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# Iridium(III)-Catalyzed C-7 Selective C−H Alkynylation of Indolines at Room Temperature

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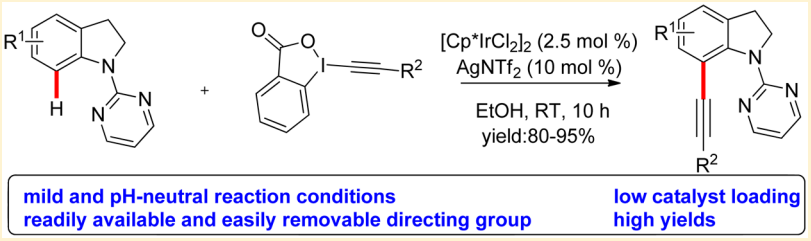
Supporting Information



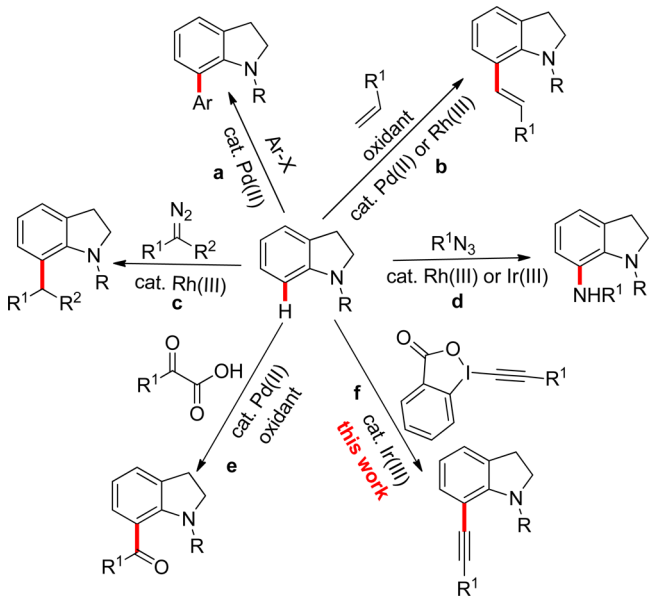

**ABSTRACT:** An iridium-catalyzed direct C-7 selective C−H alkynylation of indolines at room temperature, for the first time, has been developed via C−H bond activation. Furthermore, the first example of direct C−H alkynylation of carbazoles at the C1 position is also achieved. More importantly, the resulting product can be readily transformed into C7-alkynylated indoles, further widening the C-7 derivatization of indoles and highlighting the synthetic utility of this methodology.

The indoles and indolines are among the most privileged structures due to their ubiquity in numerous natural bioactive products, pharmaceutically important compounds, marketed drugs, and other functional molecules.[1] With the development of catalytic C−H functionalization, tremendous studies have been carried out on transition-metal-mediated C-2 or C-3 selective C−H functionalization of indoles.[2] In sharp contrast, similar approaches to access C7-functionalized indole derivatives have very limited reports,[3] although C7-substituted indoles are prevalent in important pharmaceutical agents.[4]

Recently, some examples of transition-metal-catalyzed direct C7-functionalization of indolines have been disclosed by several groups and us,[5−9] including the palladium-catalyzed C-7 arylation of indolines (Scheme 1a),[5] the oxidative transition-metal-catalyzed C-7 alkenylation of indolines with alkenes (Scheme 1b),[6] the Ir(I)- and Ir(III)-catalyzed C-7 alkylation of indolines (Scheme 1c),[7] the transition-metal-catalyzed amidation of indolines with azides (Scheme 1d),[8] and Pd-catalyzed C7-acylation of indolines (Scheme 1e).[9] However, to the best of our knowledge, there has been no previous report on catalytic C-7 C−H alkynylation of indolines, although alkynes are arguably one of the most versatile functionalities in synthetic chemistry.[10]

Over the past decade, transition-metal-catalyzed aromatic C−H bond functionalization, removing the need for prefunctionalization, represents a burgeoning field.[11] Recently, the C−H activation strategies have been successfully employed in the alkynylation of aromatic C−H bonds by palladium, ruthenium, and rhodium catalysis.[12] With our ongoing interest in the metal-catalyzed C−H functionalization,[13] we described herein a facile Ir(III)-catalyzed C7-selective alkynylation of indolines with the hypervalent iodine reagent (Scheme 1f), wherein the pyrimidyl directing group proves to be the key point for the success of this alkynylation. More importantly, this catalytic reaction can be carried out under very mild and pH-neutral reaction conditions (room temperature) and the resulting products can be readily transformed into C7-alkynylated indoles.

