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Cp*Co^{III}-Catalyzed C(7)−H Bond Annulation of Indolines with Alkynes

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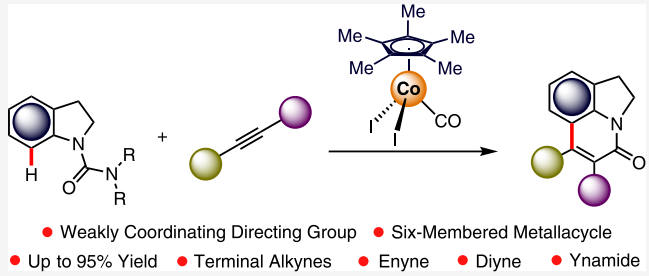
ABSTRACT: An efficient protocol for the synthesis of biologically essential pyrroloquinolinones has been developed under Cp*Co^{III} catalysis, which involves a cascade reaction of C(7)−H alkenylation with alkynes followed by nucleophilic addition. A wide variety of internal alkynes including enyne, diyne, and ynamide and more challenging terminal alkynes were successfully employed for the annulation in good to excellent yield with high regioselectivity.



INTRODUCTION

Over the past few decades, directing-group-assisted catalytic C−H bond functionalizations have been paramount in the field of synthetic organic chemistry to construct new carbon−carbon and carbon−heteroatom bonds.[1,2] The scarcity of abundance and extensive use of precious transition metals such as [Ir], [Rh], [Ru], etc. in catalytic C−H bond functionalization call for the synthetic community to look for an economical and sustainable alternative. In the past few years, catalysts based on earth-abundant 3d metals have been explored extensively for the aforementioned processes.[3] Among them, the Cp*Co^{III} catalytic system has demonstrated its significance complementary to the other group 9 congeners such as [Rh] and [Ir] because of its unique and versatile reactivity, as pioneered by Matsunaga and Kanai[4] and later by many other groups.[5] However, the overdependence on strongly coordinating directing groups such as pyridyl, pyrimidyl, and pyrazoyl is a major problem in cobalt-catalyzed C−H functionalizations.[6,7] Hence, it is important to develop novel C−H functionalization protocols using a Cp*Co^{III} catalyst with weakly coordinating directing groups. However, only handful of examples have been explored using directing groups such as amides, ketones, and carboxylic acids with Cp*Co^{III} catalysts, probably because of the less favored formation of the key metallacyclic intermediate.[8,9]

Indole and its derivatives are omnipresent in various natural products and bioactive molecules.[10] More specifically, heterocycles such as the pyrroloquinolinone unit constitute the core structure of various natural products and medicinally important molecules toward asthma, obesity, and epilepsy and inhibit antiacetylcholinesterase activity (Figure 1).[11] In this context, precious 4d and 5d transition metals have been utilized for their synthesis via the coupling of *N*-carbamoyl-protected indoline with alkyne. However, these protocols suffer

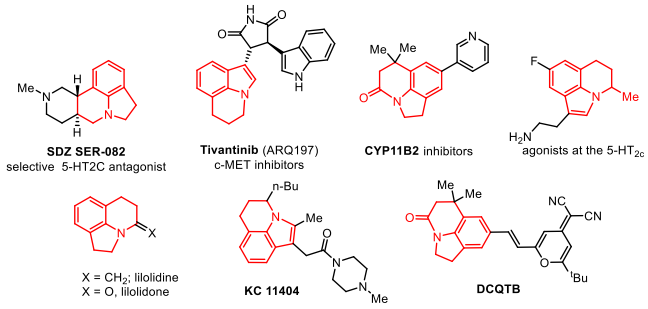


Figure 1. Representative Examples of Bio-Relevant Molecules Containing the Pyrroloquinolinone Core Unit.

from limited scope, as only internal alkynes are amenable to annulation and no reactivity has been observed with terminal alkynes.[12] Inspired by the unique nucleophilic activity of organocobalt species over organorhodium species reported by Matsunaga and Kanai,[9b,e] we envisaged annulating the C(7)−H bond of indoline with various alkynes. It is expected that the cobalt catalyst may undergo six-membered cyclometalation at the C(7) position[13,14] of indoline assisted by a carbamoyl directing group.[15] The alkyne further inserts into the organocobalt species to produce an alkenyl−cobalt intermediate that subsequently facilitates the nucleophilic attack of [Co]−C to the less electrophilic carbamoyl group, leading to the annulation product with the liberation of a secondary

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amine. In a continuation of our earlier work on weakly coordinating directing-group-assisted Cp*Co^{III}-catalyzed C−H bond functionalizations,[16] we sought to access such biologically important skeletons via coupling with a diverse range of alkynes, including terminal alkynes, diynes, enynes, ynamides, etc.

RESULTS AND DISCUSSION

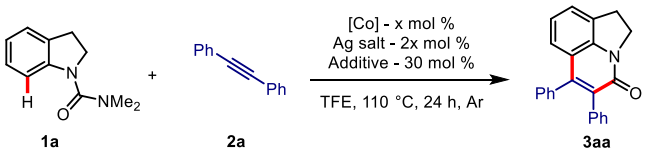
We began our studies with 0.2 mmol of *N*,*N*-dimethylindoline-1-carboxamide (**1a**) as the limiting reagent and 1,2-diphenylethyne (**2a**) as the coupling partner in the presence of Cp*Co(CO)I_2 (10 mol %), $AgSbF_6$ (20 mol %), and sodium acetate (30 mol %) in TFE (0.2 M) at 110 °C (Table 1). To our delight, the desired annulated product **3aa** was isolated in 42% yield after 24 h (Table 1, entry 1). In order to improve the efficiency of the reaction, we optimized various reaction parameters, including additives (entries 2−6), solvents (entries 6 and 7), silver salts (entries 6 and 8), cobalt catalyst precursors (entries 9 and 10), solvent concentration (entries 11 and 12), and reaction temperature (entry 13). Among the various additives screened, zinc triflate was found to be optimal (entry 6) and provided the expected product **3aa** in 72% yield. Although the role of the zinc triflate is not clear at this point, we believe that it may likely play a role in the cyclization. A change of solvent from 2,2,2-trifluoroethanol (TFE) to 1,2-dichloroethane (DCE) did not improve the reactivity (entry 7); however, a satisfactory yield of **3aa** was obtained when AgOTf was used in place of $AgSbF_6$ (entries 6 and 8).

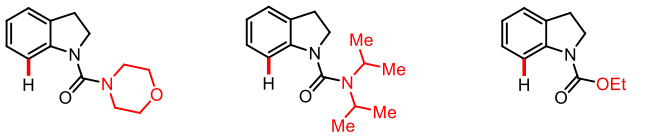
To our surprise, the chloride and iodide dimers of Cp*Co^{III} both failed to provide a satisfactory yield of **3aa** (Table 1, entries 9 and 10). Finally, the product **3aa** was isolated in an excellent yield of 95% when the reaction was performed using a 0.1 M concentration (entry 11). A further lowering of temperature or catalyst loading did not show promising results (entries 13 and 14). Control experiments revealed that both silver salt and additive are crucial to deliver the product **3aa** in high yield (entries 15 and 16). A blank experiment revealed that the catalyst is essential to obtain the annulated product **3aa** (entry 17). We further examined various indoline derivatives protected with different weakly coordinating directing groups such as indolin-1-yl(morpholino)methanone (**1j**), *N*,*N*-diisopropylindoline-1-carboxamide (**1k**), and ethyl indoline-1-carboxylate (**1l**). The sterically hindered carbamoyl groups were less suitable in delivering the desired product, whereas the ester failed to provide the desired product.

With the optimized conditions in hand, the scope of the annulation reactions was explored. As shown in Scheme 1, a wide variety of internal symmetrical alkynes containing electron-donating and electron-withdrawing substituents annulated smoothly with *N*,*N*-dimethylindoline-1-carboxamide (**1a**) to provide the corresponding pyrroindolinone derivatives in 72−91% yields (**3ab**−**ah**) (Scheme 1a). The scalability of the reaction was further checked on a 1.0 mmol scale, and to our delight an excellent yield of 92% was obtained (**3aa**).

