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Visible-Light-Catalyzed Cascade Radical Cyclization of N-propargylindoles with Acyl Chlorides for the Synthesis of 2-Acyl-*9H*-pyrrolo[1,2-*a*]indoles

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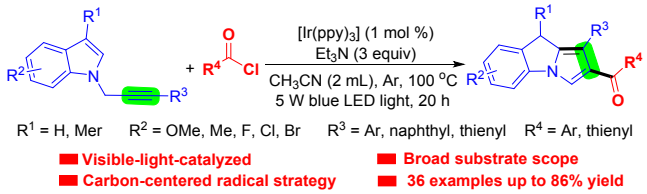
Abstract



A novel and convenient visible-light-catalyzed tandem radical cyclization of *N*-propargylindoles with acyl chlorides for accessing 2-acyl-*9H*-pyrrolo[1,2-*a*]indoles is established. This transformation undergoes sequential addition of acyl radical to the carbon–carbon triple bond, intramolecular cylization with 2-position of indole and isomerisation of carbon–carbon double bond. The experiment results

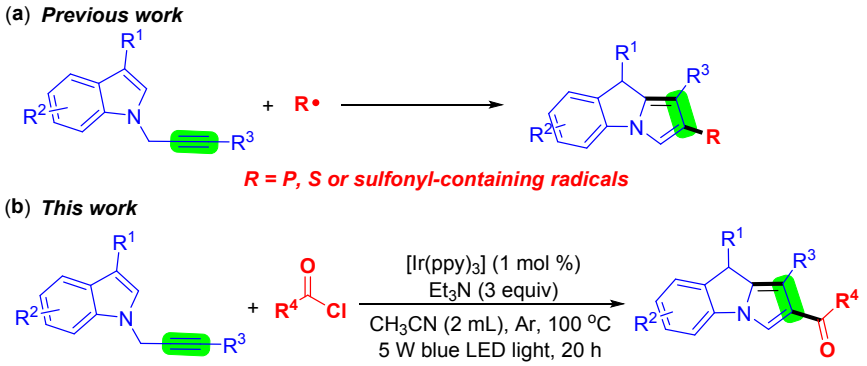
indicate that show that this reaction contains a radical pathway and radical chain process is not the majoy pathway for the formation of product.

Introduction

Indole derivatives, especially polycyclic indoles, are important heterocycle structures, due to their particular pharmacological and biological activities.[1] For instance, the pyrrolo[1,2-*a*]indole skeletons are distinctive motifs existed in numerous pharmaceutical chemicals and natural products.[2] Pyrrolo[1,2-*a*]indoles, which possess the characteristics of anti-tumor, anti-diabetes and anti-cancer, have become a class of indispensable pharmacophores.[3] Additionally, they also show unique optical and electrical prooerties.[4] Herein, the development of simple and efficient methods for the preparation of pyrrolo[1,2-*a*]indoles has attracted considerable attention.[5] Recently, several groups have reported that *N*-propargylindoles could capture free radicals (including P, S and sulfonyl-containing radicals), which underwent cascade cyclization to access 2-substituted pyrrolo[1,2-*a*]indole compounds (Scheme 1a).[6-7] Zhao's group[6a] and Zhu's group[6b] developed the tandem cyclization of *N*-propargylindoles with P(O)-H derivatives for the generation of 2-phosphoryl-pyrrolo[1,2-*a*]indoles. In 2017, Cheng and co-workers[6c] developed the cascade cyclization of *N*-propargylindoles with arylsulfonyl hydrazides for the preparation of 2-arylthiolyl-*3H*-pyrrolo[1,2-*a*]indoles. Several chemists presented sulfonylation/cyclization of *N*-propargylindoles with different kinds of sulfonyl radical sources (such as sulfonyl hydrazides,[7a–c] sulfinic acids,[7d] aryldiazonium tetrafluoroborates and DABCO·$(SO_2)_2$[7e] or sulfonyl chlorides[7f]) to furnish 2-sulfonyl-pyrrolo[1,2-*a*]indoles. However, these methods only disclosed the tandem annulations of *N*-propargylindoles with hetero–centered radicals. The methods for cascade radical cyclization of *N*-propargylindoles with carbon–centered radicals are lacking.

Acyl radicals, which can generate from aldehydes,[8] α-ketoacids,[9] aromatic carboxylic acids,[10] acyl chlorides,[11] and other acyl radical sources,[12] are valuable reaction intermediates. However, beside high temperature and transition-metals, the generation of acyl radicals usually needs strong oxidants. These strict conditions limited the application of acyl radicals in pharmaceutical and organic synthesis.

In recent years, visible-light-catalysis, which possessed the advantages of high efficiency, safety, availability and mild reaction conditions, was considered as an efficient and fascinating tool in organic synthesis.[13-15] Therefore, we report the visible-light-mediated cascade radical cyclization of *N*-propargylindoles with acyl chlorides to prepare 2-acyl-*9H*-pyrrolo[1,2-*a*]indoles, which sequentially undergoes addition of acyl radical to the carbon–carbon triple bond, intramolecular cyclization with the 2-position of indole and isomerisation of carbon–carbon double bond (Scheme 1b).



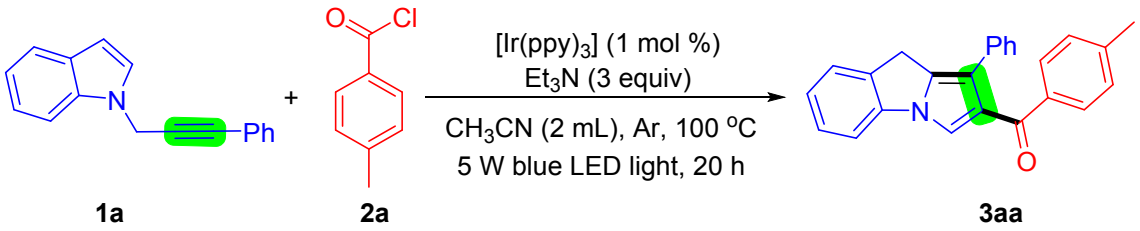
Scheme 1. The Cascade Radical Cyclization of *N*-propargylindoles

Results and discussion

We started our investigation by using 1-(3-phenylprop-2-yn-1-yl)-*1H*-indole (**1a**, 0.2 mmol) and 4-methylbenzoyl chloride (**2a**, 61.6 mg, 0.4 mmol) as the model substrates to identify the best reaction conditions (Table 1). To our surprise, the desired acylation product (1-phenyl-*9H*-pyrrolo[1,2-*a*]indol-2-yl)(*p*-tolyl)methanone (**3aa**) could be obtained in 80% yield by employing [Ir(ppy)$_3$] (1.3 mg, 0.002mmol) as photocatalyst, Et$_3$N (60.6 mg, 0.6 mmol) as base and MeCN (2 mL) as solvent at 100 °C (oil bath) in Ar atmosphere under blue LED light for 20 h (entry 1). Inspired by this result, two other photocatalysts, Ru(bpy)$_3$Cl$_2$ and Eosin Y, were examined. However, they were failed to increase the reaction yields (entries 2–3). The photocatalyst was indispensable for this transformation as the cyclization product could not be obtained in the absence of photocatalyst (entry 4). Next, a series of different visible-light sources, including 36 W compact fluorescent light, 12 W blue LED light and 3 W blue LED light, were successively studied. None of them afforded higher yields (entries 5–7). The experimental results indicated that the visible-light irradiation was also indispensable for the tandem

cyclization (entry 8). Other bases, such as Cs_2CO_3, Na_2CO_3, DABCO and 2,6-lutidine, were screened. All of them were inferior to Et_3N according to the reaction yields (entries 9–12). However, DABCO and 2,6-lutidine provided the target pyrrolo[1,2-*a*]indole **3aa** in 78% and 74% yields, respectively (entries 11–12). Several solvents, including DCE,

Table 1. Screening Optimal Conditions[a]



