Temperature-Controlled Divergent Synthesis of Tetrasubstituted Alkenes and Pyrrolo[1,2-*a*]indole Derivatives *via* Iridium Catalysis

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Dedication ((optional))

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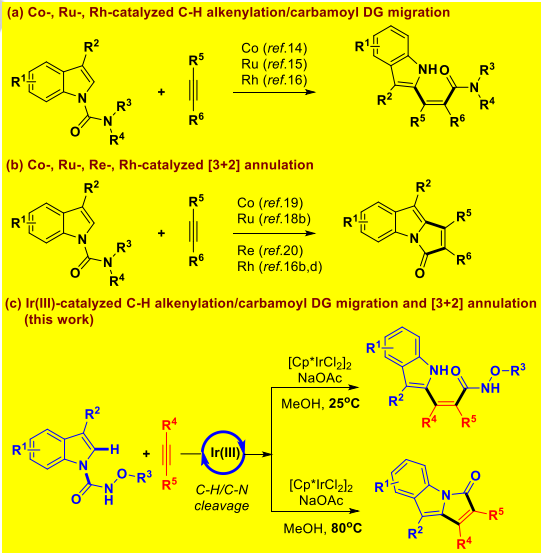
Abstract: We have achieved a Ir(III)-catalyzed temperature-controlled divergent synthesis of tetrasubstituted alkenes and pyrrolo[1,2-*a*]indole derivatives through C–H alkenylation/DG migration and [3+2] annulation, respectively. This method has various advantageous features: a) excellent regio- and stereoselectivity and good functional group tolerance, b) broad substrate scope and moderate to excellent yields, c) mild redox-neutral reaction conditions and operational simplicity.

Introduction

Transition metal-catalyzed C–H functionalization with various coupling partners assisted by directing groups (DGs) has achieved significant advances over the past decades.[1] Particularly, alkynes are one of the most frequently used coupling partners for the straightforward synthesis of alkenes through C–H alkenylation.[2] In this context, C–H alkenylation with alkynes *via* Pd,[3] Ru,[4] Rh,[5] Co,[6] Ni,[7] Mn[8] catalysis has contributed significantly to alkene synthesis. By contrast, despite Ir(III)-catalyzed C–H activation assisted by DGs has made remarkable achievements in recent years,[9-11] reports on Ir(III)-catalyzed C–H alkenylation with alkynes for the synthesis of multi-substituted alkenes are still limited.[12] Moreover, di- or trisubstituted alkenes are generally obtained in Ir(III)-catalyzed C–H alkenylation as the alkenyl-metal intermediate formed *via* C–H activation and the following alkyne insertion preferred to undergo proto-demetalation to form an alkenyl–H bond. Of note,



Scheme 1. Transition metal-catalyzed C-H alkenylation/carbamoyl DG migration and [3+2] annulation between *N*-carbamoyl indoles and alkynes.

the DGs in the abovementioned Ir(III)-catalyzed C–H alkenylation only function as auxiliary groups and keep still at their original locations. Inspired by the recent C–H alkenylation/carbamoyl[13] DG migration strategy for the synthesis of tetrasubstituted alkenes through Co,[14] Ru,[15] and

Rh[16] catalysis (Scheme 1a), we wonder if it is possible to synthesize tetrasubstituted alkenes by taking advantage of the strategy of carbamoyl DG migration *via* Ir(III) catalysis. With our experience in functional group transfer[17] and interest in C–H functionalization with alkynes,[16a-c,18] herein we describe an efficient and atom-economical method for the regio- and stereoselective synthesis of tetrasubstituted alkenes *via* Ir(III)-catalyzed C–H alkenylation/carbamoyl DG migration between *N*-carbamoyl indoles and internal alkynes (Scheme 1c). Except for acting as the auxiliary group which helps to achieve high reactivity and site selectivity, the carbamoyl DG also plays as an internal amidation reagent which migrates onto the alkene moiety of the products to deliver tetrasubstituted α,β-unsaturated amides.

In this work, we also disclose a Ir(III)-catalyzed regioselective [3+2] annulation from the same set of substrates for the synthesis of pyrrolo[1,2-*a*]indoles by elevating the reaction temperature (Scheme 1c). This process provides a useful complementarity to the preexisting [3+2] annulation for pyrrolo[1,2-*a*]indole synthesis *via* Co,[19] Ru,[18b] Re[20] and Rh[16b,d] catalysis (Scheme 1b). Considering the prevalence of the tetrasubstituted alkene and pyrrolo[1,2-*a*]indole nucleus in natural products and pharmaceutical ingredients (Figure 1),[21] our protocol is quite appealing because it allows the temperature-controlled divergent synthesis of tetrasubstituted alkenes and pyrrolo[1,2-*a*]indoles *via* Ir(III)-catalyzed C–H alkenylation/DG migration and [3+2] annulation, respectively, under redox-neutral conditions. The redox-neutral feature of this protocol also contrasts with the majority of the reported Ir(III)-catalyzed C–H functionalization, in which a silver oxidant is commonly added.[22]

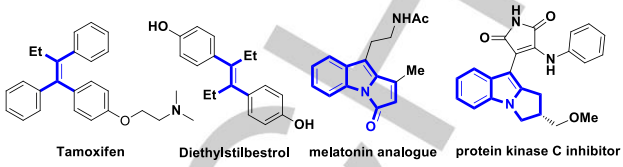
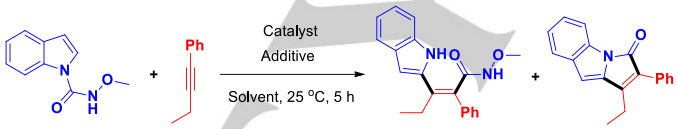


Figure 1. Representative bioactive molecules containing the tetrasubstituted alkene or pyrrolo[1,2-*a*]indole motif.

Results and Discussion

Screening experiments were carried out using indole **1aa** and but-1-yn-1-ylbenzene **2aa** as the model substrates to optimize the reaction conditions (Table 1). At first, treatment of substrates **1aa** and **2aa** with various metal catalysts in DCE at room temperature for 5 h employing NaOAc as the additive (entries 1-5) revealed that $[Cp^*IrCl_2]_2$ was an effective catalyst, which could

Table 1. Optimization of the reaction conditions.[a]

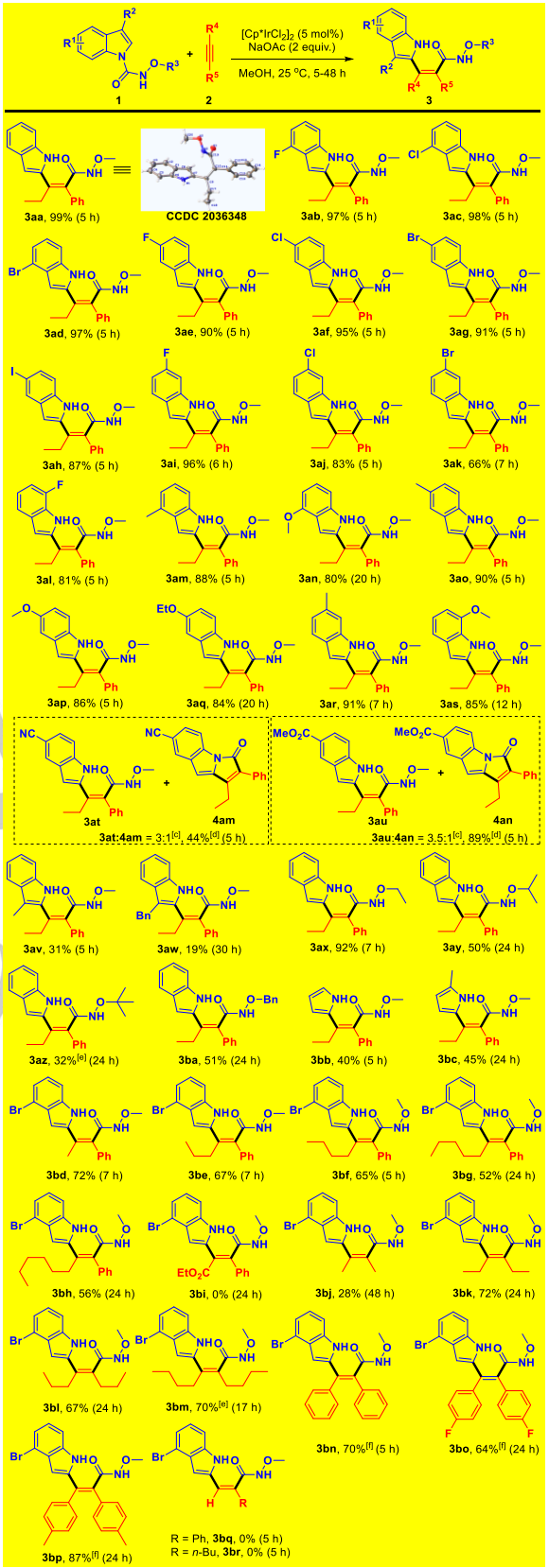


Entry	Catalyst	Additive	Solvent	Yield of **3aa** (%)[b]	Yield of **4aa** (%)[b]
1	$MnBr(CO)_5$	NaOAc	DCE	0	0
2	$Pd(OAc)_2$	NaOAc	DCE	0	0
3	$CoCp_2^*PF_6$	NaOAc	DCE	0	0
4	$[IrCl(COD)]_2$	NaOAc	DCE	0	0
5	$[Cp^*IrCl_2]_2$	NaOAc	DCE	62	0
6	$[Cp^*IrCl_2]_2$	NaOAc	Toluene	88	0
7	$[Cp^*IrCl_2]_2$	NaOAc	THF	71	0
8	$[Cp^*IrCl_2]_2$	NaOAc	Acetone	81	0
9	$[Cp^*IrCl_2]_2$	NaOAc	1,4-dioxane	50	0
10	$[Cp^*IrCl_2]_2$	NaOAc	CH_3CN	94	0
11	**$[Cp^*IrCl_2]_2$**	**NaOAc**	**MeOH**	**99**	**0**
12	$[Cp^*IrCl_2]_2$	NaOAc	EtOH	80	0
13	$[Cp^*IrCl_2]_2$	NaOAc	DMSO	0	0
14	$[Cp^*IrCl_2]_2$	CsOAc	MeOH	96	0
15	$[Cp^*IrCl_2]_2$	KOAc	MeOH	97	0
16	$[Cp^*IrCl_2]_2$	$Cu(OAc)_2$	MeOH	12	0
17	$[Cp^*IrCl_2]_2$	$Zn(OAc)_2$	MeOH	86	0
18	$[Cp^*IrCl_2]_2$	Na_2CO_3	MeOH	15	0
19	$[Cp^*IrCl_2]_2$	K_2CO_3	MeOH	18	0
20	$[Cp^*IrCl_2]_2$	NaCl	MeOH	11	0
21[c]	**$[Cp^*IrCl_2]_2$**	**NaOAc**	**MeOH**	**0**	**76**
22[d]	$[Cp^*IrCl_2]_2$	NaOAc	MeOH	62	0
23[e]	$[Cp^*IrCl_2]_2$	NaOAc	MeOH	91	0
24	-	NaOAc	MeOH	0 (0[f])	0 (0[f])
25	$[Cp^*IrCl_2]_2$	-	MeOH	0 (0[f])	0 (0[f])

