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Ruthenium-catalyzed cyclization of *N*-carbamoyl indolines with alkynes: an efficient route to pyrroloquinolinones†

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A regioselective synthesis of substituted pyrroloquinolinones *via* a ruthenium-catalyzed oxidative cyclization of substituted *N*-carbamoyl indolines with alkynes is described. The cyclization reaction was compatible with various symmetrical and unsymmetrical alkynes including substituted propiolates. Later, we performed the aromatization of pyrroloquinolinones into indole derivatives in the presence of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).

Introduction

The pyrroloquinoline unit is present in various agrochemicals, drug molecules, natural products and materials.[1] Pyrroloquinoline derivatives show potent biological activities towards asthma, obesity and epilepsy, and anti-acetylcholinesterase and melatoninergic activity.[2] In addition, pyrroloquinoline derivatives can also be used as key intermediates for synthesizing various biologically active molecules and natural products.[3] Due to the increasing importance of pyrroloquinoline molecules in medicinal and materials chemistry, the synthesis of a pyrroloquinoline framework has gained considerable attention in organic synthesis for the past three decades.[4] Traditionally, pyrroloquinoline derivatives have been prepared by Fischer indole cyclization,[2a–c] a free radical cyclization,[4a] sigmatropic rearrangement,[4b,c] and Michael-type cyclization.[4d] In addition, pyrroloquinoline derivatives can also be prepared by using metal catalysts.[5] However, these methods suffer several drawbacks such as a limited substrate scope, a number of steps being needed, poor regioselectivity and requirement of prefunctionalized substrates for the reaction.

Transition metal-catalyzed oxidative cyclization of heteroatom substituted aromatics with carbon–carbon π-components is one of the powerful methods for synthesizing heterocyclic molecules in one pot without any pre-functionalized substrates.[6,7] This method provides a step- and atom-economical route to synthesize various heterocyclic molecules from the readily available starting materials. Meanwhile, due to the high abundance of nitrogen containing heterocyclic moieties in natural products and biologically active molecules, the C–H bond functionalization of N-heterocycles has gained much attention in organic synthesis. In particular, C–H bond functionalization of indole derivatives has been highly focused on [Fig. 1]. By employing a suitable directing group on the indole nitrogen atom, the C2-H of the indole can be functionalized selectively. Subsequently, by having a directing group at the C3 position of the indole, C4-H or C2-H can be activated.[8] However, the direct C–H bond activation at C7-H of the indole skeleton is a very challenging task. But, this type of C–H bond functionalization can be indirectly achieved by the C–H bond activation at C7-H of the indoline moiety which has a directing group such as acetyl (COR), carbamoyl ($CONR_2$) or pyridyl on the nitrogen atom in the presence of metal catalysts. Later, the indoline moiety can be converted easily into an indole moiety by using a suitable oxidizing agent. By employing this protocol, various functionalizations such as arylation, alkenylation, alkylation, acylation and amination were performed at the C7 position of the indoline moiety.[9]

Recently, we have reported the hydroarylation of substituted aromatics with alkynes in the presence of a less expensive ruthenium catalyst and an organic acid, providing trisubsti-

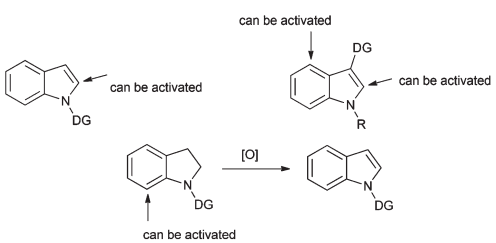

Fig. 1 Possible functionalization of indoles.

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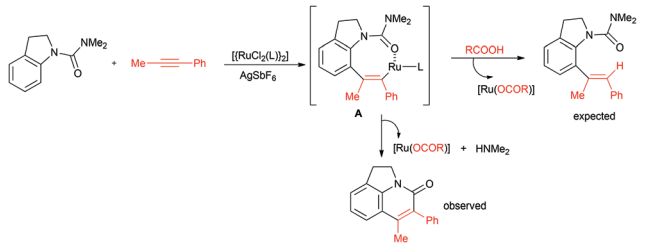
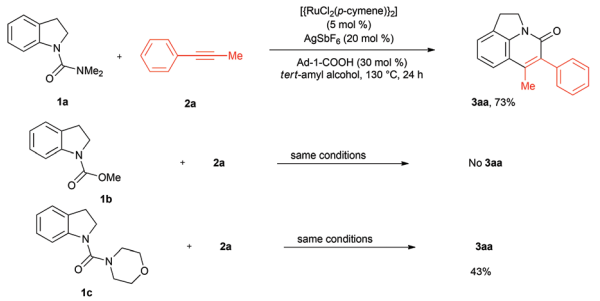
†Electronic supplementary information (ESI) available. CCDC 1059904 and 1059951. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ob01146a



Scheme 1 Observed cyclization of *N*-carbamoyl indoline with an alkyne.



Scheme 2 Cyclization of *N*-carbamoyl indolines (**1a–c**).

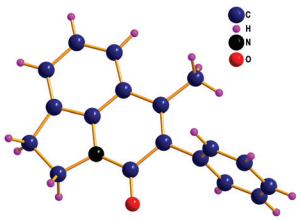


Fig. 2 Crystal structure of compound **3aa**.

tuted alkenes in a highly regio- and stereoselective manner. Our continuing interest in a ruthenium-catalyzed hydroarylation and oxidative cyclization reaction prompted us to explore the possibility of hydroarylation at C7-H of *N*-carbamoyl indolines with alkynes.[10] Herein, we wish to report a convenient route to synthesize pyrroloquinolinone derivatives *via* a ruthenium-catalyzed base free oxidative cyclization of *N*-carbamoyl indolines with alkynes. In the reaction, we expected the *ortho* alkenylation of *N*-carbamoyl indolines with alkynes in the presence of a ruthenium catalyst and an organic acid [Scheme 1].

