indole (5w)

Yellow solid (92.6 mg, 71%), mp 114-116 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.93 (s, 3H), 2.39 (s, 3H), 3.71 (s, 3H), 5.15 (s, 1H), 5.51 (s, 1H), 7.11-7.14 (m, 1H), 7.20-7.25 (m, 3H), 7.33 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 23.9, 30.5, 109.5, 113.6, 119.5, 120.0, 120.9, 121.9, 127.0, 129.1, 129.2, 132.6, 135.3, 136.7, 136.9, 138.7. HRMS calcd for $C_{19}H_{20}N$: 262.1590 $[M+H]^+$, found: 262.1583.

3-(4-Methoxyphenyl)-1-methyl-2-(prop-1-en-2-yl)-1*H*-indole (5x)

Yellow solid (90.1 mg, 65%), mp 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92 (s, 3H), 3.71 (s, 3H), 3.83 (s, 3H), 5.15 (s, 1H), 5.51 (s, 1H), 6.95 (d, J = 8.8 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.8, 30.4, 55.3, 109.5, 113.4, 113.8, 119.4, 119.9, 120.8, 121.9, 127.2, 128.0, 130.3, 136.7, 136.9, 138.6, 157.9. HRMS calcd for $C_{19}H_{20}NO$: 278.1539 $[M+H]^+$, found: 278.1539.

1-Methyl-3-(4-nitrophenyl)-2-(prop-1-en-2-yl)-1*H*-indole (5y)

Red solid (87.7 mg, 60%), mp 119-121 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.98 (s, 3H), 3.75 (s, 3H),

5.21 (s, 1H), 5.61 (s, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.70-7.74 (m, 3H), 8.23 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.8, 30.5, 110.0, 111.5, 119.0, 121.0, 122.3, 122.6, 123.9, 126.1, 129.0, 136.0, 137.2, 140.6, 143.2, 145.4. HRMS calcd for $C_{18}H_{16}N_2O_2Na$: 315.1104 $[M+Na]^+$, found: 315.1101.

3-(2-Bromophenyl)-1-methyl-2-(prop-1-en-2-yl)-1*H*-indole (5z)

Yellow solid (114.2 mg, 70%), mp 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.82 (s, 3H), 3.66 (s, 3H), 4.98 (s, 1H), 5.28 (t, *J* = 1.6 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 7.07-7.11 (m, 1H), 7.13-7.17 (m, 1H), 7.19-7.26 (m, 4H), 7.59 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.4, 30.9, 109.5, 114.0, 119.8, 120.1, 120.5, 121.9, 125.7, 127.0, 127.3, 128.5, 132.7, 133.3, 135.9, 136.8, 136.9, 139.7. HRMS calcd for $C_{18}H_{16}BrNNa$: 348.0358 $[M+Na]^+$, found: 348.0356.

2-(But-1-en-2-yl)-1-methyl-3-phenyl-1*H*-indole (5aa)

Yellow solid (58.8 mg, 45%), mp 68-69 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.92 (t, *J* = 7.2 Hz, 3H), 2.17 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 5.22 (s, 1H), 5.56 (d, *J* = 1.2 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.24-7.26 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.4, 30.1, 30.4, 109.5, 113.7, 118.9, 119.4, 120.0, 121.8, 125.8, 127.0, 128.3, 129.2, 135.7, 137.0, 138.6, 142.7. HRMS calcd for $C_{19}H_{20}N$: 262.1590 $[M+H]^+$, found: 262.1584.

2-(But-2-en-2-yl)-1-methyl-3-phenyl-1*H*-indole (5bb)

Yellow solid (26.1 mg, 20%), mp 76-78 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.79 (d, *J* = 6.6 Hz, 3H), 1.86 (s, 3H), 3.68 (s, 3H), 5.66-5.69 (m, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.22-7.25 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.36-7.39 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 17.6, 30.4, 109.4, 113.1, 119.3, 119.9, 121.6, 125.4, 126.9, 127.2, 128.2, 129.2, 130.7, 136.0, 136.7, 141.2. HRMS calcd for $C_{19}H_{20}N$: 262.1590 $[M+H]^+$, found: 262.1588.