[a] Reaction conditions: **1aa** (0.25 mmol), **2aa** (0.275 mmol), catalyst (5 mol%), additive (0.5 mmol), solvent (4.0 mL), 25 °C, 5 h. [b] Isolated yield. [c] The reaction was performed at 80 °C for 20 h. [d] $[Cp^*IrCl_2]_2$ (2.5 mol%) was used. [e] NaOAc (0.25 mmol) was used. [f] Data under 80 °C for 20 h.

catalyze the C–H alkenylation/DG migration cascade between **1aa** and **2aa** highly regioselectively and stereoselectively, providing the *cis*-adduct **3aa** with the indole moiety exclusively located at the less hindered position as the only isomer in a good yield (entry 5). Next, with $[Cp^*IrCl_2]_2$ and NaOAc as the catalyst and additive, respectively, a series of solvents were investigated (entries 6-13). MeOH was found to be the best solvent (entry 11), in which the desired tetrasubstituted alkene **3aa** precipitated out as white solids and could be simply collected by filtration in a quantitative yield (99%). Subsequent screening of a variety of additives disclosed that CsOAc, KOAc and $Zn(OAc)_2$ were also effective additives while $Cu(OAc)_2$, Na_2CO_3, K_2CO_3 and NaCl are less- or non-effective (entries 14-20). Interestingly, when the Ir(III)-catalyzed reaction of **1aa** and **2aa** was performed at a higher temperature (80 °C) for a longer time (20 h), the [3+2] annulation product **4aa** instead of the C–H alkenylation/DG migration product **3aa** was selectively afforded as the only product in a highly regioselective manner with 76% yield (entry 21). Moreover, when the same reaction was carried out at 80 °C for a shorter time (6 h), a mixture, in which the ratio of **4aa**:**3aa** is 2.15:1, was obtained (Supporting Information). The result suggests **3aa** could undergo intramolecular cyclization under heating to deliver product **4aa**. Besides, reducing the amount of $[Cp^*IrCl_2]_2$ from 5 mol% to 2.5 mol% or NaOAc from 2 to 1 equivalent both led to incomplete consumption of **1aa**, thus resulting in lower yields of product **3aa** (entries 22 and 23). At last, blank experiments showed that no formation of product **3aa** or **4aa** was observed in the presence of single catalyst or additive but with the recovery of the materials (entries 24 and 25). In this way, the Ir(III)-catalyzed temperature-controlled divergent synthesis of **3aa** and **4aa** through C–H alkenylation/DG migration and [3+2] annulation, respectively, was achieved in a highly regio- and stereoselective manner.

With the optimal reaction conditions identified, the substrate scope of the Ir(III)-catalyzed C–H alkenylation/DG migration cascade was explored (Scheme 2). At first, we examined the scope of indoles using alkyne **2aa** as the reaction partner. Overall, the reactions of a broad range of indoles **1** bearing various substituents at R^1-R^3 with **2aa** underwent smoothly to afford the desired tetrasubstituted alkenes with excellent regio- and stereoselectivity in moderate to high yields. For instance, the reactions of indoles carrying halogens (F, Cl, Br, I) occurred well to give products **3ab**-**3al** in 66-98% yields. Likewise, electron-rich indoles possessing Me, MeO or EtO reacted well to provide products **3am**-**3as** in 80-91% yields. However, the reactions of electron-deficient indoles carrying CN or CO_2Me at C5 position of the indole ring afforded a separable mixture of the C–H alkenylation/DG migration and [3+2] annulation products. This maybe because the hydrogens attached to the indole N1 position of electron-deficient indoles are more acidic, thus the C–H alkenylation/DG migration products tend to undergo further nucleophilic substitution to give some [3+2] annulation products. Indole substrates having substituents at C3 position could also take part in this reaction to yield the corresponding products **3av** and **3aw**, albeit with lower yields. This could be ascribed to the steric hindrance caused by C3 substituents. Pleasingly, indoles possessing various alkyl groups at R^3 could smoothly add to **2aa** to deliver products **3ax**-**3ba** in 32-92% yields. Additionally, this transformation could also be applicable to pyrrole substrates, which reacted with **2aa** successfully to assemble the desired products **3bb** and **3bc** in moderate yields. Subsequently, the

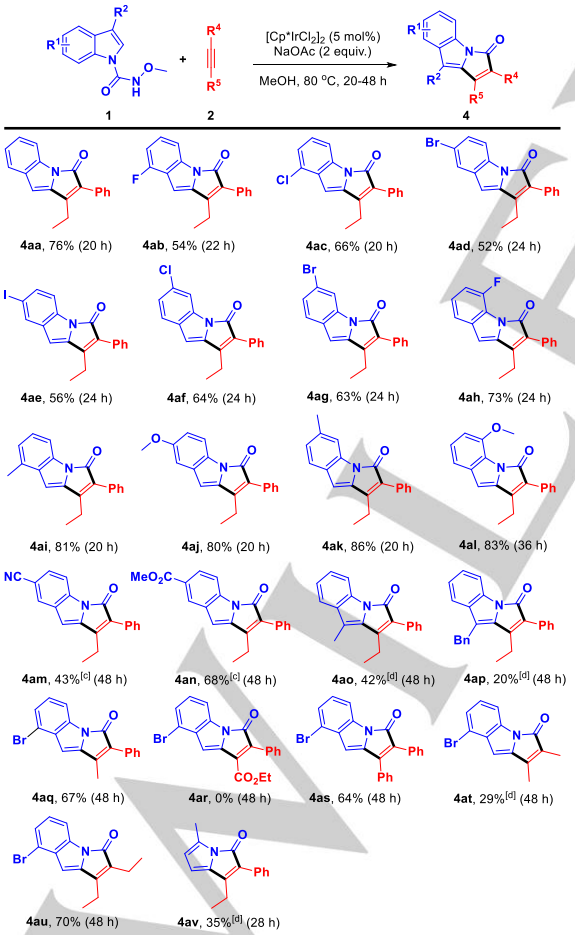


Scheme 2. Substrate scope of Ir(III)-catalyzed C–H alkenylation/DG migration.[a,b] [a] Reaction conditions: **1** (0.25 mmol), **2** (0.275 mmol), $[Cp^*IrCl_2]_2$ (5 mol%), NaOAc (0.5 mmol), MeOH (4.0 mL), 25 °C, 5-48 h. [b] Isolated yield. [c] The ratio was determined by ^1H NMR integration. [d] Combined yield. [e] $[Cp^*IrCl_2]_2$ (10 mol%) and NaOAc (1 mmol) were used. [f] DCE was used as the solvent.

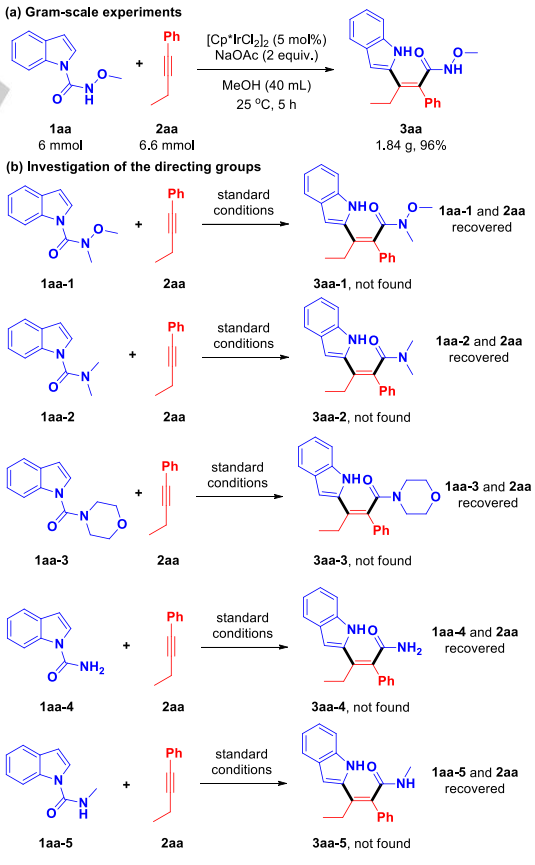
substrate scope of the alkynes was studied with indole **1ad** as the reaction partner. In general, a variety of unsymmetrical and symmetrical alkynes **2** reacted successfully with **1ad** to yield the tetrasubstituted alkenes with excellent regio- and stereoselectivities in good to high yields. For example, the reactions of a series of unsymmetrical alkyl/aryl alkynes with **1ad** took place well to produce the *cis*-adducts **3bd**-**3bh** with exclusive regio- and stereoselectivity in 52-72% yields. Ethyl phenylpropiolate failed to react to give the corresponding product **3bi**. Similarly, various symmetrical dialkylalkynes and diarylalkynes could be converted into the corresponding products **3bj**-**3bp** with excellent *cis*-stereoselectivities in 28-87% yields. Besides, terminal alkynes like phenylacetylene and 1-hexyne failed to react but with the materials untouched. Notably, the indicated products in Scheme 2 were obtained as single isomers in all cases, suggesting the excellent regio- and stereoselectivities of this process.