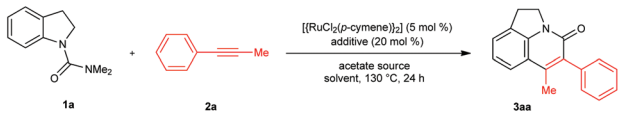
However, we observed an unexpected pyrroloquinolinone derivative *via* an intramolecular nucleophilic addition of the C–Ru bond into the carbamoyl group of intermediate **A**. Generally, a metal acetate base is used to activate the C–H bond of organic moieties. In the reaction, a catalytic amount of the organic acid, 1-adamantanecarboxylic acid (Ad-1-COOH), was used. The function of Ad-1-COOH is unique in the reaction, as it plays a role of a proton source as well as a base for activating the C7-H bond of the indoline moiety. The cyclization reaction was compatible with various hydrocarbon containing alkynes as well as functional groups such as ester containing alkynes. The cyclization reaction was also compatible with various functional group substituted indolines. The cyclization reaction is highly regioselective particularly with unsymmetrical alkynes and the coordinating groups such as aryl or ester substituents on the alkyne moiety tend to stay adjacent to the carbonyl group of the quinolinone derivative. Later, pyrroloquinolinone derivatives were aromatized into indole derivatives in the presence of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).

Results and discussion

When *N*-carbamoyl indoline (**1a**) was treated with the unsymmetrical alkyne, 1-phenyl-1-propyne (**2a**), in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol%), $AgSbF_6$ (20 mol%) and Ad-1-COOH (30 mol%) in *tert*-amyl alcohol at 130 °C for 24 h, pyrroloquinolinone derivative **3aa** was observed in 73% isolated yield in a highly regioselective manner [Scheme 2]. In the product **3aa**, methyl substituted carbon of alkyne **2a** was connected at the C7 position of **1a** and the phenyl ring substituted carbon of **2a** was connected adjacent to the carbonyl group of **3aa**. The structure and regiochemistry of compound **3aa** were confirmed by a single crystal X-ray analysis [Fig. 2].

The cyclization reaction was examined with various organic acid sources such as acetic acid (10.0 equiv.), pivalic acid (5.0 equiv.), mesitylenic acid (30 mol%), CF_3COOH (5.0 equiv.) and Ad-1-COOH (30 mol%). Pivalic acid and mesitylenic acid were partially effective, providing **3aa** in 51% and 47% GC yields, respectively (Table 1, entries 1 and 2). Ad-1-COOH was superior for the reaction, yielding **3aa** in 79% GC yield (entry 3). Other organic acids were not effective. The cyclization reaction was examined with various metal acetate sources (1.0 equiv.) such as AgOAc, CsOAc, LiOAc, NaOAc, Ag_2CO_3, $Cu(OAc)_2{\cdot}H_2O$ and CsOPiv instead of organic acids. AgOAc, $Cu(OAc)_2{\cdot}H_2O$ and NaOAc were less effective, producing product **3aa** in 29%, 37% and 25% GC yields, respectively (entries 4–6). The remaining salts were not effective. This result clearly revealed that the Ad-1-COOH was the best acetate source for the reaction (entry 3). The cyclization reaction was also examined with various solvents such as THF, DCE, CH_3CN, iso-PrOH, DMSO, DMF, *tert*-amyl alcohol, 1,2-dimethoxy ethane and toluene under similar reaction conditions. Among them, *tert*-amyl alcohol was very effective, providing **3aa** in 79% GC yield (entry 3). DCE was partially effective, giving **3aa** in 58% GC yield (entry 7). THF, iso-PrOH and 1,2-dimethoxyethane were less effective, affording product **3aa** in 15%, 20% and 32% GC yields, respectively (entries 8–10). The remaining solvents were not effective. The reaction was also tested with additives such as $AgSbF_6$, $AgBF_4$, AgOTf and KPF_6. Among them, $AgSbF_6$ was very effective, giving product **3aa** in 79% GC yield (entry 3). $AgBF_4$ was partially effective, yielding **3aa** in 41% GC yield (entry 11). AgOTf and

Table 1 Optimization studies[a]



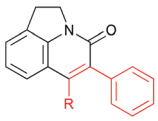
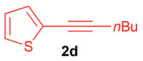
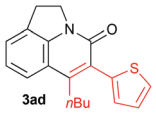
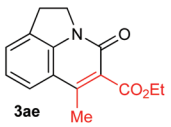
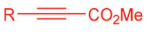
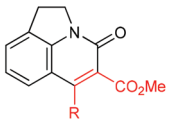
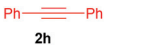
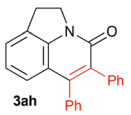
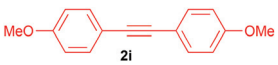
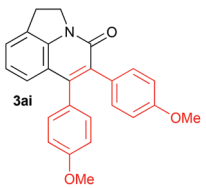
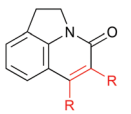
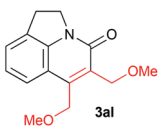
Entry	Solvent	Acetate source	Additive	Yield[b] (%)
1	*tert*-Amyl alcohol	Pivalic acid	$AgSbF_6$	51
2	*tert*-Amyl alcohol	Mesitylenic acid	$AgSbF_6$	47
3	*tert*-Amyl alcohol	Ad-1-COOH	$AgSbF_6$	79
4	*tert*-Amyl alcohol	AgOAc	$AgSbF_6$	29
5	*tert*-Amyl alcohol	$Cu(OAc)_2{\cdot}H_2O$	$AgSbF_6$	37
6	*tert*-Amyl alcohol	NaOAc	$AgSbF_6$	25
7	1,2-Dicholoroethane	Ad-1-COOH	$AgSbF_6$	58
8	THF	Ad-1-COOH	$AgSbF_6$	15
9	iso-PrOH	Ad-1-COOH	$AgSbF_6$	20
10	1,2-Dimethoxyethane	Ad-1-COOH	$AgSbF_6$	32
11	*tert*-Amyl alcohol	Ad-1-COOH	$AgBF_4$	41
12	*tert*-Amyl alcohol	Ad-1-COOH	AgOTf	—
13	*tert*-Amyl alcohol	Ad-1-COOH	KPF_6	—
14	*tert*-Amyl alcohol	Ad-1-COOH	$AgSbF_6$	45[c]

[a] All reactions were carried out using **1a** (100 mg), alkyne **2a** (1.2 equiv.), $[\{RuCl_2(p\text{-cymene})\}_2]$ (5 mol%), $AgSbF_6$ (20 mol%), acetate source and solvent (3.0 mL) at 130 °C for 24 h. [b] GC yield. [c] Reaction was performed at 110 °C for 24 h.