**Scheme 1. C-7 C−H Functionalization of Indolines**




To achieve this reaction, various *N*-protecting indolines (**1a**−**1h**) and a hypervalent iodine reagent (TIPS-EBX, **2a**) were

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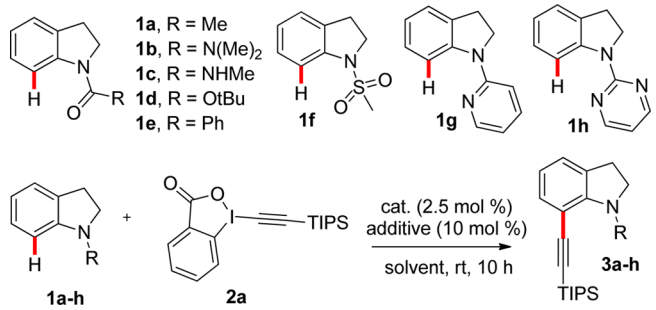
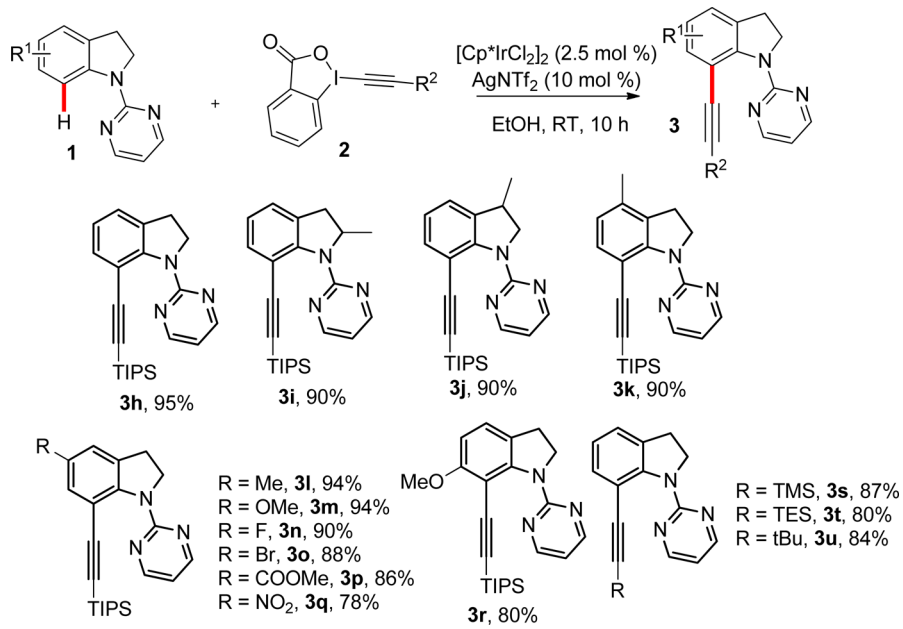
**Table 1. Reaction Optimization**[a]




| entry | substrates | catalyst (2.5 mol %) | solvents | yield (%)[b] |
|---|---|---|---|---|
| 1 | **1a−1f** | $[Cp^*RhCl_2]_2/AgSbF_6$ | DCE | 0 |
| 2 | **1g** | $[Cp^*RhCl_2]_2/AgSbF_6$ | DCE | 60 |
| 3 | **1h** | $[Cp^*RhCl_2]_2/AgSbF_6$ | DCE | 70 |
| 4 | **1h** | $[RuCl_2(p\text{-cymene})]_2/AgSbF_6$ | DCE | 63 |
| 5 | **1h** | $[Cp^*IrCl_2]_2/AgNTf_2$ | DCE | 83 |
| 6 | **1h** | $[Cp^*IrCl_2]_2/AgNTf_2$ | 1,4-dioxane | 60 |
| 7 | **1h** | $[Cp^*IrCl_2]_2/AgNTf_2$ | THF | 80 |
| 8 | **1h** | $[Cp^*IrCl_2]_2/AgNTf_2$ | EtOH | 95 |
| 9 | **1h** | $[Cp^*IrCl_2]_2/AgSbF_6$ | EtOH | 76 |
| 10 | **1h** | $[Cp^*IrCl_2]_2/AgOTf$ | EtOH | 83 |
| 11 | **1h** | $[Cp^*IrCl_2]_2/AgBF_4$ | EtOH | 75 |

[a]Conditions: **1a−1h**/**2a** = 1:1.5, 0.2 mmol scale, 2.5 mol % of catalyst; Rh, Ru or Ir/Ag = 1:4; rt for 10 h. [b]Yield of isolated product.