2-(3,3-Dimethylbut-1-en-2-yl)-1-methyl-3-phenyl-1*H*-indole (5cc)

Yellow liquid (56.4 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.79 (s, 9H), 3.60 (s, 3H), 5.29 (s, 1H), 5.73 (s, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.15-7.21 (m, 2H), 7.28-7.31 (m, 3H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.7, 30.7, 38.1, 109.4, 114.1, 119.3, 119.8, 120.3, 121.6, 125.7, 127.0, 128.1, 130.0, 136.4, 136.5, 138.0, 149.9. HRMS calcd for $C_{21}H_{23}NNa$: 312.1723 $[M+Na]^+$, found: 312.1713.

2-(Cyclopent-1-en-1-yl)-1-methyl-3-phenyl-1*H*-indole (5dd)

Yellow liquid (80.6 mg, 59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.94 (t, *J* = 7.2 Hz, 2H), 2.43 (br s, 2H), 2.53 (br s, 2H), 3.72 (s, 3H), 5.90 (s, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.22-7.26 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.0, 30.7, 33.5, 36.3, 109.4, 114.7, 119.3, 119.9, 121.9, 125.7, 127.1, 128.2, 129.4, 134.6, 134.7, 134.9, 135.9, 137.2. HRMS calcd for $C_{20}H_{20}N$: 274.1590 $[M+H]^+$, found: 274.1574.

2-(Cyclohex-1-en-1-yl)-1-methyl-3-phenyl-1*H*-indole (5ee)

Yellow solid (87.6 mg, 61%), mp 88-89 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.58-1.60 (m, 4H), 2.00-2.01 (m, 2H), 2.12-2.13 (m, 2H), 3.61 (s, 3H), 5.79-5.81 (m, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H).. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.0, 23.0, 25.8, 29.7, 30.3, 109.4, 113.2, 119.3, 119.9, 121.6, 125.5, 126.9, 128.2, 129.1, 129.9, 133.0, 136.0, 136.8, 140.1. HRMS calcd for $C_{21}H_{22}N$: 288.1747 $[M+H]^+$, found: 288.1747.

2-(Cyclohex-1-en-1-yl)-1-methyl-3-(*p*-tolyl)-1*H*-indole (5ff)

Yellow solid (90.4 mg, 60%), mp 107-109 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.68 (br s, 4H), 2.09 (br s, 2H), 2.21 (br s, 2H), 2.38 (s, 3H), 3.68 (s, 3H), 5.88 (s, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.19-7.24 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ: 21.3, 22.0, 23.0, 25.8, 29.6, 30.3, 109.4, 113.0, 119.4, 119.8, 121.5, 126.9, 128.9, 129.0, 129.9, 132.8, 132.9, 134.9, 136.7, 139.8. HRMS calcd for $C_{22}H_{24}N$: 302.1903 $[M+H]^+$, found: 302.1921.

2-(Cyclohex-1-en-1-yl)-3-(4-methoxyphenyl)-1-methyl-1*H*-indole (5gg)

Yellow solid (120.6 mg, 76%), mp 110-111 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.66-1.68 (m, 4H), 2.07-2.08 (m, 2H), 2.21-2.22 (m, 2H), 3.68 (s, 3H), 3.85 (s, 3H), 5.87 (s, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.21-7.24 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.0, 22.9, 25.7, 29.6, 30.3, 55.3, 109.4, 112.7, 113.7, 119.3, 119.7, 121.5, 126.9, 128.4, 129.9, 130.0, 132.8, 136.7, 139.6, 157.6. HRMS calcd for $C_{22}H_{23}NONa$: 340.1672 $[M+Na]^+$, found: 340.1673.