1a **2a** **3aa**

Entry	Variation from the standard conditions	Yield (%)[b]
1	none	80
2	$[Ru(bpy)_3Cl_2]$ instead of $[Ir(ppy)_3]$	44
3	Eosin Y instead of $[Ir(ppy)_3]$	31
4[c]	without $[Ir(ppy)_3]$	0
5[d]	none	62
6[e]	none	72
7[f]	none	57
8[c]	without additional light	0
9	Cs_2CO_3 instead of Et_3N	38
10	Na_2CO_3 instead of Et_3N	55
11	DABCO instead of Et_3N	78
12	2,6-lutidine instead of Et_3N	74
13	DCE instead of CH_3CN	38
14	THF instead of CH_3CN	29
15	Toluene instead of CH_3CN	40
16	DMF instead of CH_3CN	31
17[c]	DMSO instead of CH_3CN	0
18	at 110 °C	75
19	at 90 °C	66
20[c]	at room temperature	13
21	for 30 h	78
22[g]	none	63

[a] Reaction conditions: **1a** (0.2 mmol, 0.1 M), **2a** (0.6 mmol, 3 equiv), $[Ir(ppy)_3]$ (1.3 mg, 0.002 mmol), Et_3N (60.6 mg,0.6 mmol), CH_3CN (2 mL) at 100 °C (oil bath) under Ar atmosphere and irradiation by 5 W blue LED

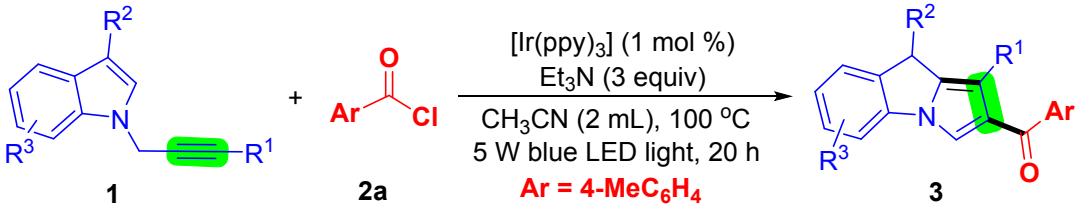
light for 20 h. [b] Isolated yield. [c] Most of the starting materials **1a** was recovered. [d] 36 W compact fluorescent light instead of 5 W blue LED light. [e] 12 W blue LED light instead of 5 W blue LED light. [f] 3 W blue LED light instead of 5 W blue LED light. [g] **1a** (1.0 g, 4.33 mmol) and solvent (10 mL) for 60 h.

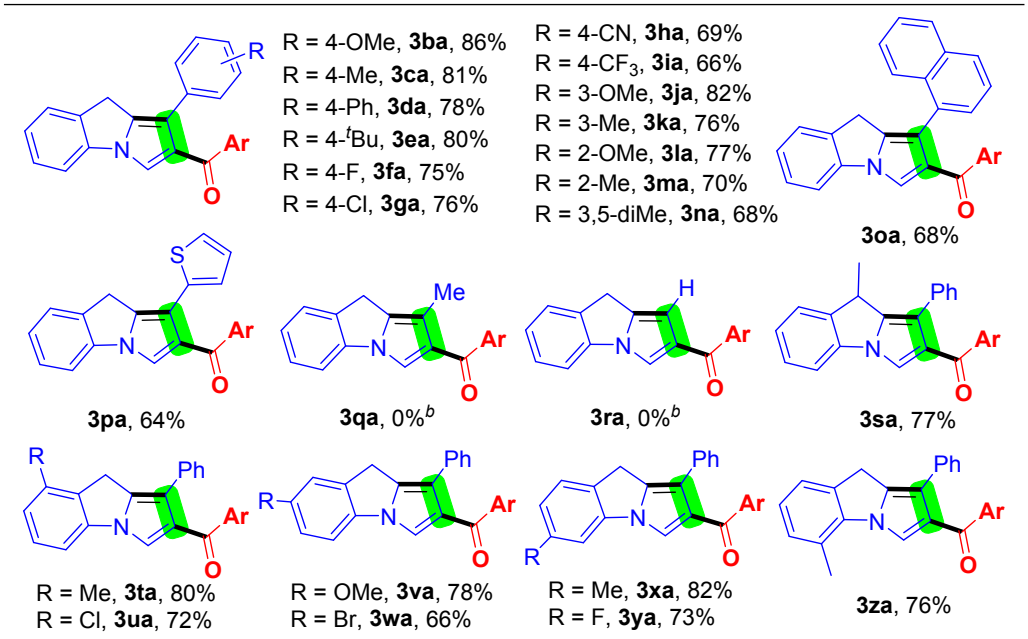
THF, toluene, DMF and DMSO, were tested. None of them gave higher yield than that of CH_3CN(entries 13–17). The isolated yield of pyrrolo[1,2-*a*]indole **3aa** also decreased when the reactions were conducted at 110 °C or at 90 °C (entries 18–19). Conducting the reaction at room temperature only afforded the product **3aa** in 13% yield and most of the starting materials **1a** was recovered (entry 20). Moreover, the prolonged time could not deliver product **3aa** in higher yield (entry 21). It is noticeable that the scale-up experiment could also assemble the acylated pyrrolo[1,2-*a*]indole **3aa** in 63% yield (entry 21).

As the standard conditions for the tandem cyclization reaction were established, we set out to study the scope of *N*-propargyl-substituted indoles in the presence of 4-methylbenzoyl chloride (**2a**) (Table 2). Firstly, a series of *N*-propargylindoles **1a**–**n**, which had different substituted phenyl groups at terminal position of the triple bonds, were investigated. The results suggested that both electricity and hindrance of the substituents had influence on the yields of products (products **3aa**–**na**). As for the *para*-substituted substrates, the substrates bearing electron-withdrawing substituents delivered lower yields than that of substrates bearing electron-donating substituents (products **3ba**–**ia**). Moreover, the *ortho*-substituted substrates showed lower reactivity than that of *para*-substituted ones (products **3ba**, **3ja** and **3la**). In particular, compounds bearing 1-naphthyl or 2-thienyl groups at terminal position of the triple bond could also install the corresponding acylation products **3oa** and **3pa** in 68% and 64% yields, respectively. Both substrate **1q** (R^1 = Me) and substrate **1r** (R^1 = H) were not suitable for this tandem cyclization (products **3qa** and **3ra**). Next, a variety of indole derivatives **1s**–**z** was used to react with acyl chloride **2a**. The indoles with methyl group on the indole skeleton, such as 3-methyl, 4-methyl, 6-methyl and 7-methyl, reacted smoothly and delivered the corresponding polycyclic indoles in 76%-82% yields (products **3sa**, **3ta**, **3xa** and **3za**). An isomerisation process must be contained in this reaction

according to the structure of product **3sa**. Halogen substituted substrates **1u**, **1w** and **1y** were tolerated in this transformation, which offer a possibility for further modification of the products (products **3ua**, **3wa** and **3ya**).

Table 2. Screening Scope of *N*-propargylindoles (**1**) [a]