We then examined the general applicability of the Ir(III)-catalyzed [3+2] annulation (Scheme 3). Generally, a diversity of indoles carrying halogens, electron-donating and electron-withdrawing groups and representative alkyl/aryl alkynes, diarylalkynes and dialkylalkynes were well tolerated, thus providing the desired 3*H*-pyrrolo[1,2-*a*]indol-3-ones with excellent regioselectivity and moderate to high yields, although slightly change of the conditions was occasionally required. For example, indoles having halogens could participate in this [3+2] annulation uneventfully to afford products **4ab**-**4ah** in 52-73% yields. The reactions of indoles bearing electron-donating (Me, MeO) and electron-withdrawing (CN, CO_2Me) groups also appeared to be reactive and produced products **4ai**-**4an** in 43-86% yields. C3-substituted indoles could also undergo this transformation to yield products **4ao** and **4ap**, albeit with lower yields. This may be attributed to the steric hindrance caused by C3 substituents. With respect to the alkynes, representative alkyl/aryl alkynes, diarylalkynes and dialkylalkynes were proved to be suitable coupling partners, which underwent this reaction smoothly to provide products **4aq**-**4au** in 29-70% yields. By contrast, ethyl phenylpropiolate failed to react to give the desired product **4ar**. In addition, pyrrole substrate could also take part in this reaction to deliver the 3*H*-pyrrolizin-3-one **4av**, albeit with a lower yield (35%). Notably, the indicated products in Scheme 3 were obtained as single regioisomers in all cases, indicating the exclusive regiochemical control of this [3+2] annulation.

To further prove the practicality of this protocol, the Ir(III)-catalyzed C–H alkenylation/DG migration between **1aa** and **2aa** was performed on a gram scale under optimal conditions (Scheme 4a). Impressively, the gram-scale reaction provided the desired product **3aa** which was collected by a simple filtration as white solids in a comparable yield (96%) as the small-scale reaction. To confirm the role of the DG, an investigation of different DGs was carried out (Scheme 4b). As a result, none of *N*-methoxy-*N*-methyl-1*H*-indole-1-carboxamide **1aa-1**, *N*,*N*-dimethyl-1*H*-indole-1-carboxamide **1aa-2**, (1*H*-indol-1-yl)(morpholino)methanone **1aa-3**, 1*H*-indole-1-carboxamide **1aa-4** and *N*-methyl-1*H*-indole-1-carboxamide **1aa-5** could react with



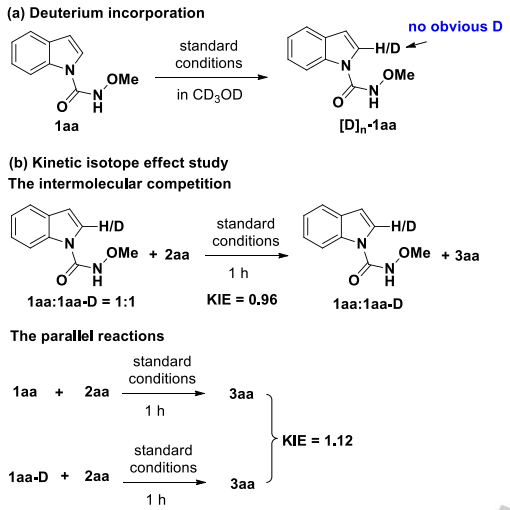
Scheme 3. Substrate scope of Ir(III)-catalyzed [3+2] annulation.[a,b] [a] Reaction conditions: **1** (0.25 mmol), **2** (0.275 mmol), $[Cp^*IrCl_2]_2$ (5 mol%), NaOAc (0.5 mmol), MeOH (4.0 mL), 80 °C, 20-48 h. [b] Isolated yield. [c] The reaction was performed at 40 °C. [d] The reaction was performed at 100 °C.



Scheme 4. Gram-scale experiments and investigation of the directing groups.

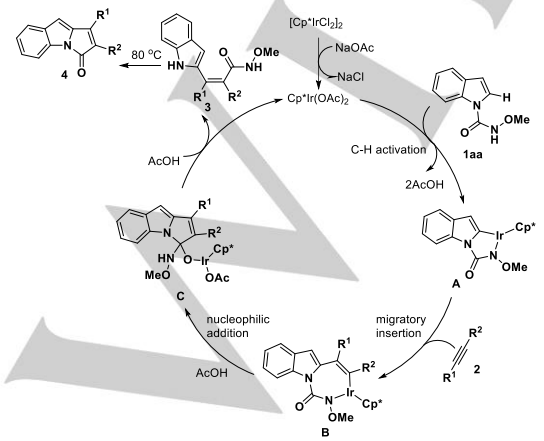
2aa to give the corresponding products but with the starting materials untouched. These results clearly suggest the free hydrogen and alkoxyl groups like OMe attached to the amide nitrogen are both essential for this reaction.

Preliminary isotope labelling experiments were conducted to gain some mechanistic insights. When CD_3OD was used as the solvent under standard conditions, there was no obvious deuteration at the C2 position of the indole (Scheme 5a). This result indicates the step of C–H cleavage could be irreversible. Subsequently, kinetic isotope effect (KIE) experiments led to low KIE values of 0.96 and 1.12 by intermolecular competition and two parallel reactions, respectively (Scheme 5b), suggesting the step of C–H bond cleavage could not be the rate-limiting step.



Scheme 5. Mechanistic studies.

On the basis of the preliminary mechanistic results and known reports,[11a,14-16,19] a possible reaction mechanism is proposed in Scheme 6. Firstly, the active $Cp^*Ir(OAc)_2$ catalyst, which is generated by the ligand exchange of $[Cp^*IrCl_2]_2$ with the additive NaOAc, coordinates with the amide of indole **1aa** and then activates the *ortho*-C–H bond to give a five-membered iridacycle **A**. Subsequently, the regioselective coordination and migratory insertion of alkynes into the Ir−C bond of iridacycle **A** form a seven-membered iridacycle **B**, which undergoes the nucleophilic addition of Ir–C bond to the carbonyl group to give intermediate



Scheme 6. Proposed reaction mechanism.

C. After the cleavage of C−N bond and protonation, it produces tetrasubstituted alkenes **3** and regenerates the catalyst. On the other hand, when increasing the reaction temperature to 80 °C, products **3** undergoes intramolecular cyclization to form the pyrrolo[1,2-*a*]indole derivatives **4**.

Conclusion

In conclusion, we have developed a Ir(III)-catalyzed temperature-controlled divergent synthesis of tetrasubstituted alkenes and pyrrolo[1,2-*a*]indole derivatives through the C–H alkenylation/DG migration and [3+2] annulation, respectively. This protocol features rare Ir(III)-catalyzed DG migration through C–N bond cleavage, excellent regio- and stereoselectivity, broad substrate scope, good functional group tolerance, moderate to excellent yields, mild redox-neutral conditions and operational simplicity. Further bioactivity studies of the tetrasubstituted alkenes and pyrrolo[1,2-*a*]indole derivatives are undergoing in our laboratory, and we anticipate these heterocyclic compounds incorporating the privileged indole motif may find their pharmaceutical applications.

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 Starting Materials

All the indole substrates were prepared according to the literature procedure,[18d,23] and their characterization data were in accordance with the published ones.[18d,23] All the alkynes were 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[24] and the NMR spectral data match published data.[25] **1aa-D** was synthesized from 2-Deuterium indole with 96% D incorporation following the reported method.[23]

General Procedure for Iridium(III)-Catalyzed C–H Alkenylation/Directing Group Migration

To a mixture of indoles **1** (0.25 mmol), $[Cp^*IrCl_2]_2$ (5 mol% or 10 mol%) and NaOAc (0.5 mmol or 1 mmol) in a 25 mL Schlenk tube was added a solution of alkynes **2** (0.275 mmol) in MeOH or DCE (4.0 mL). Then the

tube was capped with septa, and the resulting mixture was stirred at 25 °C for the time indicated (For specific reaction conditions, please see Scheme 2). In most cases, the desired products precipitated out as solids, and the vast majority of the products were simply collected by filtration. The filtrate was subjected to flash chromatography on silica gel to give the rest of the products. If the precipitation did not occur, the reaction mixture was subjected directly to flash chromatography on silica gel to provide the desired products.

(*Z*)-3-(1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3aa): white solid (79.6 mg, yield 99%), mp 195-196 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.22 (s, 1H), 11.00 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.46-7.42 (m, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.11-7.07 (m, 1H), 7.00-6.96 (m, 1H), 6.62 (s, 1H), 3.35 (s, 3H), 2.47 (q, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.96, 137.21, 136.51, 135.78, 135.65, 133.31, 128.50, 128.24, 127.79, 127.63, 121.53, 119.95, 119.12, 111.25, 102.65, 62.22, 24.65, 13.50; HRMS (ESI) *m/z* calculated for $C_{20}H_{21}N_2O_2^+$ [M+H]$^+$ 321.1598, found: 321.1587.

(*Z*)-3-(4-fluoro-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3ab): white solid (82.1 mg, yield 97%), mp 177-178 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.41 (s, 1H), 11.30 (s, 1H), 7.47-7.42 (m, 2H), 7.39-7.31 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.10-7.03 (m, 1H), 6.79-6.74 (m, 1H), 6.66 (s, 1H), 3.36 (s, 3H), 2.46 (q, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.72, 155.32 (d, $J_{C\text{-}F}$ = 244.1 Hz), 139.15 (d, $J_{C\text{-}F}$ = 11.4 Hz), 136.98, 136.29, 135.13, 134.20, 128.53, 128.19, 127.74, 122.00 (d, $J_{C\text{-}F}$ = 7.6 Hz), 116.58 (d, $J_{C\text{-}F}$ = 21.9 Hz), 107.89 (d, $J_{C\text{-}F}$ = 3.1 Hz), 103.60 (d, $J_{C\text{-}F}$ = 18.6 Hz), 97.87, 62.13, 24.70, 13.38; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}FN_2O_2^+$ [M+H]$^+$ 339.1503, found: 339.1497.

(*Z*)-3-(4-chloro-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3ac): white solid (86.8 mg, yield 98%), mp 181-182 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.57 (s, 1H), 11.39 (s, 1H), 7.47-7.42 (m, 2H), 7.39-7.36 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.11-7.03 (m, 2H), 6.69 (s, 1H), 3.37 (s, 3H), 2.46 (q, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.61, 137.22, 137.04, 136.97, 135.02, 134.49, 128.51, 128.18, 127.72, 126.31, 123.96, 122.28, 118.61, 110.44, 100.57, 62.01, 24.67, 13.39; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}ClN_2O_2^+$ [M+H]$^+$ 355.1208, found: 355.1199.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3ad): white solid (96.4 mg, yield 97%), mp 182-183 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.47 (s, 1H), 11.31 (s, 1H), 7.47-7.43 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.36-7.32 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.06-7.01 (m, 1H), 6.65 (s, 1H), 3.40 (s, 3H), 2.46 (q, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.60, 136.98, 136.78, 136.77, 135.01, 134.41, 128.54, 128.20, 128.16, 127.76, 122.71, 121.75, 113.04, 110.88, 102.37, 62.09, 24.58, 13.39; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}BrN_2O_2^+$ [M+H]$^+$ 399.0703, found: 399.0694.

