Redox-Neutral Rhodium(III)-Catalyzed Chemo- and Regiospecific [4+1] Annulation between Indoles and Alkenes for the Synthesis of Functionalized Imidazo[1,5-*a*]indoles

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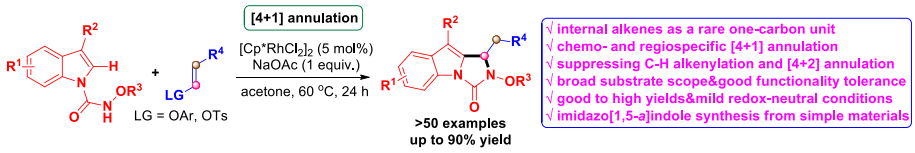
Supporting Information Placeholder

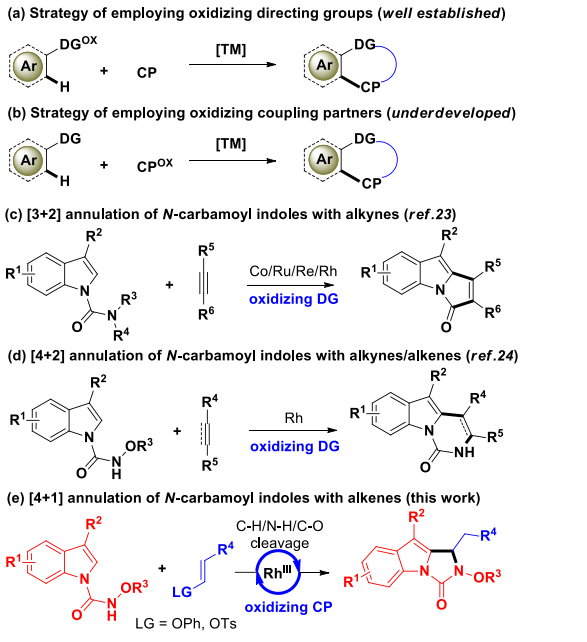


ABSTRACT: Exploiting internal alkenes embedded with an oxidizing function/leaving group as a rare and unconventional one-carbon unit, a redox-neutral rhodium(III)-catalyzed chemo- and regiospecific [4+1] annulation between indoles and alkenes for the synthesis of functionalized imidazo[1,5-*a*]indoles has been achieved. Internal alkenes employed here can fulfil an unusual [4+1] annulation rather than normal [4+2] annulation/C−H alkenylation. This method is characterized by excellent chemo- and regioselectivity, broad substrate scope, good functional group tolerance, good to high yields and redox-neutral conditions.

INTRODUCTION

Transition-metal (TM)-catalyzed C−H functionalization assisted by directing groups (DGs) has made remarkable advances in recent decades and become a powerful tool for the synthesis of a broad range of valuable molecules.[1] In particular, TM-catalyzed cycloaddition reactions triggered by C−H activation constitute an efficient strategy to access various heterocyclic compounds.[2] However, stoichiometric amounts of external oxidants are usually required because of the oxidative character of these C−H annulation reactions, and thus results in unsatisfactory selectivity and compatibility of functional groups, undesired side reactions and environmental pollution. An emerging dominant strategy to address this issue is to employ oxidizing DGs (working as an internal oxidant), which has been well established (Scheme 1a).[3] A variety of oxidizing DGs, including N^{+}–O^{-},[4] N–OAc,[5] N–OH,[6] N–OMe,[7] N–OPiv,[8] N–OBoc,[9] O–NHAc,[10] O–NEt_2,[11] N–N=O,[12] N–NHAc,[13] N–N=C,[14] N–NMe_2,[15] *etc*, have been exploited. By contrast, an alternative strategy to avoid using external oxidants by incorporating the oxidizing function (typically a leaving group which could be eliminated during the annulation) into the coupling partners (CPs) is comparatively underdeveloped (Scheme 1b). This is mainly because of the relative

Scheme 1. Redox-neutral C−H annulations employing oxidizing DGs or CPs



scarcity of available synthons which can behave as reactive CPs and simultaneously act as efficient internal oxidants in C−H annulations. Nevertheless, several groups have made their efforts in adopting the strategy of employing oxidizing CPs to achieve cycloadditions under external-oxidant-free conditions. For example, Loh's group pioneered an intriguing assembly of isoindolin-1-ones using α,α-difluoromethylene alkynes as the oxidizing CPs, which underwent two consecutive β-F eliminations to allow the annulation to occur under redox-neutral conditions.[16] The group of Glorius disclosed a facile furnishment of isoquinolines with propargylic carbonates as the oxidizing CPs, in this case, external oxidants were also not needed thanks to the β-elimination of the carbonate group.[17] In this context, it is still highly desirable to explore new types of oxidizing CPs to fulfil redox-neutral cycloadditions to construct novel heterocycles.

On the other hand, indole-fused polyheterocycles play an important role among numerous heterocycles as they are widely found in natural products and active pharmaceutical ingredients.[18] Therefore, TM-catalyzed C−H annulations between indoles and CPs for the direct construction of indole-fused polyheterocycles have captured the attention of synthetic community.[19,20] Within this field, *N*-carbamoyl indoles are popular indole substrates, not only because the carbamoyl[21] DG is easy to install and can display as an oxidizing DG to avoid using external oxidants, but also because different annulation modes could be provided by *N*-carbamoyl indoles. With regard to CPs, alkynes/alkenes are hot CPs as they are readily available and reactive.[22] The reported external-oxidant-free cycloadditions between *N*-carbamoyl indoles and alkynes/alkenes could be categorized into two patterns. (a) [3+2] annulation with alkynes for the synthesis of 3*H*-pyrrolo[1,2-*a*]indol-3-ones via Co,[23a] Ru,[23b] Re,[23c] Rh[23d, e] catalysis (Scheme 1c); (b) [4+2] annulation with alkynes/alkenes for the synthesis of pyrimido[1,6-*a*]indol-1(2*H*)-ones[24]/3,4-dihydropyrimido[1,6-*a*]indol-1(2*H*)-ones[24a,25] via Rh catalysis (Scheme 1d). Despite the remarkable achievements made, however, the [4+1] annulation between *N*-carbamoyl indoles and alkynes/alkenes for the synthesis of imidazo[1,5-a]indoles has never been reported to date. Moreover, it should be noted that both annulation reactions mentioned above avoided the use of external oxidants by taking advantage of the oxidizing carbamoyl DG. With our interests in Rh(III)-catalyzed C−H activation[23b,23d,24d,26] and indole compound synthesis,[27] herein we developed an unprecedented Rh(III)-catalyzed chemo- and regiospecific [4+1] annulation between *N*-carbamoyl indoles and internal alkenes embedded with an oxidizing function/leaving group for the synthesis of functionalized imidazo[1,5-*a*]indoles (Scheme 1e). Notably, our protocol does not require external oxidants by the strategy of employing oxidizing CPs, namely oxidizing internal alkenes, which is conceptually different from the aforementioned two annulations. Of note, this transformation has the following valuable advantageous features. (a) Internal alkenes embedded with an oxidizing function/leaving group are firstly used as a rare and unconventional one-carbon unit, which has not been disclosed before and is unusual since internal alkenes normally act as two-carbon partners to participate [n+2] annulations;[28] (b) a chemoselective [4+1] annulation, in which the background reactions such as [4+2] annulation[24a] as well as C−H alkenylation[29] are completely suppressed; (c) a regioselective [4+1] annulation, in which both C−C and C−N bonds are formed at the same proximal sp^2 hybridized carbon; (d) a mild redox-neutral process because of the detachment of the oxidizing function/leaving group; (e) the activation of C−H bond, the cleavage of C−O/N−H bonds, and the construction of C−C/C−N bonds are integrated in a single process, indicating the high bond-cleaving/forming efficiency. Despite the elegant assembly of the imidazo[1,5-*a*]indole scaffold from indoles with hazardous diazo compounds (the group of Cui[24a,30] and Song[31]), 4-hydroxyphenylboronic acid under Ag oxidant (Cui's group[32]) or isocyanides under O_2 (Yu's group[33]), to the best of our knowledge, our work stands as the first example of imidazo[1,5-*a*]indole synthesis via redox-neutral Rh(III)-catalyzed [4+1] cycloaddition reaction employing oxidizing internal alkenes as the one-carbon CPs and internal oxidants. Considering the large presence of the imidazo[1,5-*a*]indole nucleus in bioactive molecules (Figure 1),[34] our protocol is quite appealing as it allows the rapid and efficient synthesis of imidazo[1,5-*a*]indoles from simple materials via Rh(III)-catalyzed chemo- and regiospecific [4+1] annulation.

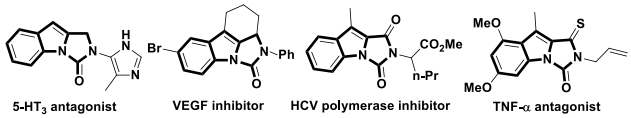
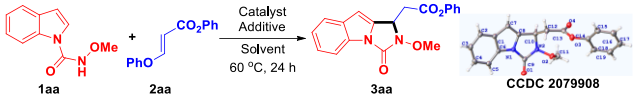


Figure 1. Representative bioactive molecules bearing the imidazo[1,5-*a*]indole motif.

RESULTS AND DISCUSSION

Optimization of the reaction conditions was carried out with indole **1aa** and (*E*)-phenyl 3-phenoxyacrylate **2aa** as the model substrates (Table 1). At first, with NaOAc as the additive, the reaction of **1aa** and **2aa** was performed with a series of metal catalysts in DCE at 60 °C for 24 h (entries 1-6). To our delight, when $[Cp^*RhCl_2]_2$ was employed (entry 6), the desired [4+1] annulation product **3aa** was obtained in 67% yield with excellent regioselectivity, in which the C−H activation occurred at the indole C2 position and the C−C/C−N bonds were formed at the same proximal sp^2 hybridized carbon. Next, with $[Cp^*RhCl_2]_2$ and NaOAc as the catalyst and additive, respectively, various solvents were screened (entries 7-17). As a result, except for DMF (entry 17), the [4+1] annulation could be tolerated in a diversity of solvents. Acetone was found to be the best solvent in which product **3aa** was obtained in 88% yield (entry 10). Interestingly, when MeOH was used as the solvent, the transesterification product of **3aa**, namely **4aa**, was observed as the final product (entry 13), while the reaction in TFE gave a ratio of 1:1.9 mixture of **3aa** and the transesterification product of TFE in 89% combined yield, which were inseparable by chromatography (entry 15). Subsequently, a variety of additives were investigated in acetone (entries 18-24), and NaOAc was proved to be the most effective additive. Besides, an investigation on the amount of the catalyst and additive was also carried out. The results showed that reducing the amount of $[Cp^*RhCl_2]_2$ from 5 mol% to 2.5 mol% or NaOAc from 1 to 0.1 equivalent both caused incomplete conversion of **1aa**, thus leading to lower yields of product **3aa** (entries 25 and 26). Of note, the detachment of the PhO group was confirmed by the detection of PhOH during condition optimization. At last, blank experiments were conducted (entries 27 and 28). The result shows that the catalytic system of $[Cp^*RhCl_2]_2$/NaOAc is crucial for the title [4+1] annulation. Notably, the background reaction products of [4+2] annulation and C−H alkenylation were not observed during condition optimization, suggesting the excellent chemoselectivity of this

Table 1. Optimization of the reaction conditions[a]