2-(Cyclohex-1-en-1-yl)-1-methyl-3-(4-nitrophenyl)-1*H*-indole (5hh)[33]

Red solid (119.2 mg, 72%), mp 128-129 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.67-1.71 (m, 4H), 2.06-2.07 (m, 2H), 2.21 (br s, 2H), 3.67 (s, 3H), 5.87-5.88 (m, 1H), 7.16-7.18 (m, 1H), 7.24-7.27 (m, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.9, 22.9, 25.8, 29.7, 30.5, 110.0, 111.3, 118.9, 120.9, 122.4, 123.8, 126.2, 128.7, 129.4, 134.2, 137.1, 141.9, 143.7, 145.1. HRMS calcd for $C_{21}H_{20}N_2O_2Na$: 355.1417 $[M+Na]^+$, found: 355.1421.

3-Butyl-1-methyl-2-(prop-1-en-2-yl)-1*H*-indole (5ii)

Yellow liquid (73.8 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, *J* = 7.6 Hz, 3H), 1.35-1.42 (m, 2H), 1.57-1.65 (m, 2H), 2.06-2.07 (m, 3H), 2.69-2.73 (m, 2H), 3.61(s, 1H), 5.07-5.08 (m, 1H), 5.48-5.49 (m, 1H), 7.06-7.10 (m, 1H), 7.16-7.20 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.56-7.58 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.1, 23.0, 24.2, 24.6, 30.4, 33.7, 109.1, 112.3, 118.8, 119.1, 119.9, 121.3, 127.9, 136.5, 137.0, 139.2. HRMS calcd for $C_{16}H_{22}N$: 228.1747 $[M+H]^+$, found: 228.1747.

3-Butyl-1,6-dimethyl-2-(prop-1-en-2-yl)-1*H*-indole (5jj)

Yellow liquid (83.3 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.93 (t, J = 7.2 Hz, 3H), 1.35-1.40 (m, 2H), 1.56-1.62 (m, 2H), 2.05-2.05 (m, 3H), 2.45 (s, 3H), 2.67 (t, J = 8.0 Hz, 2H), 3.58 (s, 3H), 5.05-5.06 (m, 1H), 5.46-5.47 (m, 1H), 7.00 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.1, 21.6, 23.0, 24.2, 24.6, 30.4, 33.7, 108.8, 111.8, 118.8, 119.7, 122.8, 127.9, 128.0, 135.5, 136.6, 139.3. HRMS calcd for $C_{17}H_{24}N$: 242.1903 $[M+H]^+$, found: 242.1901.

3-Butyl-6-chloro-1-methyl-2-(prop-1-en-2-yl)-1*H*-indole (5kk)

Yellow liquid (75.7 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, J = 7.6 Hz, 3H), 1.33-1.41 (m, 2H), 1.53-1.61 (m, 2H), 2.06 (s, 3H), 2.65 (t, J = 8.0 Hz, 2H), 3.59 (s, 3H), 5.08-5.09 (m, 1H), 5.50-5.51 (m, 1H), 7.09-7.15 (m, 2H), 7.51 (d, J = 1.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.1, 22.9, 24.0, 24.4, 30.5, 33.6, 110.1, 112.0, 118.5, 120.3, 121.4, 124.5, 128.9, 135.3, 136.1, 140.6. HRMS calcd for $C_{16}H_{21}ClN$: 262.1357 $[M+H]^+$, found: 262.1363.

3. Large scale synthesis of 5a

To a reaction tube equipped with a stir bar were added *N*-methyl-*N*-nitrosobenzamide (**1a**, 680.8 mg, 5 mmol), 2-methyl-4-phenylbut-3-yn-2-ol (**4a**, 160.2 mg, 10 mmol), DCE (30 mL), AgOAc (417.3 mg, 2.5 mmol), $[RhCp^*Cl_2]_2$ (154.5 mg, 0.25 mmol) and $AgSbF_6$ (343.6 mg, 1.0 mmol) with stirring. The mixture was stirred under N_2 at 120 °C for 10 h. Then, it was cooled to room temperature. The resulting mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (500:1) as eluent to afford **5a** (619.0 mg, 50%).

