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ARTICLE

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Synthesis of 5-Iodopyrrolo[1,2-*a*]quinolines and Indolo[1,2-*a*]quinolines via Iodine-Mediated Electrophilic and Regioselective 6-*endo*-*dig* Ring Closure

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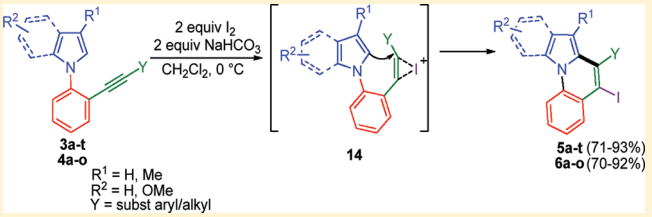
Supporting Information

ABSTRACT: The *endo*-cyclic ring closure of 1-(2-(substituted ethynyl)phenyl)-1*H*-pyrroles **3a**−**t** and 1-(2-(substituted ethynyl)-phenyl)-*H*-indole **4a**−**o** mediated by Lewis acid (I_2) under mild conditions afforded substituted 5-iodopyrrolo[1,2-*a*]-quinolines **5a**−**t** and 5-iodoindolo[1,2-*a*]quinolines **6a**−**o** in good to excellent yields. The reaction shows selective C−C bond formation on the more electrophilic alkynyl carbon, resulting in the regioselective 6-*endo*-*dig*-cyclized product. Iodo derivatives of pyrrolo- and indoloquinolines allow functional group diversification on the quinoline nucleus, which proves to be highly advantageous for structural and biological activity assessments.



INTRODUCTION

Numerous natural products and biologically active molecules are comprised of nitrogen-containing subunits. Synthesis of hetrocycles has been a prominent research objective for over a century, and a variety of well-established methods are available in the literature. Development of new approaches for their syntheses, employing efficient and economical routes, is currently a popular research area. Among different *N*-heterocycles, indole and pyrrole rings are known to exert biological activity in many active pharmaceutical ingredients.[1] Pyrrolo[1,2-*a*]quinolines and indolo[1,2-*a*]quinolines are such molecules which have unique nitrogen-containing tricyclic and tetracyclic stuctures derived from pyrrole and indole, and their reduced and oxidized forms occur widely among natural products.[2] These polycyclic compounds are also identified as rigid molecular platforms critical to advances in various areas of chemical research such as host−guest chemistry,[3] liquid crystal chemistry,[4] and even biochemical studies of synthetic peptides.[5]

Synthesis of pyrrolo- and indoloquinolines is one of the least explored areas. Reported methods[6] for the synthesis of pyrrolo- and indoloquinolines are limited and multistep and suffer from availability of starting materials. Few of the recently reported methods include Lautens's protocol, which employed the synthesis of pyrrolo- and indolo[1,2-*a*]quinolines from *gem*-dibromovinyl substrates by the sequential Suzuki−Miyuara coupling/direct arylation using S-Phos ligand under palladium catalysis at 100 °C (Scheme 1A).[7] Furthermore, in another report, $Pd(OAc)_2$ along with norbornene ligand and PPh_3 as a coligand in toluene at 110 °C was used for the synthesis of fused heterocyclic scaffolds (Scheme 1B).[8]

However, in keeping with the recently reported synthesis of halo derivatives of numerous heterocycles such as benzoxepine,[9] pyrrazoles,[10] pyranoquinolines, pyranoquinolinones, and isocumarins,[11] indoles, quinolines, and quinolinones,[12] benzo[*b*]-thiophenes,[13] pyrroles,[14] naphthalenes,[15] isochromenes,[16] phosphaisocoumarins,[17] and other heterocycles[18] by electrophilic cyclization of the alkynes using Lewis acids such as ICl and I_2, an alternate method for the preparation of iodo derivatives of pyrrolo- and indoloquinolines has been reported. This method allows functional group variation on the quinoline nucleus, which subsequently proves highly desirable for structural and biological activity assessments. In continuation of our efforts to adapt heterocyclic chemistry,[11,19] we herein report an electrophilic cyclization reaction employing the use of I_2, which is more economical and convenient to handle than other reported media. Furthermore, this cyclization method leads to the synthesis of halogen-containing quinoline derivatives which thereafter can be elaborated using various palladium- and copper-catalyzed coupling reactions, such as the Suzuki−Miyaura, Sonogashira, Heck, and Ullmann reactions.