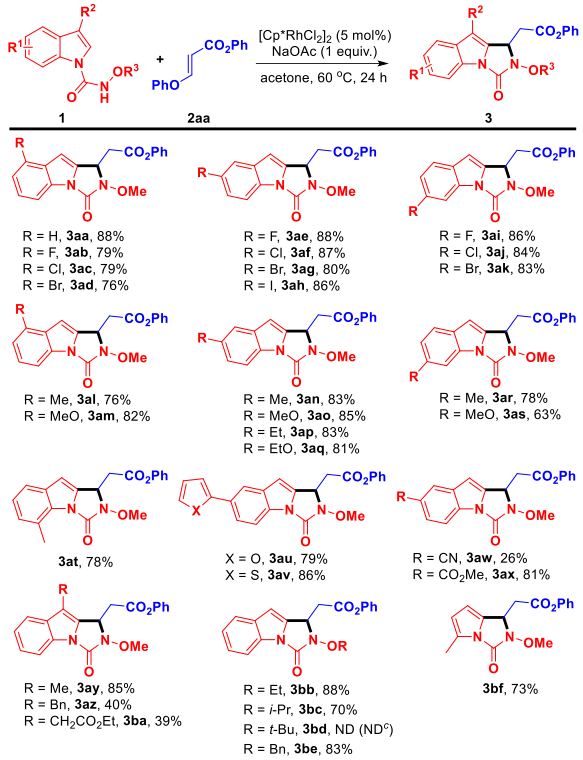
Entry	Catalyst	Additive	Solvent	Yield (%)[b]
1	$MnBr(CO)_5$	NaOAc	DCE	0
2	$Pd(OAc)_2$	NaOAc	DCE	0
3	$[Cp^*IrCl_2]_2$	NaOAc	DCE	0
4	$[RuCl_2(p\text{-cym})]_2$	NaOAc	DCE	0
5	$CoCp_2^*PF_6$	NaOAc	DCE	0
6	$[Cp^*RhCl_2]_2$	NaOAc	DCE	67
7	$[Cp^*RhCl_2]_2$	NaOAc	Toluene	54
8	$[Cp^*RhCl_2]_2$	NaOAc	CH_2Cl_2	71
9	$[Cp^*RhCl_2]_2$	NaOAc	THF	82
10	**$[Cp^*RhCl_2]_2$**	**NaOAc**	**Acetone**	**88**
11	$[Cp^*RhCl_2]_2$	NaOAc	Dioxane	73
12	$[Cp^*RhCl_2]_2$	NaOAc	CH_3CN	59
13	$[Cp^*RhCl_2]_2$	NaOAc	MeOH	87[c]
14	$[Cp^*RhCl_2]_2$	NaOAc	EtOH	76
15	$[Cp^*RhCl_2]_2$	NaOAc	TFE	89[d]
16	$[Cp^*RhCl_2]_2$	NaOAc	HFIP	27
17	$[Cp^*RhCl_2]_2$	NaOAc	DMF	<10
18	$[Cp^*RhCl_2]_2$	CsOAc	Acetone	37
19	$[Cp^*RhCl_2]_2$	KOAc	Acetone	78
20	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	Acetone	12
21	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	Acetone	54
22	$[Cp^*RhCl_2]_2$	Na_2CO_3	Acetone	78
23	$[Cp^*RhCl_2]_2$	K_2CO_3	Acetone	<10
24	$[Cp^*RhCl_2]_2$	NaCl	Acetone	0
25[e]	$[Cp^*RhCl_2]_2$	NaOAc	Acetone	79
26[f]	$[Cp^*RhCl_2]_2$	NaOAc	Acetone	58
27	-	NaOAc	Acetone	0
28	$[Cp^*RhCl_2]_2$	-	Acetone	0

[a]Reaction conditions: **1aa** (0.25 mmol), **2aa** (0.3 mmol), catalyst (5 mol%), additive (0.25 mmol), solvent (4.0 mL), 60 °C, 24 h. [b]Isolated yield. [c]The yield refers to the yield of transesterification product **4aa**. [d]The yield refers to the combined yield of **3aa** and transesterification product of TFE, and the ratio was determined to be 1:1.9 by ^{1}H NMR integration of the crude products. [e]$[Cp^*RhCl_2]_2$ (2.5 mol%) was used. [f]NaOAc (10 mol%) was used. DCE = 1,2-dichloroethane; THF = tetrahydrofuran; TFE = 2,2,2-trifluoroethanol; HFIP = 1,1,1,3,3,3-hexafluoroisopropanol; DMF = *N*,*N*-dimethylformamide.

transformation.

With the optimal reaction conditions in hands, the scope of indoles was explored at first with **2aa** as the reaction partner (Scheme 2). Overall, a broad range of indoles **1** carrying diverse substituents at R^1-R^3 could react with **2aa** to deliver the regiospecific [4+1] annulation products **3** in moderate to high yields. For example, halogenated indoles having F, Cl, Br, I at C4-C6 positions underwent this reaction smoothly to give products **3ab**-**3ak** in 76-88% yields. Likewise, the reactions of electron-rich indoles possessing Me, MeO, Et, EtO at C4-C7 positions also took place uneventfully to afford products **3al**-

Scheme 2. Substrate scope of the indoles [a,b]

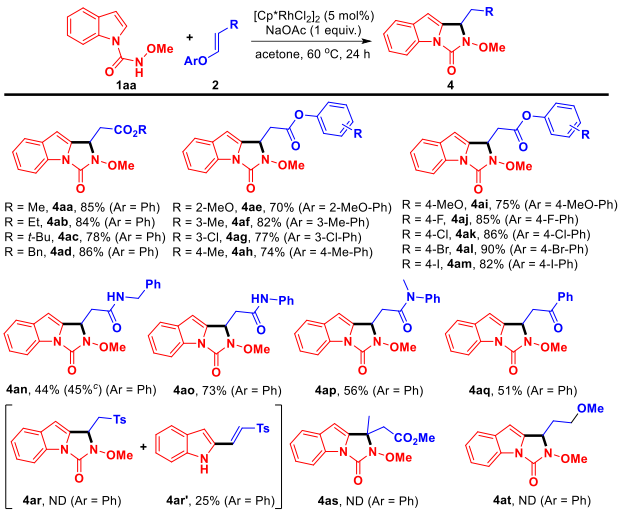


[a]Reaction conditions: **1** (0.25 mmol), **2aa** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), NaOAc (0.25 mmol), acetone (4.0 mL), 60 °C, 24 h. [b]Isolated yield. ND = not detected. [c]The reaction was performed at 100 °C.

3at in 63-85% yields. Of note, indoles bearing a heterocycle such as furan or thiophene ring at C5 position were also well tolerated and converted into the corresponding products **3au** and **3av** in 79% and 86% yields, respectively. Electron-deficient indoles carrying CN, CO_2Me at C5 position were also suitable substrates, and the desired products **3aw** and **3ax** were prepared in 26% and 81% yields, respectively. The [4+1] transformation was also compatible with indoles owning functional groups at C3 position, which could participate in this reaction to provide products **3ay**-**3ba** in 39-85% yields. Although lower yields were observed with indoles bearing bulky C3 substituents such as Bn and CH_2CO_2Et, the result is rationalized by the steric hindrance near the reaction centre. Besides, the reactions of indoles containing diverse alkyl groups such as Et, *i*-Pr and Bn at R^3 appeared to be reactive, and the desired products **3bb**, **3bc** and **3be** were synthesized in 70-88% yields. By contrast, indole substrate bearing a *t*-Bu group at R^3 failed to react to yield the corresponding product **3bd** even at a higher temperature but with most of the materials untouched. This result could also be ascribed to the steric hindrance caused by the huge *t*-Bu group. Pleasingly, *N*-carbamoyl pyrrole could take part in this reaction as well, assembling 1*H*-pyrrolo[1,2-*c*]imidazol-3(2*H*)-one product **3bf** in 73% yield.

Next, we examined the scope of alkenes with indole **1aa** as the reaction partner (Scheme 3). In general, a variety of alkenes **2** having diverse groups at R and Ar positions could interact with **1aa** to furnish the [4+1] annulation products **4** highly chemo- and regioselectively with good to high yields. For instance, the reactions of various alkyl acrylates such as (*E*)-methyl/ethyl/*tert*-butyl/benzyl 3-phenoxyacrylates worked

Scheme 3. Substrate scope of the alkenes [a,b]



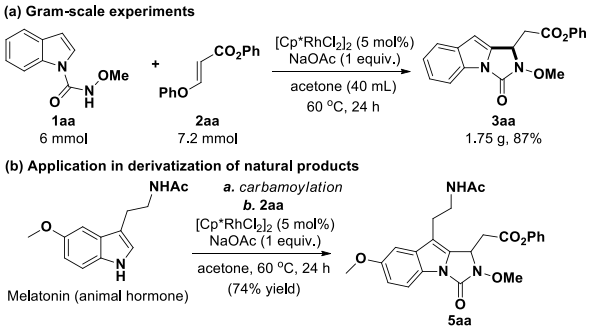
[a]Reaction conditions: **1aa** (0.25 mmol), **2** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), NaOAc (0.25 mmol), acetone (4.0 mL), 60 °C, 24 h. [b]Isolated yield. [c](*Z*)-*N*-benzyl-3-phenoxyacrylamide was used. ND = not detected.

well to afford products **4aa**-**4ad** in 78-86% yields. Likewise, a series of (*E*)-aryl 3-aryloxyacrylates could undergo this transformation smoothly to give products **4ae**-**4am** in 70-90% yields. Notably, both (*E*)- and (*Z*)-*N*-benzyl-3-phenoxyacrylamide could react successfully to deliver the desired product **4an** in comparable yields, suggesting *E*- and *Z*-configuration of the C=C bond of the alkenes are both suitable. Similarly, the reactions of (*E*)-3-phenoxy-*N*-phenylacrylamide or (*E*)-*N*-methyl-3-phenoxy-*N*-phenylacrylamide with **1aa** underwent smoothly, providing products **4ao** and **4ap** in 73% and 56% yields, respectively. Moreover, (*E*)-3-phenoxy-1-phenylprop-2-en-1-one was also tolerated, producing product **4aq** in 51% yield. The reaction of (*E*)-1-methyl-4-((2-phenoxyvinyl)sulfonyl)benzene with **1aa** under standard conditions failed to give the [4+1] annulation product **4ar**, but gave the C–H alkenylation/DG cleavage product **4ar'** in 25% yield with the majority of the materials untouched. Besides, (*E*)-methyl 3-phenoxybut-2-enoate could not be converted into the corresponding product **4as**, maybe because of the steric hindrance caused by the Me group attached to the alkene carbon. Alkenes like (*E*)-((3-methoxyprop-1-en-1-yl)oxy)benzene failed to react to provide the corresponding product **4at**, indicating that alkenes **2** possessing electron-withdrawing groups rather than electron-donating groups at the R position are suitable alkene components for this [4+1] annulation.

Gram-scale experiments were conducted to further prove the efficiency and practicality of this protocol. Impressively, the Rh(III)-catalyzed [4+1] annulation between **1aa** and **2aa** could be easily scaled up at a 6 mmol scale, providing product **3aa** in 87% yield (Scheme 4a). Moreover, our method could also be applied to the derivatization of natural products. For example, melatonin,[35] an animal hormone, underwent carbamoylation and the following Rh(III)-catalyzed [4+1] annulation with **2aa** smoothly to give melatonin derivative **5aa** bearing an imidazo[1,5-*a*]indole nucleus in a good yield (Scheme 4b).