(*Z*)-3-(5-fluoro-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3ae): white solid (75.9 mg, yield 90%), mp 185-186 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.26 (s, 1H), 11.19 (s, 1H), 7.47-7.41 (m, 2H), 7.40-7.31 (m, 4H), 7.27 (dd, *J* = 9.8, 1.9 Hz, 1H), 6.96-6.90 (m, 1H), 6.61 (s, 1H), 3.34 (s, 3H), 2.45 (q, *J* = 7.2 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.75, 157.02 (d, $J_{C\text{-}F}$ = 231.2 Hz), 137.85, 137.12, 135.35, 133.92, 133.19, 128.50, 128.22, 127.97 (d, $J_{C\text{-}F}$ = 10.4 Hz), 127.68, 112.18 (d, $J_{C\text{-}F}$ = 9.9 Hz), 109.64 (d, $J_{C\text{-}F}$ = 26.2 Hz), 104.37 (d, $J_{C\text{-}F}$ = 23.1 Hz), 102.68 (d, $J_{C\text{-}F}$ = 4.8 Hz), 62.19, 24.72, 13.45; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}FN_2O_2^+$ [M+H]$^+$ 339.1503, found: 339.1494.

(*Z*)-3-(5-chloro-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3af): white solid (84.4 mg, yield 95%), mp 180-181 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.32 (s, 2H), 7.56 (d, *J* = 1.8 Hz, 1H), 7.46-7.42 (m, 2H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.08 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.60 (s, 1H), 3.34 (s, 3H), 2.44 (q, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.66, 137.66, 137.06, 135.21, 134.93, 134.19, 128.91, 128.50, 128.21, 127.70, 123.66, 121.40, 119.01, 112.74, 102.19, 62.19, 24.73, 13.41; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}ClN_2O_2^+$ [M+H]$^+$ 355.1208, found: 355.1199.

(*Z*)-3-(5-bromo-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3ag): white solid (90.7 mg, yield 91%), mp 174-175 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.33 (s, 2H), 7.71 (s, 1H), 7.46-7.41 (m, 2H), 7.38-7.30 (m, 4H), 7.19 (dd, *J* = 8.6, 1.5 Hz, 1H), 6.60 (s, 1H), 3.34 (s, 3H), 2.44 (q, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.63, 137.47, 137.04, 135.17, 135.14, 134.22, 129.64, 128.50, 128.20, 127.70, 123.91, 122.05, 113.21, 111.63, 102.07, 62.19, 24.73, 13.39; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}BrN_2O_2^+$ [M+H]$^+$ 399.0703, found: 399.0693.

(*Z*)-3-(5-iodo-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3ah): white solid (96.6 mg, yield 87%), mp 179-180 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.32 (s, 2H), 7.88 (d, *J* = 1.1 Hz, 1H), 7.47-7.41 (m, 2H), 7.38-7.30 (m, 4H), 7.25 (d, *J* = 8.5 Hz, 1H), 6.57 (s, 1H), 3.34 (s, 3H), 2.44 (q, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.63, 137.06, 136.99, 135.49, 135.15, 134.17, 130.57, 129.35, 128.49, 128.25, 128.19, 127.68, 113.72, 101.70, 82.81, 62.20, 24.74, 13.39; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}IN_2O_2^+$ [M+H]$^+$ 447.0564, found: 447.0552.

(*Z*)-3-(6-fluoro-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3ai): white solid (81.5 mg, yield 96%), mp 184-185 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.23 (s, 1H), 11.09 (s, 1H), 7.50 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.47-7.41 (m, 2H), 7.38-7.31 (m, 3H), 7.16-7.11 (m, 1H), 6.87-6.82 (m, 1H), 6.62 (s, 1H), 3.35 (s, 3H), 2.44 (q, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.87, 158.98 (d, $J_{C\text{-}F}$ = 234.8 Hz), 137.10, 136.54 (d, $J_{C\text{-}F}$ = 3.5 Hz), 136.37 (d, $J_{C\text{-}F}$ = 12.7 Hz), 135.35, 133.34, 128.51, 128.22, 127.66, 124.59, 121.04 (d, $J_{C\text{-}F}$ = 10.0 Hz), 107.69 (d, $J_{C\text{-}F}$ = 24.4 Hz), 102.66, 97.13 (d, $J_{C\text{-}F}$ = 25.5 Hz), 62.23, 24.62, 13.46; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}FN_2O_2^+$ [M+H]$^+$ 339.1503, found: 339.1494.

(*Z*)-3-(6-chloro-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3aj): white solid (73.3 mg, yield 83%), mp 173-174 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.25 (s, 1H), 11.16 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.46-7.42 (m, 2H), 7.41 (s, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.35-7.31 (m, 2H), 7.00 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.64 (d, *J* = 1.2 Hz, 1H), 3.34 (s, 3H), 2.45 (q, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.74, 136.99, 136.97, 136.85, 135.25, 133.90, 128.52, 128.20, 127.72, 126.55, 126.08, 121.34, 119.51, 110.77, 102.69, 62.24, 24.68, 13.41; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}ClN_2O_2^+$ [M+H]$^+$ 355.1208, found: 355.1199.

(*Z*)-3-(6-bromo-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3ak): pale yellow solid (66.0 mg, yield 66%), mp 182-183 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.23 (s, 1H), 11.15 (s, 1H), 7.54 (s, 1H), 7.49-7.41 (m, 3H), 7.39-7.35 (m, 1H), 7.35-7.30 (m, 2H), 7.11 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.62 (d, *J* = 1.4 Hz, 1H), 3.33 (s, 3H), 2.44 (q, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 165.70, 137.31, 136.97, 136.85, 135.20, 133.96, 128.52, 128.18, 127.72, 126.77, 122.03, 121.72, 114.10, 113.70, 102.70, 62.23, 24.67, 13.38; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}BrN_2O_2^+$ [M+H]$^+$ 399.0703, found: 399.0692.

(*Z*)-3-(7-fluoro-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3al): white solid (68.4 mg, yield 81%), mp 186-187 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.51 (s, 1H), 11.28 (s, 1H), 7.48-7.42 (m, 2H), 7.39-7.32 (m, 4H), 6.98-6.90 (m, 2H), 6.68 (d, *J* = 3.3 Hz, 1H), 3.34 (s, 3H), 2.55-2.51 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.72, 148.97 (d, $J_{C\text{-}F}$ = 242.9 Hz), 137.38, 137.04, 135.49,

134.41, 131.69 (d, J_{C-F} = 5.9 Hz), 128.49, 128.21, 127.69, 124.27 (d, J_{C-F} = 12.9 Hz), 119.36 (d, J_{C-F} = 6.1 Hz), 116.13 (d, J_{C-F} = 3.2 Hz), 106.29 (d, J_{C-F} = 16.1 Hz), 103.52 (d, J_{C-F} = 1.7 Hz), 62.11, 24.60, 13.30; HRMS (ESI) *m/z* calculated for $C_{20}H_{20}FN_2O_2^+$ $[M+H]^+$ 339.1503, found: 339.1492.

(*Z*)-*N*-methoxy-3-(4-methyl-1*H*-indol-2-yl)-2-phenylpent-2-enamide (3am): white solid (73.6 mg, yield 88%), mp 182-183 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1H), 11.06 (s, 1H), 7.48-7.40 (m, 2H), 7.39-7.30 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.02-6.94 (m, 1H), 6.78 (d, *J* = 7.0 Hz, 1H), 6.66 (s, 1H), 3.38 (s, 3H), 2.49-2.37 (m, 5H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.92, 137.39, 136.17, 135.57, 135.15, 133.21, 128.64, 128.43, 128.22, 127.76, 127.51, 121.57, 119.09, 108.93, 101.18, 61.94, 24.62, 18.49, 13.51; HRMS (ESI) *m/z* calculated for $C_{21}H_{23}N_2O_2^+$ $[M+H]^+$ 335.1754, found: 335.1746.

(*Z*)-*N*-methoxy-3-(4-methoxy-1*H*-indol-2-yl)-2-phenylpent-2-enamide (3an): white solid (69.7 mg, yield 80%), mp 183-184 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 10.98 (s, 1H), 7.48-7.40 (m, 2H), 7.39-7.28 (m, 3H), 7.06-6.94 (m, 2H), 6.66 (s, 1H), 6.53-6.43 (m, 1H), 3.86 (s, 3H), 3.37 (s, 3H), 2.45 (q, *J* = 7.0 Hz, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.97, 152.65, 137.78, 137.30, 135.48, 134.11, 132.84, 128.44, 128.22, 127.52, 122.42, 118.47, 104.63, 100.05, 99.03, 62.12, 54.91, 24.56, 13.48; HRMS (ESI) *m/z* calculated for $C_{21}H_{23}N_2O_3^+$ $[M+H]^+$ 351.1703, found: 351.1693.

(*Z*)-*N*-methoxy-3-(5-methyl-1*H*-indol-2-yl)-2-phenylpent-2-enamide (3ao): white solid (75.1 mg, yield 90%), mp 185-186 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.19 (s, 1H), 10.87 (s, 1H), 7.48-7.39 (m, 2H), 7.38-7.30 (m, 3H), 7.30-7.21 (m, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.53 (s, 1H), 3.36 (s, 3H), 2.44 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.92, 137.30, 135.79, 135.65, 134.87, 133.07, 128.42, 128.22, 128.04, 127.52, 127.49, 123.13, 119.42, 110.93, 102.14, 62.15, 24.62, 21.16, 13.49; HRMS (ESI) *m/z* calculated for $C_{21}H_{23}N_2O_2^+$ $[M+H]^+$ 335.1754, found: 335.1744.