III. Mechanistic studies

1. Study on the reversibility of C−H bond activation

To a reaction tube equipped with a stir bar were added **1b** (60.1 mg, 0.4 mmol), DCE (4 mL), CD_3OD (0.2 mL, 2.4 mmol), $[RhCp^*Cl_2]_2$ (12.4 mg, 0.02 mmol), $AgSbF_6$ (27.5 mg, 0.08 mmol) and AgOAc

(33.4 mg, 0.2 mmol) with stirring. The mixture was stirred under N_2 at 120 °C for 40 min. Then, it was cooled to room temperature. The resulting mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (30/1) as eluent to give a mixture of **1b** and **1b**-d_n. The mixture was analyzed using ^{1}H NMR spectrometer. The deuterated percentage was calculated as 67%.

2. Intermolecular kinetic isotope effect study

To a reaction tube equipped with a stir bar were added **1a** (40.8 mg, 0.3 mmol), **1a**-d_3[34] (41.8 mg, 0.3 mmol), DCE (3 mL), **4a** (48.1 mg, 0.3 mmol), $[RhCp^*Cl_2]_2$ (9.3 mg, 0.015 mmol), $AgSbF_6$ (20.6 mg, 0.06 mmol) and AgOAc (25.0 mg, 0.15 mmol) with stirring. The mixture was stirred under N_2 at 120 °C for 1 h. Then, it was cooled to room temperature. The resulting mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (500:1) as eluent to afford a mixture of **5a** and **5a**-d_2. Upon analyzing the ^{1}H NMR spectrum of the mixture, the ratio of **5a** to **5a**-d_2 was determined as about 0.8:0.2. Accordingly, the intermolecular KIE (k_H/k_D) was calculated as 4.0.

3. Competition study of substrates with different electronic characteristics

To a reaction tube equipped with a stir bar were added **1b** (45.1 mg, 0.3 mmol), **1j** (46.2 mg, 0.3 mmol), DCE (5 mL), $[RhCp^*Cl_2]_2$ (9.3 mg, 0.015 mmol), $AgSbF_6$ (20.6 mg, 0.06 mmol), AgOAc (24.3 mg, 0.15 mmol) and **4a** (48.1 mg, 0.3 mmol) with stirring. The mixture was stirred under N_2 at 120 °C for 10 h. Then, it was cooled to room temperature. The resulting mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (500/1) as eluent to give a mixture of **5b** and **5d**. The mixture was analyzed using ^{1}H NMR spectrometer, and the ratio of the amount of **5b** to **5d** was calculated as about 3:1.

4. A control experiment

To a 15 mL reaction tube equipped with a stir bar were added **B** (53.5 mg, 0.5 mmol), DCE (5 mL), AgOAc (41.7 mg, 0.25 mmol), $[RhCp^*Cl_2]_2$ (15.4 mg, 0.025 mmol), $AgSbF_6$ (34.3 mg, 0.1 mmol) and 2-methyl-4- phenylbut-3-yn-2-ol (**4a**, 160.2 mg, 1.0 mmol) with stirring. The mixture was stirred under N_2 at 120 °C for 10 h. Then, it was cooled to room temperature. The resulting mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (20:1) as eluent to recover **B** (48.2 mg, 90%). Meanwhile, **5a** was not obtained.

IV. Structural elaborations

1. Structural elaboration of 5z

1.1. Procedure for the synthesis of 6[35]

To a reaction tube equipped with a stir bar were added **5z** (162.6 mg, 0.5 mmol), DMF (5 mL), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PivOH (51.0 mg, 0.5 mmol), PPh_3 (13.1 mg, 0.05 mmol), TBAB (161.2 mg, 0.5 mmol) and K_2CO_3 (69.1 mg, 0.5 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 90 °C for 20 h. Upon completion, the resulting mixture was diluted with ethyl acetate (20 mL), and washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (100:1) to give prodcut **6**.

6,7-Dimethyl-7*H*-benzo[*c*]carbazole (6)[20]

White solid (100 mg, 82%), 149-151 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.88 (s, 3H), 3.84 (s, 3H), 7.43-7.52 (m, 2H), 7.53-7.55 (m, 2H), 7.57-7.61 (m, 1H), 7.81 (t, J = 7.6 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.64 (d, J = 7.6 Hz, 1H), 8.90 (d, J = 8.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.8, 29.0, 109.1,

111.3, 113.5, 119.7, 121.7, 122.6, 123.6, 123.7, 125.4, 126.6, 128.3, 130.3, 133.5, 138.3, 139.7. HRMS calcd for $C_{18}H_{16}N$: 246.1277 $[M+H]^+$, found: 246.1278.