**Scheme 2. Ir(III)-Catalyzed C−H Alkynylation of Indolines**[a]




[a]The reaction was performed with 0.2 mmol of **1**, 0.25 mmol of **2**, 0.005 mmol of $[Cp^*IrCl_2]_2$, and 0.02 mmol of $AgNTf_2$ at room temperature in 3 mL of EtOH. The reported yields are of isolated product.

initially used as cross-coupling partners in the presence of $[Cp^*RhCl_2]_2$ (2.5 mol %) and $AgSbF_6$ (10 mol %) in DCE at room temperature for 10 h (Table 1). The choice of the N-protecting group was found to be crucial for this alkynylation reaction, and only pyridinyl- and pyrimidyl-protected indolines (**1g** and **1h**) afforded desired alkynylated products **3g** and **3h** in 60% and 70% yields, respectively (entries 2 and 3). By changing Rh(III) catalyst to Ru(II) catalyst, a relatively low yield was obtained (entry 4). To our delight, switching the Rh(III) catalyst to Ir(III) congener (2.5 mol %) in the presence of $AgNTf_2$ (10 mol %) gave an improved yield (83%) (entry 5). After a screen of solvents (entries 6−8), EtOH was proven to be optimal, providing **3h** in 95% yield (entry 8). Other halide abstractors were also explored (entries 9−11), but $AgNTf_2$ proved to be optimal (entry 8). It is noteworthy to mention that the C−H at the 2-position was untouched.

With the optimal conditions in hand, the substrate scope was examined with respect to indolines (Scheme 2). It was found that the electronic nature of the substituents on the indoline ring did not play a key role. Both electron-rich (**3i−3m**, **3r**) and



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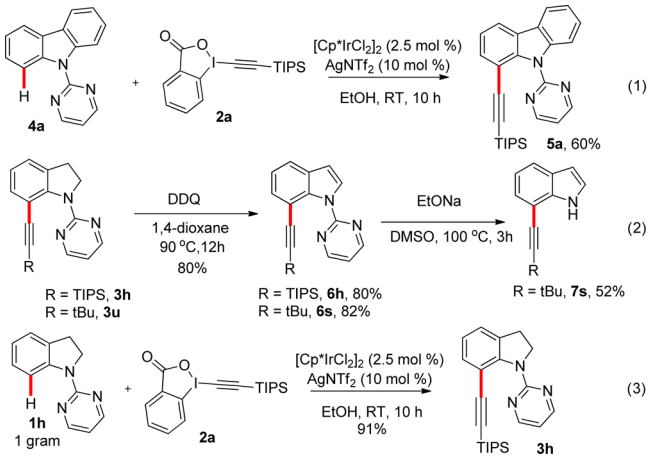
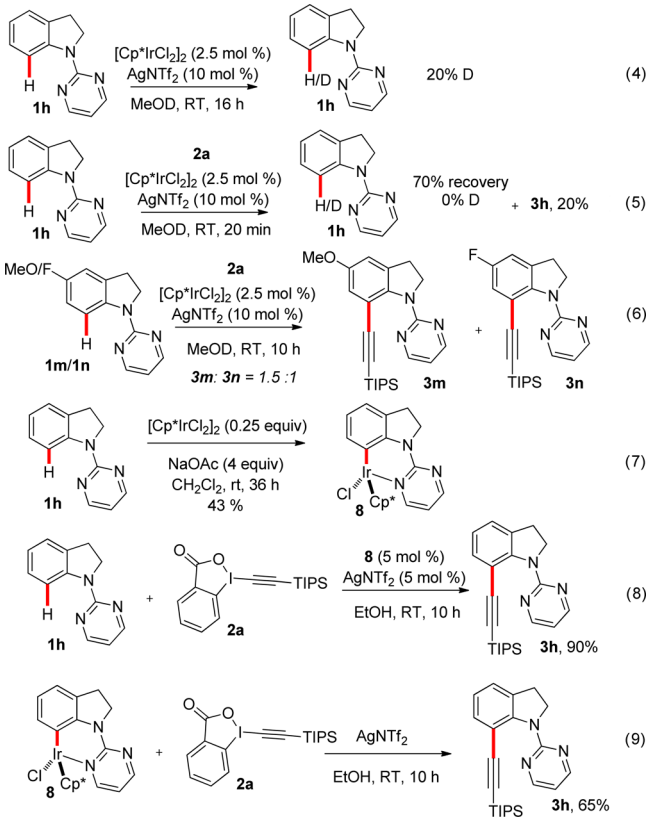
electron-poor (**3n**−**3q**) indolines gave the corresponding alkynylation products in excellent yields. Substitutions at the C2, C3, C4, C5, and even C6 positions of the phenyl ring, were all well tolerated, providing the corresponding products in excellent yields. Notably, the tolerance of halogens offers the opportunity for further transformations. Encouraged by these results, we further examined this alkynylation reaction with various hypervalent alkynyl iodine reagents. To our delight, other alkynes such as TMS-EBX, TES-EBX, and *t*Bu-EBX also afforded the corresponding products (**3s**−**3u**) in excellent yield.

Besides indolines, we were also intrigued by developing an alkynylation of carbazoles, given the unique structural features and biological activities of carbazoles.[14] Pleasingly, carbazole **4a** was readily converted to the alkynylation product **5a** in 60% yield (eq 1). To the best of our knowledge, this is the first example of transition-metal-catalyzed direct C−H alkynylation of carbazoles at the C1 position.[15]




The utility of this C-7 selective alkynylation reaction was further highlighted by its successful conversion of indolines into indoles (eq 2). Moreover, the pyrimidyl group can be successfully removed by the treatment of NaOEt in DMSO at 100 °C for 3 h, affording C7-alkynylated indole **7s** in 52% yield (eq 2). Finally, it merits mentioning that this reaction was successfully scalable to gram amounts of substrate without a decrease in yield (eq 3).