(*Z*)-*N*-methoxy-3-(5-methoxy-1*H*-indol-2-yl)-2-phenylpent-2-enamide (3ap): white solid (75.6 mg, yield 86%), mp 174-175 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.19 (s, 1H), 10.85 (s, 1H), 7.47-7.40 (m, 2H), 7.38-7.30 (m, 3H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.00 (s, 1H), 6.74 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.55 (s, 1H), 3.74 (s, 3H), 3.37 (s, 3H), 2.43 (q, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.93, 153.44, 137.32, 136.32, 135.60, 133.04, 131.68, 128.43, 128.22, 128.15, 127.52, 111.90, 111.87, 102.44, 101.40, 62.19, 55.27, 24.64, 13.52; HRMS (ESI) *m/z* calculated for $C_{21}H_{23}N_2O_3^+$ $[M+H]^+$ 351.1703, found: 351.1694.

(*Z*)-3-(5-ethoxy-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3aq): white solid (76.2 mg, yield 84%), mp 182-183 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.17 (s, 1H), 10.77 (s, 1H), 7.48-7.39 (m, 2H), 7.39-7.30 (m, 3H), 7.27 (d, *J* = 8.7 Hz, 1H), 6.99 (s, 1H), 6.73 (d, *J* = 8.7 Hz, 1H), 6.54 (s, 1H), 4.00 (q, *J* = 6.8 Hz, 2H), 3.37 (s, 3H), 2.43 (q, *J* = 6.9 Hz, 2H), 1.33 (t, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.96, 152.60, 137.26, 136.22, 135.65, 132.94, 131.69, 128.44, 128.21, 128.17, 127.54, 112.35, 111.86, 102.47, 102.38, 63.24, 62.22, 24.61, 14.88, 13.51; HRMS (ESI) *m/z* calculated for $C_{22}H_{25}N_2O_3^+$ $[M+H]^+$ 365.1860, found: 365.1850.

(*Z*)-*N*-methoxy-3-(6-methyl-1*H*-indol-2-yl)-2-phenylpent-2-enamide (3ar): white solid (76.3 mg, yield 91%), mp 184-185 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.19 (s, 1H), 10.79 (s, 1H), 7.46-7.41 (m, 2H), 7.39-7.30 (m, 4H), 7.17 (s, 1H), 6.81 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.56 (d, *J* = 1.4 Hz, 1H), 3.35 (s, 3H), 2.45 (q, *J* = 7.3 Hz, 2H), 2.39 (s, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 166.00, 137.28, 136.95, 135.72, 135.08, 132.80, 130.62, 128.47, 128.24, 127.55, 125.70, 120.92, 119.66, 111.00, 102.56, 62.19, 24.60, 21.51, 13.51; HRMS (ESI) *m/z* calculated for $C_{21}H_{23}N_2O_2^+$ $[M+H]^+$ 335.1754, found: 335.1744.

(*Z*)-*N*-methoxy-3-(7-methoxy-1*H*-indol-2-yl)-2-phenylpent-2-enamide (3as): white solid (74.2 mg, yield 85%), mp 173-174 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.17 (s, 1H), 10.78 (s, 1H), 7.47-7.40 (m, 2H), 7.38-7.30 (m, 3H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.95-6.87 (m, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 6.59 (s, 1H), 3.92 (s, 3H), 3.34 (s, 3H), 2.55-2.49 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.03, 145.88, 137.13, 136.10, 135.68, 133.24, 129.13, 128.43, 128.22, 127.56, 126.64, 119.67, 112.73, 103.36, 102.04, 62.17, 55.08, 24.56, 13.38; HRMS (ESI) *m/z* calculated for $C_{21}H_{23}N_2O_3^+$ $[M+H]^+$ 351.1703, found: 351.1693.

(*Z*)-3-(5-cyano-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3at): pale yellow solid (28.6 mg, yield 33%), mp 174-175 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.61 (s, 1H), 11.24 (s, 1H), 8.08 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.48-7.41 (m, 3H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 7.1 Hz, 2H), 6.73 (s, 1H), 3.32 (s, 3H), 2.48-2.41 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.48, 138.49, 138.12, 136.73, 134.86, 128.53, 128.13, 127.82, 127.50, 125.60, 124.17, 120.67, 112.41, 103.17, 101.21, 62.23, 24.64, 13.25; HRMS (ESI) *m/z* calculated for $C_{21}H_{20}N_3O_2^+$ $[M+H]^+$ 346.1550, found: 346.1541.

(*Z*)-methyl 2-(1-(methoxyamino)-1-oxo-2-phenylpent-2-en-3-yl)-1*H*-indole-5-carboxylate (3au): white solid (65.3 mg, yield 69%), mp 174-175 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.43 (s, 1H), 11.24 (s, 1H), 8.22 (s, 1H), 7.78-7.69 (m, 1H), 7.50-7.42 (m, 3H), 7.40-7.30 (m, 3H), 6.75 (s, 1H), 3.84 (s, 3H), 3.33 (s, 3H), 2.46 (q, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 167.20, 165.63, 139.05, 137.73, 136.91, 135.22, 134.34, 128.55, 128.19, 127.78, 127.34, 122.55, 122.50, 120.68, 111.21, 103.81, 62.23, 51.69, 24.71, 13.38; HRMS (ESI) *m/z* calculated for $C_{22}H_{23}N_2O_4^+$ $[M+H]^+$ 379.1652, found: 379.1645.

(*Z*)-*N*-methoxy-3-(3-methyl-1*H*-indol-2-yl)-2-phenylpent-2-enamide (3av): white solid (25.8 mg, yield 31%), mp 183-184 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (s, 1H), 10.65 (s, 1H), 7.50-7.40 (m, 3H), 7.40-7.29 (m, 4H), 7.10-7.02 (m, 1H), 7.01-6.92 (m, 1H), 3.01 (s, 3H), 2.34 (q, *J* = 6.9 Hz, 2H), 2.21 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.08, 137.17, 136.81, 136.44, 135.93, 133.15, 128.41, 128.36, 127.64, 121.07, 118.16, 118.12, 110.85, 108.78, 62.01, 26.45, 12.71, 9.42; HRMS (ESI) *m/z* calculated for $C_{21}H_{23}N_2O_2^+$ $[M+H]^+$ 335.1754, found: 335.1754.

(*Z*)-3-(3-benzyl-1*H*-indol-2-yl)-*N*-methoxy-2-phenylpent-2-enamide (3aw): white solid (19.2 mg, yield 19%), mp 198-201 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.81 (s, 1H), 10.65 (s, 1H), 7.47-7.43 (m, 2H), 7.38-7.32 (m, 4H), 7.24-7.20 (m, 5H), 7.15-7.11 (m, 1H), 7.06-7.02 (m, 1H), 6.90-6.85 (m, 1H), 4.08 (s, 2H), 3.08 (s, 3H), 2.30 (q, *J* = 7.5 Hz, 2H), 0.68 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.29, 142.03, 137.12, 136.74, 136.57, 136.06, 133.84, 128.50, 128.43, 128.38, 128.03, 127.78, 127.76, 125.52, 121.16, 118.90, 118.40, 112.47, 111.04, 62.26, 30.46, 26.66, 12.67; HRMS (ESI) *m/z* calculated for $C_{27}H_{25}N_2O_2^-$ $[M-H]^-$ 409.1922, found: 409.1921.

(*Z*)-*N*-ethoxy-3-(1*H*-indol-2-yl)-2-phenylpent-2-enamide (3ax): white solid (76.5 mg, yield 92%), mp 166-167 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.11 (s, 1H), 10.96 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.47-7.41 (m, 2H), 7.40-7.33 (m, 4H), 7.11-7.06 (m, 1H), 7.00-6.95 (m, 1H), 6.62 (d, *J* = 1.4 Hz, 1H), 3.59 (q, *J* = 7.0 Hz, 2H), 2.46 (q, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 166.07, 137.30, 136.50, 135.88, 135.45, 133.49, 128.46, 128.23, 127.82, 127.58, 121.48, 119.91, 119.08, 111.22, 102.55, 69.71, 24.67, 13.48, 13.24; HRMS (ESI) *m/z* calculated for $C_{21}H_{23}N_2O_2^+$ $[M+H]^+$ 335.1754, found: 335.1745.

(*Z*)-3-(1*H*-indol-2-yl)-*N*-isopropoxy-2-phenylpent-2-enamide (3ay): pale yelow solid (43.2 mg, yield 50%), mp 142-143 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.99 (s, 1H), 10.94 (s, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.46-7.41 (m, 2H), 7.41-7.31 (m, 4H), 7.11-7.05 (m, 1H), 7.01-6.94 (m, 1H), 6.61 (d, *J* = 1.4 Hz, 1H), 3.89-3.78 (m, 1H), 2.46 (q, *J* = 7.4 Hz, 2H),

0.90 (t, *J* = 7.4 Hz, 3H), 0.84 (d, *J* = 6.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 166.20, 137.39, 136.50, 135.97, 135.26, 133.72, 128.41, 128.24, 127.86, 127.55, 121.42, 119.88, 119.05, 111.19, 102.50, 75.64, 24.70, 20.36, 13.46; HRMS (ESI) *m/z* calculated for $C_{22}H_{25}N_2O_2^+$ $[M+H]^+$ 349.1911, found: 349.1903.

(*Z*)-*N*-(*tert*-butoxy)-3-(1*H*-indol-2-yl)-2-phenylpent-2-enamide (3az): white solid (28.9 mg, yield 32%), mp 124-125 °C. ^1H NMR (600 MHz, DMSO-d_6) δ 10.95 (s, 1H), 10.55 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.46-7.42 (m, 2H), 7.40-7.32 (m, 4H), 7.10-7.05 (m, 1H), 7.00-6.95 (m, 1H), 6.60 (s, 1H), 2.43 (q, *J* = 7.2 Hz, 2H), 0.96 (s, 9H), 0.89 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 167.64, 137.72, 136.47, 136.02, 134.71, 134.00, 128.36, 128.25, 127.89, 127.50, 121.38, 119.90, 119.03, 111.22, 102.54, 81.02, 26.40, 24.78, 13.49; HRMS (ESI) *m/z* calculated for $C_{23}H_{27}N_2O_2^+$ $[M+H]^+$ 363.2067, found: 363.2058.