Symmetrical bis-aliphatic alkynes (**2e**−**h**) underwent annulation smoothly with excellent yields, whereas moderate yields were obtained under the optimized conditions reported previously.[10] A further examination revealed that a variety of unsymmetrical alkynes also afforded the expected products (**3ai**−**at**) in moderate to good yields (39−78%) with high regioisomeric ratios (Scheme 1b). The regioselectivity was further confirmed by determining the X-ray structure of **3aj**.[17] Aryl/aliphatic alkynes having phenyl, naphthyl, and aliphatic variants with different chain lengths were amenable under the reaction conditions. Interestingly, alkynes such as (3-(benzyloxy)prop-1-yn-1-yl)benzene (**2o**), 3-phenylprop-2-yn-1-ol (**2p**), and 4-methyl-*N*-(3-phenylprop-2-yn-1-yl)-benzenesulfonamide (**2q**) provided the corresponding products in moderate to good yields (**3ao**−**aq**). In addition to alkynes, the methodology was also quite effective with a diyne (**2r**), an enyne (**2s**), and an ynamide (**2t**), affording the regioselective annulated products (**3ar**−**3at**) with acceptable yields (39−46%) using 30 mol % of NaOPiv as an additive instead of $Zn(OTf)_2$. Subsequently, the scope of the indolines was examined under the optimized reaction conditions (Scheme 1c). Indolines containing electron-donating as well as electron-withdrawing substituents present on the phenyl ring underwent annulation smoothly to produce the cyclized products (**3ba**−**ga**) in good to excellent yields (81−94%). Useful functional groups such as −OMe, −Cl, and −Br were kept intact after annulation, which can be used as additional handles for further transformations. Both 2-methyl *N*-carbamoyl indoline (**2h**) and 3-methyl *N*-carbamoyl indoline (**2i**) underwent cyclization with diphenylacetylene to provide

Table 1. Results of Optimization[a]





entry	[Co] (mol %)	[Ag] (mol %)	additive (mol %)	yield[b] (%)
1	Cp*Co(CO)I_2 (10)	$AgSbF_6$ (20)	NaOAc (30)	42
2	Cp*Co(CO)I_2 (10)	$AgSbF_6$ (20)	NaOPiv (30)	40
3	Cp*Co(CO)I_2 (10)	$AgSbF_6$ (20)	AgOPiv (30)	54
4	Cp*Co(CO)I_2 (10)	$AgSbF_6$ (20)	PivOH (30)	43
5	Cp*Co(CO)I_2 (10)	$AgSbF_6$ (20)	$AdCO_2H$ (30)	50
6	Cp*Co(CO)I_2 (10)	$AgSbF_6$ (20)	$Zn(OTf)_2$ (30)	72
7	Cp*Co(CO)I_2 (10)	$AgSbF_6$ (20)	$Zn(OTf)_2$ (30)	43[c]
8	Cp*Co(CO)I_2 (10)	AgOTf (20)	$Zn(OTf)_2$ (30)	82
9	$[Cp^*CoI_2]_2$ (5)	AgOTf (20)	$Zn(OTf)_2$ (30)	23
10	$[Cp^*CoCl_2]_2$ (5)	AgOTf (20)	$Zn(OTf)_2$ (30)	16
11	Cp*Co(CO)I_2 (10)	AgOTf (20)	$Zn(OTf)_2$ (30)	95[d]
12	Cp*Co(CO)I_2 (10)	AgOTf (20)	$Zn(OTf)_2$ (30)	24[e]
13	Cp*Co(CO)I_2 (10)	AgOTf (20)	$Zn(OTf)_2$ (30)	82[f]
14	Cp*Co(CO)I_2 (5)	AgOTf (10)	$Zn(OTf)_2$ (30)	58
15	Cp*Co(CO)I_2 (10)	AgOTf (10)		55
16	Cp*Co(CO)I_2 (10)		$Zn(OTf)_2$ (30)	53
17		AgOTf (10)	$Zn(OTf)_2$ (30)	ND

[a]All of the reactions were carried out under an argon atmosphere, unless otherwise stated, using 0.2/0.24/0.02/0.04/0.06 mmol of **1a**/**2a**/[Co]/[Ag]/additive at 110 °C in TFE (0.2 M). Abbreviations: TFE, 2,2,2-trifluoroethanol; DCE, 1,2-dichloroethane; ND, not determined. [b]Isolated yield. [c]DCE (0.2 M) was used as the solvent. [d]Reaction performed in TFE (0.1 M). [e]Reaction performed in TFE (0.4 M). [f]Reaction performed at 90 °C.

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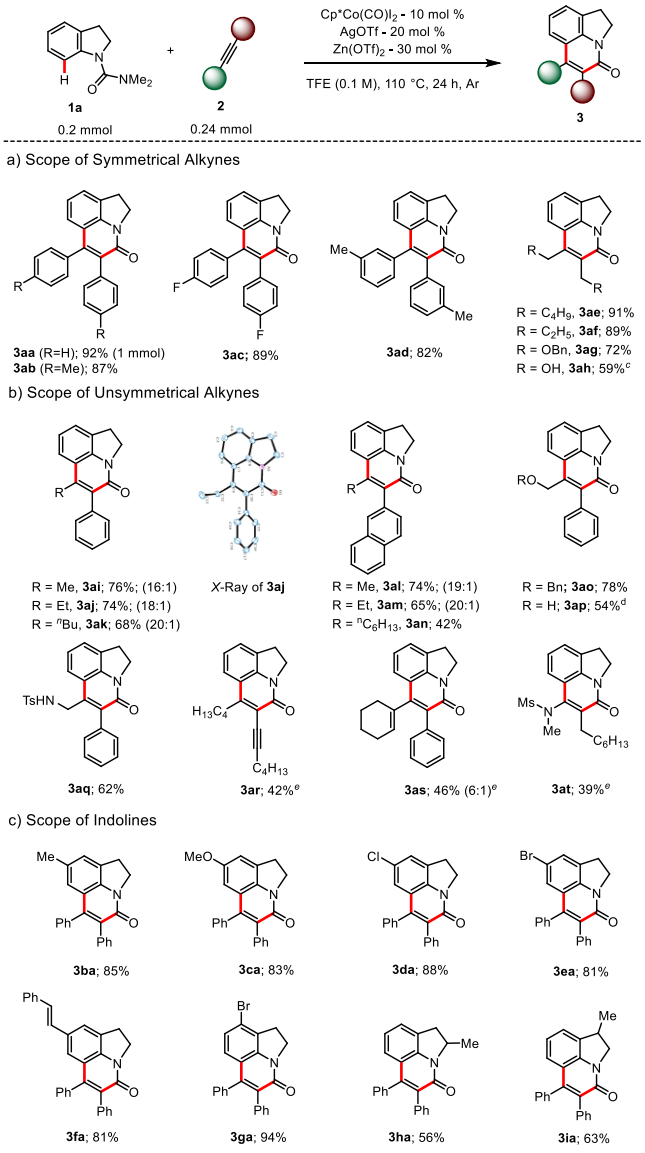
Scheme 1. Substrate Scope[a,b]

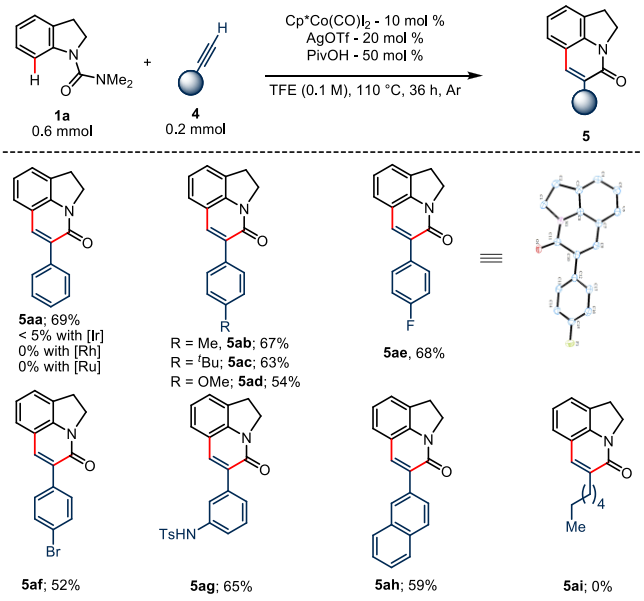


[a]All of the reactions, unless stated otherwise, were carried out under an argon atmosphere using 0.2/0.24/0.02/0.04/0.06 mmol of **1**/**2**/[Co]/[Ag]/additive at 110 °C in TFE (0.1 M) for 24 h. [b]Isolated yield of single regioisomer. [c]Reaction time 48 h. [d]3-Phenylprop-2-yn-1-yl acetate was used as the alkyne. [e]30 mol % of NaOPiv was used in place of $Zn(OTf)_2$, and the reaction was carried out for 36 h.

the expected annulated products (**3ha,ia**) in good yields (56−63%).

We next examined the scope of annulation using more challenging terminal alkynes (Scheme 2). In comparison to internal alkynes, terminal alkynes have been considered as nontrivial coupling partners in transition-metal-catalyzed C−H bond functionalizations due to competent self-dimerization or -trimerization.[18] Under the conditions optimized for internal alkynes, phenylacetylene **4a** failed to deliver the annulated product **5aa**. A brief screening of additives and reaction stoichiometry revealed that 50 mol % of pivalic acid (PivOH) is sufficient to acquire 5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (**5aa**) in 69% yield as a single regioisomeric product. On the other hand, widely explored metal precursors such as $[Cp^*RhCl_2]_2$, Ru(*p*-cymene)$_2Cl_2$, and $[Cp^*IrCl_2]_2$ for

Scheme 2. Scope with Terminal Alkynes[a]

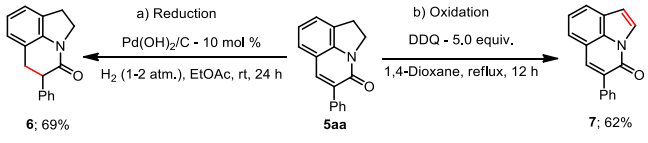


[a]All of the reactions were carried out under an argon atmosphere using 0.6/0.2/0.02/0.04/0.06 mmol of **1a**/**4**/[Co]/[Ag]/PivOH at 110 °C in TFE (0.1 M) for 36 h.