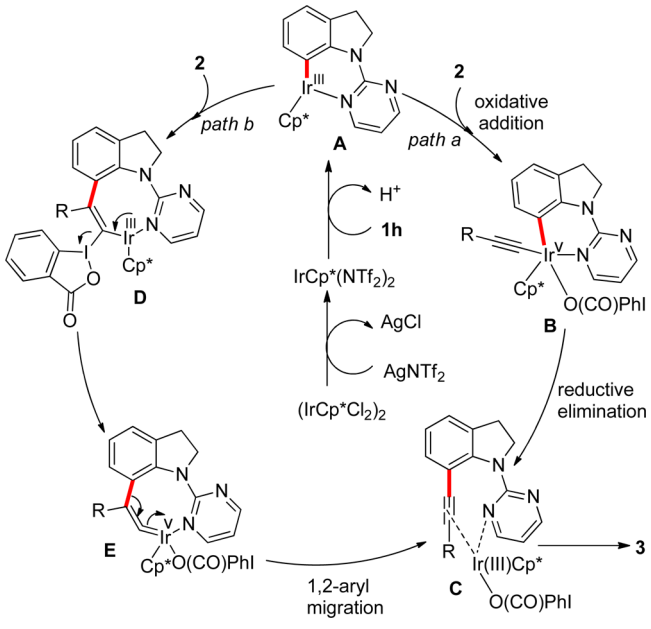
To gain insight into the mechanism, the following experiments were carried out. First, a moderate deuterium incorporation was observed in the C7 position of indoline when **1h** was treated with a catalytic amout of $(IrCp^*Cl_2)_2$ and $AgNTf_2$ in MeOD for 16 h, indicating that the C−H bond cleavage was a reversible process in the absence of TIPS-EBX **2a** (eq 4). When the reaction was carried out in the presence of **2a**, no deuterium incorporation was observed in the recovered **1h**, indicating the alkynylation process to be much faster than the deuteration (eq 5). Moreover, the competitive reaction of an equimolar amount of **1m**, **1n**, and **2a** under the standard conditions gave a mixture of **3m** and **3n** in a 1.5:1 ratio, suggesting that the more electron-rich indoline is kinetically favored (eq 6). In addition, treatment of **1h** with $(IrCp^*Cl_2)_2$ and NaOAc afforded a stable cyclometalated Ir(III) complex **8**, which was further characterized by single-crystal X-ray diffraction analysis (eq 7).[16] More importantly, complex **8** successfully catalyzed the alkynylation reaction of **1h** with **2a** (eq 8), and alkynylation reaction also occurred when treating **8** with $AgNTf_2$ and **2a** at room temperature (eq 9), indicating




that the cationic metalacycle is indeed an active species in the catalytic cycle.

On the basis of the observed experimental results, a plausible mechanistic pathway is proposed (Scheme 3). First, treatment of a dimeric iridium species with $AgNTf_2$ affords monomeric $IrCp^*(NTf_2)_2$, and then a six-membered cyclometalated Ir(III) complex **A** is formed via a Ir(III)-catalyzed C-7 C−H bond cleavage.[17] Then, an oxidative addition to the hypervalent iodine occurs to give an Ir(V) alkynyl **B**, which undergo a

**Scheme 3. Proposed Catalytic Cycle**



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reductive elimination to generate an Ir(III) alkyne intermediate **C** (path a).[18] Alternatively, **A** may undergo a regioselective migratory insertion into the alkyne to produce intermediate **D**. Then, an $\alpha$-elimination of 2-iodobenzoic acid from **D** occurs to generate iridium vinylidene species **E**, which undergoes a concerted or stepwise aryl-migration and elimination to afford the same intermediate **C**.[19] Finally, alkyne dissociation from **C** releases the C7-alkynylated indoline **3** and an active Ir(III) benzoate catalyst, which may undergo a C−H activation with indoline **1h** to regenerate **A**.

In conclusion, we have developed an iridium-catalyzed direct C-7 selective C−H alkynylation of indolines at room temperature that can be readily scaled up. A broad range of C-7 alkynylated indolines can be accessible in excellent yields. Synthetic utility of the current approach was demonstrated by the successful access to C-7 alkynylated indoles and the removal of a pyrimidyl group. Moreover, in addition to indolines, alkynylation of carbazoles is also developed. Considering the valuable structure of the products, we expect this regioselective alkynylation reaction to gain broad synthetic utility.