(*Z*)-*N*-(benzyloxy)-3-(1*H*-indol-2-yl)-2-phenylpent-2-enamide (3ba): white solid (50.7 mg, yield 51%), mp 120-121 °C. ^1H NMR (600 MHz, DMSO-d_6) δ 11.25 (s, 1H), 11.00 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.45-7.39 (m, 3H), 7.38-7.34 (m, 1H), 7.34-7.29 (m, 2H), 7.28-7.24 (m, 1H), 7.23-7.18 (m, 2H), 7.12-7.08 (m, 1H), 7.06 (d, *J* = 7.1 Hz, 2H), 7.01-6.96 (m, 1H), 6.66 (d, *J* = 1.4 Hz, 1H), 4.56 (s, 2H), 2.46 (q, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 166.31, 137.16, 136.56, 135.93, 135.81, 135.56, 133.36, 128.76, 128.42, 128.32, 128.09, 127.86, 127.58, 121.52, 119.99, 119.13, 111.25, 102.69, 76.07, 24.65, 13.46; HRMS (ESI) *m/z* calculated for $C_{26}H_{25}N_2O_2^+$ $[M+H]^+$ 397.1911, found: 397.1902.

(*Z*)-*N*-methoxy-2-phenyl-3-(1*H*-pyrrol-2-yl)pent-2-enamide (3bb): white solid (27.0 mg, yield 40%), mp 156-158 °C. ^1H NMR (600 MHz, DMSO-d_6) δ 11.16 (s, 1H), 10.69 (s, 1H), 7.41-7.37 (m, 2H), 7.32-7.29 (m, 1H), 7.28 (d, *J* = 7.5 Hz, 2H), 6.81 (s, 1H), 6.35-6.29 (m, 1H), 6.08-6.02 (m, 1H), 3.45 (s, 3H), 2.33 (q, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 166.59, 137.87, 135.27, 129.05, 128.77, 128.37, 128.35, 127.18, 119.07, 109.54, 108.25, 62.28, 24.29, 13.89; HRMS (ESI) *m/z* calculated for $C_{16}H_{17}N_2O_2^-$ $[M-H]^-$ 269.1296, found: 269.1296.

(*Z*)-*N*-methoxy-3-(5-methyl-1*H*-pyrrol-2-yl)-2-phenylpent-2-enamide (3bc): pale yellow solid (31.8 mg, yield 45%), mp 165-166 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 11.08 (s, 1H), 10.35 (s, 1H), 7.42-7.34 (m, 2H), 7.32-7.21 (m, 3H), 6.23-6.14 (m, 1H), 5.74 (s, 1H), 3.47 (s, 3H), 2.31 (q, *J* = 7.1 Hz, 2H), 2.20 (s, 3H), 0.89 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 166.86, 138.08, 135.38, 128.55, 128.41, 128.27, 127.78, 127.48, 127.01, 109.93, 106.64, 62.18, 24.09, 13.99, 12.83; HRMS (ESI) *m/z* calculated for $C_{17}H_{21}N_2O_2^+$ $[M+H]^+$ 285.1598, found: 285.1595.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-*N*-methoxy-2-phenylbut-2-enamide (3bd): pale yellow solid (69.3 mg, yield 72%), mp 172-173 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 11.46 (s, 1H), 11.34 (s, 1H), 7.48-7.40 (m, 3H), 7.39-7.32 (m, 3H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.07-7.00 (m, 1H), 6.69 (d, *J* = 1.8 Hz, 1H), 3.47 (s, 3H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 165.78, 138.07, 137.00, 136.66, 134.34, 128.60, 128.56, 128.44, 128.15, 127.71, 122.81, 121.88, 113.16, 110.91, 101.42, 62.12, 18.62; HRMS (ESI) *m/z* calculated for $C_{19}H_{18}BrN_2O_2^+$ $[M+H]^+$ 385.0546, found: 385.0538.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-*N*-methoxy-2-phenylhex-2-enamide (3be): pale yellow solid (69.0 mg, yield 67%), mp 175-176 °C. ^1H NMR (600 MHz, DMSO-d_6) δ 11.53 (s, 1H), 11.31 (s, 1H), 7.47-7.42 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.38-7.35 (m, 1H), 7.35-7.30 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.05-6.99 (m, 1H), 6.62 (s, 1H), 3.37 (s, 3H), 2.45-2.34 (m, 2H), 1.33-1.21 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 165.53, 137.08, 137.03, 136.71, 135.13, 133.63, 128.44, 128.27, 128.16, 127.68, 122.61, 121.70, 113.00, 110.85, 102.03, 62.05, 33.05, 21.52, 13.64; HRMS (ESI) *m/z* calculated for $C_{21}H_{22}BrN_2O_2^+$ $[M+H]^+$ 413.0859, found: 413.0851.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-*N*-methoxy-2-phenylhept-2-enamide (3bf): pale yellow solid (69.7 mg, yield 65%), mp 180-181 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 11.43 (s, 1H), 11.26 (s, 1H), 7.47-7.42 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.38-7.35 (m, 1H), 7.35-7.30 (m, 2H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.06-6.99 (m, 1H), 6.63 (d, *J* = 1.6 Hz, 1H), 3.38 (s, 3H), 2.48-2.39 (m, 2H), 1.27-1.20 (m, 2H), 1.20-1.12 (m, 2H), 0.70 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 165.55, 137.06, 136.92, 136.71, 134.86, 133.89, 128.43, 128.26, 128.16, 127.72, 122.64, 121.72, 113.02, 110.86, 102.11, 62.10, 30.82, 30.47, 21.81, 13.59; HRMS (ESI) *m/z* calculated for $C_{22}H_{24}BrN_2O_2^+$ $[M+H]^+$ 427.1016, found: 427.1007.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-*N*-methoxy-2-phenyloct-2-enamide (3bg): pale yellow solid (57.1 mg, yield 52%), mp 154-155 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 11.49 (s, 1H), 11.29 (s, 1H), 7.47-7.42 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.38-7.35 (m, 1H), 7.35-7.31 (m, 2H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.06-6.99 (m, 1H), 6.62 (s, 1H), 3.37 (s, 3H), 2.48-2.37 (m, 2H), 1.30-1.19 (m, 2H), 1.18-1.03 (m, 4H), 0.73 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 165.52, 137.11, 137.00, 136.71, 134.92, 133.87, 128.41, 128.24, 128.16, 127.69, 122.61, 121.70, 113.00, 110.86, 102.06, 62.05, 31.01, 30.83, 27.87, 21.60, 13.73; HRMS (ESI) *m/z* calculated for $C_{23}H_{26}BrN_2O_2^+$ $[M+H]^+$ 441.1172, found: 441.1161.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-*N*-methoxy-2-phenylnon-2-enamide (3bh): pale yellow solid (63.3 mg, yield 56%), mp 156-157 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 11.45 (s, 1H), 11.26 (s, 1H), 7.48-7.42 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.39-7.36 (m, 1H), 7.36-7.30 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.06-7.01 (m, 1H), 6.62 (s, 1H), 3.37 (s, 3H), 2.46-2.39 (m, 2H), 1.30-1.21 (m, 2H), 1.20-1.10 (m, 4H), 1.09-1.01 (m, 2H), 0.76 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 165.54, 137.10, 137.00, 136.72, 134.91, 133.87, 128.40, 128.26, 128.16, 127.69, 122.61, 121.70, 113.01, 110.86, 102.08, 62.06, 31.02, 30.70, 28.25, 28.13, 21.89, 13.80; HRMS (ESI) *m/z* calculated for $C_{24}H_{28}BrN_2O_2^+$ $[M+H]^+$ 455.1329, found: 455.1320.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-*N*-methoxy-2-methylbut-2-enamide (3bj): light yellow solid (22.9 mg, yield 28%), mp 134-136 °C. ^1H NMR (600 MHz, DMSO-d_6) δ 11.29 (s, 1H), 10.97 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.00-6.97 (m, 1H), 6.43 (s, 1H), 3.43 (s, 3H), 2.09 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.84, 138.71, 136.43, 129.53, 128.13, 126.58, 122.37, 121.67, 112.92, 110.76, 100.55, 62.07, 17.44, 17.41; HRMS (ESI) *m/z* calculated for $C_{14}H_{14}BrN_2O_2^-$ $[M-H]^-$ 321.0244, found: 321.0242.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-2-ethyl-*N*-methoxypent-2-enamide (3bk): white solid (63.5 mg, yield 72%), mp 158-159 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 11.21 (s, 1H), 10.83 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.16 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.01-6.94 (m, 1H), 6.42 (d, *J* = 1.7 Hz, 1H), 3.36 (s, 3H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.34 (q, *J* = 7.5 Hz, 2H), 1.03 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 166.85, 137.69, 136.54, 135.29, 132.53, 128.15, 122.26, 121.55, 112.81, 110.72, 101.58, 62.01, 23.70, 23.42, 13.17, 12.89; HRMS (ESI) *m/z* calculated for $C_{16}H_{20}BrN_2O_2^+$ $[M+H]^+$ 351.0703, found: 351.0693.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-*N*-methoxy-2-propylhex-2-enamide (3bl): pale yellow solid (63.8 mg, yield 67%), mp 165-166 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 11.20 (s, 1H), 10.77 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.99-6.92 (m, 1H), 6.37 (d, *J* = 1.7 Hz, 1H), 3.31 (s, 3H), 2.50-2.47 (m, 2H), 2.35-2.25 (m, 2H), 1.47-1.36 (m, 2H), 1.27-1.22 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.83 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 166.87, 138.00, 136.48, 134.91, 131.73, 128.10, 122.19, 121.50, 112.77, 110.69, 101.38, 61.95, 32.38, 32.24, 21.24, 21.02, 13.75, 13.50; HRMS (ESI) *m/z* calculated for $C_{18}H_{24}BrN_2O_2^+$ $[M+H]^+$ 379.1016, found: 379.1007.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-2-butyl-*N*-methoxyhept-2-enamide (3bm): white solid (71.6 mg, yield 70%), mp 143-144 °C. ^1H NMR (600 MHz, DMSO-d_6) δ 11.23 (s, 1H), 10.80 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.01-6.93 (m, 1H), 6.38 (d, *J* = 1.7 Hz, 1H), 3.32