1.2. Procedure for the synthesis of 7 [36]

To a reaction tube equipped with a stir bar were added $CuCl_2 \cdot 2H_2O$ (0.01 mmol, dissolved in 0.1 mL of H_2O) and neocuproine (2.1 mg, 0.01 mmol). Then, H_2O (0.7 mL), DCE (0.7 mL), **5z** (65 mg, 0.2 mmol) and *tert*-butyl hydroperoxide (200 μL, 1.55 mmol) were added. The resulting mixture was stirred at room temperature for 20 h. Afterwards, it was extracted with DCM (3×10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (50:1) as the eluent to give **7**.

1-(3-(2-Bromophenyl)-1-methyl-1*H*-indol-2-yl)ethan-1-one (7)

Yellow solid (48.6 mg, 74%), 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.14 (s, 3H), 4.12 (s, 3H), 7.14-7.18 (m, 1H), 7.30-7.36 (m, 2H), 7.40-7.48 (m, 4H), 7.79 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.4, 32.7, 110.4, 120.9, 121.8, 124.0, 125.3, 126.1, 126.5, 127.6, 129.7, 132.5, 132.9, 133.1, 136.5, 138.5, 193.0. HRMS calcd for $C_{17}H_{14}BrNNaO$: 350.0151 $[M+Na]^+$, found: 350.0149.

1.3. Procedure for the synthesis of 8 [37]

To a reaction tube equipped with a stir bar were added **7** (130.9 mg, 0.4 mmol), mesitylene (4 mL), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), PPh_3 (20.9 mg, 0.08 mmol), PivOH (12.3 mg, 0.12 mmol) and $CsCO_3$ (260.7 mg, 0.8 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 140 °C for 16 h. Upon completion, the resulting mixture was diluted with ethyl acetate (20 mL), and washed with water (5 mL) and brine (5 mL). The organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to give **8**.

7-Methyl-7*H*-benzo[*c*]carbazol-6-ol (8)

Yellow liquid (42.5 mg, 43%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.16 (s, 3H), 5.10 (s, 1H), 6.86 (s, 1H), 7.33-7.38 (m, 2H), 7.45-7.47 (m, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.68 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 32.2, 108.5, 109.4, 117.6, 119.9, 122.1, 123.0, 123.3, 123.5, 124.4, 124.5, 126.2, 127.0, 129.57, 129.61, 140.6, 143.2. HRMS calcd for $C_{17}H_{14}NO$: 248.1070 $[M+H]^+$, found: 248.1072.

1.4. Procedure for the synthesis of 9[38]

To a reaction tube equipped with a stir bar were added **7** (163.6 mg, 0.5 mmol), DMF (5 mL), $NH_3 \cdot H_2O$ (0.5 mL), CuI (9.5 mg, 0.2 mmol), L-proline (11.5 mg, 0.1 mmol) and K_2CO_3 (69.1 mg, 0.5 mmol) with stirring. The tube was then sealed, and the mixture was stirred at 100 °C for 20 h. Upon completion, the resulting mixture was diluted with ethyl acetate (20 mL), and washed with water (5 mL) and brine (5 mL). The organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane/ methanol (100:1) to give **9**.

6,7-Dimethyl-7*H*-indolo[2,3-*c*]quinoline (9)

Yellow solid (116.8 mg, 95%), 156-158 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.07 (s, 3H), 4.04 (s, 3H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.47-7.51 (m, 1H), 7.52-7.56 (m, 2H), 8.07 (d, *J* = 7.8 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.52 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 25.3, 32.5, 110.0, 120.4, 121.2, 121.8, 122.8, 123.1, 124.1, 12.6, 126.3, 126.5, 129.2, 133.0, 140.9, 142.2, 145.7. HRMS calcd for $C_{17}H_{15}N_2$: 247.1230 $[M+H]^+$, found: 247.1230.