## EXPERIMENT SECTION

**General Information.** $^1$H NMR (400 or 300 MHz) and $^{13}$C NMR (125, 100 MHz) spectra were determined with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in ppm from internal TMS ($\delta$). All coupling constants ($J$ values) were reported in hertz (Hz). High-resolution mass spectra were recorded using the EI method with a double focusing magnetic mass analyzer. Reactions were monitored by thin-layer chromatography or LC-MS analysis. Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200−300 mesh). All of the reagents were used directly as obtained commercially unless otherwise noted.

**Typical Experimental Procedure for Synthesis of 3h−3u, and 5a.** $(IrCp^*Cl_2)_2$ (2.5 mol %), $Ag(NTf)_2$ (10 mol %), indolines **1** (0.2 mmol), alkyne **2** (0.3 mmol, 1.5 equiv), and EtOH (2 mL, 0.1 M) were added to a test tube. The reaction mixture was stirred at room temperature for 12 h. The crude mixture was filtered through Celite and concentrated under reduced pressure. The residue was then purified by flash column chromatography with PE/EtOAc (10:1) to give the desired product.

*Compound* ***3g***. Amorphous solid (45 mg, 60%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.31 (d, $J$ = 4.4 Hz, 1H), 7.49 (t, $J$ = 7.1 Hz, 1H), 7.34−7.27 (m, 1H), 7.20 (d, $J$ = 7.3 Hz, 1H), 6.99 (d, $J$ = 8.4 Hz, 1H), 6.89 (t, $J$ = 7.5 Hz, 1H), 6.83−6.77 (m, 1H), 4.37 (t, $J$ = 8.2 Hz, 2H), 3.10 (t, $J$ = 8.2 Hz, 2H), 0.95 (s, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 155.9, 147.6, 146.0, 136.1, 134.8, 132.6, 125.1, 121.5, 115.9, 112.8, 104.3, 99.7, 53.8, 28.7, 18.5, 11.1; HRMS (EI) Calcd for $C_{24}H_{32}N_2Si$ $[M]^+$ 376.2335, found 376.2331.

*Compound* ***3h***. Amorphous solid (71 mg, 95%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.46 (d, $J$ = 4.8 Hz, 2H), 7.35 (d, $J$ = 7.8 Hz, 1H), 7.18 (d, $J$ = 7.4 Hz, 1H), 6.93 (t, $J$ = 7.6 Hz, 1H), 6.71 (t, $J$ = 4.8 Hz, 1H), 4.38 (t, $J$ = 8.0 Hz, 2H), 3.09 (t, $J$ = 8.1 Hz, 2H), 0.96 (s, 21H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 160.3, 157.4, 144.7, 134.6, 132.6, 124.8, 122.8, 112.8, 112.7, 105.1, 98.1, 52.9, 29.2, 18.6, 11.2; HRMS (EI) Calcd for $C_{23}H_{31}N_3Si$ $[M]^+$ 377.2287, found 377.2281.

*Compound* ***3i***. Amorphous solid (70 mg, 90%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.46 (d, $J$ = 4.8 Hz, 2H), 7.38 (d, $J$ = 7.8 Hz, 1H), 7.20 (d, $J$ = 7.3 Hz, 1H), 6.96 (t, $J$ = 7.6 Hz, 1H), 6.76−6.64 (m, 1H), 4.93−4.77 (m, 1H), 3.48 (dd, $J$ = 15.4, 8.6 Hz, 1H), 2.54 (d, $J$ = 15.5 Hz, 1H), 1.44 (d, $J$ = 6.5 Hz, 3H), 1.04−0.94 (m, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 160.1, 157.4, 143.6, 133.4, 132.4, 132.4, 125.3, 122.9, 113.3, 112.8, 105.3, 97.9, 60.5, 36.7, 21.4, 18.6, 11.2; HRMS (EI) Calcd for $C_{24}H_{33}N_3Si$ $[M]^+$ 391.2444, found 391.2442.

*Compound* ***3j***. Amorphous solid (70 mg, 90%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.48 (d, $J$ = 4.8 Hz, 2H), 7.39 (d, $J$ = 7.7 Hz, 1H), 7.17 (d, $J$ = 7.4 Hz, 1H), 6.98 (t, $J$ = 7.6 Hz, 1H), 6.75−6.69 (m, 1H), 4.56 (dd, $J$ = 10.8, 8.4 Hz, 1H), 3.93 (dd, $J$ = 10.9, 7.2 Hz, 1H), 3.53−3.35 (m, 1H), 1.30 (t, $J$ = 7.1 Hz, 3H), 0.98 (s, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 160.4, 157.4, 144.4, 139.8, 132.8, 123.6, 123.0, 112.8, 112.6, 105.1, 98.1, 60.7, 35.9, 18.9, 18.6, 11.2; HRMS (EI) Calcd for $C_{24}H_{33}N_3Si$ $[M]^+$ 391.2444, found 391.2438.