(s, 3H), 2.54-2.50 (m, 2H), 2.36-2.27 (m, 2H), 1.42-1.32 (m, 4H), 1.31-1.25 (m, 2H), 1.24-1.18 (m, 2H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-*d*$_6$) δ 166.87, 138.05, 136.49, 134.79, 131.74, 128.12, 122.19, 121.50, 112.78, 110.71, 101.38, 61.95, 30.34, 30.32, 29.99, 29.96, 21.95, 21.86, 13.88, 13.82; HRMS (ESI) *m/z* calculated for $C_{20}H_{28}BrN_2O_2^+$ $[M+H]^+$ 407.1329, found: 407.1318.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-*N*-methoxy-2,3-diphenylacrylamide (3bn): pale yellow solid (78.1 mg, yield 70%), mp 190-191 °C. ^1H NMR (600 MHz, DMSO-*d*$_6$) δ 11.61 (s, 1H), 10.89 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.27-7.22 (m, 3H), 7.22-7.14 (m, 4H), 7.10-7.03 (m, 4H), 7.02-6.98 (m, 1H), 6.73 (d, *J* = 2.0 Hz, 1H), 3.46 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-*d*$_6$) δ 165.69, 138.16, 137.80, 137.11, 136.95, 135.28, 134.08, 130.48, 129.06, 128.18, 128.12, 127.99, 127.94, 127.38, 122.96, 121.83, 113.12, 111.26, 103.38, 62.23; HRMS (ESI) *m/z* calculated for $C_{24}H_{20}BrN_2O_2^+$ $[M+H]^+$ 447.0703, found: 447.0694.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-2,3-bis(4-fluorophenyl)-*N*-methoxyacrylamide (3bo): white solid (76.9 mg, yield 64%), mp 173-174 °C. ^1H NMR (600 MHz, DMSO-*d*$_6$) δ 11.63 (s, 1H), 10.90 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.16-7.04 (m, 8H), 7.03-6.99 (m, 1H), 6.76 (d, *J* = 1.7 Hz, 1H), 3.48 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-*d*$_6$) δ 165.49, 161.77 (d, $J_{C\text{-}F}$ = 245.5 Hz), 161.19 (d, $J_{C\text{-}F}$ = 245.6 Hz), 137.40, 137.11, 134.30 (d, $J_{C\text{-}F}$ = 2.7 Hz), 134.19, 133.38, 133.26 (d, $J_{C\text{-}F}$ = 2.9 Hz), 132.69 (d, $J_{C\text{-}F}$ = 8.4 Hz), 131.20 (d, $J_{C\text{-}F}$ = 8.3 Hz), 127.95, 123.13, 121.92, 115.37 (d, $J_{C\text{-}F}$ = 6.3 Hz), 115.23 (d, $J_{C\text{-}F}$ = 6.3 Hz), 113.19, 111.24, 103.47, 62.25; HRMS (ESI) *m/z* calculated for $C_{24}H_{18}BrF_2N_2O_2^+$ $[M+H]^+$ 483.0514, found: 483.0507.

(*Z*)-3-(4-bromo-1*H*-indol-2-yl)-*N*-methoxy-2,3-di-*p*-tolylacrylamide (3bp): yellow solid (103.1 mg, yield 87%), mp 132-133 °C. ^1H NMR (600 MHz, DMSO-*d*$_6$) δ 11.52 (s, 1H), 10.82 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 2H), 7.03-6.97 (m, 3H), 6.97-6.87 (m, 4H), 6.71 (d, *J* = 1.0 Hz, 1H), 3.44 (s, 3H), 2.27 (s, 3H), 2.22 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-*d*$_6$) δ 165.96, 138.16, 137.20, 137.04, 136.65, 135.42, 134.81, 134.20, 133.41, 130.44, 128.97, 128.85, 128.76, 127.95, 122.83, 121.75, 113.06, 111.21, 103.26, 62.16, 20.83, 20.74; HRMS (ESI) *m/z* calculated for $C_{26}H_{24}BrN_2O_2^+$ $[M+H]^+$ 475.1016, found: 475.1008.

General Procedure for Iridium(III)-Catalyzed [3+2] Annulation

To a mixture of indoles **1** (0.25 mmol), $[Cp^*IrCl_2]_2$ (5 mol%) and NaOAc (0.5 mmol) in a 25 mL Schlenk tube was added a solution of alkynes **2** (0.275 mmol) in MeOH (4.0 mL). Then the tube was capped with septa, and the resulting mixture was stirred at the temperature for the time indicated (For specific reaction conditions, please see Scheme 3). Then the reaction mixture was subjected directly to flash chromatography on silica gel to provide the desired products.

1-ethyl-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4aa): orange red solid (51.6 mg, yield 76%), mp 90-91 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.52-7.48 (m, 2H), 7.47-7.43 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.39-7.35 (m, 1H), 7.29-7.26 (m, 1H), 7.12-7.07 (m, 1H), 6.48 (s, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.35 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 164.85, 146.34, 141.85, 134.43, 134.13, 133.09, 130.89, 129.20, 128.55, 128.35, 127.21, 123.23, 122.57, 112.52, 106.41, 20.21, 13.98; HRMS (ESI) *m/z* calculated for $C_{19}H_{16}NO^+$ $[M+H]^+$ 274.1226, found: 274.1219.

1-ethyl-8-fluoro-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4ab): yellow solid (39.1 mg, yield 54%), mp 124-125 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.50-7.47 (m, 2H), 7.47-7.43 (m, 2H), 7.41-7.35 (m, 1H), 7.24-7.18 (m, 1H), 6.83-6.77 (m, 1H), 6.58 (s, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.35 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 164.84, 156.65 (d, $J_{C\text{-}F}$ = 250.7 Hz), 146.45, 141.66, 136.07 (d, $J_{C\text{-}F}$ = 9.1 Hz), 133.43, 130.63, 129.19, 128.61, 128.55, 128.42 (d, $J_{C\text{-}F}$ = 7.7 Hz), 122.26 (d, $J_{C\text{-}F}$ = 20.8 Hz), 109.29 (d, $J_{C\text{-}F}$ = 19.2 Hz), 108.68 (d, $J_{C\text{-}F}$ = 3.7 Hz), 101.79, 20.21, 13.90; HRMS (ESI) *m/z* calculated for $C_{19}H_{15}FNO^+$ $[M+H]^+$ 292.1132, found: 292.1128.

8-chloro-1-ethyl-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4ac): yellow solid (50.9 mg, yield 66%), mp 130-131 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.53-7.42 (m, 4H), 7.42-7.35 (m, 1H), 7.21-7.14 (m, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.59 (s, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 164.75, 146.52, 142.09, 134.97, 133.34, 132.75, 130.58, 129.19, 128.62, 128.58, 127.96, 127.55, 123.20, 110.92, 104.16, 20.23, 13.92; HRMS (ESI) *m/z* calculated for $C_{19}H_{15}ClNO^+$ $[M+H]^+$ 308.0837, found: 308.0829.

7-bromo-1-ethyl-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4ad): orange red solid (45.4 mg, yield 52%), mp 120-121 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.56-7.52 (m, 1H), 7.50-7.43 (m, 4H), 7.41-7.35 (m, 2H), 6.41 (s, 1H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 164.61, 146.30, 142.86, 135.82, 133.50, 133.01, 130.57, 129.77, 129.19, 128.62, 128.59, 125.22, 116.12, 113.65, 105.20, 20.22, 13.90; HRMS (ESI) *m/z* calculated for $C_{19}H_{15}BrNO^+$ $[M+H]^+$ 352.0332, found: 352.0326.

1-ethyl-7-iodo-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4ae): orange red solid (56.2 mg, yield 56%), mp 119-120 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 1.2 Hz, 1H), 7.55 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.52-7.42 (m, 5H), 7.40-7.36 (m, 1H), 6.39 (s, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 164.63, 146.24, 142.48, 136.34, 135.50, 133.51, 131.23, 130.57, 129.19, 128.62, 128.58, 114.17, 104.97, 86.48, 20.23, 13.90; HRMS (ESI) *m/z* calculated for $C_{19}H_{15}INO^+$ $[M+H]^+$ 400.0193, found: 400.0194.

6-chloro-1-ethyl-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4af): yellow solid (49.1 mg, yield 64%), mp 136-137 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.8 Hz, 1H), 7.50-7.43 (m, 4H), 7.40-7.36 (m, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.06 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.44 (s, 1H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.34 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 164.58, 146.59, 142.22, 134.66, 133.17, 133.16, 132.61, 130.63, 129.18, 128.61, 128.53, 123.63, 123.10, 112.91, 105.83, 20.24, 13.91; HRMS (ESI) *m/z* calculated for $C_{19}H_{15}ClNO^+$ $[M+H]^+$ 308.0837, found: 308.0832.

6-bromo-1-ethyl-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4ag): yellow solid (55.1 mg, yield 63%), mp 149-150 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 0.5 Hz, 1H), 7.50-7.42 (m, 4H), 7.41-7.34 (m, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.21 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.43 (s, 1H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.34 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 164.57, 146.58, 142.09, 134.86, 133.23, 132.99, 130.63, 129.18, 128.62, 128.54, 126.40, 123.45, 120.98, 115.75, 105.86, 20.25, 13.91; HRMS (ESI) *m/z* calculated for $C_{19}H_{15}BrNO^+$ $[M+H]^+$ 352.0332, found: 352.0323.

1-ethyl-5-fluoro-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4ah): yellow solid (53.3 mg, yield 73%), mp 136-137 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.3 Hz, 2H), 7.47-7.42 (m, 2H), 7.40-7.36 (m, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.07-6.99 (m, 2H), 6.51 (d, *J* = 1.9 Hz, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.35 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 163.15, 149.53 (d, $J_{C\text{-}F}$ = 251.4 Hz), 146.08, 142.97, 137.52 (d, $J_{C\text{-}F}$ = 5.3 Hz), 132.94, 130.72, 129.31, 128.53, 128.52, 124.06 (d, $J_{C\text{-}F}$ = 6.0 Hz), 121.64 (d, $J_{C\text{-}F}$ = 14.0 Hz), 118.12 (d, $J_{C\text{-}F}$ = 3.5 Hz), 113.86 (d, $J_{C\text{-}F}$ = 18.4 Hz), 105.87 (d, $J_{C\text{-}F}$ = 1.8 Hz), 20.15, 13.92; HRMS (ESI) *m/z* calculated for $C_{19}H_{15}FNO^+$ $[M+H]^+$ 292.1132, found: 292.1123.