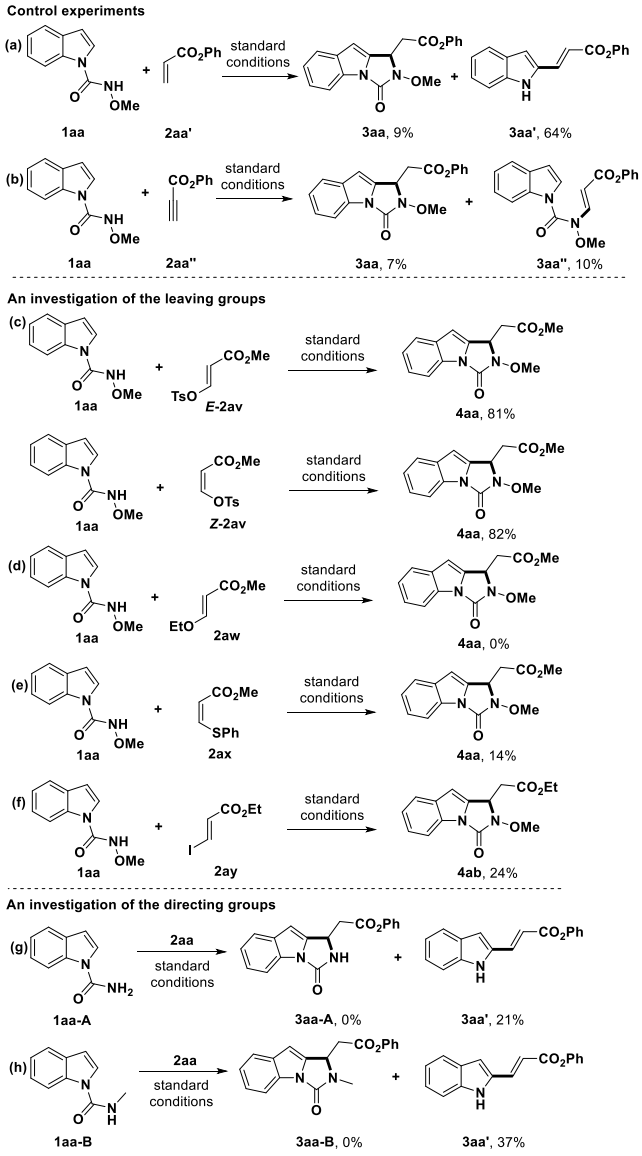
A series of control experiments were performed to further

Scheme 4. Gram-scale experiments and derivatization of natural products



probe the Rh(III)-catalyzed [4+1] annulation. The reaction of **1aa** with phenyl acrylate **2aa'** under standard conditions gave the desired product **3aa** and C–H alkenylation/DG cleavage product **3aa'** in 9% and 64% yields, respectively (Scheme 5a). This indicates the PhO group attached to the alkene carbon of

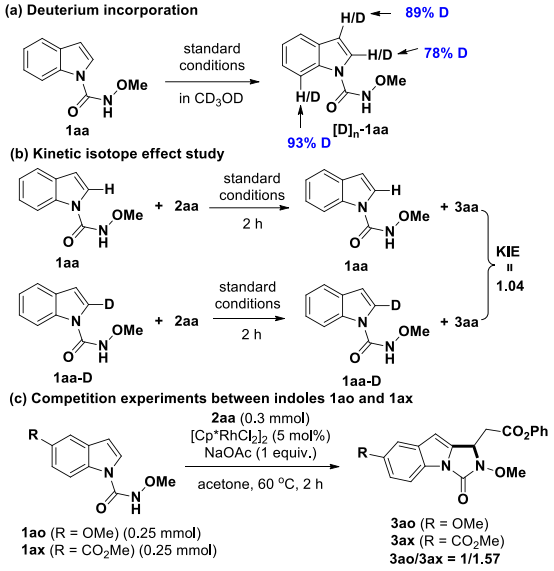
Scheme 5. Control experiments and investigation of the leaving groups and directing groups



the alkene component **2aa** is essential. The reaction of **1aa** with phenyl propiolate **2aa''** under standard conditions afforded the desired product **3aa** and *aza*-Michael addition product **3aa''** in 7% and 10% yields, respectively, along with the majority of the starting materials untouched (Scheme 5b). This suggests the possibility that alkene **2aa** acts as a masked alkyne could be excluded. In addition, an investigation of the leaving groups was carried out. The replacement of the PhO group in **2ab** with TsO group has no impact on the yield of the desired product **4aa** (Scheme 5c). By contrast, the replacement of the PhO group with groups such as EtO, PhS or I caused a sharp decrease in the yield of the desired product (Scheme 5d-5f). This indicates the PhO and TsO groups display as better leaving groups than EtO, PhS and I. At last, an investigation of the directing groups was conducted. As a result, the reaction of indole **1aa-A** or **1aa-B** with **2aa** under standard conditions failed to deliver the corresponding [4+1] annulation product **3aa-A** or **3aa-B**, but both provided the C–H alkenylation/DG cleavage product **3aa'** in low yields with partial starting materials untouched (Scheme 5g and 5h). This shows the alkoxy groups like MeO attached to the amide N is indispensable for the [4+1] annulation.

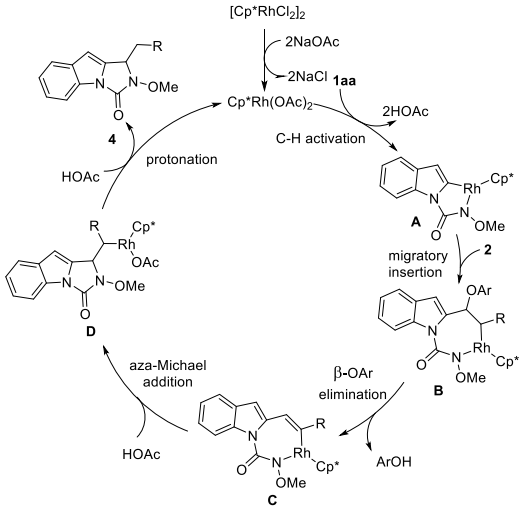
Mechanistic experiments were carried out to gain some insights into the reaction mechanism. Treatment of **1aa** in CD_3OD under standard conditions led to high deuterations at C2, C3 and C7 positions of **1aa** (Scheme 6a). This shows the cleavage of C−H bond is reversible. Kinetic isotope effect (KIE) study through two parallel reactions gave a low KIE value of 1.04 (Scheme 6b), indicating the step of C−H bond cleavage is unlikely to be the rate-limiting step. In addition, intermolecular competition experiments between electron-rich indole **1ao** and electron-deficient indole **1ax** resulted in a ratio of 1/1.57 of desired products **3ao**/**3ax** (Scheme 6c), suggesting electron-deficient indole was favored. Thus, a concerted metalation/deprotonation mechanism[36] maybe involved in the step of C−H bond cleavage.

Scheme 6. Mechanistic experiments



Based on the mechanistic studies and literature reports,[22b] a possible reaction mechanism was proposed in Scheme 7. Initially, the ligand exchange between $[Cp^*RhCl_2]_2$ and NaOAc generates the active catalyst $Cp^*Rh(OAc)_2$, which activates the C–H bond at C2 position of indole selectively to

Scheme 7. Proposed reaction mechanism



form the rhodacycle **A**. The regioselective migratory insertion of the alkene into the Rh–C bond of **A** gives intermediate **B**. The polarization of the C=C bond by the electron-withdrawing substituents is believed to guarantee the regioselectivity as well as reactivity. Then, intermediate **B** undergoes β-OAr elimination to afford intermediate **C**, which undergoes intramolecular *aza*-Michael addition to yield intermediate **D**. Finally, the protonation of intermediate **D** occurs to afford the product with concomitant regeneration of the active rhodium catalyst. We speculated that the alkoxy groups like MeO may enable the amide N to possess an appropriate electronic property to coordinate with the rhodium catalyst to commence the catalytic cycle, and may also stabilize complexes **B** and **C** by electron donation effect to ensure the successful occurrence the [4+1] annulation.

CONCLUSIONS

In conclusion, we have achieved the synthesis of imidazo[1,5-*a*]indoles via Rh(III)-catalyzed chemo- and regiospecific [4+1] annulation, in which internal alkenes embedded with an oxidizing function/leaving group are firstly exploited as a rare and unconventional one-carbon reaction partner, and thus can fulfil an unusual [4+1] annulation rather than common [4+2] annulation or C−H alkenylation. Additionally, the detachment of the oxidizing function/leaving group allows the [4+1] annulation to occur under redox-neutral conditions. This approach exhibits excellent chemo- and regioselectivity, broad substrate scope, good functional group tolerance and good to high yields. Further applications of this unique one-carbon unit in TM-catalyzed [n+1] annulations and biological studies of the indole-fused polyheterocycles incorporating the privileged imidazo[1,5-*a*]indole motif is undergoing in our laboratory.

EXPERIMENTAL SECTION

General Information. If not otherwise specified, the reagents were obtained from commercial sources and used directly without purification. Heating source: all the reactions that require heating were carried out in an oil bath. Analytical thin-layer chromatography (TLC): HSGF 254 (0.15-0.2 mm thickness). Detection under UV light at 254 nm. Column chromatography: separations were carried out on silica gel FCP 200-300. Yields refer to isolated compounds. Melting point apparatus: a micro melting point apparatus, values are uncorrected.

Nuclear magnetic resonance (NMR) apparatus: a Brucker 400, 500 or 600 MHz instrument. Chemical shifts (δ) are given in ppm. Proton coupling patterns were recorded as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). HRMS (high-resolution mass) were measured on a Thermo Scientific LTQ Orbitrap Discovery (Bremen, Germany). The linear ion trap (LTQ) part of the hybrid MS system was equipped with electrospray ionization (ESI) probe and operated in both positive and negative ion modes.

Preparation of the Indole Materials. All the indole substrates were prepared according to the literature procedure and their characterization data were in accordance with the published ones.[24d, 25b]

Preparation of the Alkene Materials

(*E*)-phenyl 3-phenoxyacrylate (2aa): to a mixture of phenol (10 mmol, 1.0 equiv) and DMAP (10 mmol, 1.0 equiv) in dichloromethane (20 mL) at 0 °C in an ice bath was added phenyl propiolate (12 mmol, 1.2 equiv) dropwise. After addition, the resulting mixture was stirred at room temperature for 24 h. After removal of the solvent, the residue was purified by flash chromatography (Petroleum/EtOAc: 64:1→Petroleum/EtOAc: 32/1) on silica gel to provide the desired product **2aa** as a pale yellow oil (1.92 g, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 12.2 Hz, 1H), 7.44-7.36 (m, 4H), 7.25-7.21 (m, 2H), 7.17-7.09 (m, 4H), 5.74 (d, *J* = 12.2 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.8, 160.9, 155.9, 150.8, 130.2, 129.5, 125.8, 125.4, 121.9, 118.3, 101.4; HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{15}H_{11}O_3$ 239.0714; Found 239.0711.

(*E*)-methyl 3-phenoxyacrylate (2ab): compound **2ab** was prepared as a pale yellow oil (1.49 g, 84% yield) following the similar procedure carried out for **2aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 12.2 Hz, 1H), 7.41-7.33 (m, 2H), 7.22-7.15 (m, 1H), 7.10-7.03 (m, 2H), 5.56 (d, *J* = 12.2 Hz, 1H), 3.73 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.8, 159.3, 156.0, 130.1, 125.1, 118.1, 101.9, 51.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{11}O_3$ 179.0703; Found 179.0702.

(*E*)-ethyl 3-phenoxyacrylate (2ac): compound **2ac** was prepared as a pale yellow oil (1.64 g, 85% yield) following the similar procedure carried out for **2aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 12.2 Hz, 1H), 7.42-7.32 (m, 2H), 7.22-7.14 (m, 1H), 7.11-7.02 (m, 2H), 5.55 (d, *J* = 12.2 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.4, 159.2, 156.0, 130.1, 125.1, 118.2, 102.3, 60.2, 14.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{13}O_3$ 193.0859; Found 193.0861.

(*E*)-*tert*-butyl 3-phenoxyacrylate (2ad): compound **2ad** was prepared as a pale yellow oil (1.28 g, 58% yield) following the similar procedure carried out for **2aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 12.2 Hz, 1H), 7.40-7.33 (m, 2H), 7.21-7.15 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 5.47 (d, *J* = 12.2 Hz, 1H), 1.49 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.7, 158.5, 156.0, 130.0, 124.9, 118.2, 104.0, 80.3, 28.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}O_3$ 221.1172; Found 221.1166.