KPF_6 were not suitable for the reaction (entries 12 and 13). The reaction temperature 130 °C was also crucial to obtain a better yield of product **3aa**. Product **3aa** was observed only in 45% yield at reaction temperature 110 °C (entry 14). Under the optimized reaction conditions, the cyclization reaction was tested with other *N*-substituted indolines **1b–c** with **2a** (Scheme 2). In the substrate **1c**, product **3aa** was observed only in 43% yield. In the substrate **1b**, no product **3aa** was observed. No cyclization product **3aa** was observed in the blank reaction such as without $AgSbF_6$, $[\{RuCl_2(p\text{-cymene})\}_2]$ catalyst and Ad-1-COOH. These optimization studies clearly revealed that $[\{RuCl_2(p\text{-cymene})\}_2]$ (5.0 mol%), $AgSbF_6$ (20 mol%) and Ad-1-COOH (30 mol%) in *tert*-amyl alcohol at 130 °C are the best conditions for the cyclization reaction.

The scope of the cyclization reaction was examined with other unsymmetrical alkynes **2b–g** (Table 2). Thus, 1-phenyl-1-butyne (**2b**), 1-phenyl-1-hexyne (**2c**) and 2-thienyl substituted alkyne **2d** reacted with **1a** under the optimized reaction conditions, yielding the corresponding cyclization products **3ab–ad** in 65%, 60% and 61% yields, respectively (entries 1–3). In these reactions, C7-H of **1a** was selectively inserted at the alkyl substituted carbon of alkynes **2b–d**. Encouraged by this result, we further examined the cyclization reaction with substituted propiolates such as ethyl 2-butynoate (**2e**), methyl hex-2-ynoate (**2f**), and methyl oct-2-ynoate (**2g**). Interestingly, these alkynes also participated well in the reaction, yielding products **3ae–ag** in 56%, 53%, and 48% yields, respectively (entries 4–6). In these reactions also, the alkyl substituted carbon of alkynes **2e–g** was regioselectively connected at the carbon-7 position of **1a**. The structure and regiochemistry of compound **3af** were confirmed by a single crystal X-ray analysis [Fig. 3]. Next, the

Table 2 Scope of alkynes **2b–l**[a]

Entry	Alkyne **2**	Product **3**	Yield[b] [%]
			
1	**2b**: R = Et	**3ab**: R = Et	65
2	**2c**: R = *n*-Bu	**3ac**: R = *n*-Bu	60
3			61
4			56
			
5	**2f**: R = *n*-Pr	**3af**: R = *n*-Pr	53
6	**2g**: R = *n*-Pentyl	**3ag**: R = *n*-Pentyl	48
7			67
8			68
			
9	**2j**: R = Me	**3aj**: R = Me	47
10	**2k**: R = Et	**3ak**: R = Et	61
11			65

[a] All reactions were carried out using **1a** (100 mg, 0.46 mmol), alkynes **2a–l** (1.2 equiv.), $[\{RuCl_2(p\text{-cymene})\}_2]$ (5 mol%), $AgSbF_6$ (20 mol%) and Ad-1-COOH (30 mol%) in *tert*-amyl alcohol (3.0 mL) at 130 °C for 24 h. [b] Isolated yield.

cyclization reaction was examined with symmetrical alkynes **2h–l**. Diphenylacetylene (**2h**) and 1,2-bis(4-methoxyphenyl)-ethyne (**2i**) reacted well with **1a**, providing the corresponding cyclization products **3ah–ai** in 67% and 68% yields, respectively (entries 7 and 8). Less reactive aliphatic alkynes such as 2-butyne (**2j**) and 3-hexyne (**2k**) were also involved well in the reaction, affording products **3aj–ak** in 47% and 61% yields, respectively (entries 9 and 10). 1,4-Dimethoxy-2-butyne (**2l**)

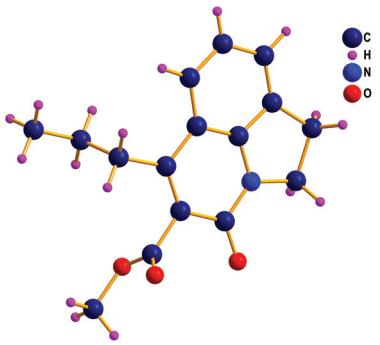


Fig. 3 Crystal structure of compound **3af**.

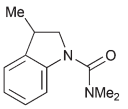
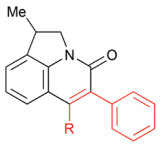
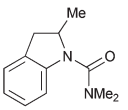
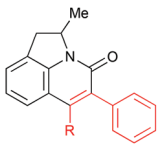
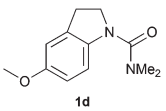
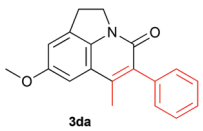
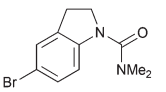
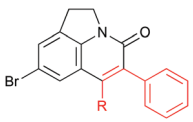
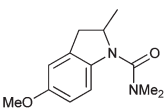
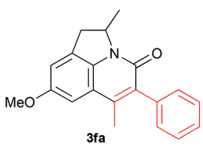
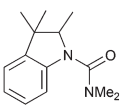
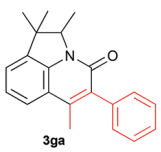
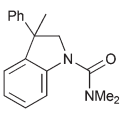
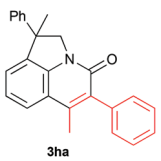
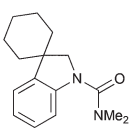
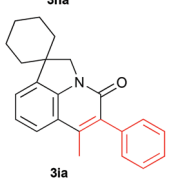
also reacted well with **1a**, giving product **3al** in 65% yield (entry 11). Meanwhile, the cyclization reaction was also examined with terminal alkynes such as phenylacetylene and 1-butyne. However, terminal alkynes were not compatible with the reaction.