*Compound* ***3k***. Amorphous solid (70 mg, 90%); $^1$H NMR (400 MHz, $CDCl_3$) $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.47 (d, $J$ = 4.8 Hz, 2H), 7.30 (d, $J$ = 8.7 Hz, 1H), 6.79 (d, $J$ = 7.9 Hz, 1H), 6.72 (t, $J$ = 4.7 Hz, 1H), 4.40 (t, $J$ = 8.0 Hz, 2H), 3.02 (t, $J$ = 8.0 Hz, 2H), 2.27 (s, 3H), 0.97 (s, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 160.5, 157.4, 144.4, 134.6, 133.0, 132.5, 124.1, 112.8, 110.1, 105.3, 97.1, 52.7, 27.9, 18.8, 18.6, 11.2; HRMS (EI) Calcd for $C_{24}H_{33}N_3Si$ $[M]^+$ 391.2444, found 391.2440.

*Compound* ***3l***. Amorphous solid (70.5 mg, 94%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.43 (d, $J$ = 4.8 Hz, 2H), 7.15 (s, 1H), 7.00 (s, 1H), 6.67 (t, $J$ = 4.8 Hz, 1H), 4.36 (t, $J$ = 7.9 Hz, 2H), 3.04 (t, $J$ = 7.9 Hz, 2H), 2.28 (s, 3H), 0.96 (s, 21H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 160.6, 157.4, 142.6, 134.8, 132.6, 132.5, 125.8, 112.6, 112.5, 105.2, 97.4, 52.9, 29.3, 20.7, 18.6, 11.2; HRMS (EI) Calcd for $C_{24}H_{33}N_3Si$ $[M]^+$ 391.2444, found 391.2439.

*Compound* ***3m***. Amorphous solid (76.5 mg, 94%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.43 (d, $J$ = 4.8 Hz, 2H), 6.83 (d, $J$ = 11.4 Hz, 2H), 6.66 (t, $J$ = 4.7 Hz, 1H), 4.38 (t, $J$ = 7.8 Hz, 1H), 3.79 (s, 2H), 3.05 (t, $J$ = 7.8 Hz, 1H), 0.96 (s, 10H); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 160.2, 156.9, 155.2, 138.4, 135.9, 115.2, 112.7, 112.3, 111.9, 104.3, 97.3, 55.4, 52.6, 29.1, 18.1, 10.7; HRMS (EI) Calcd for $C_{24}H_{33}N_3OSi$ $[M]^+$ 407.2393, found 407.2391.

*Compound* ***3n:*** Amorphous solid (74 mg, 94%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.46 (d, $J$ = 4.8 Hz, 2H), 7.04 (dd, $J$ = 9.5, 2.4 Hz, 1H), 6.95−6.91 (m, 1H), 6.72 (t, $J$ = 4.8 Hz, 1H), 4.42 (t, $J$ = 7.9 Hz, 2H), 3.08 (t, $J$ = 7.9 Hz, 2H), 0.96 (s, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 159.9, 157.9 (d, $J$ = 240 Hz), 156.9, 140.7, 136.2 (d, $J$ = 9.0 Hz), 117.5 (d, $J$ = 23.6 Hz), 113.0 (d, $J$ = 10.1 Hz), 112.4, 112.2, 103.3 (d, $J$ = 2.0 Hz), 98.7, 52.7, 28.9, 18.0, 10.6; HRMS (EI) Calcd for $C_{23}H_{30}FN_3Si$ $[M]^+$ 395.2193, found 395.2190.

*Compound* ***3o***. Amorphous solid (80 mg, 88%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.48 (d, $J$ = 4.7 Hz, 2H), 7.48 (s, 1H), 7.31 (s, 1H), 6.76 (t, $J$ = 4.6 Hz, 1H), 4.41 (t, $J$ = 8.0 Hz, 2H), 3.11 (t, $J$ = 7.9 Hz, 2H), 0.98 (s, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 159.7, 156.9, 143.6, 136.3, 134.0, 127.3, 114.2, 113.7, 112.7, 103.1, 99.3, 52.4, 28.5, 18.1, 10.6; HRMS (EI) Calcd for $C_{23}H_{30}BrN_3Si$ $[M]^+$ 455.1392, found 455.1392.

*Compound* ***3p***. Amorphous solid (74 mg, 86%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.51 (d, $J$ = 3.6 Hz, 2H), 8.07 (s, 1H), 7.84 (s, 1H), 6.80 (s, 1H), 4.42 (t, $J$ = 7.8 Hz, 2H), 3.91 (s, 3H), 3.16 (t, $J$ = 7.4 Hz, 2H), 0.97 (s, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 166.5, 159.9, 157.4, 148.6, 135.3, 134.7, 125.7, 124.4, 113.8, 111.6, 104.1, 99.3, 53.1, 52.0, 28.5, 18.6, 11.1; HRMS (EI) Calcd for $C_{25}H_{33}N_3O_2Si$ $[M]^+$ 435.2342, found 435.2338. Compound **3q**: Amorphous solid (65 mg, 78%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.56 (d, $J$ = 4.8 Hz, 2H), 8.28 (d, $J$ = 2.2 Hz, 1H), 8.05−8.01 (m, 1H), 6.89 (t, $J$ = 4.8 Hz, 1H), 4.48 (t, $J$ = 8.3 Hz, 2H), 3.23 (t, $J$ = 8.3 Hz, 2H), 0.98 (s, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 159.4, 157.5, 150.1, 142.6, 135.7, 129.8, 119.9, 114.6, 111.3, 102.8, 101.4, 53.3, 28.2, 18.6, 11.1; HRMS (EI) Calcd for $C_{23}H_{30}N_4O_2Si$ $[M]^+$ 422.2318, found 422.2315.