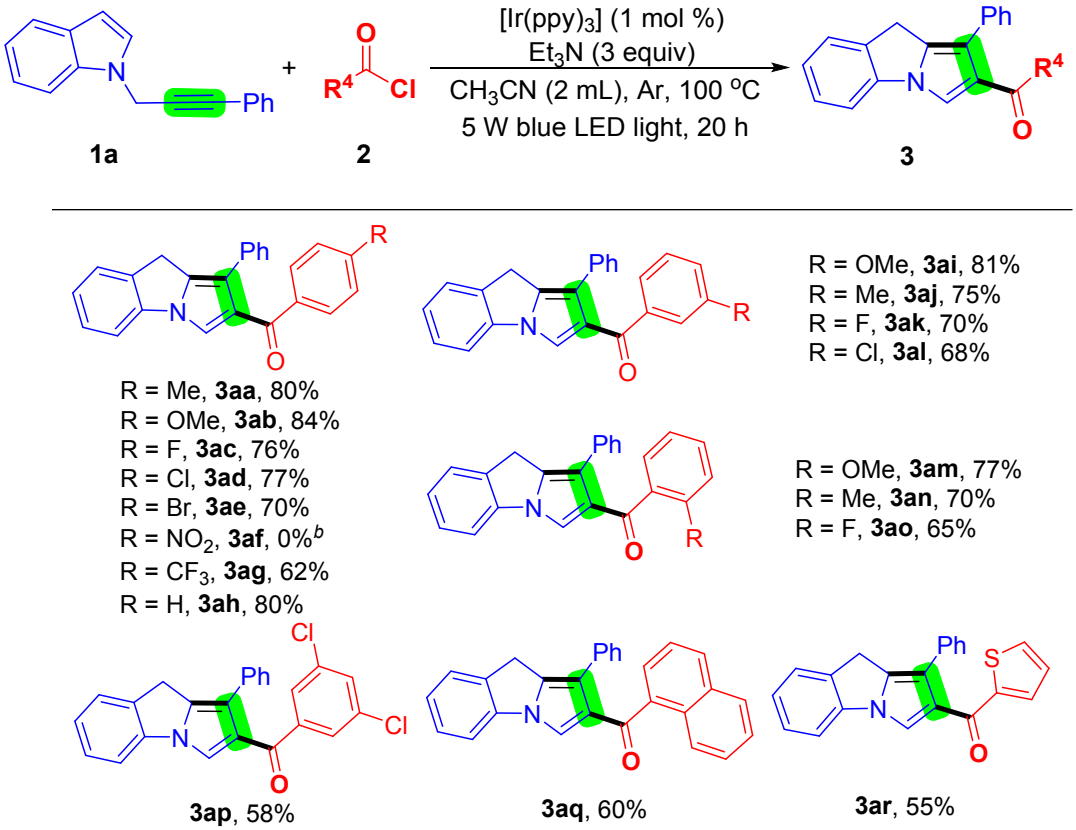


[a] Reaction conditions: **1** (0.2 mmol, 0.1 M), **2a** (0.6 mmol, 3 equiv), [Ir(ppy)$_3$] (1.3 mg, 0.002 mmol), Et$_3$N (60.6 mg, 0.6 mmol), CH$_3$CN (2 mL) at 100 °C (oil bath) under Ar atmosphere and irradiation by 5 W blue LED light for 20 h; isolated yields are reported. [b] Most of the starting materials **1** was decomposed.

Subsequently, a variety of acyl chlorides **2** were used to react with *N*-propargylindole **1a** under the best conditions (Table 3). To our delight, a series of benzoyl chlorides (**2b**−**p**) bearing substituents on the benzene rings underwent the radical cyclization smoothly and installed the corresponding polycyclic indoles **3** in moderate to good yields (products **3ab**−**ap**). Both electron-withdrawing and electron-donating group substituted benzoyl chlorides were all good candidates in the transformation. Furthermore, the results indicated that the electronic effects and steric effects had influence on the

reaction, and the cyclization order of benzoyl chlorides is electron-donating > electron-withdrawing (products **3ab**−**ah**) and *para* > *meta* > *ortho* (products **3aa**, **3aj** and **3an**). However, 4-nitrobenzoyl chloride **2f** could not convert into the desired product **3af** as the formation of 4-nitrobenzoyl radical under this conditions was difficult due to its instability. Dichloro-substituted benzoyl chloride **2p** could undergo this cascade cycylization smoothly (product **3ap**). 1-naphthoyl chloride **2q** and thenoyl chloride **2r** were suitable for this cascade cylcization and led to the corresponding products **3aq** and **3ar** in 60% and 55% yields, respectively. Finally, cinnamoyl chloride, 2-phenylacetyl chloride and pentanoyl chloride were tested and all of them failed to assemble the acylation products.

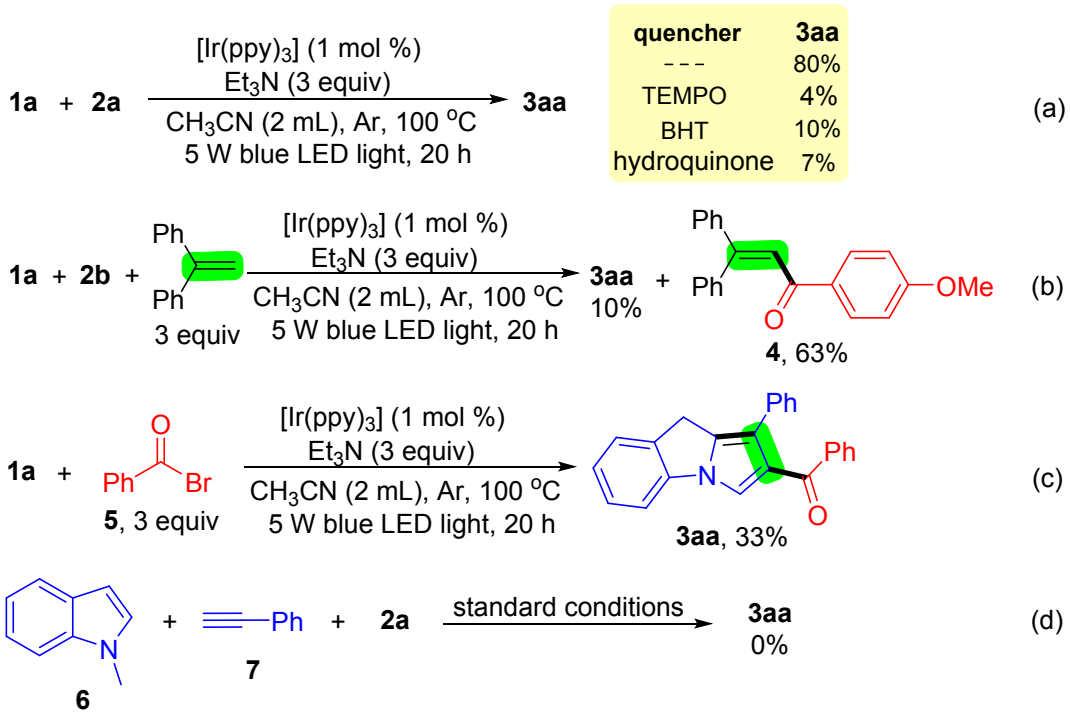
Table 3. Screening Scope of Acyl Chlorides (**2**) [a]



[a] Reaction conditions: **1** (0.2 mmol, 0.1 M), **2a** (0.6 mmol, 3 equiv), $[Ir(ppy)_3]$ (1.3 mg, 0.002 mmol), Et_3N (60.6 mg, 0.6 mmol), CH_3CN (2 mL) at 100 °C (oil bath) under Ar atmosphere and irradiation by 5 W blue LED light for 20 h; isolated yields are reported. [b] Most of the starting materials **1** was decomposed.

Several control experiments were carried out as shown in Scheme 2 to understand the mechanism of this cascade radical cyclization. Initially, subjecting of radical scavengers, including TEMPO, BHT, hydroquinone and 1,1-diphenylethylene, to the optimized conditions afforded the product **3aa** in very low yields (Scheme 2a−b). The trapping product **4** (1-(4-methoxyphenyl)-3,3-diphenylprop-2-en-1-one) could be isolated in 63% yields when 1,1-diphenylethylene was employed into the reaction (Scheme 2b). These results showed that this transformation definitely contained an acyl radical forming process. Then, another acyl group source **5** (benzoyl bromide) was employed into the reaction and generated the product **3aa** in 33% yield (Scheme 2c). We have tested the ternary system 1-methyl-*1H*-indole **6**, phenylacetylene **7** and acylchloride **2a** under the conditions. The GC-MS analysis result showed that no target product was detected (Scheme 2d).

Scheme 2. Control Experiments.



The light on/off experiment verified the necessity of continuous irradiation of visible light and suggested that chain propagation is not the predominant mechanistic pathway (Figure 1).