The cyclization reaction was further examined with substituted *N*-carbamoyl indolines **1b–i** (Table 3). In the cyclization reaction, a less reactive 1-phenyl-1-propyne (**2a**) efficiently reacted with indoline derivatives, yielding the corresponding cyclization products in good yields compared with a highly reactive diphenylacetylene (**2h**). 3-Methyl *N*-carbamoyl indoline (**1b**) reacted with 1-phenyl-1-propyne (**2a**) or diphenylacetylene (**2h**) under similar reaction conditions, affording the cyclization products **3ba** and **3bh** in 76% and 62% yields, respectively (entries 1 and 2). Similarly, 2-methyl *N*-carbamoyl indoline (**1c**) reacted with **2a** or **2h**, providing the cyclization products **3ca** and **3ch** in 57% and 55% yields, respectively (entries 3 and 4). The cyclization reaction was also compatible with OMe and Br substituted indolines **1d–f**. Thus, 5-methoxy (**1d**) and bromo (**1e**) substituted *N*-carbamoyl indolines reacted well with **2a** or **2h**, giving pyrroloquinolinones **3da–3eh** in 68%, 56% and 51% yields, respectively (entries 5–7). Similarly, 5-methoxy-2-methyl *N*-carbamoyl indoline (**1f**) provided the corresponding cyclic compound **3fa** in 63% yield (entry 8). Substituted indolines **1g–h** also efficiently reacted with **2a**, giving pyrroloquinolinones **3ga** and **3ha** in 73% and 47% yields, respectively (entries 9 and 10). Interestingly, spiro indoline **1i** was also efficiently involved in the reaction with **2a**, affording a multi cyclic spiro compound **3ia** in 69% yield (entry 11).

Later, we tried to aromatize pyrroloquinolinones into indole derivatives in the presence of DDQ [Scheme 3]. Treatment of **3aa** and **3ah** with DDQ in 1,4-dioxane at 130 °C for 12 h gave indole derivatives **4a** and **4b** in 65% and 81% yields, respectively. It is important to note that the pyrroloindolone unit is highly useful and is present in various natural products and biologically active molecules.[11]

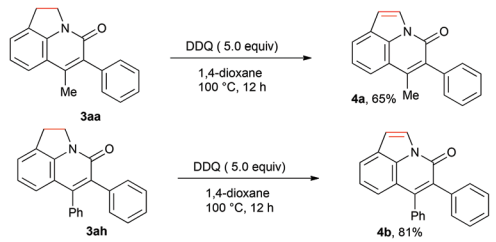
A plausible reaction mechanism is proposed to account for the present cyclization reaction in Scheme 4. The active cationic ruthenium species **5** was generated by the ligand exchange reaction between $[\{RuCl_2(p\text{-cymene})\}_2]$ and $AgSbF_6$. Chelation of the oxygen atom of the carbamoyl group into the active ruthenium species **5** followed by selective deprotonation

Table 3 Reaction of substituted *N*-carbamoyl indolines **1** with 1-phenyl-1-propyne (**2a**) or diphenylacetylene (**2h**)[a]

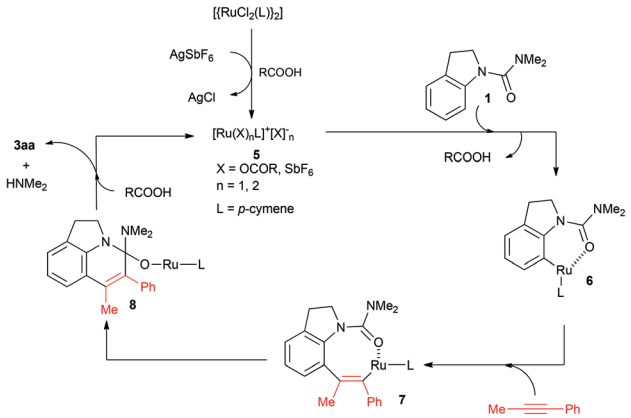
Entry	1	Product 3	Yield[b] [%]
			
1	**1b**	**3ba:** R = Me	76
2	**1b**	**3bh:** R = Ph	62
			
3	**1c**	**3ca:** R = Me	57
4	**1c**	**3ch:** R = Ph	55
5	 **1d**	 **3da**	68
			
6	**1e**	**3ea:** R = Me	56
7	**1e**	**3eh:** R = Ph	51
8	 **1f**	 **3fa**	63
9	 **1g**	 **3ga**	73
10	 **1h**	 **3ha**	47
11	 **1i**	 **3ia**	69

[a] All reactions were carried out using **1b–i** (100 mg), alkynes **2a** and **2h** (1.2 equiv.), $[\{RuCl_2(p\text{-cymene})\}_2]$ (5 mol%), $AgSbF_6$ (20 mol%) and Ad-1-COOH (30 mol%) in *tert*-amyl alcohol (3.0 mL) at 130 °C for 24 h. [b] Isolated yield.

at C7-H of the indoline moiety affords a six-membered ruthenacycle **6**. Regioselective coordinative insertion of an alkyne into the C–Ru bond of intermediate **6** provides an alkenyl–Ru intermediate **7**. It is important to note that the coordinating



Scheme 3 Aromatization of pyrroloquinolinones.



Scheme 4 Plausible mechanism.

group Ph or ester of unsymmetrical alkynes always tend to stay close to the ruthenium metal of intermediate **7**. An intramolecular nucleophilic addition of the alkene–Ru bond of intermediate **7** into the carbamoyl group produces intermediate **8**. Later, protonation at the O–Ru bond of intermediate **8** in the presence of 1-Ad-COOH affords the cyclization product **3** along with the release of *N*, *N*-dimethyl amine and regenerates the active cationic Ru complex **5** for the next catalytic cycle.