C−H bond functionalizations provided only trace amounts of products under our optimized conditions. We further tested phenylacetylene toward annulation with the previously reported reaction conditions with [Ru] and [Rh] metal precursors, and similar results were encountered with no desired product. To understand the stereoelectronic effect involved in the reaction, several phenylacetylenes having electron-donating and electron-withdrawing substituents were tested under the optimized reaction conditions (Scheme 2). All of the alkynes irrespective of their substituents present at either *meta* or *para* positions reacted smoothly to provide the annulated products (**5ab**−**ag**) as single regioisomers with moderate to good yields (59−69%). The product regiochemistry of **5ae** was further established by an X-ray crystal structure determination.[17] Functional groups such as −F, −Br, and −NHTs were tolerated and hence could serve as additional handles for postsynthetic derivatizations. Delightfully, 2-ethynylnaphthalene (**2h**) underwent the desired annulation smoothly, whereas electron-rich aliphatic terminal alkynes (**4i**) failed to provide the desired product under the optimized conditions.

To further illustrate the synthetic utility of this protocol, 5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (**5aa**) was subjected to oxidation and reduction separately (Scheme 3). The reduction of **5aa** using [Pd] catalyst and molecular hydrogen as the sole reductant gave 5-phenyl-5,6-dihydro-1*H*-pyrrolo[3,2,1-*ij*]quinolin-4(2*H*)-one (**6**) in 69% yield (Scheme 3a). On the other hand, DDQ oxidation provided the

Scheme 3. Applications of 5aa



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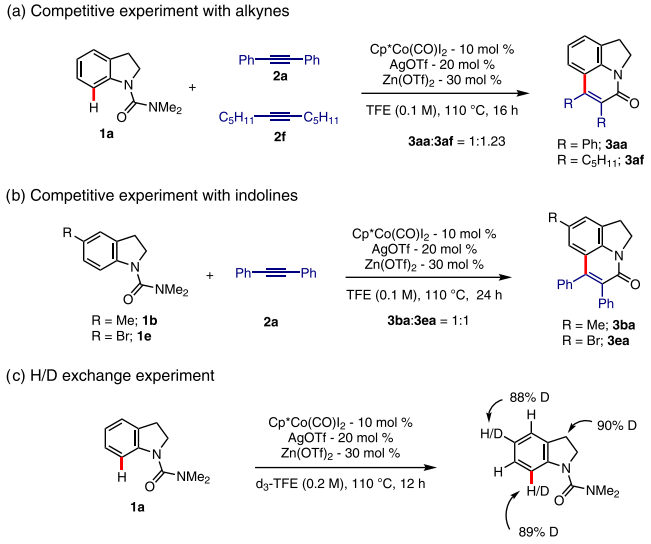
synthetically important 5-phenyl-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (**7**) in 62% yield (Scheme 3b).

To get an insight into the reaction mechanism, preliminary control experiments were carried out as shown in Scheme 4. At

Scheme 4. Mechanistic Studies



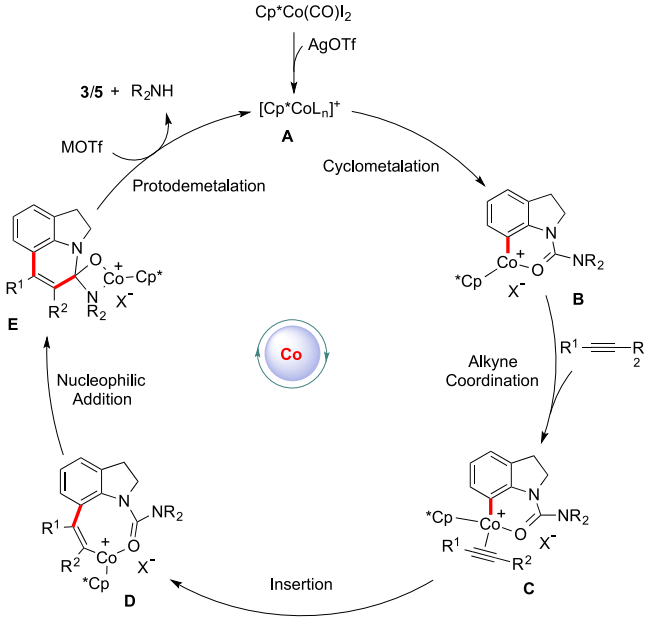
first, intermolecular competitive experiments with equimolar amounts of alkyne implied the faster formation of product **3ae** with the aliphatic alkyne **2e** in comparison with the aromatic alkyne **2a** (**3aa**:**3ae** = 1:1.23) (Scheme 4a). This is probably due to facile insertion into the M−C bond with the electron-rich alkyne **2e** over the electron-deficient partner **2a**. Other intermolecular competitive experiments with equimolar amount of *N*-carbamoyl indoline **1b**,**e** were carried out, and it was found that both substrates react with 1,2-diphenylacetylene (**2a**) with similar efficiency (**3ba**:**3ea** = 1:1) (Scheme 4b). Deuterium incorporation at the C(7) and C(5) positions observed to be 89% and 88%, respectively, in H/D scrambling experiments suggested that the cyclometalation step is reversible in nature and that the C−H bond cleavage follows an electrophilic activation pathway (Scheme 4c).

On the basis of the preliminary experiments and previous literature,[8,9,14] a plausible mechanism is proposed in Scheme 5. The reaction mechanism is initiated by the formation of the *in situ* generated cationic [Co] complex **A**. Substrate binding to the metal via weak coordination followed by cyclometalation leads to intermediate **B**. Subsequent coordination of the alkyne to **B**, followed by insertion of the alkyne into the [Co]−C bond, provides the intermediate **D**. Nucleophilic addition of the alkenyl−Co(III) bond to an electrophilic carbamoyl group leads to intermediate **E**, which finally undergoes protodemetalation to give the desired [4 + 2] annulated product **3**/**5** with concomitant release of a secondary amine and the active catalyst **A** back into the catalytic cycle.

CONCLUSION

In summary, we have developed an efficient Cp*Co^{III}-catalyzed regioselective protocol for the synthesis of biologically important pyrroloquinolinones. A diverse range of alkynes, including internal alkynes, terminal alkynes, diyne, ynamide, and enyne, were amenable in delivering the pyrroloquinolinone derivatives in good to excellent yields. Preliminary experiments revealed that the electrophilic cyclometalation step is reversible. The isolation of reaction intermediates and further mechanistic investigations are currently ongoing in our laboratory.

Scheme 5. Plausible Mechanism



EXPERIMENTAL SECTION

General Information. Unless otherwise mentioned, all reactions were carried out under an argon atmosphere. 1,2-Dichloroethane (1,2-DCE) was dried using calcium hydride according to the established protocol. Reagent-grade 2,2,2-trifluoroethanol (TFE) and 1,4-dioxane and HPLC-grade ethyl acetate (EtOAc) were used as such from the commercial sources. ^{1}H and ^{13}C NMR were recorded on JEOL 400 and 500 MHz spectrometers using $CDCl_3$ and DMSO-d_6 as solvents. Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) in Hz. The solvent signals used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$, δ_C 77.0 ppm, δ_H 7.26 ppm; DMSO-d_6, δ_C 39.52 ppm, δ_H 2.50 ppm). All of the reactions were monitored by analytical thin-layer chromatography (TLC) using commercial aluminum sheets precoated with silica gel. Column chromatography was conducted on silica gel (Merck, 200−400 mesh). HRMS measurements were recorded on a quadrupole time-of-flight mass spectrometer. Unless otherwise mentioned, all other chemicals were received and used as such from the commercial sources. Alkynes, enynes, diynes, and ynamides were prepared according to the literature procedure.[19]

General Procedure for the Synthesis of *N*-Acyl or *N*-Carbamoyl Indolines 1a−l. To a stirred solution of the indoline derivative (10 mmol, 1.0 equiv) prepared by the literature procedure and triethylamine (30 mmol, 3.0 equiv) in DCM (30 mL) was added dropwise a solution of *N*-acyl or *N*-carbamoyl chloride (1.5 equiv) in DCM (10 mL) at 0 °C. The reaction mixture was further stirred at room temperature for 6−8 h. The reaction mixture was quenched with water and portioned between DCM and water layers. The organic layer was further dried with Na_2SO_4 and purified by silica gel chromatography using *n*-hexanes/EtOAc to give the corresponding products **1a−l**. Characterization data of these compounds matched well those of previous reports.[20]

General Procedure A of Catalytic Couplings of *N*-Carbamoyl Indoline 1 with Internal Alkynes 2a−q. An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %) and AgOTf (10.3 mg, 0.04 mmol, 20 mol %) under an argon atmosphere. A small amount of 1,2-TFE (0.5 mL) was placed in the Schlenk tube, and the mixture was stirred for 1−2 min. *N*-Carbamoyl indoline **1** (0.2 mmol,

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J. Org. Chem. 2021, 86, 9407−9417

1.0 equiv) and alkyne **2** (0.24 mmol, 1.2 equiv) followed by $Zn(OTf)_2$ (21.8 mg; 0.06 mmol, 30 mol %) and 1.5 mL of TFE were successively placed in the Schlenk tube. The closed tube was placed in a preheated oil bath at 110 °C, and the contents were stirred for 24 h. After completion of the reaction, the reaction mixture was then cooled to room temperature. The crude mixture was purified by flash column chromatography (ethyl acetate/hexane) on silica gel, affording **3** as the desired product.