(*E*)-benzyl 3-phenoxyacrylate (2ae): compound **2ae** was prepared as a pale yellow oil (2.06 g, 81% yield) following the similar procedure carried out for **2aa**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 12.2 Hz, 1H), 7.43-7.36 (m, 6H), 7.35-7.31 (m, 1H), 7.23-7.16 (m, 1H), 7.12-7.04 (m, 2H), 5.61 (d, *J* = 12.2 Hz, 1H), 5.20 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 167.2, 159.7, 155.9, 136.3, 130.1, 128.7, 128.3, 128.3, 125.2, 118.3, 101.9, 66.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}O_3$ 255.1016; Found 255.1017.

(*E*)-2-methoxyphenyl 3-(2-methoxyphenoxy)acrylate (2af): compound **2af** was prepared as a white solid (0.726 g, 48% yield) following the similar procedure carried out for **2ak**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 12.2 Hz, 1H), 7.23-7.17 (m, 2H), 7.12 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.07 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.00 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.99-6.92 (m, 3H), 5.64 (d, *J* = 12.3 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 165.5, 162.6, 151.5, 150.6, 144.3, 139.8, 126.8, 126.6, 123.2, 121.2, 120.9, 120.7, 113.0, 112.5, 99.8, 56.1, 56.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}O_5$ 301.1071; Found 301.1069.

(*E*)-*m*-tolyl 3-(*m*-tolyloxy)acrylate (2ag): compound **2ag** was prepared as a colorless oil (1.13 g, 84% yield) following the similar procedure carried out for **2ak**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 12.2 Hz, 1H), 7.30-7.26 (m, 2H), 7.08-7.01 (m, 2H), 6.97-6.89 (m, 4H), 5.73 (d, *J* = 12.2 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.0, 160.9, 155.9, 150.7, 140.5, 139.7, 129.9, 129.2, 126.6, 126.2, 122.5, 118.9, 118.8, 115.2, 101.2, 21.5, 21.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}O_3$ 269.1172; Found 269.1176.

(*E*)-3-chlorophenyl 3-(3-chlorophenoxy)acrylate (2ah): compound **2ah** was prepared as a yellow oil (0.657 g, 43% yield) following the similar procedure carried out for **2ak**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 12.1 Hz, 1H), 7.37-7.28 (m, 2H), 7.24-7.19 (m, 2H), 7.19-7.12 (m, 2H), 7.06-7.00 (m, 2H), 5.76 (d, *J* = 12.2 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 165.1, 160.3, 156.2, 151.1, 135.6, 134.8, 131.0, 130.3, 126.2, 125.8, 122.5, 120.2, 118.9, 116.5, 102.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{11}Cl_2O_3$ 309.0080; Found 309.0080.

(*E*)-*p*-tolyl 3-(p-tolyloxy)acrylate (2ai): compound **2ai** was prepared as a white solid (0.701 g, 52% yield) following the similar procedure carried out for **2ak**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 12.2 Hz, 1H), 7.22-7.16 (m, 4H), 7.03-6.98 (m, 4H), 5.69 (d, *J* = 12.2 Hz, 1H), 2.36 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.1, 161.3, 153.7, 148.5, 135.4, 135.1, 130.6, 130.0, 121.5, 118.2, 100.9, 21.0, 20.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}O_3$ 269.1172; Found 269.1174.

(*E*)-4-methoxyphenyl 3-(4-methoxyphenoxy)acrylate (2aj): compound **2aj** was prepared as a white solid (1.20 g, 80% yield) following the similar procedure carried out for **2ak**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 12.2 Hz, 1H), 7.07-6.99 (m, 4H), 6.94-6.86 (m, 4H), 5.62 (d, *J* = 12.2 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.3, 162.0, 157.2, 157.1, 149.5, 144.2, 122.6, 119.7, 115.1, 114.5, 100.5, 55.8, 55.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}O_5$ 301.1071; Found 301.1076.

(*E*)-4-fluorophenyl 3-(4-fluorophenoxy)acrylate (2ak): to a mixture of 4-fluorophenol (11 mmol, 2.2 equiv), DCC (6 mmol, 1.2 equiv) and DMAP (5 mmol, 1.0 equiv) in DCM (20 mL) at 0 °C in an ice bath was added a solution of propiolic acid (5 mmol, 1.0 equiv) in DCM (20 mL) dropwise. After addition, the resulting mixture was stirred at room temperature for 24 h. After removal of the solvent, the residue was purified by flash chromatography (Petroleum/EtOAc: 64:1→Petroleum/EtOAc: 32/1) on silica gel to provide the desired product **2ak** as a white solid (0.824 g, 60% yield). ^{1}H

NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 12.2 Hz, 1H), 7.14-7.02 (m, 8H), 5.67 (d, *J* = 12.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 165.7, 161.3, 160.3 (d, J_{C-F} = 244.1 Hz), 160.0 (d, J_{C-F} = 244.4 Hz), 151.7 (d, J_{C-F} = 2.7 Hz), 146.5 (d, J_{C-F} = 2.8 Hz), 123.2 (d, J_{C-F} = 8.5 Hz), 120.0 (d, J_{C-F} = 8.5 Hz), 116.9 (d, J_{C-F} = 23.7 Hz), 116.2 (d, J_{C-F} = 23.4 Hz), 101.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{11}F_2O_3$ 277.0671; Found 277.0674.

(*E*)-4-chlorophenyl 3-(4-chlorophenoxy)acrylate (2al): compound **2al** was prepared as a white solid (0.821 g, 53% yield) following the similar procedure carried out for **2ak**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 12.2 Hz, 1H), 7.43-7.30 (m, 4H), 7.13-7.00 (m, 4H), 5.72 (d, *J* = 12.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.3, 160.6, 154.2, 149.1, 131.2, 130.9, 130.3, 129.6, 123.2, 119.6, 101.6; HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{15}H_9Cl_2O_3$ 306.9934; Found 306.9940.

(*E*)-4-bromophenyl 3-(4-bromophenoxy)acrylate (2am): compound **2am** was prepared as a white solid (1.51 g, 76% yield) following the similar procedure carried out for **2ak**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 12.2 Hz, 1H), 7.57-7.43 (m, 4H), 7.07-6.95 (m, 4H), 5.73 (d, *J* = 12.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.2, 160.5, 154.8, 149.7, 133.2, 132.6, 123.6, 120.0, 119.0, 118.4, 101.7; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{10}Br_2NaO_3$ 418.8889; Found 418.8892.

(*E*)-4-iodophenyl 3-(4-iodophenoxy)acrylate (2an): compound **2an** was prepared as a white solid (1.42 g, 58% yield) following the similar procedure carried out for **2ak**. ^1H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 12.2 Hz, 1H), 7.74-7.64 (m, 4H), 6.92-6.83 (m, 4H), 5.73 (d, *J* = 12.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 165.2, 160.3, 155.6, 150.5, 139.2, 138.6, 124.0, 120.4, 101.8, 89.9, 89.0; HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{15}H_9I_2O_3$ 490.8647; Found 490.8655.

(*E*)-*N*-benzyl-3-phenoxyacrylamide (*E*-2ao): compound ***E*-2ao** was prepared as a pale yellow solid (0.927 g, 37% yield) following the similar procedure carried out for **2aa**. ^1H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 11.8 Hz, 1H), 7.37-7.30 (m, 4H), 7.30-7.26 (m, 3H), 7.19-7.13 (m, 1H), 7.09-7.02 (m, 2H), 5.88 (s, 1H), 5.59 (d, *J* = 11.8 Hz, 1H), 4.49 (d, *J* = 5.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 166.1, 156.7, 156.2, 138.4, 130.0, 128.8, 128.0, 127.6, 124.7, 117.9, 104.3, 43.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_2$ 254.1176; Found 254.1175.

(*Z*)-*N*-benzyl-3-phenoxyacrylamide (*Z*-2ao): compound ***Z*-2ao** was prepared as a pale yellow solid (0.889 g, 35% yield) following the similar procedure carried out for **2aa**. ^1H NMR (600 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.36-7.29 (m, 5H), 7.29-7.26 (m, 1H), 7.23-7.17 (m, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 7.1 Hz, 1H), 5.28 (d, *J* = 7.1 Hz, 1H), 4.59 (d, *J* = 5.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 164.9, 156.3, 148.9, 138.7, 130.2, 128.8, 127.6, 127.4, 125.2, 117.5, 106.0, 43.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_2$ 254.1176; Found 254.1178.

(*E*)-3-phenoxy-*N*-phenylacrylamide (2ap): compound **2ap** was prepared as a white solid (1.08 g, 45% yield) following the similar procedure carried out for **2aa**. ^1H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 11.7 Hz, 1H), 7.60-7.48 (m, 3H), 7.38-7.33 (m, 2H), 7.33-7.28 (m, 2H), 7.20-7.14 (m, 1H), 7.13-7.08 (m, 1H), 7.07-7.03 (m, 2H), 5.76 (d, *J* = 11.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 157.6, 156.2, 130.1, 129.1, 124.9, 117.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}NO_2$ 240.1019; Found 240.1022.

(*E*)-*N*-methyl-3-phenoxy-*N*-phenylacrylamide (2aq): compound **2aq** was prepared as a pale yellow oil (1.99 g, 79% yield) following the similar procedure carried out for **2aa**. ^1H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 11.6 Hz, 1H), 7.44-7.39 (m, 2H), 7.35-7.29 (m, 3H), 7.23-7.18 (m, 2H), 7.14-7.08 (m, 1H), 7.03-6.97 (m, 2H), 5.61 (d, *J* = 11.6 Hz, 1H), 3.36 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 166.6, 156.6, 156.5, 143.8, 129.9, 129.7, 127.7, 127.5, 124.4, 117.3, 103.4, 37.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_2$ 254.1176; Found 254.1176.

(*E*)-3-phenoxy-1-phenylprop-2-en-1-one (2ar): compound **2ar** was prepared as a yellow oil (0.202 g, 9% yield) following the similar procedure carried out for **2aa**. ^1H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 11.8 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.58-7.54 (m, 1H), 7.50-7.45 (m, 2H), 7.43-7.37 (m, 2H), 7.24-7.19 (m, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.75 (d, *J* = 11.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 190.4, 160.2, 156.1, 138.3, 132.7, 130.1, 128.6, 128.2, 125.2, 118.0, 106.8; LRMS (ESI) *m/z*: 225 $[M+H]^+$. Compound **2ar** is a known compound and the characterization data were in accordance with the published ones.[37]

(*E*)-1-methyl-4-((2-phenoxyvinyl)sulfonyl)benzene (2as): compound **2as** was prepared as a white solid (1.07 g, 39% yield) following the similar procedure carried out for **2aa**. ^1H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 11.9 Hz, 1H), 7.79-7.75 (m, 2H), 7.40-7.36 (m, 2H), 7.35-7.31 (m, 2H), 7.24-7.20 (m, 1H), 7.08-7.03 (m, 2H), 6.00 (d, *J* = 11.9 Hz, 1H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 157.7, 155.5, 144.1, 139.1, 130.3, 130.0, 127.2, 125.8, 118.4, 112.2, 21.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}O_3S$ 275.0736; Found 275.0738.

(*E*)-methyl 3-phenoxybut-2-enoate (2at): to a mixture of phenol (10 mmol, 1.0 equiv) and DMAP (10 mmol, 1.0 equiv) in dichloromethane (20 mL) at 0 °C in an ice bath was added methyl but-2-ynoate (12 mmol, 1.2 equiv) dropwise. After addition, the resulting mixture was stirred at 50 °C for 48 h. After removal of the solvent, the residue was purified by flash chromatography (Petroleum/EtOAc: 64:1→Petroleum/EtOAc: 32/1) on silica gel to provide the desired product **2at** as a pale yellow oil (0.826 g, 43% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.24-7.20 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.87 (s, 1H), 3.62 (s, 3H), 2.49 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 173.1, 168.2, 153.4, 130.1, 125.8, 121.7, 95.9, 51.0, 18.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{13}O_3$ 193.0859; Found 193.0860.