Conclusions

In conclusion, we have described a highly regioselective, atom- and step-economical route to synthesize very useful pyrroloquinolinone derivatives by a ruthenium-catalyzed cyclization of *N*-carbamoyl indolines with alkynes. The cyclization reaction was compatible with various functional group substituted indolines and symmetrical as well as unsymmetrical alkynes including substituted propiolates. Later, we performed the aromatization of pyrroloquinolinones in the presence of DDQ.

Experimental section

General information

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with nitrogen prior to use (three times). Dry solvents were used for the reaction. Column chromatographical purifications were performed using SiO_2 (120–200 mesh ASTM) from Merck if not indicated otherwise. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Starting materials: commercially available starting materials, metal complexes and metal salts were purchased from commercial sources and used without further purification.

General procedure for the preparation of pyrroloquinolinones catalyzed by ruthenium complex

A 15 mL pressure tube with a septum containing [{$RuCl_2$-(*p*-cymene)}$_2$] (5.0 mol%), *N*-carbamoyl indolines **1** (100 mg), Ad-1-COOH (30 mol%), alkyne **2** (1.2 equiv.) (if the alkyne is a solid) and $AgSbF_6$ (20 mol%) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the tube was then added *tert*-amyl alcohol (3.0 mL) *via* a syringe, after that the reaction mixture was evacuated and purged with nitrogen gas three times (liquid alkynes were added at this stage *via* a syringe). After that, the septum was taken out and immediately a screw cap was used to cover the tube under a nitrogen atmosphere and the reaction mixture was stirred at room temperature for 5 minutes. Then, the reaction mixture was allowed to stir at 130 °C for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, and filtered through Celite and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluents to give pure product **3**.

Spectral data of compounds

6-Methyl-5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3aa). White solid; mp: 167–169 °C; eluent (40% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 73% (99 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2960, 1611, 1231, 793, 608 and 653. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.2 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.30–7.23 (m, 2H), 7.20–7.14 (m, 1H), 4.47–4.41 (t, J = 8.0 Hz, 2H), 3.42 (t, J = 8.0 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 142.6, 141.2, 136.3, 133.6, 130.8, 130.3, 128.3, 127.6, 124.8, 123.2, 121.7, 119.00, 47.3, 27.3, 16.3. HRMS (ESI): calc. for [($C_{18}H_{15}NO$)H] (M + H) 262.1232, measured 262.1233.

6-Ethyl-5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3ab). White solid; mp: 169–171 °C; eluent (35% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 65% (95 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2956, 1620, 1606, 1277, 1066 and 706. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.2 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.39–7.31 (m, 2H), 7.28–7.22 (m, 2H), 7.21–7.14 (m, 1H), 4.43 (t, J = 8.0, 2H), 3.41 (t, J = 8.0 Hz, 2H), 2.67 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 148.3, 141.8, 136.5, 133.4, 131.0, 129.9, 128.4, 127.5, 124.6, 123.0, 121.7, 117.6, 47.11, 27.2, 22.9, 14.6. HRMS (ESI): calc. for [($C_{19}H_{17}NO$)H] (M + H) 276.1388, measured 276.1389.

6-Butyl-5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3ac). White solid; mp: 173–175 °C; eluent (40% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 60% (96 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2960, 1621, 1615, 1277, 1071 and 743. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.2 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.38–7.29 (m, 2H), 7.28–7.20 (m, 2H), 7.20–7.11 (m, 1H), 4.44 (t, J = 8.0 Hz, 2H), 3.41 (t, J = 8.0 Hz, 2H), 2.70–2.59 (m, 2H), 1.52 (dd, J = 11.4, 4.6 Hz, 2H), 1.26 (dd, J = 14.6, 7.2 Hz, 2H), 0.78 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 147.4, 141.7, 136.4, 133.6, 130.9, 129.9, 128.3, 127.5, 124.6, 122.9, 121.8, 118.0, 47.1, 32.3, 29.4, 27.2, 22.9, 13.7. HRMS (ESI): calc. for $[(C_{21}H_{21}NO)H]$ (M + H) 304.1701, measured 304.1707.

6-Butyl-5-(thiophen-2-yl)-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3ad). Brown solid; mp: 124–128 °C; eluent (45% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 61% (99 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2850, 1641, 1232, 823, 697 and 743. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 7.8 Hz, 1H), 7.43 (dd, J = 5.2, 1.2 Hz, 1H), 7.35–7.30 (m, 1H), 7.21–7.13 (m, 1H), 7.10 (dd, J = 5.2, 3.6 Hz, 1H), 7.02 (dd, J = 3.6, 1.2 Hz, 1H), 4.48–4.37 (m, 2H), 3.45–3.34 (m, 2H), 2.85–2.74 (m, 2H), 1.66–1.55 (m, 2H), 1.37 (dd, J = 14.8, 7.4 Hz, 2H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 149.7, 141.8, 136.5, 131.0, 128.3, 126.6, 126.6, 126.1, 125.0, 123.1, 121.9, 117.7, 47.2, 32.8, 29.9, 27.2, 23.1, 13.8. HRMS (ESI): calc. for $[(C_{19}H_{19}NOS)H]$ (M + H) 310.1266, measured 310.1261.

Ethyl 6-methyl-4-oxo-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxylate (3ae). Brown liquid; eluent (50% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 56% (72 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3006, 1725, 1644, 1614, 1161 and 741. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.2, 1H), 7.36 (d, J = 7.4, 1H), 7.17 (dd, J = 8.2, 7.4 Hz, 1H), 4.49–4.36 (m, 4H), 3.40 (t, J = 8.2 Hz, 2H), 2.44 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 157.8, 144.3, 141.7, 130.9, 127.6, 126.0, 123.5, 121.8, 117.8, 61.9, 46.9, 27.2, 15.5, 14.4. HRMS (ESI): calc. for $[(C_{15}H_{15}NO_3)H]$ (M + H) 258.1130, measured 258.1133.