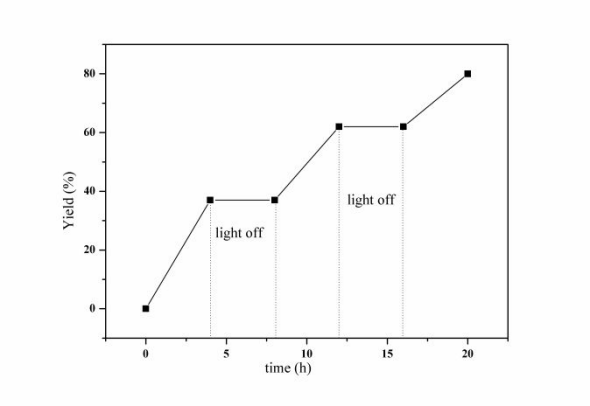
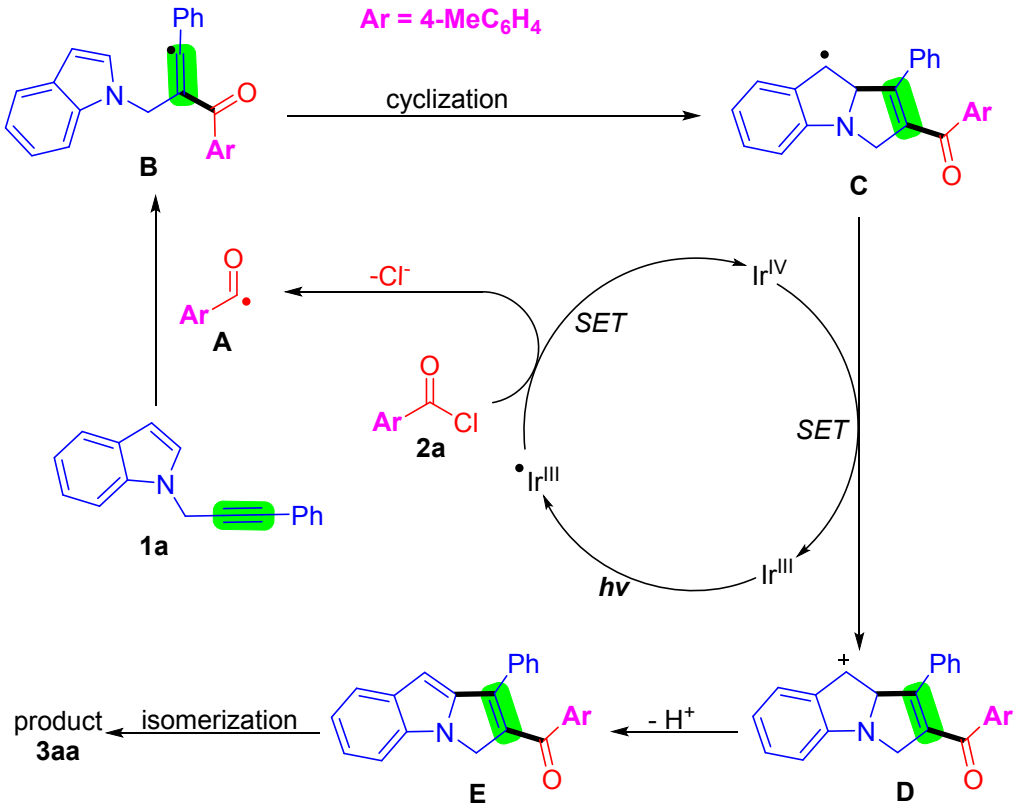


Figure 1. Profile of **3aa** with Light on or off over Time. GC yield using biphenyl as an internal standard.

Based on recent reports and our experimental results,[7,12-14] a possible mechanistic pathway was proposed as outline in Scheme 3. First, $Ir^{III}(ppy)_3$ is converted into the strong reductant $*Ir^{III}(ppy)_3$ under the irradiation of visible-light. Then, acyl chloride **2a** is reduced by $*Ir^{III}(ppy)_3$ *via* single-electron transfer (*SET*) process and releases of chloride ion to give the acyl radical **A** and producing $Ir^{IV}(ppy)_3$. Next, the intermediate **A** attacks the carbon−carbon triple bond of *N*-propargylindole **1a** to produce the stable benzyl radical **B**. The intermediate **B** goes through intramolecular cyclization with 2-position of indole to deliver intermediate **C**, which is oxidized by $Ir^{IV}(ppy)_3$ to provide cation **D**, accompany with regenerating $Ir^{III}(ppy)_3$. The intermediate **E**, which comes from deprotonation of the intermediate **D**, goes through isomerization to furnish the target product **3aa**.

Scheme 3. Possible Mechanisms.



Conclusions

In conclusion, we have reported the visible-light-catalyzed tandem radical cyclization of *N*-propargylindoles with acyl chlorides for accessing 2-acyl-*9H*-pyrrolo[1,2-*a*]indoles. This cyclization reaction proceeds sequentially addition of acyl radical to the carbon–carbon triple bond, intramolecular cyclization with 2-position of indole and isomerisation of carbon–carbon double bond. This reaction is a simple and green strategy for accessing 2-acyl-*9H*-pyrrolo[1,2-*a*]indole skeletons. The results of the control experiments show that this reaction contains a radical pathway and radical chain process is not the majoy pathway for the formation of product. Further researches on the mechanism and development of tandem radical cyclization are currently underway in our laboratory.

Experimental Section

General Considerations:

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a NMR spectrometer using TMS as internal standard. LRMS was performed on a GC-MS instrument and HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

Preparation of *N*-propargylindoles **1:**

N-propargylindoles **1**[5-7] were synthesized according to the literatures.

N-propargylindoles **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1i**, **1k, 1m, 1o, 1p, 1q, 1s, 1v, 1x, 1y, 1z**;[6a] **1t**;[6b] **1h, 1w**;[6c] **1n**;[7d] and **1r**[5d] were reported in previous literatures, *N*-propargylindoles **1j, 1l** and **1u** were reported for the first time and its physical data and spectroscopic were presented as follow:

*1-(3-(3-Methoxyphenyl)prop-2-yn-1-yl)-1H-indole (**1j**):* Yield: 555.9 mg, 71%; brown solid; mp 45.0-46.5 °C (uncorrected); ^{1} H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.4 Hz, 1H), 7.27-7.25 (m, 2H), 7.23-7.14 (m, 2H), 7.02-7.00 (m, 1H), 6.93-6.92 (m, 1H), 6.87-6.84 (m, 1H), 6.54-6.53 (m, 1H), 5.06 (s, 2H), 3.74 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 159.2, 135.8, 129.3, 128.3, 127.3, 124.2, 123.2, 121.8, 121.0, 119.7, 116.5, 115.1, 109.4, 101.8, 85.0, 82.9, 55.2, 36.5; HRMS (ESI-TOF) *m/z*: $C_{18}H_{16}NO$ $(M + H)^+$ calcd for 262.1226, found 262.1230.

*1-(3-(2-Methoxyphenyl)prop-2-yn-1-yl)-1H-indole (**1l**):* Yield: 532.4 mg, 68%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.37-7.34 (m, 2H), 7.27-7.22 (m, 2H), 7.14 (t, *J* = 6.8 Hz, 1H), 6.88-6.83 (m, 2H), 6.53-6.52 (m, 1H), 5.12 (s, 2H), 3.85 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 160.1, 135.8, 133.7, 130.0, 128.8, 127.4, 121.6, 120.9, 120.4, 119.6, 111.4, 110.5, 109.5, 101.6, 86.9, 81.8, 55.7, 36.9; HRMS (ESI-TOF) *m/z*: $C_{18}H_{16}NO$ $(M + H)^+$ calcd for 262.1226, found 262.1230.

*4-Chloro-1-(3-phenylprop-2-yn-1-yl)-1H-indole (**1u**):* Yield: 604.2 mg, 76%; yellow solid; mp 80.6-81.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42-7.39 (m, 2H), 7.38-7.35 (m, 1H), 7.32-7.28 (m, 4H), 7.23-7.14 (m, 2H), 6.65-6.64 (m, 1H), 5.07 (s, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 136.5,

131.7, 128.7, 128.3, 127.9, 127.6, 126.2, 122.4, 122.0, 119.6, 108.1, 100.5, 85.5, 82.5, 37.0; HRMS (ESI-TOF) *m/z*: $C_{17}H_{13}ClN$ $(M + H)^+$ calcd for 266.0731, found 266.0736.