1-ethyl-8-methyl-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4ai): orange red solid (58.3 mg, yield 81%), mp 140-141 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.53-7.48 (m, 2H), 7.48-7.42 (m, 2H), 7.40-7.34 (m, 1H), 7.20-7.14 (m, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.52 (s, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 2.47 (s, 3H), 1.36 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 164.97, 146.31, 141.27, 134.25, 133.64, 132.77, 132.30, 130.98, 129.19, 128.53, 128.28, 127.30, 124.02, 110.09, 105.01, 20.21, 18.57, 14.06; HRMS (ESI) *m/z* calculated for $C_{20}H_{18}NO^+$ $[M+H]^+$ 288.1383, found: 288.1375.

1-ethyl-7-methoxy-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4aj): red solid (60.8 mg, yield 80%), mp 117-118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.6 Hz, 1H), 7.51-7.47 (m, 2H), 7.47-7.42 (m, 2H), 7.39-7.34 (m, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.40 (s, 1H), 3.82 (s, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 164.61, 156.28, 146.04, 142.75, 135.04, 132.96, 130.94, 129.18, 128.53, 128.31, 114.39, 112.88, 106.73, 106.23, 55.91, 20.16, 13.98; HRMS (ESI) *m/z* calculated for $C_{20}H_{18}NO_2^+$ $[M+H]^+$ 304.1332, found: 304.1323.

1-ethyl-6-methyl-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4ak): red solid (61.6 mg, yield 86%), mp 107-108 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.52-7.48 (m, 2H), 7.47-7.42 (m, 2H), 7.39-7.34 (m, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.43 (s, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.34 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 164.92, 146.42, 141.26, 137.89, 134.83, 132.65, 131.76, 131.03, 129.19, 128.52, 128.24, 124.44, 122.16, 113.05, 106.58, 21.98, 20.22, 14.01; HRMS (ESI) *m/z* calculated for $C_{20}H_{18}NO^+$ $[M+H]^+$ 288.1383, found: 288.1379.

1-ethyl-5-methoxy-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4al): orange red solid (62.8 mg, yield 83%), mp 108-109 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.46-7.41 (m, 2H), 7.397.33 (m, 1H), 7.08-7.01 (m, 2H), 6.84 (dd, *J* = 7.4, 1.1 Hz, 1H), 6.47 (s, 1H), 3.98 (s, 3H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.34 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 163.48, 147.29, 145.71, 142.90, 136.18, 132.67, 131.10, 129.34, 128.42, 128.24, 124.73, 124.23, 115.21, 110.39, 106.10, 56.77, 20.03, 14.00; HRMS (ESI) *m/z* calculated for $C_{20}H_{18}NO_2^+$ $[M+H]^+$ 304.1332, found: 304.1324.

1-ethyl-3-oxo-2-phenyl-3*H*-pyrrolo[1,2-*a*]indole-7-carbonitrile (4am): yellow solid (32.4 mg, yield 43%), mp 137-138 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.05 (s, 1H), 7.72 (s, 2H), 7.54-7.41 (m, 5H), 6.99 (s, 1H), 2.70 (q, *J* = 7.4 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 163.76, 147.18, 142.75, 135.31, 134.11, 132.79, 130.81, 129.84, 128.98, 128.59, 128.45, 127.27, 119.20, 112.26, 106.29, 105.43, 19.63, 13.18; HRMS (ESI) *m/z* calculated for $C_{20}H_{15}N_2O^+$ $[M+H]^+$ 299.1179, found: 299.1178.

methyl 1-ethyl-3-oxo-2-phenyl-3*H*-pyrrolo[1,2-*a*]indole-7-carboxylate (4an): yellow solid (56.6 mg, yield 68%), mp 154-155 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.00 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.51-7.42 (m, 4H), 7.42-7.36 (m, 1H), 6.53 (s, 1H), 3.92 (s, 3H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.35 (t, *J* = 7.7 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 167.20, 164.64, 146.80, 142.76, 136.93, 134.03, 133.54, 130.51, 129.19, 128.93, 128.63, 125.22, 124.53, 111.96, 106.29, 52.24, 20.27, 13.90; HRMS (ESI) *m/z* calculated for $C_{21}H_{18}NO_3^+$ $[M+H]^+$ 332.1281, found: 332.1273.

1-ethyl-9-methyl-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4ao): orange solid (30.1 mg, yield 42%), mp 85-86 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.50-7.47 (m, 2H), 7.47-7.43 (m, 2H), 7.39-7.34 (m, 2H), 7.30-7.26 (m, 1H), 7.12-7.09 (m, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.37 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.50, 146.89, 137.34, 135.48, 134.30, 132.82, 131.10, 129.18, 128.53, 128.15, 127.50, 122.89, 120.45, 117.81, 112.33, 19.85, 14.13, 9.81; HRMS (ESI) *m/z* calculated for $C_{20}H_{18}NO^+$ $[M+H]^+$ 288.1383, found: 288.1381.

9-benzyl-1-ethyl-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4ap): orange viscous oil (18.6 mg, yield 20%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.48-7.43 (m, 2H), 7.39-7.36 (m, 1H), 7.32-7.27 (m, 4H), 7.26-7.21 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.02-6.98 (m, 1H), 4.18 (s, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.60, 146.81, 138.69, 138.17, 134.77, 134.56, 133.49, 130.97, 129.21, 128.87, 128.58, 128.35, 128.31, 127.50, 126.77, 123.04, 121.42, 120.14, 112.43, 30.70, 19.91, 14.40; HRMS (ESI) *m/z* calculated for $C_{26}H_{22}NO^+$ $[M+H]^+$ 364.1696, found: 364.1692.

8-bromo-1-methyl-2-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4aq): orange red solid (56.3 mg, yield 67%), mp 123-124 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.49-7.43 (m, 2H), 7.41-7.35 (m, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.14-7.09 (m, 1H), 6.52 (s, 1H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 164.68, 143.31, 140.38, 134.90, 134.70, 133.74, 130.61, 129.20, 128.60, 128.52, 128.17, 126.21, 116.14, 111.41, 105.27, 12.36; HRMS (ESI) *m/z* calculated for $C_{18}H_{13}BrNO^+$ $[M+H]^+$ 338.0175, found: 338.0173.

8-bromo-1,2-diphenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4as): orange red solid (64.2 mg, yield 64%), mp 176-177 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.50-7.47 (m, 2H), 7.46-7.39 (m, 5H), 7.36-7.32 (m, 3H), 7.28-7.26 (m, 1H), 7.18-7.12 (m, 1H), 6.58 (d, *J* = 0.6 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 164.61, 141.99, 141.75, 135.01, 134.51, 132.21, 131.22, 130.34, 130.09, 129.69, 129.09, 128.79, 128.66, 128.54, 128.38, 126.50, 116.30, 111.61, 107.66; HRMS (ESI) *m/z* calculated for $C_{23}H_{15}BrNO^+$ $[M+H]^+$ 400.0332, found: 400.0325.

8-bromo-1,2-dimethyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4at): yellow solid (20.1 mg, yield 29%), mp 138-140 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.09-7.04 (m, 1H), 6.35 (s, 1H), 2.07 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.11, 143.77, 140.28, 134.92, 134.67, 131.89, 127.65, 125.86, 115.97, 111.09, 103.77, 11.04, 8.81; HRMS (ESI) *m/z* calculated for $C_{13}H_{11}BrNO^+$ $[M+H]^+$ 276.0019, found: 276.0018.

8-bromo-1,2-diethyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (4au): yellow solid (53.5 mg, yield 70%), mp 87-88 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.09-7.04 (m, 1H), 6.38 (s, 1H), 2.51 (q, *J* = 7.7 Hz, 2H), 2.33 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.7 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.94, 145.79, 142.63, 136.77, 134.78, 134.69, 127.65, 125.88, 115.89, 111.10, 104.39, 19.44, 17.21, 13.86, 13.81; HRMS (ESI) *m/z* calculated for $C_{15}H_{15}BrNO^+$ $[M+H]^+$ 304.0332, found: 304.0331.

1-ethyl-5-methyl-2-phenyl-3*H*-pyrrolizin-3-one (4av): red oil (20.9 mg, yield 35%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.38 (m, 4H), 7.33-7.29 (m, 1H), 6.01 (d, *J* = 3.0 Hz, 1H), 5.73 (dd, *J* = 2.9, 1.2 Hz, 1H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.43, 149.60, 136.34, 133.40, 131.34, 129.08, 128.45, 127.65, 127.21, 113.01, 110.35, 20.39, 13.74, 12.52; HRMS (ESI) *m/z* calculated for $C_{16}H_{16}NO^+$ $[M+H]^+$ 238.1226, found: 238.1223.

Gram-scale preparation of compound 3aa

To a mixture of indole **1aa** (6 mmol), $[Cp^*IrCl_2]_2$ (5 mol%) and NaOAc (12 mmol) in a 100 mL flask was added a solution of **2aa** (6.6 mmol) in MeOH (40.0 mL). Then the flask was capped with septa, and the resulting mixture was stirred at 25 °C for 5 h. After that, the vast majority of the product precipitated out was simply collected by filtration. The filtrate was subjected to flash chromatography on silica gel to give the rest of the product. The combined product was obtained as white solids (1.84 g, yield 96%).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Iridium • C-H activation • [3+2] annulation • Tetrasubstituted alkene • pyrrolo[1,2-*a*]indole

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[22] In Ir(III)-catalyzed C–H functionalization, a silver salt is commonly combined with a Ir(III) catalyst such as $[Cp^*IrCl_2]_2$ to help to generate an active cationic iridium species *in situ*. For examples, see references 10 and 11.

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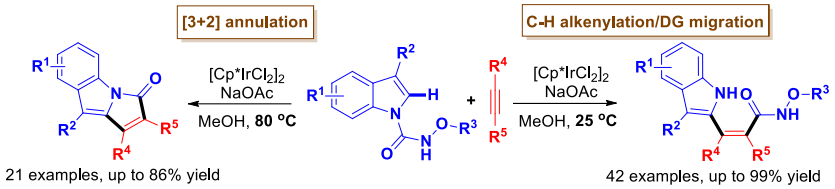

We report a Ir(III)-catalyzed temperature-controlled divergent synthesis of tetrasubstituted alkenes and pyrrolo[1,2-*a*]indole derivatives through C–H alkenylation/DG migration and [3+2] annulation, respectively. This protocol is characterized by excellent regio- and stereoselectivity, broad substrate scope, good functional group tolerance, moderate to excellent yields, mild redox-neutral reaction conditions and operational simplicity.

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