4-Methyl 4-oxo-6-propyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxylate (3af). Brown liquid; eluent (45% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 53% (76 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2920, 1727, 1640, 1606, 1231 and 809. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8.2 Hz, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.16 (dd, J = 8.2, 7.4 Hz, 1H), 4.51–4.33 (m, 2H), 3.93 (s, 3H), 3.39 (t, J = 8.0 Hz, 2H), 2.84–2.69 (m, 2H), 1.75–1.62 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 157.9, 148.8, 142.1, 131.2, 127.0, 125.9, 123.5, 122.0, 116.9, 52.6, 46.9, 32.0, 27.2, 23.5, 14.5. HRMS (ESI): calc. for $[(C_{16}H_{17}NO_3)Na]$ (M + Na) 294.1106, measured 294.1105.

Methyl 4-oxo-6-pentyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxylate (3ag). Brown solid; mp: 141–143 °C; eluent (45% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 48% (76 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2956, 1728, 1643, 1612, 1154 and 744. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.2 Hz, 1H), 7.35 (d, J = 7.2, Hz, 1H), 7.17 (dd, J = 8.0, 7.2 Hz, 1H), 4.53–4.18 (m, 2H), 3.93 (s, 3H), 3.39 (t, J = 8.0 Hz, 2H), 2.76 (dd, J = 9.2, 7.2 Hz, 2H), 1.65 (dd, J = 8.8, 6.6 Hz, 2H), 1.43–1.27 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 157.9, 149.1, 142.1, 131.2, 126.8, 125.9, 123.5, 121.9, 116.9, 52.6, 46.9, 32.1, 30.0, 29.8, 27.2, 22.4, 14.0. HRMS (ESI): calc. for $[(C_{18}H_{21}NO_3)H]$ (M + H) 300.1599, measured 300.1600.

5,6-Diphenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3ah). White solid; mp: 209–212 °C; eluent (40% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 67% (114 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2997, 1636, 1604, 1443, 1237, 1070 and 772. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, J = 6.8, 1.2 Hz, 1H), 7.28–7.22 (m, 3H), 7.18–7.02 (m, 9H), 4.53 (t, J = 8.2 Hz, 2H).3.48 (t, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 146.9, 141.7, 136.0, 135.5, 133.4, 130.9, 130.4, 129.8, 127.9, 127.6, 127.4, 126.9, 124.8, 123.7, 122.9, 118.6, 47.3, 27.2. HRMS (ESI): calc. for $[(C_{23}H_{17}NO)H]$ (M + H) 324.1388, measured 324.1393.

5,6-bis(4-Methoxyphenyl)-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]-quinolin-4-one (3ai). White semisolid; eluent (40% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 68% (137 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2867, 1640, 1630, 1501, 1247, 1085 and 748. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 8.0 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 7.09–6.99 (m, 5H), 6.80 (d, J = 8.4 Hz, 2H), 6.73–6.67 (m, 2H), 4.60–4.45 (m, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 3.46 (t, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 158.8, 158.3, 146.8, 141.4, 132.6, 132.3, 131.1, 130.6, 128.3, 127.8, 124.7, 123.7, 123.2, 119.0, 113.6, 113.0, 55.2, 55.1, 47.5, 27.2. HRMS (ESI): calc. for $[(C_{25}H_{21}NO_3)H]$ (M + H) 384.1600, measured 384.1607.

5,6-Dimethyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3aj). White solid; mp: 131–135 °C; eluent (30% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 47% (49 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2924, 1637, 1620, 1597, 1245, 1022 and 809. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.2 Hz, 1H), 7.26 (d, J = 7.2 Hz, 1H), 7.18–7.07 (m, 1H), 4.49–4.32 (m, 2H), 3.38 (t, J = 8.0 Hz, 2H), 2.41 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 140.8, 140.4, 130.6, 128.5, 123.8, 122.9, 120.9, 118.9, 47.0, 27.3, 14.7, 13.2. HRMS (ESI): calc. for $[(C_{13}H_{13}NO)H]$ (M + H) 200.1075, measured 200.1076.

5,6-Diethyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3ak). White solid; mp: 139–141 °C; eluent (35% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 61% (73 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2960, 1651, 1615, 1247, 1041 and 643. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 7.0, Hz, 1H), 7.18–7.06 (m, 1H), 4.43 (t, J = 8.0 Hz, 2H), 3.39 (t, J = 8.0 Hz, 2H), 2.89 (q, J = 7.6 Hz, 2H), 2.76 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H), 1.18 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 146.1, 140.9, 133.8, 130.8, 123.7, 122.8, 120.9, 117.9, 46.9, 27.2, 21.7, 20.4, 14.4, 14.0. HRMS (ESI): calc. for $[(C_{15}H_{17}NO)H]$ (M + H) 228.1388, measured 228.1392.

5,6-bis(Methoxymethyl)-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3al). White solid; mp: 134–137 °C; eluent (35% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1a** (100 mg); yield is 65% (89 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2975, 1644, 1525, 1177, 1071, 950 and 743. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.2 Hz, 1H), 7.31 (d, J = 7.0 Hz, 1H), 7.18–7.09 (m, 1H), 4.79 (s, 2H), 4.67 (s, 2H), 4.41 (t, J = 8.0 Hz, 2H), 3.42 (s, 3H), 3.41 (s, 3H), 3.38 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 144.6, 141.8, 130.7, 129.7, 125.4, 123.5, 122.7, 117.7, 67.7, 65.0, 58.6, 47.4, 27.2. HRMS (ESI): calc. for [($C_{15}H_{17}NO_3$)Na] (M + Na) 282.1106, measured 282.1107.