General Procedure B of Catalytic Couplings of *N*-Carbamoyl Indoline 2a with Alkynes 2r−t. An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cp^*Co(CO)I_2$ (9.5 mg, 0.02 mmol, 10 mol %) and AgOTf (10.3 mg, 0.04 mmol, 20 mol %) under argon atmosphere. A small amount of 1,2-TFE (0.5 mL) was placed in the Schlenk tube, and the mixture was stirred for 1−2 min. *N*-Carbamoyl indoline **1** (0.2 mmol, 1.0 equiv) and alkynes **2r−t** (0.24 mmol, 1.2 equiv) followed by NaOPiv (7.4 mg; 0.06 mmol, 30 mol %) and 1.5 mL of TFE were successively placed in the Schlenk tube. The closed tube was placed in a preheated oil bath at 110 °C, and the contents were stirred for 36 h. After completion of the reaction, the reaction mixture was then cooled to room temperature. The crude mixture was purified by flash column chromatography (ethyl acetate/hexane) on silica gel, affording **3** as the desired product.

General Procedure C of Catalytic Couplings of *N*-Carbamoyl Indoline 1a with Terminal Alkynes 4. An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cp^*Co(CO)I_2$ (9.5 mg, 0.02 mmol, 10 mol %) and AgOTf (10.3 mg, 0.04 mmol, 20 mol %) under an argon atmosphere. 1,2-TFE (1.0 mL) was placed in the Schlenk tube, and the contents were stirred for 1−2 min. *N*-Carbamoyl indoline **1a** (38.0 mg, 0.2 mmol, 1.0 equiv) and PivOH (10.2 mg; 0.1 mmol, 50 mol %) followed by alkyne **4** (0.24 mmol, 1.2 equiv) and 1.0 mL of TFE were successively placed in the Schlenk tube. The closed tube was placed in a preheated oil bath at 110 °C, and the contents were stirred for 36 h. After completion of the reaction, the reaction mixture was then cooled to room temperature. The crude mixture was purified by flash column chromatography (ethyl acetate/hexane) on silica gel, affording **5** as the desired product.

Synthesis of 5,6-Diphenyl-1*H*-pyrrolo[3,2,1-*ij*]quinolin-4(2*H*)-one (3aa) on a 1.0 mmol Scale. An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cp^*Co(CO)I_2$ (47.5 mg, 0.1 mmol, 10 mol %) and AgOTf (51.4 mg, 0.02 mmol, 20 mol %) under an argon atmosphere. A 2.0 mL portion of 1,2-TFE was placed in the Schlenk tube, and the contents were stirred for 2−3 min. *N*-Carbamoyl indoline **1a** (192.2 mg, 1.0 mmol, 1.0 equiv) and alkyne **2a** (213.8 mg, 1.2 mmol, 1.2 equiv) followed by $Zn(OTf)_2$ (109.1 mg; 0.3 mmol, 30 mol %) and 8.0 mL of TFE were successively placed in the Schlenk tube. The closed tube was placed in a preheated oil bath at 110 °C, and the contents were stirred for 36 h. After completion of the reaction, the reaction mixture was then coolrf to room temperature. The crude mixture was purified by flash column chromatography (ethyl acetate/hexane) on silica gel, affording **3aa** in 92% (297.5 mg) yield.

*5,6-Diphenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3aa**).* Compound **3aa** was prepared according to general procedure A and was purified by flash column chromatography (EtOAc/hexane 20/80), affording 61.4 mg of **3aa** in 95% yield as a white solid. The NMR data of **3aa** are in accordance with the literature.[12b] ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 6.5 Hz, 1H), 7.26−7.21 (m, 3H), 7.16−7.08 (m, 8H), 7.05−7.01 (m, 1H), 4.50 (t, J = 8.1 Hz, 2H), 3.42 (t, J = 8.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.2, 146.9, 141.6, 135.9, 135.5, 133.2, 130.9, 130.4, 129.7, 127.9, 127.5, 127.4, 126.8, 124.8, 123.6, 123.0, 118.4, 47.3, 27.1. IR (neat): 3043, 2921, 2856, 1638, 1612, 1309, 774, 712 cm^{-1}. Mp: 166−170 °C.

*5,6-Di-p-tolyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ab**).* Compound **3ab** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 20/80) to afford 61.1 mg of **3ab** in 87% yield as a white solid. The NMR data of **3ab** are in accordance with the literature.[12c] ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 6.9 Hz, 1H), 7.12−6.97 (m, 10H), 4.53 (t, J = 8.1 Hz, 2H), 3.47 (t, J = 8.1 Hz, 2H), 2.32 (s, 3H), 2.26 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.6, 146.9, 141.6, 137.2, 136.4, 133.3, 133.2, 132.6, 130.9, 130.4, 129.7, 128.8, 128.3, 124.7, 123.8, 123.0, 118.9, 47.4, 27.3, 21.3 (overlapped).

*5,6-Bis(4-fluorophenyl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ac**).* Compound **3ac** was prepared according to the general procedure A and then was purified by flash column chromatography (EtOAc/hexane 15:95) to afford 64.0 mg of **3ac** in 89% yield as a white solid. The NMR data of **3ac** are in accordance with the literature.[12c] ^1H NMR (400 MHz, $CDCl_3$): δ 7.37−7.35 (m, 1H), 7.11−7.07 (m, 6H), 7.02−6.96 (m, 2H), 6.90−6.84 (m, 2H), 4.53 (t, J = 8.1 Hz, 2H), 3.48 (t, J = 8.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 162.1, (d, $^1J_{C-F}$ = 246.7 Hz), 161.8 (d, $^1J_{C-F}$ = 245.1 Hz), 160.2, 146.3, 141.7, 132.7 (d, $^3J_{C-F}$ = 8.0 Hz), 132.6, 131.8 (d, $^4J_{C-F}$ = 3.2 Hz), 131.6 (d, $^3J_{C-F}$ = 8.0 Hz), 131.3 (d, $^4J_{C-F}$ = 3.3 Hz), 130.7, 125.2, 123.4 (d, $^2J_{C-F}$ = 19.6 Hz), 115.4 (d, $^2J_{C-F}$ = 21.5 Hz), 114.75 (d, $^2J_{C-F}$ = 21.4 Hz), 47.5, 27.2. ^{19}F NMR (372 MHz, $CDCl_3$): −113.3, −114.7. IR (neat): 2922, 2853, 1633, 1617, 1599, 817, 772 cm^{-1}. Mp: 184−186 °C.

*6-m-Tolyl-5-p-tolyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ad**).* Compound **3ad** was prepared according to the general procedure A and then was purified by flash column chromatography (EtOAc/hexane 20/80) o afford 57.6 mg of **3ad** in 82% yield as a colorless solid. The NMR data of **3ad** are in accordance with the literature.[12c] ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, J = 6.7, 1.1 Hz, 1H), 7.16−7.12 (m, 2H), 7.08−7.02 (m, 3H), 6.98 (br s, 1H), 6.93−6.87 (m, 4H), 4.54 (t, J = 8.2 Hz, 2H), 3.48 (t, J = 8.1 Hz, 2H), 2.26 (s, 3H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.6, 147.1, 141.7, 135.5, 136.8, 136.0, 135.5, 133.5, 131.6, 130.51, 130.47, 128.3, 128.0, 127.9, 127.8, 127.4, 126.9, 124.7, 123.9, 123.0, 118.8, 47.4, 27.3, 21.4 (overlapped). IR (neat): 2922, 2852, 1646, 1600, 738 cm^{-1}. Mp: 149−152 °C.

*5,6-Dipentyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ae**).* Compound **3ae** was prepared according to the general procedure A and then was purified by flash column chromatography (EtOAc/hexane 20/80) to afford 56.7 mg of **3ae** in 91% yield as a colorless solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.2 Hz, 1H), 7.25 (d, J = 5.7 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 4.41 (t, J = 8.1 Hz, 2H), 3.37 (t, J = 8.0 Hz, 2H), 2.82 (t, J = 8.2 Hz, 2H), 2.70 (t, J = 7.9 Hz, 2H), 1.64−1.52 (m, 4H), 1.48−1.34 (m, 8H), 0.94−0.88 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 162.2, 145.1, 141.0, 133.0, 130.8, 123.7, 122.8, 121.1, 118.4, 46.9, 32.42, 32.40, 29.8, 29.3, 28.8, 27.4, 27.2, 22.7, 22.6, 14.2, 14.1. HRMS: calcd for $C_{21}H_{29}NNaO$ is $[M + Na]^+$: 334.2147; found: 334.2139. IR (2871, 2919, 2850, 1635, 1609, 771 cm^{-1}. Mp: 128−131 °C.

*5,6-Dipropyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3af**).* Compound **3af** was prepared according to the general procedure A and then was purified by flash column chromatography (EtOAc/hexane 20/80) to afford 45.4 mg of **3af** in 89% yield as a colorless solid. The NMR data of **3af** are in accordance with the literature.[12c] ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 7.4 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 4.41 (t, J = 8.1 Hz, 2H), 3.37 (t, J = 8.2 Hz, 2H), 2.84−2.80 (m, 2H), 2.71−2.67 (m, 2H), 1.68−1.52 (m, 4H), 1.07 (t, J = 7.4 Hz, 3H), 1.02 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.1, 145.0, 140.9, 132.9, 130.7, 123.7, 122.8, 121.1, 118.3, 46.9, 30.7, 29.5, 27.2, 23.4, 22.8, 14.7, 14.6. IR (neat): 2926, 2864, 1634, 1602, 1462, 740 cm^{-1}. Mp: 117−119 °C.