(*E*)-((3-methoxyprop-1-en-1-yl)oxy)benzene (2au): to a solution of (*E*)-3-phenoxyprop-2-en-1-ol[38] (3 mmol, 1.0 equiv) in anhydrous DMF (15 mL) was added NaH (6 mmol, 2.0 equiv) by portion at 0 °C, 30 minutes later, CH_3I (6 mmol, 2.0 equiv) was added dropwise at 0 °C. The resulting mixture was stirred at room temperature for 4 h. Then water was added and the reaction mixture was extracted with ethyl acetate, the organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide **2au** as a colorless oil (0.406 g, 82%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.36-7.30 (m, 2H), 7.11-7.06 (m, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 12.2 Hz, 1H), 5.51-5.40 (m, 1H), 3.94 (d, *J* = 7.3 Hz, 2H), 3.35 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 156.9, 146.3, 129.8, 123.4, 117.2,

108.0, 69.3, 57.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{13}O_2$ 165.0910; Found 165.0909.

(*Z*)-methyl 3-(tosyloxy)acrylate (*Z*-2av): this compound was prepared according to the literature procedure and the characterization data were in accordance with the publ ished ones.[39]

(*E*)-methyl 3-(tosyloxy)acrylate (*E*-2av): this compound was prepared according to the literature procedure and the characterization data were in accordance with the publ ished ones.[39]

(*E*)-methyl 3-ethoxyacrylate (2aw): this compound was prepared according to the literature procedure and the characterization data were in accordance with the publ ished ones.[38]

(*Z*)-methyl 3-(phenylthio)acrylate (2ax): this compound was prepared according to the literature procedure and the characterization data were in accordance with the publ ished ones.[40]

ethyl (*E*)-3-iodoacrylate (2ay): this compound is a known compound[41] and was obtained from commercial sources and used directly without purification.

Preparation of 2-Deuterium Indole and 1aa-D. 2-Deuterium indole (96% Deuteration) was prepared according to the reported procedure[42] and the characterization data match published data.[43] **1aa-D** was synthesized from 2-Deuterium indole with 96% D incorporation following the reported method[25b] and the characterization data match published data.[25b]

General Procedure for the Rhodium-Catalyzed Chemo- and Regiospecific [4+1] Annulation between Indoles and Alkenes. To a mixture of indoles **1** (0.25 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol%) and NaOAc (0.25 mmol, 1.0 equiv) in a 25 mL Schlenk tube was added a solution of alkenes **2** (0.3 mmol, 1.2 equiv) in acetone (4.0 mL). Then the tube was capped with septa, and the resulting mixture was stirred at 60 °C in an oil bath for 24 h. After removal of the solvent, the residue was purified by flash chromatography on silica gel to give the desired products.

phenyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3aa): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow amorphous solid (74.2 mg, yield 88%), mp 128-129 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.46-7.38 (m, 2H), 7.37-7.31 (m, 1H), 7.30-7.26 (m, 2H), 7.16-7.08 (m, 2H), 6.47 (s, 1H), 5.38-5.30 (m, 1H), 4.01 (s, 3H), 3.31 (dd, *J* = 16.5, 6.2 Hz, 1H), 3.08 (dd, *J* = 16.5, 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.5, 152.5, 150.4, 134.8, 132.8, 131.0, 129.7, 126.3, 124.2, 123.5, 121.5, 121.4, 113.0, 100.2, 65.1, 55.3, 37.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_4$ 337.1183; Found 337.1177.

phenyl 2-(8-fluoro-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ab): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a white amorphous solid (70.0 mg, yield 79%), mp 122-123 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.44-7.39 (m, 2H), 7.30-7.26 (m, 2H), 7.14-7.08 (m, 2H), 6.96 (ddd, *J* = 10.0, 8.1, 0.5 Hz, 1H), 6.59 (dd, *J* = 1.5, 0.7 Hz, 1H), 5.38-5.32 (m, 1H), 4.01 (s, 3H), 3.33 (dd, *J* = 16.6, 6.1 Hz, 1H), 3.10 (dd, *J* = 16.6, 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.4, 156.0 (d, $J_{C\text{-}F}$ = 249.0 Hz), 152.1, 150.4, 134.8, 133.0 (d, $J_{C\text{-}F}$ = 9.9 Hz), 129.8, 126.5, 125.2 (d, $J_{C\text{-}F}$ = 7.4 Hz), 121.6, 121.4, 109.2 (d, $J_{C\text{-}F}$ = 3.9 Hz), 108.9 (d, $J_{C\text{-}F}$ = 18.8 Hz), 96.2, 65.2, 55.2, 37.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}FN_2O_4$ 355.1089; Found 355.1083.

phenyl 2-(8-chloro-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ac): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a white amorphous solid (73.6 mg, yield 79%), mp 78-79 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.45-7.39 (m, 2H), 7.30-7.24 (m, 3H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.61 (s, 1H), 5.40-5.33 (m, 1H), 4.01 (s, 3H), 3.33 (dd, *J* = 16.6, 6.1 Hz, 1H), 3.11 (dd, *J* = 16.6, 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.4, 152.0, 150.3, 135.3, 131.6, 131.5, 129.8, 126.5, 125.0, 123.3, 121.4, 111.5, 98.7, 65.2, 55.2, 37.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}ClN_2O_4$ 371.0793; Found 371.0792.

phenyl 2-(8-bromo-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ad): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a pale yellow amorphous solid (79.4 mg, yield 76%), mp 97-98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.46-7.39 (m, 3H), 7.30-7.26 (m, 1H), 7.23-7.17 (m, 1H), 7.15-7.10 (m, 2H), 6.58 (dd, *J* = 1.5, 0.7 Hz, 1H), 5.41-5.31 (m, 1H), 4.01 (s, 3H), 3.33 (dd, *J* = 16.6, 6.1 Hz, 1H), 3.11 (dd, *J* = 16.6, 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.4, 152.0, 150.4, 135.4, 133.4, 131.3, 129.8, 126.5, 125.3, 121.5, 114.9, 112.1, 100.4, 65.2, 55.2, 37.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}BrN_2O_4$ 415.0288; Found 415.0283.

phenyl 2-(7-fluoro-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ae): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a white amorphous solid (78.1 mg, yield 88%), mp 119-120 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.8, 4.5 Hz, 1H), 7.46-7.37 (m, 2H), 7.30-7.26 (m, 1H), 7.24 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 2H), 7.09-7.05 (m, 1H), 6.45 (s, 1H), 5.37-5.28 (m, 1H), 4.00 (s, 3H), 3.33 (dd, *J* = 16.6, 6.1 Hz, 1H), 3.09 (dd, *J* = 16.6, 7.3 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.5, 159.7 (d, $J_{C\text{-}F}$ = 240.2 Hz), 152.2, 150.4, 136.5, 133.7 (d, $J_{C\text{-}F}$ = 10.3 Hz), 129.8, 127.4, 126.4, 121.4, 113.8 (d, $J_{C\text{-}F}$ = 9.6 Hz), 112.3 (d, $J_{C\text{-}F}$ = 25.9 Hz), 107.1 (d, $J_{C\text{-}F}$ = 24.4 Hz), 100.2 (d, $J_{C\text{-}F}$ = 4.2 Hz), 65.2, 55.3, 37.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}FN_2O_4$ 355.1089; Found 355.1088.

phenyl 2-(7-chloro-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3af): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a pale yellow amorphous solid (80.4 mg, yield 87%), mp 87-88 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 1H), 7.55 (s, 1H), 7.45-7.38 (m, 2H), 7.31-7.26 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.42 (s, 1H), 5.36-5.30 (m, 1H), 4.00 (s, 3H), 3.33 (dd, *J* = 16.6, 6.0 Hz, 1H), 3.09 (dd, *J* = 16.6, 7.3 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.4, 152.0, 150.3, 136.2, 133.9, 129.8, 129.3, 129.2, 126.5, 124.5, 121.4, 121.2, 113.9, 99.8, 65.2, 55.2, 37.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}ClN_2O_4$ 371.0793; Found 371.0791.

phenyl 2-(7-bromo-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ag): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a white amorphous solid (83.4 mg, yield 80%), mp 112-113 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.45-7.38 (m, 3H), 7.30-7.26 (m, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.42 (s, 1H), 5.37-5.31 (m, 1H), 4.00 (s, 3H), 3.33 (dd, *J* = 16.6, 6.1 Hz, 1H), 3.08 (dd, *J* = 16.6, 7.4 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.4, 152.0, 150.3, 136.0, 134.4, 129.8, 129.6, 127.2, 126.5, 124.2, 121.4, 116.8, 114.3, 99.6, 65.2, 55.2, 37.7; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{19}H_{16}BrN_2O_4$ 415.0288; Found 415.0278.

phenyl 2-(7-iodo-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ah): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (99.2 mg, yield 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.1 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.60 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.45-7.38 (m, 2H), 7.30-7.26 (m, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.40 (s, 1H), 5.37-5.31 (m, 1H), 4.00 (s, 3H), 3.33 (dd, *J* = 16.6, 6.1 Hz, 1H), 3.08 (dd, *J* = 16.6, 7.3 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.4, 152.0, 150.3, 135.6, 135.0, 132.7, 130.4, 130.1, 129.8, 126.5, 121.4, 114.7, 99.3, 87.5, 65.2, 55.1, 37.7; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{19}H_{16}IN_2O_4$ 463.0149; Found 463.0141.

phenyl 2-(6-fluoro-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ai): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow amorphous solid (75.9 mg, yield 86%), mp 116-117 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.50 (dd, *J* = 8.7, 5.0 Hz, 1H), 7.44-7.38 (m, 2H), 7.30-7.26 (m, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.05-7.00 (m, 1H), 6.45 (s, 1H), 5.36-5.29 (m, 1H), 4.00 (s, 3H), 3.33 (dd, *J* = 16.5, 6.1 Hz, 1H), 3.08 (dd, *J* = 16.5, 7.3 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.5, 160.6 (d, $J_{C\text{-}F}$ = 242.1 Hz), 152.0, 150.4, 135.0 (d, $J_{C\text{-}F}$ = 3.9 Hz), 130.9 (d, $J_{C\text{-}F}$ = 13.1 Hz), 129.8, 129.0, 126.4, 122.2 (d, $J_{C\text{-}F}$ = 9.9 Hz), 121.4, 112.0 (d, $J_{C\text{-}F}$ = 24.3 Hz), 100.3 (d, $J_{C\text{-}F}$ = 27.5 Hz), 100.1, 65.2, 55.2, 37.8; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{19}H_{16}FN_2O_4$ 355.1089; Found 355.1085.

phenyl 2-(6-chloro-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3aj): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a pale yellow amorphous solid (77.5 mg, yield 84%), mp 99-100 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.44-7.38 (m, 2H), 7.30-7.26 (m, 1H), 7.24 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.45 (s, 1H), 5.37-5.31 (m, 1H), 4.01 (s, 3H), 3.33 (dd, *J* = 16.6, 6.0 Hz, 1H), 3.08 (dd, *J* = 16.6, 7.4 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.4, 151.9, 150.3, 135.3, 131.2, 130.2, 129.8, 126.5, 124.2, 122.3, 121.4, 113.2, 100.1, 65.2, 55.2, 37.7; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{19}H_{16}ClN_2O_4$ 371.0793; Found 371.0785.

phenyl 2-(6-bromo-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ak): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a pale yellow amorphous solid (85.7 mg, yield 83%), mp 115-116 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.45-7.39 (m, 3H), 7.37 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.29-7.26 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.45 (d, *J* = 0.6 Hz, 1H), 5.36-5.28 (m, 1H), 4.00 (s, 3H), 3.33 (dd, *J* = 16.6, 6.0 Hz, 1H), 3.08 (dd, *J* = 16.6, 7.4 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.4, 151.9, 150.3, 135.2, 131.6, 131.5, 129.8, 126.9, 126.5, 122.6, 121.4, 117.7, 116.1, 100.2, 65.2, 55.2, 37.7; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{19}H_{16}BrN_2O_4$ 415.0288; Found 415.0277.