1,6-Dimethyl-5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3ba). White solid; mp: 142–144 °C; eluent (40% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1b** (100 mg); yield is 76% (102 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2870, 1640, 1609, 1229, 860 and 752. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.42–7.34 (m, 2H), 7.34–7.27 (m, 2H), 7.27–7.21 (m, 1H), 4.65 (dd, J = 12.6, 9.4 Hz, 1H), 4.03 (dd, J = 12.6, 5.6 Hz, 1H), 3.89–3.74 (m, 1H), 2.33 (s, 3H), 1.50 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 142.3, 140.6, 136.3, 135.8, 133.8, 130.2, 128.2, 127.4, 123.7, 123.0, 121.8, 118.8, 55.0, 34.8, 20.9, 16.2. HRMS (ESI): calc. for [($C_{19}H_{17}NO$)H] (M + H) 276.1388, measured 276.1389.

1-Methyl-5,6-diphenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3bh). White solid; mp: 193–195 °C; eluent (40% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1b** (100 mg); yield is 62% (103 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2770, 1629, 1596, 1123, 830 and 736. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.0 Hz, 1H), 7.31–7.26 (m, 3H), 7.21–7.10 (m, 9H), 4.74 (dd, J = 12.0, 8.0 Hz, 1H), 4.13 (dd, J = 12.0, 4.0 Hz, 1H), 3.88 (dq, J = 13.6, 7.0 Hz, 1H), 1.55 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 147.0, 141.0, 136.0, 135.6, 135.5, 133.5, 130.9, 129.8, 128.0, 127.5, 127.4, 126.9, 123.9, 123.8, 123.1, 118.5, 55.3, 34.8, 20.8. HRMS (ESI): calc. for [($C_{24}H_{19}NO$)H] (M + H) 338.1545, measured 338.1549.

2,6-Dimethyl-5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3ca). Off-white solid; mp: 157–160 °C; eluent (30% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1c** (100 mg); yield is 57% (77 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2960, 1650, 1620, 1240, 873 and 740. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.0 Hz, 1H), 7.49–7.45 (m, 2H), 7.42–7.34 (m, 2H), 7.33 (m, 1H), 7.33–7.31 (m, 1H), 7.22 (t, J = 8.0 Hz, 1H), 5.15–5.02 (m, 1H), 3.67 (dd, J = 16.8, 9.4 Hz, 1H), 3.03 (dd, J = 16.8, 3.8 Hz, 1H), 2.34 (s, 3H), 1.65 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 142.1, 140.6, 136.4, 134.2, 130.3, 129.2, 128.1, 127.4, 124.7, 122.9, 121.6, 118.7, 56.9, 36.3, 20.6, 16.1. HRMS (ESI): calc. for [($C_{19}H_{17}NO$)H] (M + H) 276.1388, measured 276.1396.

2-Methyl-5,6-diphenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3ch). Off-white solid; mp: 203–205 °C; eluent (30% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1c** (100 mg); yield is 55% (91 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2973, 1640, 1613, 1206, 793 and 720. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (t, J = 8.4 Hz, 2H), 7.31–7.24 (m, 3H), 7.22–7.15 (m, 5H), 7.14–7.01 (m, 3H), 5.19 (m, 1H), 3.72 (dd, J = 16.6, 9.4 Hz, 1H), 3.08 (dd, J = 16.6, 3.8 Hz, 1H), 1.73 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 146.9, 141.0, 136.0, 135.6, 133.8, 131.0, 129.8, 129.0, 128.0, 127.9, 127.5, 127.4, 126.8, 124.9, 123.7, 123.0, 118.4, 57.2, 36.3, 20.6. HRMS (ESI): calc. for [($C_{24}H_{19}NO$)H] (M + H) 338.1545, measured 338.1549.

8-Methoxy-6-methyl-5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]-quinolin-4-one (3da). White solid; mp: 239–242 °C; eluent (45% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1d** (100 mg); yield is 68% (90 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2965, 1640, 1607, 1483, 1314 and 780. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (t, J = 7.4 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.30 (dd, J = 8.6, 2.0 Hz, 2H), 7.09–7.03 (m, 1H), 6.93 (d, J = 2.0 Hz, 1H), 4.55–4.43 (m, 2H), 3.90 (s, 3H), 3.43 (t, J = 8.0 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 156.6, 141.8, 136.4, 136.0, 134.0, 132.1, 130.2, 128.1, 127.4, 118.7, 114.7, 103.5, 56.1, 47.3, 27.2, 16.3. HRMS (ESI): calc. for [($C_{19}H_{17}NO_2$)H] (M + H) 292.1338, measured 292.1337.

8-Bromo-6-methyl-5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]-quinolin-4-one (3ea). Brown solid; mp: 175–179 °C; eluent (40% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1e** (100 mg); yield is 56% (71 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3742, 2998, 1639, 1611, 1072 and 856. ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.46 (t, J = 7.8 Hz, 3H), 7.40 (d, J = 7.4 Hz, 1H), 7.29 (dd, J = 6.8, 1.6 Hz, 2H), 4.59–4.37 (m, 2H), 3.44 (t, J = 8.0 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 141.3, 140.2, 135.8, 134.6, 132.6, 130.1, 128.2, 127.8, 127.7, 124.3, 119.9, 115.6, 47.2, 27.0, 16.2. HRMS (ESI): calc. for [($C_{18}H_{14}BrNO$)H] (M + H) 340.0337, measured 340.0339.

8-Bromo-5,6-diphenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3eh). Brown solid; mp: 211–213 °C; eluent (40% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1e** (100 mg); yield is 51% (76 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3693, 2898, 1647, 1603, 1046 and 826. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 1.6 Hz, 1H), 7.31 (s, 1H), 7.30 (d, J = 1.6 Hz, 2H), 7.26 (s, 1H), 7.19 (d, J = 8.0 Hz, 3H), 7.15–7.09 (m, 4H), 4.58 (t, J = 8.2 Hz, 2H), 3.51 (t, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.0, 146.0, 135.3, 135.1, 132.5, 130.8, 129.6, 128.2, 128.0, 127.8, 127.5, 127.1, 126.1, 119.6, 115.7, 47.5, 27.0. HRMS (ESI): calc. for [($C_{23}H_{16}BrNO$)H] (M + H) 402.0494, measured 402.0500.