*5,6-Bis(benzyloxymethyl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ag**).* Compound **3ag** was prepared according to the general procedure A and then was purified by flash column chromatography (EtOAc/hexane 20/80) to afford 59.2 mg of **3ag** in 72% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.0 Hz, 1H), 7.37−7.27 (m, 11H), 7.15 (t, J = 7.7 Hz, 1H), 4.86 (s, 2H), 4.73 (s, 2H), 4.58 (s, 2H), 4.54 (s, 2H), 4.43 (t, J = 8.1 Hz, 2H), 3.39 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.6, 144.6, 141.9, 138.4, 137.9, 130.6, 130.1, 128.5, 128.4, 128.1, 128.0, 127.9, 127.7, 125.2, 123.3, 122.7, 117.7, 73.0, 72.8, 65.4, 63.0, 47.2, 27.1. HRMS: calcd for $C_{27}H_{26}NO_3$ $[M + H]^+$, 434.1913; found, 412.1907. IR (neat): 3043, 2925, 1630, 1611, 1599, 745 cm^{-1}. Mp: 122−125 °C.

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J. Org. Chem. 2021, 86, 9407−9417

*5,6-Bis(hydroxymethyl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ah**).* Compound **3ah** was prepared according to the general procedure A and then was purified by flash column chromatography (EtOAc/hexane 60/40) to afford 27.3 mg of **3ah** in 59% yield as a brown solid. The reaction was continued for 48 h. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.71 (d, J = 8.1 Hz, 1H), 7.37 (d, J = 7.1 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 5.27 (br s, 1H), 4.85 (br s, 1H), 4.79 (s, 2H), 4.59 (s, 2H), 4.28 (t, J = 7.9 Hz, 2H), 3.37 (t, 7.7 Hz, 2H). ^{13}C{1H} NMR (126 MHz, DMSO-d_6): δ 160.0, 145.7, 141.3, 131.2, 130.8, 124.8, 122.8, 122.3, 117.1, 56.4, 54.5, 47.0, 26.6. HRMS: calcd for $C_{13}H_{14}NO$ [M + H]$^+$, 232.0974; found, 232.0974.

*6-Methyl-5-phenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ai**).* Compound **3ai** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 15/85) to afford 39.7 mg of **3ai** in a 76% yield of the major regioisomer as a white solid. The crude ^{1}H NMR analysis shows the formation of regioisomeric products with a ratio of 14:1. The NMR data of **3ai** are in accordance with the literature.[12b] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.7 Hz, 1H), 7.45−7.42 (m, 2H), 7.38−7.34 (m, 2H), 7.29−7.26 (m, 2H), 7.19 (t, J = 7.6 Hz, 1H), 4.46 (t, J = 8.3 Hz, 2H), 3.44 (t, J = 8.1 Hz, 2H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.3, 142.2, 141.2, 136.3, 133.6, 130.6, 130.2, 128.1, 127.4, 124.6, 122.9, 121.6, 118.8, 47.0, 27.1, 16.1. IR (neat): 2922, 2852, 1646, 1600, 738 cm^{-1}. Mp: 149−152 °C.

*6-Ethyl-5-phenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3aj**).* Compound **3aj** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 15/85) to afford 40.7 mg of **3aj** in a 74% yield of the major regioisomer as a white solid. The crude ^{1}H NMR analysis shows the formation of regioisomeric products with a ratio of 12:1. The NMR data of **3aj** are in accordance with the literature.[12b] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.1, 1H), 7.44−7.40 (m, 2H), 7.35−7.31 (m, 2H), 7.26−7.24 (m, 2H), 7.17 (t, J = 7.7 Hz, 1H), 4.43 (t, J = 8.3 Hz, 2H), 3.41 (t, J = 8.1 Hz, 2H), 2.67 (q, J = 7.6 Hz, 2H), 1.14 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.7, 148.3, 141.9, 136.5, 133.4, 131.0, 129.9, 128.4, 127.5, 124.7, 123.1, 121.7, 117.7, 47.1, 27.3, 22.9, 14.6. IR (neat): 3523, 2923, 1631, 1594, 770, 708 cm^{-1}. Mp: 112−114 °C.

*6-Butyl-5-phenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ak**).* Compound **3ak** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 15/85) to afford 41.3 mg of **3ak** in a 68% yield of the major regioisomer as a white solid. The NMR data of **3ak** are in accordance with the literature.[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 7.9 Hz, 1H), 7.45−7.42 (m, 2H), 7.38−7.33 (m, 2H), 7.27−7.25 (m, 2H), 7.18(t, J = 7.6 Hz, 1H), 4.45 (t, J = 8.1 Hz, 2H), 3.43 (t, J = 8.1 Hz, 2H), 2.68−2.64 (m, 2H), 1.57−1.50 (m, 2H), 1.32−1.23 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.6, 147.1, 141.8, 136.5, 133.6, 131.0, 130.0, 128.3, 127.5, 124.6, 123.0, 121.8, 118.0, 47.1, 32.3, 29.4, 27.2, 23.0, 13.8. IR (neat): 2954, 2930, 1633, 1611, 700, 770 cm^{-1}. Mp: 121−124 °C.

*6-Methyl-5-(naphthalen-2-yl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3al**).* Compound **3al** was prepared according to the general procedure A. The crude reaction mixture was purified by flash column chromatography (EtOAc/hexane 15/85) to afford 46.1 mg of **3al** in 74% yield as a white solid. The NMR data of **3al** are in accordance with the literature.[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.4 Hz, 1H), 7.90−7.84 (m, 2H), 7.77 (s, 1H), 7.54−7.48 (m, 3H), 7.44 (dd, J = 8.3, 1.4 Hz, 1H), 7.38 (d, J = 7.3 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 4.49 (t, J = 8.1 Hz, 2H), 3.45 (t, J = 8.1 Hz, 2H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.5, 142.8, 141.3, 134.0, 133.5, 133.4, 132.8, 130.8, 129.4, 128.4, 128.1, 127.7 (overlapped), 126.0, 125.9, 124.9, 123.2, 121.7, 119.0, 47.2, 27.3, 16.3. IR (neat): 2924, 1638, 1601, 812, 746 cm^{-1}. Mp: 146−149 °C.

*6-Ethyl-5-(naphthalen-2-yl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3am**).* Compound **3am** was prepared according to the general procedure **A** and was purified by flash column chromatography (EtOAc/hexane 15/85) to afford 42.3 mg of **3am** in a 65% yield of the major regioisomer as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.4 Hz, 1H), 7.90−7.84 (m, 2H), 7.75 (s, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.52−7.47 (m, 2H), 7.42 (dd, J = 8.4, 1.7 Hz, 1H), 7.37 (d, J = 7.3 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 4.48 (t, J = 8.1 Hz, 2H), 3.46 (t, J = 8.1 Hz, 2H), 2.74−2.72 (m, 2H), 1.17 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.7, 148.7, 141.9, 134.1, 133.5, 133.3, 132.9, 131.1, 128.7, 128.23, 128.21, 128.0, 127.8, 126.03, 126.00, 124.8, 123.1, 121.8, 117.7, 47.2, 27.3, 23.0, 14.7. HRMS: calcd for $C_{23}H_{20}NO$ [M + H]$^+$, 326.1545; found, 326.1539. IR (neat): 2924, 1636, 1595, 798, 758 cm^{-1}. Mp: 117−119 °C.

*6-Ethyl-5-(naphthalen-2-yl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3an**).* Compound **3an** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 15/85) to afford 32.0 mg of **3an** in a 42% yield of the major regioisomer as a white solid. The crude ^{1}H NMR analysis shows the formation of regioisomeric products with a ratio of 10:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93−7.83 (m, 3H), 7.75 (s, 1H), 7.55−7.47 (m, 3H), 7.40 (dd, J = 8.4, 1.7 Hz, 1H), 7.36 (dd, J = 7.3, 0.8 Hz, 1H), 7.22−7.18 (m, 1H), 4.48 (t, J = 8.6 Hz, 2H), 3.45 (t, J = 8.1 Hz, 2H), 2.71−2.69 (m, 2H), 1.61−1.54 (m, 2H), 1.26−1.11 (m, 6H), 0.75 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.6, 147.4, 141.7, 134.0, 133.35, 133.33, 132.7, 130.9, 128.8, 128.2, 128.0, 127.72, 127.66, 125.84, 125.80, 124.6, 122.9, 121.7, 117.9, 47.0, 31.3, 30.3, 29.6, 29.4, 27.1, 22.4, 13.9. HRMS: calcd for $C_{27}H_{27}NNaO$ [M + Na]$^+$, 404.1990; found, 404.1976. IR (neat): 3029, 2856, 1640, 1603, 1066, 737 cm^{-1}. Mp: 122−124 °C.