*Compound* ***3r***. Amorphous solid (65 mg, 80%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.48 (d, $J$ = 4.8 Hz, 2H), 7.11 (d, $J$ = 8.2 Hz, 1H), 6.72 (dd, $J$ = 8.6, 4.1 Hz, 1H), 6.51 (d, $J$ = 8.2 Hz, 1H), 4.40 (t, $J$ = 7.9 Hz, 2H), 3.86 (s, 3H), 3.04 (t, $J$ = 7.9 Hz, 2H), 0.99 (s, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 161.2, 160.4, 157.3, 146.4, 126.5, 124.34, 124.3, 112.8, 105.2, 103.4, 102.8, 100.8, 56.2, 53.9, 28.6, 18.6, 11.3; HRMS (EI) Calcd for $C_{24}H_{33}N_3OSi$ $[M]^+$ 407.2393, found 407.2388.

*Compound* ***3s***. Amorphous solid (50.5 mg, 87%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.51 (d, $J$ = 4.8 Hz, 2H), 7.34 (d, $J$ = 7.4 Hz, 1H), 7.20 (d, $J$ = 7.3, 1.1 Hz, 1H), 6.93 (t, $J$ = 7.6 Hz, 1H), 6.75 (t, $J$ = 4.8 Hz, 1H), 4.39 (t, $J$ = 8.0 Hz, 2H), 3.12 (t, $J$ = 8.1 Hz, 2H), 0.05 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 160.1, 157.2, 144.9, 134.4, 132.1, 125.0, 122.6, 112.8, 111.6, 103.3, 101.8, 52.6, 29.1, −0.21; HRMS (EI) Calcd for $C_{17}H_{19}N_3Si$ $[M]^+$ 293.1348, found 293.1345.



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*Compound* ***3t***. Amorphous solid (53.5 mg, 80%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.47 (d, $J$ = 4.8 Hz, 2H), 7.33 (d, $J$ = 7.9 Hz, 1H), 7.16 (d, $J$ = 7.9 Hz, 1H), 6.91 (t, $J$ = 7.5 Hz, 1H), 6.71 (t, $J$ = 4.7 Hz, 1H), 4.36 (t, $J$ = 8.0 Hz, 2H), 3.09 (t, $J$ = 8.0 Hz, 2H), 0.84 (t, $J$ = 7.9 Hz, 9H), 0.46 (q, $J$ = 7.9 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 160.1, 157.3, 144.9, 134.5, 132.4, 124.9, 122.7, 112.8, 112.1, 104.3, 99.4, 52.7, 29.1, 7.4, 4.2; HRMS (EI) Calcd for $C_{20}H_{25}N_3Si$ $[M]^+$ 335.1818, found 335.1816.

*Compound* ***3u***. Amorphous solid (46.5 mg, 84%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.52 (d, $J$ = 4.8 Hz, 2H), 7.27 (d, $J$ = 7.9 Hz, 1H), 7.16 (d, $J$ = 7.3 Hz, 1H), 6.93 (t, $J$ = 7.6 Hz, 1H), 6.74 (t, $J$ = 4.8 Hz, 1H), 4.38 (t, $J$ = 8.0 Hz, 2H), 3.11 (t, $J$ = 7.9 Hz, 2H), 1.09 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 160.4, 157.3, 144.6, 134.3, 131.7, 123.9, 122.8, 112.8, 112.5, 105.8, 52.9, 30.7, 29.3, 28.0; HRMS (EI) Calcd for $C_{18}H_{19}N_3$ $[M]^+$ 277.1579, found 277.1575.

*Compound* ***5a***. Amorphous solid (51 mg, 60%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.89 (d, $J$ = 4.8 Hz, 2H), 8.07 (m, 3H), 7.67 (d, $J$ = 7.5 Hz, 1H), 7.32 (m, 4H), 0.98 (s, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 158.4, 158.1, 141.0, 133.3, 126.9, 126.5, 124.8, 122.2, 121.8, 120.6, 120.0, 118.2, 112.3, 109.8, 104.8, 98.8, 18.7, 11.3; HRMS (EI) Calcd for $C_{27}H_{31}N_3Si$ $[M]^+$ 425.2287, found 425.2282.