phenyl 2-(2-methoxy-8-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3al): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a white amorphous solid (66.3 mg, yield 76%), mp 77-78 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.46-7.40 (m, 2H), 7.30-7.27 (m, 1H), 7.26-7.22 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.51 (s, 1H), 5.38-5.31 (m, 1H), 4.01 (s, 3H), 3.33 (dd, *J* = 16.5, 5.8 Hz, 1H), 3.09 (dd, *J* = 16.5, 7.3 Hz, 1H), 2.52 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.7, 152.6, 150.4, 134.2, 132.5, 131.0, 130.7, 129.7, 126.4, 124.3, 123.9, 121.5, 110.6, 98.8, 65.1, 55.4, 38.0, 18.8; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{19}N_2O_4$ 351.1339; Found 351.1330.

phenyl 2-(2,8-dimethoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3am): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a pale yellow amorphous solid (75.4 mg, yield 82%), mp 102-103 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.45-7.38 (m, 2H), 7.29-7.27 (m, 1H), 7.27-7.25 (m, 1H), 7.15-7.09 (m, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.62-6.57 (m, 1H), 5.37-5.32 (m, 1H), 4.00 (s, 3H), 3.94 (s, 3H), 3.29 (dd, *J* = 16.5, 6.4 Hz, 1H), 3.08 (dd, *J* = 16.5, 7.0 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.5, 153.3, 152.5, 150.4, 133.1, 132.1, 129.7, 126.4, 125.3, 123.0, 121.5, 106.1, 103.8, 97.5, 65.1, 55.6, 55.3, 38.0; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{19}N_2O_5$ 367.1288; Found 367.1279.

phenyl 2-(2-methoxy-7-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3an): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (72.9 mg, yield 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.44-7.39 (m, 2H), 7.37 (s, 1H), 7.30-7.26 (m, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.39 (s, 1H), 5.35-5.29 (m, 1H), 4.00 (s, 3H), 3.31 (dd, *J* = 16.4, 6.3 Hz, 1H), 3.07 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.6, 152.6, 150.4, 134.9, 133.2, 133.1, 129.7, 129.2, 126.4, 125.6, 121.5, 121.4, 112.7, 100.0, 65.1, 55.4, 38.0, 21.7; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{19}N_2O_4$ 351.1339; Found 351.1331.

phenyl 2-(2,7-dimethoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ao): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow amorphous solid (77.9 mg, yield 85%), mp 117-118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.44-7.39 (m, 2H), 7.29-7.26 (m, 1H), 7.14-7.09 (m, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.40 (d, *J* = 0.8 Hz, 1H), 5.34-5.27 (m, 1H), 3.99 (s, 3H), 3.85 (s, 3H), 3.31 (dd, *J* = 16.4, 6.2 Hz, 1H), 3.07 (dd, *J* =

16.4, 7.3 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 168.6, 156.6, 152.6, 150.4, 135.7, 133.8, 129.7, 126.4, 125.7, 121.5, 113.7, 113.3, 104.1, 100.2, 65.2, 55.9, 55.4, 37.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_5$ 367.1288; Found 367.1281.

phenyl 2-(7-ethyl-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ap): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (75.7 mg, yield 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.44-7.38 (m, 3H), 7.30-7.26 (m, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.42 (d, *J* = 0.4 Hz, 1H), 5.36-5.30 (m, 1H), 4.00 (s, 3H), 3.31 (dd, *J* = 16.4, 6.3 Hz, 1H), 3.07 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 168.6, 152.6, 150.4, 139.8, 135.0, 133.1, 129.7, 129.4, 126.4, 124.7, 121.5, 120.1, 112.8, 100.1, 65.1, 55.4, 38.0, 29.2, 16.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_4$ 365.1496; Found 365.1488.

phenyl 2-(7-ethoxy-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3aq): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow amorphous solid (76.9 mg, yield 81%), mp 131-132 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 1H), 7.44-7.38 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 1.8 Hz, 1H), 6.95 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.39 (s, 1H), 5.34-5.26 (m, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.99 (s, 3H), 3.31 (dd, *J* = 16.4, 6.2 Hz, 1H), 3.07 (dd, *J* = 16.4, 7.2 Hz, 1H), 1.44 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 168.6, 155.9, 152.6, 150.4, 135.6, 133.8, 129.7, 126.4, 125.7, 121.5, 113.8, 113.7, 105.0, 100.2, 65.2, 64.1, 55.5, 37.9, 15.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_5$ 381.1445; Found 381.1436.

phenyl 2-(2-methoxy-6-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ar): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (68.7 mg, yield 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.44-7.39 (m, 2H), 7.30-7.26 (m, 1H), 7.14-7.08 (m, 3H), 6.42 (s, 1H), 5.36-5.30 (m, 1H), 4.00 (s, 3H), 3.30 (dd, *J* = 16.4, 6.3 Hz, 1H), 3.07 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.49 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 168.6, 152.6, 150.4, 134.5, 134.1, 131.4, 130.5, 129.7, 126.4, 125.1, 121.5, 121.0, 113.2, 100.1, 65.1, 55.4, 38.0, 21.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_4$ 351.1339; Found 351.1333.

phenyl 2-(2,6-dimethoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3as): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow amorphous solid (58.1 mg, yield 63%), mp 107-108 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 2.3 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.43-7.39 (m, 2H), 7.29-7.26 (m, 1H), 7.13-7.09 (m, 2H), 6.91 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.39 (d, *J* = 1.4 Hz, 1H), 5.35-5.29 (m, 1H), 4.00 (s, 3H), 3.88 (s, 3H), 3.30 (dd, *J* = 16.4, 6.2 Hz, 1H), 3.07 (dd, *J* = 16.4, 7.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 168.6, 157.7, 152.6, 150.4, 133.2, 131.9, 129.7, 126.4, 126.4, 122.0, 121.5, 113.5, 100.1, 96.5, 65.1, 55.9, 55.3, 38.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_5$ 367.1288; Found 367.1278.

phenyl 2-(2-methoxy-5-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3at): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a white amorphous solid (68.6 mg, yield 78%), mp 87-88 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.30-7.27 (m, 1H), 7.19-7.15 (m, 1H), 7.14-7.09 (m, 3H), 6.49 (d, *J* = 1.5 Hz, 1H), 5.34-5.27 (m, 1H), 4.01 (s, 3H), 3.30 (dd, *J* = 16.3, 6.3 Hz, 1H), 3.08 (dd, *J* = 16.4, 7.0 Hz, 1H), 2.91 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 168.6, 153.1, 150.4, 135.8, 133.5, 131.6, 129.7, 126.7, 126.4, 125.0, 123.9, 121.5, 118.8, 100.7, 65.0, 54.8, 38.1, 20.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_4$ 351.1339; Found 351.1332.

phenyl 2-(7-(furan-2-yl)-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3au): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow amorphous solid (79.0 mg, yield 79%), mp 120-121 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 1H), 7.88 (s, 1H), 7.66 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.45-7.38 (m, 2H), 7.30-7.26 (m, 1H), 7.15-7.07 (m, 2H), 6.65 (d, *J* = 3.3 Hz, 1H), 6.49 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.47 (s, 1H), 5.36-5.29 (m, 1H), 4.00 (s, 3H), 3.32 (dd, *J* = 16.5, 6.2 Hz, 1H), 3.09 (dd, *J* = 16.5, 7.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 168.5, 154.4, 152.2, 150.4, 141.9, 135.5, 133.2, 130.1, 129.7, 126.8, 126.4, 121.4, 120.7, 116.7, 113.2, 111.8, 104.6, 100.5, 65.1, 55.3, 37.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}N_2O_5$ 403.1288; Found 403.1286.

phenyl 2-(2-methoxy-3-oxo-7-(thiophen-2-yl)-2,3-dihydro-1H-imidazo[1,5-a]indol-1-yl)acetate (3av): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow amorphous solid (89.9 mg, yield 86%), mp 132-133 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.61 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.46-7.38 (m, 2H), 7.33-7.31 (m, 1H), 7.30-7.26 (m, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.49 (s, 1H), 5.38-5.32 (m, 1H), 4.01 (s, 3H), 3.34 (dd, *J* = 16.5, 6.2 Hz, 1H), 3.10 (dd, *J* = 16.5, 7.3 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 168.5, 152.3, 150.4, 144.9, 135.6, 133.4, 130.4, 130.3, 129.8, 128.2, 126.4, 124.7, 123.1, 122.9, 121.5, 118.8, 113.3, 100.4, 65.2, 55.3, 37.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}N_2O_4S$ 419.1060; Found 419.1060.

phenyl 2-(7-cyano-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3aw): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 8:1→Petroleum/EtOAc: 4/1) on silica gel to provide the product as a white amorphous solid (23.4 mg, yield 26%), mp 121-122 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.45-7.39 (m, 2H), 7.31-7.26 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.56 (s, 1H), 5.42-5.35 (m, 1H), 4.02 (s, 3H), 3.38 (dd, *J* = 16.8, 5.8 Hz, 1H), 3.12 (dd, *J* = 16.8, 7.5 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 168.3, 151.3, 150.3, 136.9, 132.6, 132.6, 129.8, 127.3, 126.5, 126.5, 121.4, 119.6, 113.8, 107.0, 100.2, 65.3, 55.0, 37.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{16}N_3O_4$ 362.1135; Found 362.1127.

methyl 2-methoxy-3-oxo-1-(2-oxo-2-phenoxyethyl)-2,3-dihydro-1*H*-imidazo[1,5-*a*]indole-7-carboxylate (3ax): The reaction mixture was subjected directly to flash chromatog-

raphy (Petroleum/EtOAc: 8:1→Petroleum/EtOAc: 4/1) on silica gel to provide the product as a pale yellow amorphous solid (79.6 mg, yield 81%), mp 126-127 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.04 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.45-7.38 (m, 2H), 7.30-7.26 (m, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.55 (s, 1H), 5.40-5.33 (m, 1H), 4.01 (s, 3H), 3.94 (s, 3H), 3.35 (dd, *J* = 16.6, 6.1 Hz, 1H), 3.10 (dd, *J* = 16.6, 7.3 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.4, 167.4, 151.8, 150.3, 135.9, 133.5, 132.5, 129.8, 126.5, 125.6, 125.5, 124.0, 121.4, 112.7, 100.9, 65.2, 55.1, 52.3, 37.7; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{21}H_{19}N_2O_6$ 395.1238; Found 395.1232.

phenyl 2-(2-methoxy-9-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ay): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a white amorphous solid (74.8 mg, yield 85%), mp 122-123 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.42-7.37 (m, 2H), 7.37-7.33 (m, 1H), 7.32-7.28 (m, 1H), 7.27-7.26 (m, 1H), 7.10-7.05 (m, 2H), 5.48-5.41 (m, 1H), 3.97 (s, 3H), 3.20-3.14 (m, 2H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.8, 152.5, 150.5, 133.9, 131.0, 129.8, 129.7, 126.3, 124.3, 123.2, 121.4, 119.4, 113.1, 109.2, 64.9, 54.8, 37.2, 8.6; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{19}N_2O_4$ 351.1339; Found 351.1333.