*6-(Benzyloxymethyl)-5-phenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ao**).* Compound **3ao** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc:/hexane 30/70) to afford 57.3 mg of **3ao** in 78% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, J = 8.0 Hz, 1H), 7.43−7.24 (m, 11H), 7.17 (t, J = 7.7 Hz, 1H), 4.55 (s, 2H), 4.47−4.44 (m, 4H), 3.43 (t, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 160.3, 141.8, 140.8, 137.8, 135.7, 135.1, 130.6, 130.4, 128.5, 128.12, 128.10, 127.98, 127.94, 124.92, 123.3, 122.7, 117.8, 73.0, 66.9, 47.3, 27.9. HRMS: calcd for $C_{25}H_{22}NO_2$ [M + H]$^+$, 368.1651; found, 368.1654. IR (neat): 2920, 1633, 1614, 1605, 1054, 699 cm^{-1}. Mp: 119−121 °C.

*6-(Hydroxymethyl)-5-phenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ap**).* Compound **3ap** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 40/60) to afford 30.0 mg of **3ap** in 54% yield as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.75 (d, J = 7.9 Hz, 1H), 7.42−7.33 (m, 4H), 7.30−7.28 (m, 2H), 7.16 (t, J = 7.7 Hz, 1H), 5.26 (t, J = 5.1 Hz, 1H), 4.43 (t, J = 5.0 Hz, 2H), 4.28 (t, J = 8.0 Hz, 2H), 3.37−3.33 (m, 2H) (overlapped with DMSO peak). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 159.2, 143.7, 141.3, 135.5, 133.0, 130.8, 130.4, 127.7, 127.4, 128.8, 122.8, 127.7, 117.0, 58.2, 47.1, 26.6. HRMS: calcd for $C_{18}H_{16}NO_2$ [M + H]$^+$, 278.1181; found, 278.1176. IR (neat): 3277, 2922, 1635, 1610, 1022, 759, 704 cm^{-1}. Mp: 210−213 °C.

*4-Methyl-N-((4-oxo-5-phenyl-2,4-dihydro-1H-pyrrolo[3,2,1-ij]-quinolin-6-yl)methyl)benzenesulfonamide (**3aq**).* Compound **3aq** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 50/50) to afford 53.4 mg of **3aq** in 62% yield as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.98 (t, J = 5.3 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.46 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 7.2 Hz, 1H) 7.31−7.26 (m, 5H), 7.21−7.18 (m, 3H), 4.29 (t, J = 8.0 Hz, 2H), 3.87 (d, J = 5.3 Hz, 2H), 3.40−3.35 (m, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6): δ 158.8, 142.7, 141.1, 139.1, 136.2, 134.9, 134.7, 130.8, 130.1, 129.4, 127.5, 127.2, 126.4, 124.9, 122.8, 122.0, 116.4, 47.0, 41.5, 26.6, 20.9. HRMS: calcd for $C_{25}H_{23}N_2O_3S$ [M + H]$^+$, 431.1249; found, 431.1434. IR (neat): 3255, 1644, 1615, 1323, 1165, 712 cm^{-1}. Mp: 218−221 °C.

*6-Butyl-5-(hex-1-ynyl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ar**).* Compound **3ar** was prepared according to the general procedure B and was purified by flash column chromatography (EtOAc/hexane 20/80) to afford 25.8 mg of **3ar** in 42% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 6.8 Hz, 1H), 7.13 (t, J = 7.7 Hz, 1H), 4.40 (t, J = 8.1 Hz, 2H), 3.37 (t, J = 8.1 Hz, 2H), 3.05−3.02 (m, 2H), 2.55 (t, J = 7.0 Hz,

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J. Org. Chem. 2021, 86, 9407−9417

2H), 1.67−1.56 (m, 4H), 1.56−1.44 (m, 4H), 0.99−0.94 (m, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 160.0, 152.9, 141.1, 130.9, 125.0, 123.2, 121.3, 117.6, 117.2, 100.8, 75.7, 47.1, 31.4, 31.0, 30.5, 27.2, 23.2, 22.2, 19.9, 14.0, 13.8. HRMS: calcd for $C_{21}H_{25}NNaO$ $[M + Na]^+$, 330.1834; found, 330.1836. IR (KBr): 3439, 2921, 1637, 1610, 771 cm^{-1}. Mp: 120−123 °C.

*6-Cyclohexenyl-5-phenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3as**).* Compound **3as** was prepared according to the general procedure **B** and was purified by flash column chromatography (EtOAc/hexane 15:85) to afford 30.1 mg of **3as** in a 46% yield of the major regioisomer as a white solid. The crude ^1H NMR analysis shows the formation of regioisomeric products with a ratio of 6:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 8.0 Hz, 1H), 7.38−7.23 (m, 6H), 7.13 (t, J = 7.6 Hz, 1H), 5.67−5.65 (m, 1H), 4.50−4.46 (m, 2H), 3.45−3.42 (m, 2H), 2.15−1.87 (m, 4H), 1.72−1.36 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 160.7, 149.6, 142.0, 136.2, 133.2, 131.8, 130.6, 130.5, 129.7, 127.6, 127.3, 124.7, 123.3, 122.9, 118.1, 47.3, 28.9, 27.3, 25.2, 22.7, 21.9. HRMS: calcd for $C_{23}H_{21}NNaO$ $[M + Na]^+$, 350.1521; found, 350.1523. IR (neat): 2921, 1638, 1613, 1598, 773, 717, 699 cm^{-1}. Mp: 169−172 °C.

*N-(5-Heptyl-4-oxo-2,4-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-6-yl)-N-methylmethanesulfonamide (**3at**).* Compound **3at** was prepared according to the general procedure B and was purified by flash column chromatography (EtOAc/hexane 30/70) to afford 29.4 mg of **3at** in 39% yield as an off-white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, J = 8.1 Hz, 1H), 7.31 (d, J = 7.1 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 4.43 (t, J = 8.0 Hz, 2H), 3.42 (t, J = 8.0 Hz, 2H), 3.28 (s, 3H), 3.15 (s, 3H), 2.76−2.66 (m, 2H), 1.68−1.61 (m, 3H), 1.47−1.41 (m, 2H), 1.38−1.28 (m, 5H), 0.87 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 161.0, 143.0, 141.3, 137.7, 130.8, 124.8, 123.8, 121.0, 117.3, 47.2, 40.1, 37.9, 31.9, 30.6, 29.2, 28.6, 28.5, 27.3, 22.8, 14.2. HRMS: calcd for $C_{26}H_{28}N_2NaO_3S$ $[M + Na]^+$, 399.1718; found, 399.1720. IR (KBr): 3431, 2924, 2852, 1635, 1617, 1337, 1159 cm^{-1}. Mp: 102−105 °C.

*8-Methyl-5,6-diphenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ba**).* Compound **3ba** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 20/80) to afford 57.4 mg of **3ba** in 85% yield as a white solid. The NMR data of **3ba** are in accordance with the literature.[12c] ^1H NMR (400 MHz, $CDCl_3$): δ 7.30−7.24 (m, 3H), 7.19 (s, 1H), 7.16−7.09 (m, 7H), 6.88 (s, 1H), 4.53 (t, J = 8.0 Hz, 2H), 3.44 (t, J = 8.0 Hz, 2H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.3, 146.9, 140.0, 136.1, 135.7, 133.4, 133.0, 131.0, 130.7, 129.9, 128.1, 127.6, 127.5, 126.9, 126.5, 123.1, 118.3, 47.6, 27.2, 21.7.

*8-Methoxy-5,6-diphenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ca**).* Compound **3ca** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 20/80) to afford 58.7 mg of **3ca** in 83% yield as a white solid. The NMR data of **3ca** are in accordance with the literature.[12c] ^1H NMR (400 MHz, $CDCl_3$): δ 7.29−7.24 (m, 3H), 7.16−7.11 (m, 7H), 7.02 (d, J = 1.3 Hz, 1H), 6.54 (d, J = 1.8 Hz, 1H), 4.55 (t, J = 7.9 Hz, 2H), 3.68 (s, 3H), 3.40 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.9, 156.6, 146.6, 136.7, 136.1, 135.8, 133.8, 132.0, 131.1, 129.8, 128.1, 127.7, 127.5, 127.0, 118.4, 115.0, 105.4, 56.1, 47.6, 27.3.

*8-Chloro-5,6-diphenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3da**).* Compound **3da** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 15/85) to afford 63.0 mg of **3da** in 88% yield as a white solid. The NMR data of **3da** are in accordance with the literature.[12c] ^1H NMR (400 MHz, $CDCl_3$): δ 7.31−7.25 (m, 4H), 7.19−7.08 (m, 8H), 4.55 (t, J = 8.0 Hz, 2H), 3.47 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.0, 146.0, 140.2, 135.3, 135.0, 134.3, 132.2, 130.8, 129.6, 128.4, 128.2, 127.8, 127.5, 127.1, 125.4, 123.0, 119.0, 47.5, 27.0.

*8-Bromo-5,6-diphenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ea**).* Compound **3ea** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 15/85) to afford 50.9 mg of **3ea** in 81% yield as a white solid. The NMR data of **3ea** are in accordance with the literature.[12c] ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 1.2 Hz, 1H), 7.29−7.26 (m, 3H), 7.23 (br s, 1H), 7.17−7.08 (m, 7H), 4.54 (t, J = 8.0 Hz, 2H), 3.46 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.1, 146.1, 140.7, 135.4, 135.1, 134.4, 132.7, 130.9, 129.7, 128.3, 128.1, 128.0, 127.6, 127.2, 126.1, 119.7, 115.8, 47.6, 27.1. IR (neat): 3057, 3023, 1640, 1619, 861, 709 cm^{-1}. Mp: 188−190 °C.