2. Structural elaboration of 3a

2.1. Procedure for the synthesis of 10

To a reaction tube equipped with a stir bar were added **3a** (73.0 mg, 0.3 mmol) and polyphosphoric

acid (PPA, 16.9 mg, 0.05 mmol) with stirring. The tube was then sealed, and the mixture was stirred at 135 °C for 4 h. Upon completion, the resulting mixture was diluted with saturated $KHCO_3$ solution (5 mL), and extracted with ethyl acetate (10 mL×3). The combined organic layers were washed with water (5 mL) and brine (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as the eluent to give **10**.

4-Methyl-3-methylene-3,4-dihydrocyclopenta[*b*]indol-1(2*H*)-one (10)

Yellow solid (31.4 mg, 53%), 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.53 (s, 2H), 3.95 (s, 3H), 5.35 (s, 1H), 5.69 (s, 1H), 7.28-7.32 (m, 1H), 7.35-7.39 (m, 2H), 7.99 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.4, 47.6, 108.7, 110.1, 120.7, 121.7, 122.6, 123.1, 124.9, 134.0, 144.1, 158.5, 192.0. HRMS calcd for $C_{13}H_{11}NONa$: 220.0733 $[M+Na]^+$, found: 220.0742.

2.2. Procedure for the synthesis of 11[36]

To a reaction tube equipped with a stir bar were added $CuCl_2 \cdot 2H_2O$ (0.01 mmol, dissolved in 0.1 mL of H_2O) and neocuproine (2.1 mg, 0.01 mmol). Then, H_2O (0.7 mL), DCE (0.7 mL), **10** (39.4 mg, 0.2 mmol) and *tert*-butyl hydroperoxide (200 μL, 1.55 mmol) were added. The resulting mixture was stirred at room temperature for 20 h. Afterwards, it was extracted with DCM (3×10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as the eluent to give **11**.

4-Methylcyclopenta[*b*]indole-1,3(2*H*,4*H*)-dione (11)

Colorless solid (20.3 mg, 51%), 233-235 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.37 (s, 2H), 3.98 (s, 3H), 7.33 (t, J = 7.2 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.3, 50.2, 111.4, 120.1, 123.4, 124.0, 128.0, 132.9, 145.0, 149.6, 188.6,

188.9. HRMS calcd for $C_{12}H_{10}NO_2$: 200.0706 $[M+H]^+$, found: 200.0719.

3. Structural elaboration of 3z and procedure for the synthesis of 12

To a 15 mL reaction tube equipped with a stir bar were added **3z** (85.0 mg, 0.3 mmol) and polyphosphoric acid (PPA, 16.9 mg, 0.05 mmol) with stirring. The tube was sealed, and the mixture was stirred at 135 °C for 4 h. Upon completion, the resulting mixture was diluted with saturated $KHCO_3$ solution (5 mL), and extracted with ethyl acetate (10 mL×3). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over anhydrous $MgSO_4$, The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as the eluent to give **12**.

5-Methyl-1,3,5,10a-tetrahydroindeno[1,2-*b*]indol-10(2*H*)-one (12)

Yellow solid (40.6 mg, 57%), 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.33-1.37 (m, 1H), 1.62-1.65 (m, 1H), 2.03-2.07 (m, 1H), 2.22-2.30 (m, 1H), 2.37-2.41 (m, 1H), 2.46-2.54 (m, 1H), 3.24-3.29 (m, 1H), 3.84 (s, 3H), 6.17 (d, J = 1.6 Hz, 1H), 7.23-7.33 (m, 3H), 7.94 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.9, 23.5, 25.9, 31.4, 53.7, 109.9, 119.8, 121.3, 121.6, 122.1, 122.4, 124.1, 129.9, 143.7, 158.3, 194.0. HRMS calcd for $C_{16}H_{16}NO$: 238.1226 $[M+H]^+$, found: 238.1234.

Supporting Information. Copies of ^{1}H and ^{13}C NMR spectra of all products and the X-ray crystal structure and data of **5a**. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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