Typical Experimental Procedure for the Visible-Light-Catalyzed Cascade Radical Cyclization of *N*-propargylindoles with Acyl Chlorides for the Synthesis of 2-Acyl-*9H*-pyrrolo[1,2-*a*]indoles

To a Schlenk tube were added *N*-propargylindoles **1** (0.2 mmol, 0.1 M), acyl chlorides **2** (0.6 mmol, 3 equiv), $[Ir(ppy)_3]$ (1.3 mg, 0.002 mmol), Et_3N (60.6 mg, 0.6 mmol) and CH_3CN (2 mL). Then the tube was stirred at 100 °C (oil bath) in Ar atmosphere under 5 W blue LED light for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 15 : 1) to afford the desired products **3**. An amplified experiment conducted in the presence of *N*-propargylindole **1a** (1155 mg, 5 mmol), 4-methylbenzoyl chloride **2a** (3 equiv, 15 mmol), $[Ir(ppy)_3]$ (32.8 mg, 0.05 mmol), Et_3N (1515 mg, 15 mmol) and CH_3CN (50 mL) at 100 °C under argon atmosphere for 120 h could deliver the target product **3aa** in 51% yield (890.0 mg).

*(1-Phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3aa**):* Yield: 55.8 mg, 80%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.0 Hz, 2H), 7.53 (s, 1H), 7.46 (t, *J* = 6.8 Hz, 3H), 7.37-7.30 (m, 4H), 7.22-7.19 (m, 4H), 4.05 (s, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 191.2, 142.3, 139.8, 137.1, 134.7, 134.5, 134.4, 129.8, 128.7, 128.6, 128.6, 128.1, 127.8, 126.2, 126.1, 124.8, 119.7, 117.7, 110.6, 29.4, 21.6; HRMS (ESI-TOF) *m/z*: $C_{25}H_{20}NO$ $(M + H)^+$ calcd for 350.1539, found 350.1544.

*(1-(4-Methoxyphenyl)-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3ba**):* Yield: 65.2 mg, 86%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.0 Hz, 2H), 7.48 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 8.8 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.19-7.16 (m, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.00 (s, 2H), 3.80 (s, 3H), 2.41 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 191.2,

157.9, 142.2, 139.7, 137.2, 134.5, 134.1, 129.7, 129.7, 128.7, 127.7, 126.8, 126.1, 125.9, 124.7, 119.3, 117.7, 113.5, 110.5, 55.2, 29.3, 21.5; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO_2$ $(M + H)^+$ calcd for 380.1645, found 380.1650.

*p-Tolyl(1-(p-tolyl)-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ca**):* Yield: 58.8 mg, 81%; yellow solid; mp 156.0-156.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.4 Hz, 2H), 7.50 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.36-7.32 (m, 4H), 7.23-7.18 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.03 (s, 2H), 2.41 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.1, 142.3, 139.8, 137.2, 135.7, 134.5, 134.4, 131.4, 129.7, 128.8, 128.7, 128.4, 127.8, 126.2, 126.1, 124.7, 119.6, 117.6, 110.5, 29.3, 21.6, 21.2; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO$ $(M + H)^+$ calcd for 364.1696, found 364.1703.

*(1-([1,1'-Biphenyl]-4-yl)-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3da**):* Yield: 66.3 mg, 78%; yellow solid; mp 159.8-160.7°C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.58-7.52 (m, 5H), 7.49-7.42 (m, 3H), 7.37-7.31 (m, 3H), 7.24-7.20 (m, 3H), 4.09 (s, 2H), 2.42 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.2, 142.4, 141.1, 139.7, 138.8, 137.2, 134.8, 134.5, 133.4, 129.8, 128.9, 128.8, 128.8, 128.7, 127.8, 127.0, 126.8, 126.2, 126.1, 124.8, 119.3, 117.9, 110.6, 29.5, 21.6; HRMS (ESI-TOF) *m/z*: $C_{31}H_{24}NO$ $(M + H)^+$ calcd for 426.1852, found 426.1860.

*(1-(4-(tert-Butyl)phenyl)-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3ea**):* Yield: 64.8 mg, 80%; yellow solid; mp 156.4-157.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.4 Hz, 2H), 7.52 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.40-7.32 (m, 6H), 7.22-7.18 (m, 3H), 4.05 (s, 2H), 2.40 (s, 3H), 1.32 (s, 9H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.3, 148.8, 142.2, 139.8, 137.3, 134.6, 134.5, 131.3, 129.8, 128.6, 128.2, 127.8, 126.2, 126.1, 125.0, 124.7, 119.6, 117.7, 110.5, 34.4, 31.3, 29.4, 21.5; HRMS (ESI-TOF) *m/z*: $C_{29}H_{28}NO$ $(M + H)^+$ calcd for 406.2165, found 406.2174.

*(1-(4-Fluorophenyl)-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3fa**):* Yield: 55.1 mg, 75%; white solid; mp 154.7-155.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.44-7.40 (m, 2H), 7.39-7.34 (m, 2H), 7.24-7.20 (m, 3H), 7.05-

6.99 (m, 2H), 4.01 (s, 2H), 2.42 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 191.2, 161.4 (d, *J* = 243.6 Hz, 1C), 142.4, 139.7, 137.1, 134.6, 134.4, 130.2 (d, *J* = 7.9 Hz, 1C), 129.7, 128.8, 127.9, 126.2, 125.9, 124.9, 118.7, 117.8, 115.1, 114.8, 110.6, 29.2, 21.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ: -116.5 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{25}H_{19}{}^{19}FNO$ $(M + H)^+$ calcd for 368.1445, found 368.1450.

*(1-(4-Chlorophenyl)-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3ga**):* Yield: 58.3 mg, 76%; yellow solid; mp 105.3-105.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.40-7.34 (m, 4H), 7.31-7.27 (m, 2H), 7.24-7.20 (m, 3H), 4.02 (s, 2H), 2.43 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 191.1, 142.5, 139.6, 137.1, 134.9, 134.3, 132.9, 131.8, 129.8, 129.7, 128.8, 128.2, 127.9, 126.2, 125.9, 124.9, 118.6, 118.0, 110.6, 29.3, 21.6; HRMS (ESI-TOF) *m/z*: $C_{25}H_{19}{}^{35}ClNO$ $(M + H)^+$ calcd for 384.1150, found 384.1158.

*4-(2-(4-Methylbenzoyl)-9H-pyrrolo[1,2-a]indol-1-yl)benzonitrile (**3ha**):* Yield: 51.6 mg, 69%; yellow solid; mp 90.0-90.6°C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.0 Hz, 2H), 7.62-7.60 (m, 2H), 7.56-7.54 (m, 3H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.42-7.36 (m, 2H), 7.26-7.23 (m, 3H), 4.06 (s, 2H), 2.44 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 190.9, 142.9, 139.5, 139.4, 136.8, 135.9, 134.0, 131.9, 129.7, 129.0, 128.9, 128.1, 126.2, 126.0, 125.2, 119.3, 118.5, 118.1, 110.8, 109.3, 29.6, 21.6; HRMS (ESI-TOF) *m/z*: $C_{26}H_{19}N_2O$ $(M + H)^+$ calcd for 375.1492, found 375.1499.

*p-Tolyl(1-(4-(Trifluoromethyl)phenyl)-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ia**):* Yield: 55.0 mg, 66%; yellow solid; mp 152.8-153.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.4 Hz, 2H), 7.59-7.53 (m, 5H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.41-7.36 (m, 2H), 7.25-7.22 (m, 3H), 4.05 (s, 2H), 2.42 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 190.9, 142.6, 139.5, 136.9, 138.2 (2C), 135.5, 134.2, 129.7, 128.4, 128.0, 127.9 (q, *J* = 32.1 Hz, 1C), 126.2, 126.0, 125.1, 125.0 (q, *J* = 3.8 Hz, 1C), 124.3 (q, *J* = 270.1 Hz, 1C), 118.4, 118.2, 110.7, 29.4, 21.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ: -62.3 (s, 3F);HRMS (ESI-TOF) *m/z*: $C_{26}H_{19}{}^{19}F_3NO$ $(M + H)^+$ calcd for 418.1413, found 418.1420.

*(1-(3-Methoxyphenyl)-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3ja**):* Yield: 62.2 mg, 82%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.0 Hz, 2H), 7.53 (s, 1H), 7.46 (d, *J* = 7.2 Hz,

1H), 7.38-7.33 (m, 2H), 7.23-7.19 (m, 4H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.99 (s, 1H), 6.77-6.75 (m, 1H), 4.05 (s, 2H), 3.77 (s, 3H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 191.2, 159.3, 142.4, 139.7, 137.1, 135.8, 134.8, 134.5, 129.8, 129.0, 128.7, 127.8, 126.3, 126.2, 124.8, 121.1, 119.4, 117.6, 114.2, 111.8, 110.6, 55.2, 29.5, 21.6; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO_2$ $(M + H)^+$ calcd for 380.1645, found 380.1650.