*(E)-5,6-Diphenyl-8-styryl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3fa**).* Compound **3fa** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 15/85) to afford 67.0 mg of **3fa** in 81% yield as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.44 (d, J = 7.4 Hz, 1H), 7.33−7.28 (m, 5H), 7.25−7.13 (m, 10H), 7.05 (d, J = 16.3 Hz, 1H), 6.96 (d, J = 16.2 Hz, 1H), 4.57 (t, J = 8.1 Hz, 2H), 3.50 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 160.3, 147.0, 141.7, 137.3, 136.0, 135.6, 133.8, 133.1, 131.3, 131.1, 130.0, 128.8, 128.7, 128.2, 127.82, 127.80, 127.65, 127.60, 127.1, 126.4, 123.1. 122.3, 118.5, 47.8, 27.2. HRMS: calcd for $C_{31}H_{23}NNaO$ $[M + Na]^+$, 448.1677; found, 448.1672.

*9-Bromo-5,6-diphenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ga**).* Compound **3ga** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 20/80) to afford 75.6 mg of **3ga** in 94% yield as a white solid. The NMR data of **3ga** are in accordance with the literature.[12b] ^1H NMR (400 MHz, $CDCl_3$): δ 7.28−7.21 (m, 3H), 7.17−7.14 (m, 8H), 6.97 (d, J = 8.6 Hz, 1H), 4.53 (t, J = 8.1 Hz, 2H), 3.40 (t, J = 8.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.5, 146.8, 142.2, 135.6, 135.2, 133.4, 131.0, 130.9, 129.8, 128.2, 127.9, 127.6, 127.2, 126.0, 125.7, 119.6, 117.4, 47.0, 28.7.

*2-Methyl-5,6-diphenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ha**).* Compound **3ha** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 20/80) to afford 37.8 mg of **3ha** in 56% yield as a white solid. The NMR data of **3ha** are in accordance with the literature.[12b] ^1H NMR (500 MHz, $CDCl_3$): δ 7.33−7.29 (m, 2H), 7.23−7.20 (m, 3H), 7.16−7.04 (m, 7H), 7.01 (d, J = 7.1 Hz, 1H), 5.18−5.12 (m, 1H), 3.69 (dd, J = 16.7, 9.4 Hz, 1H), 3.05 (dd, J = 16.7, 3.7 Hz, 1H), 1.69 (d, J = 6.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 160.4, 147.0, 141.2, 136.2, 135.7, 134.0, 131.2, 130.0, 129.9, 129.2, 128.2, 128.0, 127.7, 127.6, 127.0, 125.0, 123.9, 123.1, 118.6, 57.3, 36.5, 20.8.

*1-Methyl-5,6-diphenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**3ia**).* Compound **3ia** was prepared according to the general procedure A and was purified by flash column chromatography (EtOAc/hexane 20/80) to afford 42.5 mg of **3ia** in 63% yield as a white solid. The NMR data of **3ia** are in accordance with the literature.[12b] ^1H NMR (500 MHz, $CDCl_3$): δ 7.33 (dd, J = 6.8, 1.1 Hz, 1H), 7.28−7.24 (m, 3H), 7.17−7.07 (m, 9H), 4.71 (dd, J = 12.9, 9.5 Hz, 1H), 4.09 (dd, J = 12.8, 5.4 Hz, 1H), 3.88−3.80 (m, 1H), 1.52 (d, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 160.4, 147.1, 141.2, 136.2, 135.74, 135.70, 133.6, 131.1, 129.9, 128.1, 127.7, 127.6, 127.0, 124.02, 124.0, 123.2, 118.6, 55.4, 34.9, 21.0.

*5-Phenyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**5aa**).* Compound **5aa** was prepared according to the general procedure C and was purified by flash column chromatography (EtOAc/hexane 10/90) to afford 34.1 mg of **5aa** in 69% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.73 (d, J = 7.3 Hz, 2H), 7.43−7.42 (m, 3H), 7.38 (d, J = 7.0 Hz, 1H), 7.34 (d, J = 7.3 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 4.53 (m, 2H), 3.47 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.3, 142.2, 136.8, 135.4, 134.9, 130.5, 129.2, 128.3, 128.2, 124.8, 123.7, 123.4, 117.9, 47.8, 27.5. HRMS: calcd for $C_{17}H_{13}NNaO$ $[M + Na]^+$, 270.0895; found, 270.0890. IR (KBr): 3431, 2924, 1644, 1618, 1261, 775 cm^{-1}. Mp: 122−124 °C.

*5-p-Tolyl-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**5ab**).* Compound **5ab** was prepared according to the general procedure C and was purified by flash column chromatography (EtOAc/hexane 10/90) to afford 35.0 mg of **5ab** in 67% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.63 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 7.15

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J. Org. Chem. 2021, 86, 9407−9417

(t, J = 7.4 Hz, 1H), 4.50 (t, J = 8.0 Hz, 2H), 3.44 (t, J = 8.0 Hz, 2H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 160.3, 142.1, 138.0, 134.7, 133.9, 130.4, 129.02, 129.0 (overlapped), 124.6, 123.6, 123.3, 117.9, 47.6, 27.4, 21.4. HRMS: calcd $C_{18}H_{16}NO$ is $[M + H]^+$, 262.1232; found, 262.1224. IR (KBr): 3429, 2961, 1642, 1611, 1020, 819 cm^{-1}. Mp: 115−118 °C.

*5-(4-tert-butylphenyl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**5ac**).* Compound **5ac** was prepared according to the general procedure C and was purified by flash column chromatography (EtOAc/hexane 7/93) to afford 38.2 mg of **5ac** in 63% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 4.52 (t, J = 8.0 Hz, 2H), 3.45 (t, J = 8.0 Hz, 2H), 1.35 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.3, 151.1, 142.1, 134.8, 134.6, 133.9, 130.4, 128.8, 125.3, 124.6, 123.6, 123.3, 117.9, 47.6, 34.7, 31.4, 27.4. HRMS: calcd for $C_{21}H_{21}NNaO$ $[M + Na]^+$, 326.1521; found, 326.1521. IR (neat): 2959, 2852, 1644, 1618, 1606, 834, 773 cm^{-1}. Mp: 122−125 °C.

*5-(4-Methoxyphenyl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**5ad**).* Compound **5ad** was prepared according to the general procedure C and was purified by flash column chromatography (EtOAc/hexane 15/85) to afford 30.0 mg of **5ad** in 54% yield as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.71−7.69 (m, 2H), 7.40 (d, J = 7.9 Hz, 1H), 7.31−7.29 (m, 1H), 7.14 (t, J = 7.6 hz, 1H), 6.97−6.95 (m, 2H), 4.50 (t, J = 8.1 Hz, 2H), 3.85 (s, 3H), 3.44 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 160.2, 159.5, 141.8, 134.1, 134.0, 130.2 (overlapped), 129.1, 124.3, 123.4, 123.2, 117.8, 113.6, 55.3, 47.4, 27.3. HRMS: calcd for $C_{18}H_{16}NO_2$ $[M + H]^+$, 278.1181; found, 278.1176. IR (KBr): 3436, 2924, 2853, 1647, 1607, 1246, 1176, 830 cm^{-1}. Mp: 98−100 °C.

*5-(4-Fluorophenyl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**5ae**).* Compound **5ae** was prepared according to the general procedure C and was purified by flash column chromatography (EtOAc/hexane 10/90) to afford 36.1 mg of **5ae** in 68% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.72−7.69 (m, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.14−7.08 (m, 2H), 4.50 (t, J = 8.0 Hz, 2H), 3.45 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 162.8 (d, $^1J_{C-F}$ = 247.3 Hz), 160.1, 142.2, 135.1, 133.7, 132.8 (d, $^4J_{C-F}$ = 3.0 Hz), 130.9 (d, $^3J_{C-F}$ = 8.1 Hz), 130.5, 124.8, 123.7, 123.4, 117.7, 115.2 (d, $^2J_{C-F}$ = 21.4 Hz), 47.6, 27.4. ^{19}F (373 Mz, $CDCl_3$): −113.86. HRMS: calcd for $C_{17}H_{13}FNO$ $[M + H]^+$, 266.0981; found, 266.0966. IR (KBr): 3431, 2923, 1640, 1604, 1233, 776, 831 cm^{-1}. Mp: 162−164 °C.

*5-(4-Bromophenyl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**5af**).* Compound **5af** was prepared according to the general procedure C and was purified by flash column chromatography (EtOAc/hexane 10/90) to afford 34.0 mg of **5af** in 52% yield as a brown solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 4.51 (t, J = 8.0 Hz, 2H), 3.46 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 159.9, 142.3, 135.7, 135.3, 113.6, 131.4, 130.8, 130.6, 125.0, 123.8, 123.6, 122.4, 117.7, 47.7, 27.4. HRMS: calcd for $C_{17}H_{13}BrNO$ $[M + H]^+$, 326.0181; found, 326.0172. IR (KBr): 3431, 2961, 2920, 1617, 1644, 1103, 813 cm^{-1}. Mp: 150−152 °C.