8-Methoxy-2,6-dimethyl-5-phenyl-1,2-dihydro-4*H*-yrrolo-[3,2,1-*ij*]quinolin-4-one (3fa). Yellow oil; eluent (45% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1f** (80 mg); yield is 63% (66 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3012, 1653, 1621, 1260, 1069 and 783. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (t, J = 7.4 Hz, 2H), 7.36 (d, J = 7.4 Hz, 1H), 7.29 (d, J = 6.8 Hz, 2H), 7.01 (d, J = 2.0 Hz, 1H), 6.92 (d, J = 2.0 Hz, 1H), 5.15–4.97 (m, 1H), 3.88 (s, 3H), 3.67–3.57 (m, 1H), 2.97 (dd, J = 16.0, 3.8 Hz, 1H), 2.28 (s, 3H), 1.62 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 156.6, 141.6, 136.5, 135.5, 134.6, 130.7, 130.3, 128.1, 127.3, 118.6, 114.6, 103.6,

57.1, 56.1, 36.3, 20.6, 16.3. HRMS (ESI): calc. for [($C_{20}H_{19}NO_2$)H] (M + H) 306.1494, measured 306.1495.

1,1,2,6-Tetramethyl-5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]-quinolin-4-one (3ga). White semisolid; eluent (30% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1g** (100 mg); yield is 73% (99 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2989, 1640, 1607, 1265, 1077 and 893. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0, Hz, 1H), 7.47 (t, J = 7.4 Hz, 2H), 7.39 (d, J = 7.4 Hz, 1H), 7.34–7.31 (m, 3H), 7.28–7.23 (m, 1H), 4.66 (q, J = 6.8 Hz, 1H), 2.34 (s, 3H), 1.52 (d, J = 6.8 Hz, 3H), 1.46 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 142.2, 139.2, 138.7, 136.4, 134.4, 130.3, 128.1, 127.4, 123.2, 122.4, 121.8, 118.7, 67.7, 44.1, 31.3, 22.3, 16.1, 14.7. HRMS (ESI): calc. for [($C_{21}H_{21}NO$)H] (M + H) 304.1701, measured 304.1707.

1,6-Dimethyl-1,5-diphenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]-quinolin-4-one (3ha). White semisolid; eluent (20% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1h** (100 mg); yield is 47% (59 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2354, 1693, 1646, 1531, 1231 and 772. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J = 7.4, 1.8 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.40 (d, J = 7.4 Hz, 1H), 7.39–7.29 (m, 6H), 7.26 (t, J = 2.4 Hz, 3H), 4.62 (d, J = 12.6 Hz, 1H), 4.52 (d, J = 12.6 Hz, 1H), 2.38 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 146.4, 142.5, 140.1, 138.7, 136.2, 134.1, 130.2, 128.6, 128.2, 127.5, 126.8, 126.3, 124.3, 123.3, 122.2, 118.9, 64.1, 48.7, 28.0, 16.2. HRMS (ESI): calc. for [($C_{25}H_{21}NO$)H] (M + H) 352.1701, measured 352.1709.

2,6-Dimethyl-5-phenyl-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (3ia). Yellow oil; eluent (25% ethyl acetate in hexanes); the representative general procedure **A** was followed using **1i** (100 mg); yield is 69% (88 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2960, 1651, 1515, 1277, 1071 and 743. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0, Hz, 1H), 7.51–7.44 (m, 2H), 7.42–7.36 (m, 1H), 7.36–7.29 (m, 3H), 7.24 (dd, J = 8.0, 7.4 Hz, 1H), 4.30 (s, 2H), 2.33 (s, 3H), 1.92–1.73 (m, 7H), 1.58–1.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 142.3, 140.0, 139.8, 136.4, 133.8, 130.2, 128.2, 127.4, 123.0, 122.8, 121.8, 118.8, 57.9, 45.6, 37.8, 25.2, 22.9, 16.1. HRMS (ESI): calc. for [($C_{23}H_{23}NO$)H] (M + H) 330.1858, measured 330.1862.

General procedure for the aromatization of pyrroloquinolinones

A 15 mL pressure tube with a septum containing pyrroloquinolinone **3aa** or **3ah** (50 mg) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (5.0 equiv.) was evacuated and purged with nitrogen gas three times. To the tube was then added 1,4-dioxane (2.0 mL) *via* a syringe, and then the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube under a nitrogen atmosphere and the reaction mixture was stirred at room temperature for 5 minutes. Then, the reaction mixture was allowed to stir at 100 °C for 12 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, and concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluents to give pure aromatized product **4a** or **4b**.

6-Methyl-5-phenyl-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (4a). Off-white solid; mp: 203–206 °C; eluent (10% ethyl acetate in hexanes); the representative general procedure **B** was followed using **3aa** (50 mg); yield is 65% (32 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3056, 2993, 1643, 1626, 1379, 1293 and 1119. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.56–7.41 (m, 4H), 7.39–7.32 (m, 2H), 6.90 (d, J = 3.6 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 158.9, 144.5, 135.7, 133.7, 131.5, 130.2, 128.3, 127.8, 127.8, 124.7, 123.9, 123.8, 121.9, 118.8, 110.4, 16.1. HRMS (ESI): calc. for [($C_{18}H_{13}NO$] (M + H) 260.1075, measured 260.1082.

5,6-Diphenyl-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (4b). Grey solid; mp: 205–208 °C; eluent (10% ethyl acetate in hexanes); the representative general procedure **B** was followed using **3ah** (50 mg); yield is 81% (40 mg). IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3046, 2979, 1669, 1638, 1400, 1373, and 1243. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.43–7.38 (m, 1H), 7.38–7.30 (m, 4H), 7.27–7.17 (m, 7H), 6.99 (d, J = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 148.6, 135.4, 135.0, 133.4, 131.6, 131.0, 130.0, 127.9, 127.9, 127.8, 127.6, 127.3, 124.9, 124.8, 124.0, 118.5, 110.9. HRMS (ESI): calc. for [($C_{23}H_{15}NO$)H] (M + H) 322.1232, measured 322.1239.

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