*p-Tolyl(1-(m-tolyl)-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ka**):* Yield: 55.2 mg, 76%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.4 Hz, 2H), 7.52 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.38-7.33 (m, 2H), 7.26-7.18 (m, 6H), 7.03 (d, *J* = 7.2 Hz, 1H), 4.05 (s, 2H), 2.41 (s, 3H), 2.32 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 191.2, 142.3, 139.8, 137.5, 137.2, 134.6, 134.5, 134.2, 129.7, 129.3, 128.7, 128.0, 127.8, 126.9, 126.2, 126.1, 125.7, 124.7, 119.7, 117.6, 110.6, 29.4, 21.6, 21.5; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO$ $(M + H)^+$ calcd for 364.1696, found 364.1703.

*(1-(2-Methoxyphenyl)-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3la**):* Yield: 58.4 mg, 77%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 8.0 Hz, 2H), 7.56(s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.38-7.34 (m, 3H), 7.22-7.17 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 2H), 3.62 (s, 3H), 2.37 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 191.2, 156.1, 142.0, 140.1, 136.7, 135.0, 134.7, 130.1, 129.6, 128.4, 127.9, 127.7, 127.6, 126.1, 124.4, 123.6, 120.4, 116.0, 115.1, 110.5, 110.4, 55.0, 29.3, 21.5; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO_2$ $(M + H)^+$ calcd for 380.1645, found 380.1650.

*p-Tolyl(1-(o-tolyl)-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ma**):* Yield: 50.8 mg, 70%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 8.4 Hz, 2H), 7.57 (s, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 4.0 Hz, 2H), 7.29-7.27 (m, 1H), 7.24-7.17 (m, 6H), 3.84 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 2.21 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 190.9, 142.0, 140.0, 137.1, 136.7, 134.8, 134.6, 134.4, 129.8, 129.8, 129.5, 128.7, 127.8, 127.4, 126.9, 126.2, 125.4, 124.7, 119.2, 116.9, 110.6, 28.8, 21.5, 20.1; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO$ $(M + H)^+$ calcd for 364.1696, found 364.1703.

*(1-(3,5-Dimethylphenyl)-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3na**):* Yield: 51.5 mg, 68%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.36-7.33 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 3H), 7.05 (s, 2H), 6.85 (s, 1H), 4.05 (s, 2H), 2.41 (s, 3H), 2.29 (s, 6H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.2, 142.2, 139.8, 137.4, 137.3, 134.6, 134.5, 134.1, 129.7, 128.7, 127.9, 127.8, 126.4, 126.3, 126.1, 124.7, 119.8, 117.6, 110.5, 29.4, 21.6, 21.3; HRMS (ESI-TOF) *m/z*: $C_{27}H_{24}NO$ $(M + H)^+$ calcd for 378.1852, found 378.1856.

*(1-(Naphthalen-1-yl)-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3oa**):* Yield: 54.3 mg, 68%; yellow solid; mp 153.8-154.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 8.4 Hz, 3H), 7.48-7.36 (m, 7H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.86-3.73 (m, 2H), 2.33 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 190.9, 141.9, 140.0, 137.1, 135.6, 134.7, 133.7, 132.6, 132.0, 129.3, 128.4, 128.3, 128.0, 127.8, 127.5, 127.2, 126.2, 125.8, 125.7, 125.4, 125.3, 124.8, 117.7, 116.9, 110.7, 29.0, 21.5; HRMS (ESI-TOF) *m/z*: $C_{29}H_{22}NO$ $(M + H)^+$ calcd for 400.1700, found 400.1708.

*(1-(Thiophen-2-yl)-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3pa**):* Yield: 45.4 mg, 64%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 3.2 Hz, 2H), 7.37-7.32 (m, 2H), 7.27 (s, 1H), 7.25-7.23 (m, 3H), 7.05-7.03 (m, 1H), 4.11 (s, 2H), 2.44 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.1, 142.5, 139.6, 137.4, 136.2, 134.9, 134.5, 129.8, 128.8, 127.9, 127.2, 126.2, 125.9, 125.8, 124.9, 123.5, 118.1, 113.1, 110.7, 30.4, 21.6; HRMS (ESI-TOF) *m/z*: $C_{23}H_{18}NOS$ $(M + H)^+$ calcd for 356.1104, found 356.1110.

*(9-Methyl-1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3sa**):* Yield: 55.9 mg, 77%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.0 Hz, 2H), 7.47-7.44 (m, 3H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.36-7.30 (m, 4H), 7.24-7.19 (m, 4H), 4.41-4.36 (m, 1H), 2.40 (s, 3H), 1.37 (d, *J* = 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.1, 142.2, 140.7, 139.6, 138.9, 137.2, 134.1, 129.7, 129.1, 128.7, 127.9, 127.8, 126.4, 126.2, 125.0, 124.9, 120.1, 117.1, 110.5, 36.1, 21.5, 17.2; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO$ $(M + H)^+$ calcd for 364.1696, found 364.1703.

*(8-Methyl-1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3ta**):* Yield: 58.1 mg, 80%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.0 Hz, 2H), 7.50 (s, 1H), 7.48-7.45 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.6Hz, 1H), 7.24-7.16 (m, 4H), 7.02 (d, *J* = 7.6 Hz, 1H), 3.93 (s, 2H), 2.40 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.2, 142.3, 139.4, 137.2, 135.8, 134.7, 134.5, 133.3, 129.7, 128.7, 128.6, 128.6, 128.1, 127.8, 126.1, 125.9, 119.6, 117.8, 108.0, 28.4, 21.6, 18.5; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO$ $(M + H)^+$ calcd for 364.1696, found 364.1703.

*(8-Chloro-1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3ua**):* Yield: 55.2 mg, 72%; yellow solid; mp 59.9-60.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 1H), 7.45-7.43 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 3H), 7.26-7.19 (m, 5H), 4.06 (s, 2H), 2.41 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.2, 142.6, 140.9, 136.9, 134.0, 133.8, 133.0, 131.8, 129.8, 129.3, 128.8, 128.5, 128.2, 126.6, 126.3, 124.9, 120.0, 117.6, 108.9, 29.2, 21.6; HRMS (ESI-TOF) *m/z*: $C_{25}H_{19}{}^{35}ClNO$ $(M + H)^+$ calcd for 384.1150, found 384.1158.

*(7-Methoxy-1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3va**):* Yield: 59.1 mg, 78%; yellow solid; mp 170.7-171.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 3H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 3.2 Hz, 1H), 7.23-7.19 (m, 3H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.89-6.86 (m, 1H), 4.01 (s, 2H), 3.84 (s, 3H), 2.41 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.1, 157.5, 142.2, 137.3, 136.1, 134.6, 134.5, 133.6, 129.7, 128.7, 128.6, 128.1, 126.1, 125.5, 119.8, 117.6, 112.6, 112.6, 110.9, 55.8, 29.6, 21.5; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO_2$ $(M + H)^+$ calcd for 380.1645, found 380.1650.

*(7-Bromo-1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3wa**):* Yield: 56.5 mg, 66%; yellow solid; mp 147.2-147.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.0 Hz, 2H), 7.57 (s, 1H), 7.48-7.46 (m, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.22-7.18 (m, 4H), 4.01 (s, 2H), 2.40 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.1, 142.5, 138.9, 136.9, 136.6, 134.2, 134.0, 130.8, 129.7, 129.3, 128.7, 128.5, 128.1, 126.6, 126.3, 120.0, 117.6, 117.5, 111.8, 29.3, 21.6; HRMS (ESI-TOF) *m/z*: $C_{25}H_{19}{}^{79}BrNO$ $(M + H)^+$ calcd for 428.0645, found 428.0653.