*4-Methyl-N-(3-(4-oxo-2,4-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-5-yl)phenyl)benzenesulfonamide (**5ag**).* Compound **5ag** was prepared according to the general procedure C and was purified by flash column chromatography (EtOAc/hexane 10/90) to afford 54.1 mg of **5ag** in 65% yield as a gummy solid. ^1H NMR (500 MHz, DMSO-d_6): δ 10.26 (bs, 1H), 7.87 (s, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.54−7.50 (m, 2H), 7.39−7.32 (m, 6H), 7.15 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 4.34 (t, J = 7.9 Hz, 2H), 3.37−3.36 (m, 2H) (overlapped with DMSO peak), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 158.6, 143.2, 141.9, 137.6, 137.5, 136.7, 135.3, 132.7, 130.7, 129.7, 128.7, 126.8, 125.0, 124.5, 123.6, 123.1, 120.5, 119.2, 116.7, 47.4, 26.8, 20.9. HRMS: calcd for $C_{24}H_{20}N_2O_3S$ $[M + H]^+$, 326.0181; found, 326.0172. IR (neat): 3392, 2853, 1640, 1608, 1157, 1003, 761 cm^{-1}.

*5-(Naphthalen-2-yl)-1H-pyrrolo[3,2,1-ij]quinolin-4(2H)-one (**5ah**).* Compound **5ah** was prepared according to the general procedure C and was purified by flash column chromatography (EtOAc/hexane 10/90) to afford 35.1 mg of **5ah** in 59% yield as white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.94 (s, 1H), 7.90−7.84 (m, 4H), 7.51−7.44 (m, 3H), 7.34 (d, J = 7.0 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 4.54 (t, J = 8.0 Hz, 2H), 3.46 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.3, 142.2, 135.6, 134.6, 134.3, 133.4, 133.1, 130.5, 128.5, 128.3, 127.6, 127.0, 126.3, 126.1, 124.8, 123.7, 123.4, 117.8, 47.6, 27.4. HRMS: calcd for $C_{21}H_{15}NNaO$ $[M + Na]^+$, 320.1051; found, 320.1054. IR (KBr): 3436, 2928, 1644, 1615, 737 cm^{-1}. Mp: 158−161 °C.

Procedure D for the Reduction of 5-Phenyl-1*H*-pyrrolo-[3,2,1-*ij*]quinolin-4(2*H*)-one (5aa). An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with 5-phenyl-1*H*-pyrrolo[3,2,1-*ij*]quinolin-4(2*H*)-one (**5aa**; 24.7 mg, 0.1 mmol, 1.0 equiv) in air followed by addition of $Pd(OH)_2/C$ (10.0 mg) and EtOAc (1.0 mL). The Schlenk tube was vacuumized and filled with H_2 (1−2 atm). The closed Schlenk tube was then placed at 40 °C for 24 h. After completion of the reaction, the reaction mixture was then cooled to room temperature. The crude mixture was purified by flash column chromatography (ethyl acetate/hexane) on silica gel, affording 5-phenyl-5,6-dihydro-1*H*-pyrrolo[3,2,1-*ij*]quinolin-4(2*H*)-one (**6**) in 69% (17.2 mg) yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.31−7.24 (m, 5H), 7.11 (d, J = 7.5 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 4.15−4.11 (m, 2H), 3.93 (t, J = 7.5 Hz, 1H), 3.32 (dd, J = 16.4, 7.1 Hz, 1H), 3.24−3.17 (m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 168.2, 141.2, 140.0, 129.0, 128.8, 128.1, 127.3, 125.5, 123.6, 123.5, 119.9, 48.2, 45.7, 33.1, 28.0. HRMS: calcd for $C_{17}H_{15}NNaO$ $[M + Na]^+$, 272.1051; found, 272.1053. IR (neat): 3027, 2924, 1651, 1479, 762, 696 cm^{-1}. Mp: 114−116 °C.

Procedure E for the Oxidation of 5-Phenyl-1*H*-pyrrolo-[3,2,1-*ij*]quinolin-4(2*H*)-one (5aa). An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with 5-phenyl-1*H*-pyrrolo[3,2,1-*ij*]quinolin-4(2*H*)-one (**5aa**; 24.7 mg, 0.1 mmol, 1.0 equiv) under an argon atmosphere followed by addition of DDQ (113.5 mg, 0.5 mmol, 5.0 equiv) and 1,4-dioxane (1.0 mL). The closed tube was placed in a preheated oil bath at 110 °C, and the contents were stirred for 12 h. After completion of the reaction, the reaction mixture was then cooled to room temperature. The crude mixture was purified by flash column chromatography (ethyl acetate/hexane 15/85) on silica gel, affording 5-phenyl-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (**7**) in 62% (15.2 mg) yield. ^1H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 3.5 Hz, 1H), 7.94 (s, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.74−7.64 (m, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.49−7.40 (m, 5H), 6.93 (d, J = 3.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 158.8, 136.6, 136.4, 135.4, 132.2, 129.2, 128.5, 128.4, 127.6, 125.0, 124.34, 124.30, 117.3, 111.1. HRMS: calcd for $C_{17}H_{11}NNaO$ $[M + Na]^+$, 268.0738; found, 268.0739. IR (neat): 2922, 1660, 1633, 783 cm^{-1}. Mp: 115−117 °C.

Competitive Experiment with Alkynes. An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cp^*Co(CO)I_2$ (9.5 mg, 0.02 mmol, 10 mol %) and AgOTf (10.2 mg, 0.04 mmol, 20 mol %) under an argon atmosphere. A small amount of TFE (0.5 mL) was placed in the Schlenk tube, and the contents were stirred for 1−2 min. Then, *N,N*-dimethylindoline-1-carboxamide (**1a**; 38.0 mg, 0.2 mmol, 1.0 equiv), 1,2-diphenylethyne (**2a**; 17.8 mg, 0.1 mmol, 0.5 equiv), and dodec-6-yne (**2e**; 16.6 mg, 0.1 mmol, 0.5 equiv) followed by $Zn(OTf)_2$ (21.8 mg, 0.06 mmol, 30 mol %) and 1.5 mL of TFE were successively placed in the Schlenk tube. The closed tube was placed in a preheated oil bath at 110 °C. After 16 h, the reaction mixture was then cooled to room temperature. The crude reaction mixture was passed through a short pad of silica, and the ratio of **3aa** and **3ae** was calculated from a ^1H NMR analysis (**3aa**:**3ae** = 1.0:1.23) (see the NMR spectra in the Supporting Information).

Competitive Experiment with *N*-Carbamoyl Indoline Derivatives. An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cp^*Co(CO)I_2$ (9.5 mg, 0.02 mmol, 10 mol %) and AgOTf (10.2 mg, 0.04 mmol, 20 mol %) under an argon

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J. Org. Chem. 2021, 86, 9407−9417

atmosphere. A small amount of TFE (0.5 mL) was placed in the Schlenk tube, and the contents were stirred for 1−2 min. Then, *N,N,5*-trimethylindoline-1-carboxamide (**1b**; 20.4 mg, 0.1 mmol, 0.5 equiv), 5-bromo-*N,N*-dimethylindoline-1-carboxamide (**1e**; 26.9 mg, 0.1 mmol, 0.5 equiv) and 1,2-diphenylethyne (**2a**; 35.6 mg, 0.2 mmol, 1.0 equiv) followed by $Zn(OTf)_2$ (21.8 mg, 0.06 mmol, 30 mol %) and 1.5 mL of TFE were successively placed in the Schlenk tube. The closed tube was placed in a preheated oil bath at 110 °C. After 24 h, the reaction mixture was then cooled to room temperature. The crude reaction mixture was passed through a short pad of silica, and the ratio of **3ba** and **3ea** was calculated from a ^{1}H NMR analysis (**3ba**:**3ea** = 1.0:1.0) (see the NMR spectra in the Supporting Information).

H/D Exchange Experiment. An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Cp*Co(CO)I_2 (4.7 mg, 0.01 mmol, 10 mol %) and AgOTf (5.1 mg, 0.02 mmol, 20 mol %) under an argon atmosphere. A small amount of d_3-TFE (0.2 mL) was placed in the Schlenk tube, and the contents were stirred for 1−2 min. Then, *N,N*-dimethylindoline-1-carboxamide (**1a**; 19.2 mg, 0.1 mmol, 1.0 equiv) followed by anhydrous $Zn(OTf)_2$ (10.9 mg, 0.03 mmol, 30 mol %) and 0.3 mL d_3-TFE were successively placed in the Schlenk tube. The closed tube was placed in a preheated oil bath at 110 °C for 12 h. After completion of the reaction, the reaction mixture was then cooled to room temperature. The crude mixture was passed through a short pad of silica, and a crude ^{1}H NMR analysis (provided in the Supporting Information) suggested 89% deuterium incorporation at the C(7) position and 88% deuterium at the C(5) position of indoline **1a**. Surprisingly, we have also observed 90% of deuterium incorporation at the C(3) position of indoline **1a**.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00713.

Experimental methods, optimization of reaction conditions, and other supplementary data (PDF)

Accession Codes

CCDC 2073046 and 2073053 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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