phenyl 2-(9-benzyl-2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3az): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a white amorphous solid (42.4 mg, yield 40%), mp 187-188 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.39-7.32 (m, 5H), 7.30-7.26 (m, 4H), 7.25-7.21 (m, 1H), 6.96 (d, *J* = 7.7 Hz, 2H), 5.19 (dd, *J* = 7.9, 3.7 Hz, 1H), 4.16 (d, *J* = 16.5 Hz, 1H), 4.10 (d, *J* = 16.9 Hz, 1H), 3.91 (s, 3H), 2.75 (dd, *J* = 16.6, 7.9 Hz, 1H), 2.68 (dd, *J* = 16.5, 3.8 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.6, 152.3, 150.5, 139.1, 133.1, 131.1, 130.7, 129.6, 129.1, 128.8, 127.0, 126.2, 124.4, 123.3, 121.4, 119.8, 113.1, 112.7, 64.8, 54.8, 37.0, 30.4; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{26}H_{23}N_2O_4$ 427.1652; Found 427.1643.

ethyl 2-(2-methoxy-3-oxo-1-(2-oxo-2-phenoxyethyl)-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-9-yl)acetate (3ba): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 8:1→Petroleum/EtOAc: 4/1) on silica gel to provide the product as a yellow viscous oil (41.7 mg, yield 39%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.40-7.34 (m, 3H), 7.32-7.28 (m, 1H), 7.26-7.21 (m, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 5.55-5.47 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.81-3.71 (m, 2H), 3.34 (dd, *J* = 16.7, 4.8 Hz, 1H), 3.20 (dd, *J* = 16.7, 7.1 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 168.9, 152.2, 150.5, 132.7, 131.9, 130.8, 129.6, 126.3, 124.5, 123.4, 121.5, 119.4, 113.1, 106.2, 64.9, 61.5, 54.9, 36.9, 30.1, 14.3; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{23}H_{23}N_2O_6$ 423.1551; Found 423.1541.

phenyl 2-(2-ethoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3bb): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 12/1) on silica gel to provide the product as a pale yellow amorphous solid (76.7 mg, yield 88%), mp 113-114 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.44-7.39 (m, 2H), 7.36-7.32 (m, 1H), 7.30-7.26 (m, 2H), 7.15-7.10 (m, 2H), 6.48 (s, 1H), 5.39-5.29 (m, 1H), 4.29-4.17 (m, 2H), 3.34 (dd, *J* = 16.6, 6.1 Hz, 1H), 3.05 (dd, *J* = 16.6, 7.4 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.6, 152.6, 150.4, 135.0, 132.8, 131.0, 129.7, 126.4, 124.2, 123.5, 121.5, 113.1, 100.2, 73.1, 55.5, 37.9, 13.9; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{19}N_2O_4$ 351.1339; Found 351.1330.

phenyl 2-(2-isopropoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3bc): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 12/1) on silica gel to provide the product as a colorless viscous oil (63.7 mg, yield 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.44-7.38 (m, 2H), 7.36-7.32 (m, 1H), 7.30-7.26 (m, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.48 (s, 1H), 5.37-5.29 (m, 1H), 4.46-4.37 (m, 1H), 3.39 (dd, *J* = 16.9, 5.9 Hz, 1H), 3.00 (dd, *J* = 16.9, 7.7 Hz, 1H), 1.39 (d, *J* = 6.2 Hz, 3H), 1.36 (d, *J* = 6.2 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.7, 153.0, 150.4, 135.3, 132.8, 131.0, 129.7, 126.4, 124.1, 123.4, 121.5, 121.4, 113.1, 100.1, 79.1, 55.8, 37.7, 21.2, 21.1; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{21}H_{21}N_2O_4$ 365.1496; Found 365.1487.

phenyl 2-(2-(benzyloxy)-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3be): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 12/1) on silica gel to provide the product as a white amorphous solid (85.3 mg, yield 83%), mp 83-84 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.54-7.47 (m, 2H), 7.44-7.39 (m, 3H), 7.39-7.33 (m, 3H), 7.30-7.27 (m, 1H), 7.26-7.24 (m, 1H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.43 (s, 1H), 5.20-5.14 (m, 2H), 5.13-5.07 (m, 1H), 3.08 (dd, *J* = 16.7, 5.7 Hz, 1H), 2.84 (dd, *J* = 16.7, 7.7 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.6, 152.8, 150.3, 135.1, 135.1, 132.8, 131.0, 130.1, 129.6, 129.3, 128.8, 126.3, 124.2, 123.5, 121.5, 113.1, 100.2, 79.4, 55.8, 37.4; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{25}H_{21}N_2O_4$ 413.1496; Found 413.1487.

phenyl 2-(2-methoxy-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-yl)acetate (3bf): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 10/1) on silica gel to provide the product as a colorless viscous oil (55.1 mg, yield 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.36 (m, 2H), 7.28-7.25 (m, 1H), 7.12-7.04 (m, 2H), 6.03 (dd, *J* = 3.0, 1.0 Hz, 1H), 5.98 (dd, *J* = 3.0, 1.3 Hz, 1H), 5.19-5.12 (m, 1H), 3.95 (s, 3H), 3.18 (dd, *J* = 16.3, 6.4 Hz, 1H), 2.97 (dd, *J* = 16.2, 6.8 Hz, 1H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.7, 152.6, 150.4, 129.7, 128.9, 126.3, 126.3, 121.5, 113.8, 103.8, 64.8, 54.6, 38.3, 11.5; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{17}N_2O_4$ 301.1183; Found 301.1175.

methyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4aa): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (58.2 mg, yield 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.34-7.29 (m, 1H), 7.27-7.24 (m, 1H), 6.40 (s, 1H), 5.24-5.18 (m, 1H), 3.96 (s, 3H), 3.78 (s, 3H), 3.09 (dd, *J* = 16.4, 5.8 Hz, 1H), 2.81 (dd, *J* = 16.4, 7.7 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.3, 152.6, 135.1, 132.8, 130.9, 124.1, 123.5, 121.4, 113.0, 100.0, 65.1, 55.4, 52.3, 37.5;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}N_2O_4$ 275.1026; Found 275.1020.

ethyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4ab): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (60.8 mg, yield 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.33-7.28 (m, 1H), 7.26-7.23 (m, 1H), 6.39 (d, *J* = 0.9 Hz, 1H), 5.24-5.16 (m, 1H), 4.27-4.19 (m, 2H), 3.95 (s, 3H), 3.07 (dd, *J* = 16.3, 5.8 Hz, 1H), 2.80 (dd, *J* = 16.3, 7.6 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.8, 152.5, 135.2, 132.8, 130.9, 124.0, 123.4, 121.4, 112.9, 99.9, 65.0, 61.3, 55.4, 37.7, 14.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}N_2O_4$ 289.1183; Found 289.1175.

***tert*-butyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4ac)**: The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (61.3 mg, yield 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.33-7.28 (m, 1H), 7.27-7.22 (m, 1H), 6.38 (d, *J* = 0.5 Hz, 1H), 5.20-5.15 (m, 1H), 3.95 (s, 3H), 2.97 (dd, *J* = 16.2, 6.1 Hz, 1H), 2.74 (dd, *J* = 16.2, 7.2 Hz, 1H), 1.47 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.1, 152.5, 135.4, 132.8, 130.9, 123.9, 123.3, 121.3, 112.9, 99.7, 81.9, 65.0, 55.6, 38.9, 28.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2O_4$ 317.1496; Found 317.1487.

benzyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4ad): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (74.9 mg, yield 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.41-7.34 (m, 5H), 7.34-7.30 (m, 1H), 7.28-7.25 (m, 1H), 6.30 (s, 1H), 5.27-5.17 (m, 3H), 3.89 (s, 3H), 3.13 (dd, *J* = 16.3, 6.0 Hz, 1H), 2.86 (dd, *J* = 16.3, 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.7, 152.5, 135.4, 135.0, 132.8, 130.9, 128.8, 128.7, 124.1, 123.4, 121.4, 113.0, 100.0, 67.1, 65.0, 55.4, 37.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_4$ 351.1339; Found 351.1330.

2-methoxyphenyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4ae): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16/1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (64.2 mg, yield 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.36-7.31 (m, 1H), 7.29-7.26 (m, 1H), 7.26-7.23 (m, 1H), 7.06 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.02-6.99 (m, 1H), 6.99-6.96 (m, 1H), 6.52 (d, *J* = 0.8 Hz, 1H), 5.36-5.29 (m, 1H), 4.02 (s, 3H), 3.84 (s, 3H), 3.40 (dd, *J* = 16.4, 5.5 Hz, 1H), 3.08 (dd, *J* = 16.4, 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.0, 152.6, 151.1, 139.4, 135.0, 133.0, 131.0, 127.5, 124.2, 123.5, 122.7, 121.5, 121.0, 113.1, 112.6, 100.4, 65.3, 55.9, 55.5, 37.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_5$ 367.1288; Found 367.1279.

***m*-tolyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4af)**: The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16/1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (71.9 mg, yield 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.36-7.32 (m, 1H), 7.31-7.26 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.95-6.87 (m, 2H), 6.48 (s, 1H), 5.38-5.30 (m, 1H), 4.01 (s, 3H), 3.31 (dd, *J* = 16.4, 6.2 Hz, 1H), 3.07 (dd, *J* = 16.4, 7.3 Hz, 1H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.6, 152.5, 150.4, 140.0, 134.9, 132.9, 131.0, 129.4, 127.2, 124.2, 123.6, 122.0, 121.5, 118.4, 113.1, 100.3, 65.2, 55.4, 37.9, 21.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_4$ 351.1339; Found 351.1328.

3-chlorophenyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4ag): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16/1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a pale yellow amorphous solid (71.7 mg, yield 77%), mp 121-122 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.37-7.31 (m, 2H), 7.30-7.26 (m, 2H), 7.17-7.13 (m, 1H), 7.02 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.47 (s, 1H), 5.37-5.30 (m, 1H), 4.00 (s, 3H), 3.30 (dd, *J* = 16.5, 6.3 Hz, 1H), 3.09 (dd, *J* = 16.5, 7.1 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.2, 152.5, 150.8, 135.0, 134.6, 132.8, 131.0, 130.5, 126.7, 124.3, 123.6, 122.2, 121.5, 119.9, 113.1, 100.3, 65.2, 55.2, 37.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}ClN_2O_4$ 371.0793; Found 371.0786.

***p*-tolyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4ah)**: The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (64.4 mg, yield 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.37-7.32 (m, 1H), 7.30-7.26 (m, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.03-6.97 (m, 2H), 6.47 (s, 1H), 5.39-5.30 (m, 1H), 4.00 (s, 3H), 3.31 (dd, *J* = 16.4, 6.3 Hz, 1H), 3.07 (dd, *J* = 16.5, 7.3 Hz, 1H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.8, 152.5, 148.2, 136.1, 134.8, 132.8, 131.0, 130.2, 124.2, 123.5, 121.5, 121.1, 113.1, 100.2, 65.1, 55.3, 37.9, 21.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_4$ 351.1339; Found 351.1332.

4-methoxyphenyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4ai): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16/1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (68.4 mg, yield 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.37-7.31 (m, 1H), 7.29-7.26 (m, 1H), 7.06-6.99 (m, 2H), 6.93-6.90 (m, 2H), 6.47 (s, 1H), 5.38-5.29 (m, 1H), 4.00 (s, 3H), 3.81 (s, 3H), 3.30 (dd, *J* = 16.4, 6.2 Hz, 1H), 3.06 (dd, *J* = 16.4, 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.9, 157.7, 152.5, 143.9, 134.9, 132.8, 131.0, 124.2, 123.5, 122.2, 121.5, 114.7, 113.1, 100.2, 65.1, 55.7, 55.4, 37.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_5$ 367.1288; Found 367.1277.