*(6-Methyl-1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3xa**):* Yield: 59.5 mg, 82%; yellow solid; mp 136.9-137.4°C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.0 Hz, 2H), 7.50 (s, 1H), 7.46-7.44 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 3H), 7.22-7.18 (m, 3H), 7.17 (s, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 4.00 (s, 2H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.2, 142.3, 139.9, 138.0, 137.2, 135.2, 134.4, 131.5, 129.7, 128.7, 128.6, 128.6, 128.1, 126.1, 125.9, 125.7, 125.5, 119.6, 117.7, 111.3, 29.1, 21.6; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO$ $(M + H)^+$ calcd for 364.1696, found 364.1703.

*(6-Fluoro-1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3ya**):* Yield: 53.6 mg, 73%; yellow solid; mp 90.2-90.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 7.6 Hz, 2H), 7.47 (s, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.40-7.37 (m, 1H), 7.34-7.30 (m, 2H), 7.23-7.20 (m, 3H), 7.07-7.05 (m, 1H), 6.93-6.88 (m, 1H), 4.00 (s, 2H), 2.41 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.1, 162.6 (d, *J* = 244.1 Hz, 1C), 142.6, 140.8 (d, *J* = 11.5 Hz, 1C), 136.9, 135.5, 134.1, 129.8 (d, *J* = 5.2 Hz, 1C), 128.8, 128.5, 128.1, 126.9, 126.8, 126.6, 126.3, 119.9, 117.5, 111.3 (d, *J* = 12.5 Hz, 1C), 99.2 (d, *J* = 17.1 Hz, 1C), 28.9, 21.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.0 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{25}H_{19}{}^{19}FNO$ $(M + H)^+$ calcd for 368.1445, found 368.1450.

*(5-Methyl-1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(p-tolyl)methanone (**3za**):* Yield: 55.2 mg, 76%; yellow solid; mp 141.3-141.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.4 Hz, 2H), 7.68 (s, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.32-7.28 (m, 3H), 7.21-7.18 (m, 3H), 7.15-7.09 (m, 2H), 4.04 (s, 2H), 2.58 (s, 3H), 2.39 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.4, 142.3, 138.7, 137.0, 135.1, 134.6, 134.4, 130.0, 129.8, 128.7, 128.6, 128.1, 126.2, 126.0, 124.6, 123.7, 122.5, 120.3, 119.1, 29.3, 21.6, 18.5; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}NO$ $(M + H)^+$ calcd for 364.1696, found 364.1703.

*(4-Methoxyphenyl)(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ab**):* Yield: 61.3 mg, 84%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.8 Hz, 2H), 7.53 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 6.8 Hz, 2H), 7.36 (t, *J* = 2.8 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23-7.18 (m, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.05 (s, 2H), 3.85 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 190.4, 162.7, 139.8,

134.5, 134.5, 134.4, 132.4, 131.9, 128.5, 128.1, 127.8, 126.3, 126.2, 126.1, 124.7, 119.5, 117.0, 113.2, 110.5, 55.4, 29.4; HRMS (ESI-TOF) *m/z*: $C_{25}H_{20}NO_2$ $(M + H)^+$ calcd for 366.1489, found 366.1495.

*(4-Fluorophenyl)(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ac**):* Yield: 53.7 mg, 76%; yellow solid; mp 84.4-84.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91-7.86 (m, 2H), 7.56 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.41-7.37 (m, 4H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.25-7.19 (m, 2H), 7.08-7.02 (m, 2H), 4.05 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 190.1, 165.0 (d, *J* = 251.0 Hz, 1C), 139.7, 135.9 (d, *J* = 2.9 Hz, 1C), 134.8, 134.5, 134.2, 132.0 (d, *J* = 8.9 Hz, 1C), 128.6, 128.1, 127.9, 126.2 (d, *J* = 4.0 Hz, 1C), 125.9, 124.9, 119.7, 117.5, 115.1, 114.9, 110.7, 29.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ: -107.5 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{24}H_{17}{}^{19}FNO$ $(M + H)^+$ calcd for 354.1289, found 354.1294.

*(4-Chlorophenyl)(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ad**):* Yield: 56.8 mg, 77%; yellow solid; mp 145.9-146.1 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.4 Hz, 2H), 7.55 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.42-7.30 (m, 8H), 7.25-7.20 (m, 2H), 4.05 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 190.2, 139.6, 138.1, 137.9, 134.9, 134.5, 134.1, 130.9, 128.6, 128.3, 128.1, 127.9, 126.3, 126.2, 125.8, 125.0, 119.7, 117.7, 110.7, 29.3; HRMS (ESI-TOF) *m/z*: $C_{24}H_{17}{}^{35}ClNO$ $(M + H)^+$ calcd for 370.0993, found 370.0998.

*(4-Bromophenyl)(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ae**):* Yield: 57.8 mg, 70%; brown solid; mp 132.9-136.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 8.4 Hz, 2H), 7.55-7.52 (m, 3H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.43-7.36 (m, 4H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.25-7.20 (m, 2H), 4.05 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 190.3, 139.6, 138.6, 134.9, 134.5, 134.1, 131.3, 131,1, 128.6, 128.1, 127.9, 126.5, 126.3, 126.2, 125.7, 125.0, 119.7, 117.8, 110.7, 29.3; HRMS (ESI-TOF) *m/z*: $C_{24}H_{17}{}^{79}BrNO$ $(M + H)^+$ calcd for 414.0488, found 414.0497.

*(1-Phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(4-(trifluoromethyl)phenyl)methanone (**3ag**):* Yield: 50.0 mg, 62%; yellow solid; mp 150.9-151.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.56 (s, 1H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.43-7.38 (m, 4H), 7.34-7.30 (m, 2H), 7.25-7.20 (m, 2H), 4.05 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 190.2, 143.0, 139.5, 135.1,

134.5, 134.0, 132.9 (q, J = 32.3 Hz, 1C), 129.6, 128.7, 128.1, 127.9, 126.4, 126.2, 125.6, 125.2, 125.0 (q, J = 3.8 Hz, 1C), 123.8 (q, J = 270.9 Hz, 1C), 119.8, 118.3, 110.8, 29.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ: -62.9 (s, 3F); HRMS (ESI-TOF) *m/z*: $C_{25}H_{17}{}^{19}F_3NO$ $(M + H)^+$ calcd for 404.1257, found 404.1265.

*Phenyl(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ah**):* Yield: 53.6 mg, 80%; yellow solid; mp 95.1-95.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (t, J = 6.8 Hz, 2H), 7.55 (s, 1H), 7.53-7.46 (m, 3H), 7.42 (t, J = 7.6 Hz, 3H), 7.37 (t, J = 6.4 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.24-7.20 (m, 2H), 4.06 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.5, 139.9, 139.7, 134.8, 134.5, 134.3, 131.7, 129.6, 128.6, 128.6, 128.1, 128.0, 127.8, 126.2, 126.0, 124.9, 119.8, 118.0, 110.7, 29.4; HRMS (ESI-TOF) *m/z*: $C_{24}H_{18}NO$ $(M + H)^+$ calcd for 336.1383, found 336.1390.

*(3-methoxyphenyl)(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ai**):* Yield: 58.4 mg, 81%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (s, 1H), 7.48-7.44 (m, 4H), 7.41-7.40 (m, 1H), 7.36-7.29 (m, 5H), 7.23-7.19 (m, 2H), 7.07-7.04 (m, 1H), 4.04 (m, 2H), 3.81 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.1, 159.3, 141.1, 139.7, 134.8, 134.5, 134.3, 129.0, 128.6, 128.1, 127.8, 126.2, 126.2, 125.9, 124.9, 122.3, 119.7, 118.3, 118.0, 113.8, 110.7, 55.4, 29.4; HRMS (ESI-TOF) *m/z*: $C_{25}H_{20}NO_2$ $(M + H)^+$ calcd for 366.1489, found 366.1495.