**Typical Experimental Procedure for Synthesis of 6h and 6s.** To a solution of **3h** or **3u** (0.2 mmol) in 1,4-dioxane (2 mL) was added DDQ (0.4 mmol). The mixture was stirred at 90 °C for 12 h. The resulting mixture was cooled to room temperature and then was poured into EtOAc (30 mL). The organic layer washed with $Na_2CO_3$ (aq.) (30 mL) and $H_2O$ (30 mL), dried ($Na_2SO_4$), and filtered. After removal of solvent, the product was purified by flash column chromatography with PE/EtOAc (10:1) to give product **6h** or **6s**.

*Compound* ***6h***. Amorphous solid (60 mg, 80%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.80 (d, $J$ = 4.8 Hz, 2H), 7.79 (d, $J$ = 3.5 Hz, 1H), 7.65 (d, $J$ = 7.8 Hz, 1H), 7.56 (d, $J$ = 7.4 Hz, 1H), 7.26–7.11 (m, 2H), 6.73 (d, $J$ = 3.5 Hz, 1H), 1.01 (s, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 158.3, 157.4, 134.1, 131.8, 131.0, 129.7, 121.9, 121.8, 117.8, 109.7, 106.6, 105.4, 98.5, 18.6, 11.3; HRMS (EI) Calcd for $C_{23}H_{29}N_3Si$ $[M]^+$ 375.2131, found 375.2127.

*Compound* ***6s***. Amorphous solid (45 mg, 82%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.80 (d, $J$ = 4.8 Hz, 2H), 7.72 (d, $J$ = 3.5 Hz, 1H), 7.58 (d, $J$ = 7.8 Hz, 1H), 7.42 (d, $J$ = 7.4 Hz, 1H), 7.16 (dd, $J$ = 9.9, 5.5 Hz, 2H), 6.70 (t, $J$ = 4.9 Hz, 1H), 1.09 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 158.3, 157.6, 157.4, 134.5, 131.6, 129.7, 129.6, 121.8, 120.9, 117.6, 110.0, 106.5, 105.7, 30.8, 28.0; HRMS (EI) Calcd for $C_{18}H_{17}N_3$ $[M]^+$ 275.1422, found 275.1420.

**Procedure for the Removal of the Pyrimidyl Group.** Under Ar, **6s** (27 mg) was dissolved in dry DMSO (1 mL), and 20% EtONa in EtOH (100 $\mu$L) was added. The mixture was stirred at 100 °C for 3 h and then cooled, and 2 N HCl was added. The mixture was diluted with EtOAc and washed brine. The combined organic phase was dried ($Na_2SO_4$). After evaporation of the solvents under reduced pressure, the crude product was purified on a silica gel column with PE/EtOAc (5:1) to afford the product **7s** (10 mg, yield 52%), amorphous solid. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.35 (s, 1H), 7.58 (d, $J$ = 7.8 Hz, 1H), 7.25 (d, $J$ = 5.5 Hz, 2H), 7.05 (t, $J$ = 7.6 Hz, 1H), 6.56 (s, 1H), 1.40 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 136.7, 127.3, 125.1, 124.2, 120.8, 119.9, 107.1, 103.4, 102.9, 75.1, 31.5, 28.5; HRMS (EI) Calcd for $C_{14}H_{15}N$ $[M]^+$ 197.1204, found 197.1201.

**The Synthesis and Characterization of Ir(III) Complex 8.** Indolines **1h** (197 mg, 1 mmol), $[IrCp^*Cl_2]_2$ (197 mg, 0.25 mmol, 0.25 equiv), and NaOAc (328 mg, 4.00 mmol, 4 equiv) were weighed into a 25 mL Schlenk tube, to which $CH_2Cl_2$ (6 mL) was added. The mixture was stirred at room temperature for 36 h. The mixture was filtered through a pad of Celite. All the volatiles were removed under reduced pressure, and the solid residue was washed with diethyl ether to give a crude product, which was recrystallized in $CH_2Cl_2$–diethyl ether to give analytically pure **8** as a brown color solid in 43% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.68 (d, $J$ = 3.6 Hz, 1H), 8.31 (s, 1H), 7.27 (d, $J$ = 6.8 Hz, 1H), 6.85 (t, $J$ = 7.4 Hz, 1H), 6.69 (d, $J$ = 7.3 Hz, 1H), 6.52 (t, $J$ = 5.0 Hz, 1H), 4.30 (m, 1H), 4.01 (m, 1H), 3.30–3.15 (m, 1H), 3.09 (m, 1H), 1.46 (s, 15H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.3, 157.3, 154.5, 142.0, 138.0, 127.1, 126.2, 125.5, 119.3, 112.1, 88.2, 47.4, 28.8, 8.81; HRMS (EI) Calcd for $C_{22}H_{25}ClN_3Ir$ $[M]^+$ 559.1366, found 559.1376.

## ■ ASSOCIATED CONTENT

### Supporting Information

Single-crystal X-ray crystallography of compound **8**. $^1$H and $^{13}$C NMR spectra of all synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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