4-fluorophenyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4aj): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a white amorphous solid (74.9 mg, yield 85%), mp 86-87 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.37-7.31 (m, 1H), 7.30-7.26 (m, 1H), 7.14-7.02 (m, 4H), 6.46 (d, *J* = 0.7 Hz, 1H), 5.37-5.29 (m, 1H), 4.00 (s, 3H), 3.30 (dd, *J* = 16.5, 6.3 Hz, 1H), 3.08 (dd, *J* = 16.5, 7.1 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.6, 160.6 (d, J_{C-F} = 245.2 Hz), 152.5, 146.2 (d, J_{C-}

$_F$ = 2.9 Hz), 134.7, 132.8, 131.0, 124.3, 123.6, 122.9 (d, J_{C-F} = 8.5 Hz), 121.5, 116.4 (d, J_{C-F} = 23.5 Hz), 113.1, 100.2, 65.1, 55.2, 37.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}FN_2O_4$ 355.1089; Found 355.1083.

4-chlorophenyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4ak): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16/1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a white amorphous solid (79.4 mg, yield 86%), mp 93-94 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.40-7.32 (m, 3H), 7.30-7.26 (m, 1H), 7.10-7.02 (m, 2H), 6.46 (d, *J* = 0.7 Hz, 1H), 5.37-5.29 (m, 1H), 3.99 (s, 3H), 3.30 (dd, *J* = 16.5, 6.3 Hz, 1H), 3.08 (dd, *J* = 16.5, 7.1 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.3, 152.5, 148.8, 134.7, 132.8, 131.8, 131.0, 129.8, 124.3, 123.6, 122.8, 121.5, 113.1, 100.3, 65.1, 55.2, 37.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}ClN_2O_4$ 371.0793; Found 371.0791.

4-bromophenyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4al): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16/1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (93.7 mg, yield 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.37-7.31 (m, 1H), 7.30-7.26 (m, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.45 (s, 1H), 5.36-5.28 (m, 1H), 3.99 (s, 3H), 3.29 (dd, *J* = 16.5, 6.3 Hz, 1H), 3.08 (dd, *J* = 16.5, 7.0 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.2, 152.4, 149.4, 134.6, 132.8, 131.0, 124.3, 123.6, 123.2, 121.5, 119.5, 113.1, 100.2, 65.1, 55.2, 37.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}BrN_2O_4$ 415.0288; Found 415.0284.

4-iodophenyl 2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (4am): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16/1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow viscous oil (94.4 mg, yield 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01-7.96 (m, 1H), 7.74-7.68 (m, 2H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.37-7.32 (m, 1H), 7.29-7.26 (m, 1H), 6.91-6.85 (m, 2H), 6.45 (d, *J* = 0.8 Hz, 1H), 5.36-5.29 (m, 1H), 3.99 (s, 3H), 3.29 (dd, *J* = 16.5, 6.3 Hz, 1H), 3.08 (dd, *J* = 16.5, 7.0 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.2, 152.5, 150.2, 138.8, 134.6, 132.8, 131.0, 124.3, 123.6, 121.5, 113.1, 100.3, 90.5, 65.1, 55.2, 37.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}IN_2O_4$ 463.0149; Found 463.0143.

***N*-benzyl-2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetamide (4an)**: The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 8:1→Petroleum/EtOAc: 4/1) on silica gel to provide the product as a white amorphous solid ((*Z*)-*N*-benzyl-3-phenoxyacrylamide: 39.4 mg, yield 45%; (*E*)-*N*-benzyl-3-phenoxyacrylamide: 38.4 mg, yield 44%), mp 130-131 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.32-7.26 (m, 4H), 7.26-7.22 (m, 3H), 6.30 (s, 1H), 6.16 (s, 1H), 5.39-5.31 (m, 1H), 4.47 (d, *J* = 5.7 Hz, 2H), 3.85 (s, 3H), 2.94 (dd, *J* = 14.9, 6.2 Hz, 1H), 2.60 (dd, *J* = 14.9, 7.3 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.6, 152.3, 137.9, 135.3, 132.8, 130.9, 128.9, 128.0, 127.8, 124.0, 123.4, 121.4, 112.9, 100.0, 64.7, 55.3, 43.9, 39.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}N_3O_3$ 350.1499; Found 350.1490.

2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)-*N*-phenylacetamide (4ao): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 8:1→Petroleum/EtOAc: 4/1) on silica gel to provide the product as a yellow amorphous solid (61.2 mg, yield 73%), mp 134-135 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.37-7.31 (m, 2H), 7.26-7.22 (m, 1H), 7.22-7.18 (m, 1H), 7.16-7.11 (m, 1H), 6.39 (s, 1H), 5.46-5.40 (m, 1H), 3.84 (s, 3H), 3.07 (dd, *J* = 15.0, 6.4 Hz, 1H), 2.72 (dd, *J* = 15.0, 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 167.2, 152.4, 137.7, 135.2, 132.8, 130.8, 129.2, 124.8, 124.1, 123.5, 121.5, 120.2, 112.8, 100.3, 64.7, 55.2, 40.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}N_3O_3$ 336.1343; Found 336.1338.

2-(2-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)-*N*-methyl-*N*-phenylacetamide (4ap): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 8:1→Petroleum/EtOAc: 4/1) on silica gel to provide the product as a pale yellow amorphous solid (49.3 mg, yield 56%), mp 125-126 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.40-7.35 (m, 2H), 7.33-7.31 (m, 1H), 7.29-7.27 (m, 1H), 7.25-7.22 (m, 1H), 7.16-7.12 (m, 2H), 6.42 (d, *J* = 0.7 Hz, 1H), 5.46-5.39 (m, 1H), 3.87 (s, 3H), 3.35 (s, 3H), 2.84 (dd, *J* = 16.2, 6.0 Hz, 1H), 2.44 (dd, *J* = 16.2, 7.7 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.0, 152.0, 143.2, 136.1, 132.8, 130.9, 130.2, 128.4, 127.3, 123.8, 123.3, 121.3, 112.9, 99.9, 64.5, 55.3, 37.8, 37.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}N_3O_3$ 350.1499; Found 350.1492.

2-methoxy-1-(2-oxo-2-phenylethyl)-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4aq): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the product as a yellow amorphous solid (40.7 mg, yield 51%), mp 128-129 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02-7.94 (m, 3H), 7.63-7.59 (m, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.52-7.47 (m, 2H), 7.33-7.29 (m, 1H), 7.26-7.22 (m, 1H), 6.39 (s, 1H), 5.56-5.50 (m, 1H), 3.95 (s, 3H), 3.84 (dd, *J* = 17.5, 5.2 Hz, 1H), 3.35 (dd, *J* = 17.5, 8.2 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 196.5, 152.5, 136.3, 136.0, 133.9, 132.9, 130.9, 128.9, 128.2, 123.9, 123.4, 121.4, 112.9, 100.5, 64.8, 55.0, 41.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_3$ 321.1234; Found 321.1226.

(*E*)-2-(2-tosylvinyl)-1*H*-indole (4ar'): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 8:1→Petroleum/EtOAc: 4/1) on silica gel to provide the product as a white amorphous solid (18.5 mg, yield 25%), mp 161-162 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.55 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 15.3 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.36 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.23 (d, *J* = 15.3 Hz, 1H), 7.22-7.18 (m, 1H), 7.05-6.99 (m, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 144.2, 138.2, 138.1, 132.1, 131.7, 130.2, 127.7, 127.1, 125.1, 124.5, 121.4, 120.0, 111.6, 109.8, 21.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}NO_2S$ 298.0896; Found 298.0891.

phenyl 2-(9-(2-acetamidoethyl)-2,7-dimethoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (5aa): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 2:1→Petroleum/EtOAc: 1/1) on silica gel to provide the product as a pale yellow amorphous solid (84.0 mg, yield 74%), mp 111-112 °C. ^{1}H NMR (600

MHz, DMSO-d_6) δ 8.01 (t, J = 5.7 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.44-7.36 (m, 2H), 7.28-7.23 (m, 1H), 7.22 (d, J = 2.2 Hz, 1H), 7.04 (d, J = 7.9 Hz, 2H), 6.94 (dd, J = 8.8, 2.3 Hz, 1H), 5.49 (dd, J = 6.6, 3.9 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.48 (dd, J = 16.6, 3.8 Hz, 1H), 3.34-3.26 (m, 2H), 3.24 (dd, J = 16.7, 6.9 Hz, 1H), 2.91-2.80 (m, 2H), 1.80 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) δ 169.3, 168.4, 155.8, 151.5, 150.1, 133.9, 132.1, 129.6, 126.0, 124.7, 121.5, 112.5, 112.5, 110.2, 102.6, 64.1, 55.5, 54.2, 38.7, 35.5, 23.6, 22.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{26}N_3O_6$ 452.1816; Found 452.1815.

Gram-scale preparation of compound 3aa. To a mixture of **1aa** (6 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol%) and NaOAc (6 mmol, 1.0 equiv) in a 100 mL round-bottom flask was added a solution of **2aa** (7.2 mmol, 1.2 equiv) in acetone (40.0 mL). Then the flask was capped with septa, and the resulting mixture was stirred at 60 ºC in an oil bath for 24 h. After removal of the solvent, the residue was purified by flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to provide the desired product **3aa** as a yellow amorphous solid (1.75 g, yield 87%).

Control experiments. To a mixture of **1aa** (0.25 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol%), NaOAc (0.25 mmol, 1.0 equiv) in a 25 mL Schlenk tube was added a solution of **2aa'** (0.3 mmol, 1.2 equiv) in acetone (4.0 mL). Then the tube was capped with septa, and the resulting mixture was stirred at 60 ºC in an oil bath for 24 h. After removal of the solvent, the residue was purified by flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to give the product **3aa** (7.9 mg, yield 9%) and **3aa'** (41.9 mg, yield 64%).

(*E*)-phenyl 3-(1*H*-indol-2-yl)acrylate (3aa'): yellow amorphous solid (41.9 mg, yield 64%), mp 157-158 ºC. ^1H NMR (600 MHz, DMSO-d_6) δ 11.72 (s, 1H), 7.85 (d, J = 15.9 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.47-7.43 (m, 2H), 7.42 (d, J = 8.2 Hz, 1H), 7.31-7.27 (m, 1H), 7.25-7.21 (m, 3H), 7.08-7.02 (m, 1H), 7.01 (s, 1H), 6.76 (d, J = 15.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) δ 165.1, 150.6, 138.3, 136.7, 133.6, 129.5, 127.8, 125.8, 124.4, 121.9, 121.4, 119.9, 114.3, 111.6, 109.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}NO_2$ 264.1019; Found 264.1013.

Control experiments. To a mixture of **1aa** (0.25 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol%), NaOAc (0.25 mmol, 1.0 equiv) in a 25 mL Schlenk tube was added a solution of **2aa''** (0.3 mmol, 1.2 equiv) in acetone (4.0 mL). Then the tube was capped with septa, and the resulting mixture was stirred at 60 ºC in an oil bath for 24 h. After removal of the solvent, the residue was purified by flash chromatography (Petroleum/EtOAc: 16:1→Petroleum/EtOAc: 8/1) on silica gel to give the product **3aa** (6.0 mg, yield 7%) and **3aa''** (8.1 mg, yield 10%).

(*E*)-phenyl 3-(*N*-methoxy-1*H*-indole-1-carboxamido)acrylate (3aa''): yellow viscous oil (8.1 mg, yield 10%). ^1H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, J = 13.7 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 3.8 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.43-7.39 (m, 2H), 7.39-7.36 (m, 1H), 7.33-7.29 (m, 1H), 7.26-7.23 (m, 1H), 7.19-7.14 (m, 2H), 6.70 (d, J = 3.8 Hz, 1H), 5.89 (d, J = 13.7 Hz, 1H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 165.4, 150.8, 148.3, 138.9, 136.7, 130.0, 129.6, 126.1, 125.9, 124.9, 123.9, 121.8, 121.2, 115.5, 109.3, 98.8, 62.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_4$ 337.1183; Found 337.1183.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Investigation of the leaving groups and directing groups, mechanistic experiments, X-ray data of compound **3aa**, copies of ^1H NMR and $^{13}C\{^1H\}$ NMR Spectra of all isolated compounds (PDF)

Accession Codes

CCDC 2079908 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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