*(1-Phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(m-tolyl)methanone (**3aj**):* Yield: 52.4 mg, 75%; yellow solid; mp 106.2-106.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (t, J = 5.2 Hz, 2H), 7.55 (s, 1H), 7.47-7.43 (m, 3H), 7.36 (t, J = 3.6 Hz, 2H), 7.33-7.28 (m, 4H), 7.23-7.18 (m, 2H), 4.05 (s, 2H), 2.36 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 191.7, 139.8, 139.7, 137.8, 134.7, 134.5, 134.4, 132.5, 130.2, 128.6, 128.0, 128.0, 127.9, 127.8, 126.8, 126.2, 126.1, 124.8, 119.7, 117.9, 110.6, 29.4, 21.3; HRMS (ESI-TOF) *m/z*: $C_{25}H_{20}NO$ $(M + H)^+$ calcd for 350.1539, found 350.1544.

*(3-fluorophenyl)(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ak**):* Yield: 49.4 mg, 70%; yell ow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 7.6 Hz, 1H), 7.57-7.53 (m, 2H), 7.48-7.30 (m, 8H), 7.25-7.16 (m, 3H), 4.04 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 189.9, 162.3 (d, J = 245.6 Hz, 1C), 141.9 (d, J = 6.1 Hz, 1C), 139.6, 135.0, 134.5, 134.1, 129.6 (d, J = 7.7 Hz, 1C), 128.6, 128.1, 127.9,

126.3, 126.2, 125.6, 125.3 (d, J = 3.0 Hz, 1C), 125.0, 119.8, 118.6 (d, J = 21.3 Hz, 1C), 118.0, 116.3 (d, J = 22.1 Hz, 1C), 110.8, 29.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ: -112.8 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{24}H_{17}{}^{19}FNO$ $(M + H)^+$ calcd for 354.1289, found 354.1294.

*(3-chlorophenyl)(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3al**):* Yield: 50.3 mg, 68%; yellow solid; mp 133.9-134.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (t, J = 2.0 Hz, 1H), 7.73-7.70 (m, 1H), 7.57 (s, 1H), 7.48-7.43 (m, 2H), 7.42-7.40 (m, 4H), 7.39-7.30 (m, 3H), 7.25-7.21 (m, 2H), 4.04 (s, 2H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ: 189.9, 141.4, 139.6, 135.0, 134.5, 134.1, 131.6, 129.5, 129.3, 128.6, 128.6, 128.1, 127.9, 127.6, 126.3, 126.2, 125.6, 125.0, 119.8, 117.9, 110.8, 29.3; HRMS (ESI-TOF) *m/z*: $C_{24}H_{17}{}^{35}ClNO$ $(M + H)^+$ calcd for 370.0993, found 370.0998.

*(2-methoxyphenyl)(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3am**):* Yield: 56.2 mg, 77%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.47 (m, 3H), 7.44-7.40 (m, 2H), 7.35-7.28 (m, 5H), 7.22-7.19 (m, 2H), 6.95 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 3.99 (s, 2H), 3.74 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 190.8, 157.1, 139.7, 134.9, 134.5, 134.2, 131.1, 131.0, 129.3, 129.0, 127.8, 127.7, 127.6, 126.2, 126.1, 124.8, 119.9, 119.5, 118.8, 111.2, 110.7, 55.6, 29.2; HRMS (ESI-TOF) *m/z*: $C_{25}H_{20}NO_2$ $(M + H)^+$ calcd for 366.1489, found 366.1495.

*(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(o-tolyl)methanone (**3an**):* Yield: 48.9 mg, 70%; yellow solid; mp 129.3-129.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (t, J = 7.2 Hz, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.38-7.28 (m, 6H), 7.27-7.18 (m, 4H), 4.02 (s, 2H), 2.42 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 193.3, 140.7, 139.6, 136.6, 135.3, 134.5, 134.2, 130.7, 129.6, 128.8, 128.5, 128.0, 127.8, 127.2, 126.4, 126.2, 125.0, 124.9, 119.6, 119.4, 110.7, 29.3, 19.9; HRMS (ESI-TOF) *m/z*: $C_{25}H_{20}NO$ $(M + H)^+$ calcd for 350.1539, found 350.1544.

*(2-Fluorophenyl)(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ao**):* Yield: 45.9 mg, 65%; yellow solid; mp 125.9-126.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57-7.53 (m, 2H), 7.48-7.43 (m, 3H), 7.40-7.38 (m, 1H), 7.36-7.29 (m, 4H), 7.23-7.19 (m, 2H), 7.17-7.13 (m, 1H), 7.02 (t, J = 8.4 Hz, 1H), 4.00 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 187.6, 159.8 (d, J = 249.7 Hz, 1C), 139.5,

135.1, 134.5, 134.0, 132.0 (d, J = 7.2 Hz, 1C), 130.4 (d, J = 3.0 Hz, 1C), 129.4, 129.2, 128.9, 127.8 (d, J = 5.9 Hz, 1C), 127.0, 126.3 (d, J = 18.3 Hz, 1C), 125.1, 123.8 (d, J = 3.6 Hz, 1C), 119.6, 118.7, 116.1, 115.8, 110.8, 29.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.0 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{24}H_{17}{}^{19}FNO$ $(M + H)^+$ calcd for 354.1289, found 354.1294.

*(3,5-Dichlorophenyl)(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ap**):* Yield: 46.7 mg, 58%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43-8.41 (m, 1H), 7.80 (s, 1H), 7.70 (d, J = 2.0 Hz, 2H), 7.56-7.53 (m, 2H), 7.44-7.39 (m, 4H), 7.36-7.32 (m, 3H), 5.17 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 187.4, 143.3, 136.7, 136.3, 135.1, 131.7, 130.9, 129.1, 128.4, 127.2, 127.0, 124.3, 123.4, 122.8, 121.5, 115.4, 110.0, 87.2, 80.9, 37.6; HRMS (ESI-TOF) *m/z*: $C_{24}H_{16}{}^{35}Cl_2NO$ $(M + H)^+$ calcd for 404.0604, found 404.0612.

*naphthalen-1-yl(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)methanone (**3ap**):* Yield: 46.2 mg, 60%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32-8.29 (m, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.88-7.86 (m, 1H), 7.77-7.75 (m, 1H), 7.56 (t, J = 7.2 Hz, 2H), 7.50-7.47 (m, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.39 (s, 1H), 7.34-7.29 (m, 3H), 7.23-7.17 (m, 3H), 4.03 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 192.5, 139.5, 138.5, 135.2, 134.5, 134.1, 133.6, 131.0, 130.6, 128.8, 128.1, 127.9, 127.8, 127.8, 127.2, 126.9, 126.4, 126.2, 126.2, 126.0, 125.0, 124.2, 119.9, 119.5, 110.8, 29.3; HRMS (ESI-TOF) *m/z*: $C_{28}H_{20}NO$ $(M + H)^+$ calcd for 386.1539, found 386.1547.

*(1-phenyl-9H-pyrrolo[1,2-a]indol-2-yl)(thiophen-2-yl)methanone (**3ar**):* Yield: 37.5 mg, 55%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (s, 1H), 7.70 (t, J = 2.4 Hz, 1H), 7.61-7.60 (m, 1H), 7.48-7.46 (m, 3H), 7.39-7.32 (m, 4H), 7.24-7.20 (m, 2H), 7.09-7.07 (m, 1H), 4.04 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 182.8, 145.6, 139.7, 134.8, 134.4, 134.2, 133.1, 132.6, 128.5, 128.2, 127.8, 127.5, 126.2, 126.0, 124.8, 119.3, 116.5, 110.6, 29.4; HRMS (ESI-TOF) *m/z*: $C_{22}H_{16}NOS$ $(M + H)^+$ calcd for 342.0947, found 342.0955.

*1-(4-Methoxyphenyl)-3,3-diphenylprop-2-en-1-one (**4**):* Yield: 39.6 mg, 63%; yellow solid; mp 95.1-95.6 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.8 Hz, 2H), 7.39-7.36 (m, 5H), 7.27-

7.25 (m, 3H), 7.19-7.17 (m, 2H), 7.08 (s, 1H), 6.86 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H); $^{13}C\{1H\}$NMR (100 MHz, $CDCl_3$) δ: 191.4, 163.2, 153.5, 141.5, 139.1, 131.1, 129.7, 128.5, 128.4, 128.2, 128.0, 113.5, 55.4; HRMS (ESI-TOF) *m/z*: $C_{22}H_{19}O_2$ $(M + H)^+$ calcd for 315.1380, found 315.1386.

Supporting Information Available: The copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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