In our preceding report for the synthesis of indolo[2,1-*a*]-isoquinolines **10**,[19a] we came up with an interesting outcome (Scheme 2). In the report we described that the initial attempt was to synthesize indolo[1,2-*a*]quinolines **11** starting from indole **7** and *o*-haloalkyne **8** via the anticipated route 1, i.e., *N*-arylation followed by intramolecular electrophilic cyclization without isolating intermediate **4**. The reaction surprisingly proceeded via route 2 and afforded the indolo[2,1-*a*]isoquinolines **10**, regioisomers of **11**, via the formation of hydroaminated intermediate **9** (Scheme 2)

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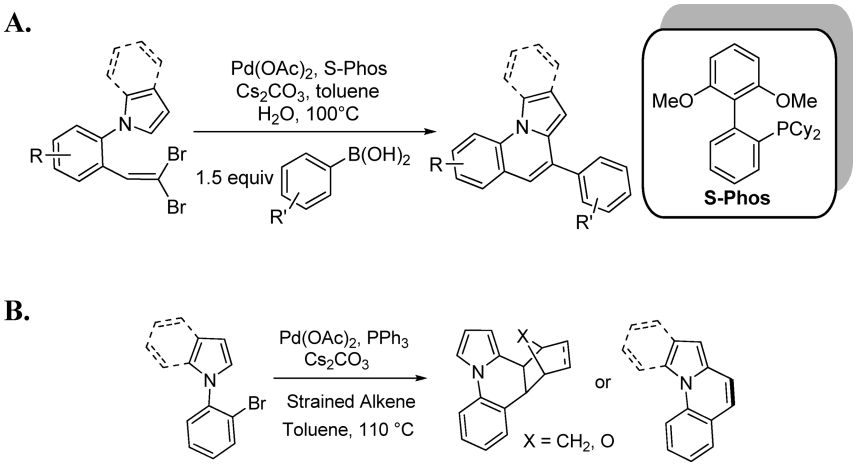
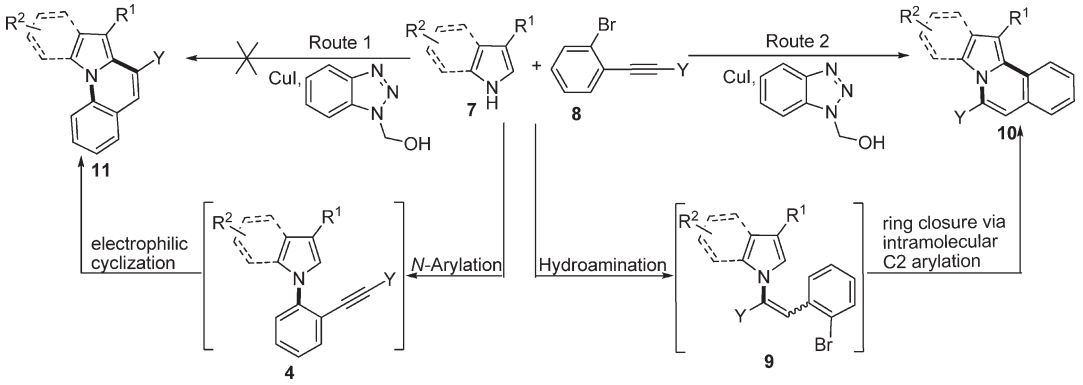
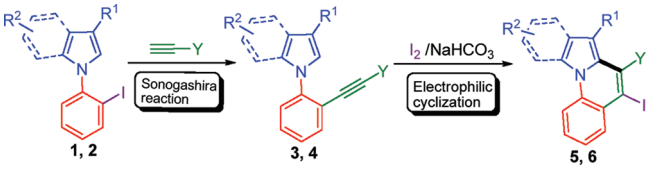
Scheme 1. Previous Approaches To Synthesize Pyrrolo/Indoloquinolines



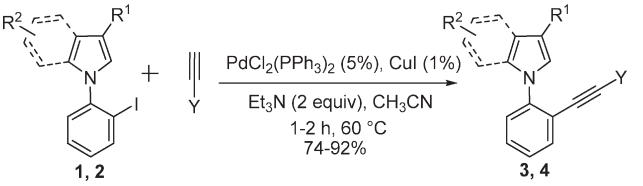
Scheme 2. Previous Effort of Our Laboratory



Scheme 3. Designed Pathway for the Synthesis of Pyrrolo/Indoloquinolines



Scheme 4



From our previous experience, we concluded that intermediates **3** and **4** (Scheme 3) are crucial for the formation of pyrrolo- and indolo[1,2-*a*]quinolines. We herein designed an alternate two-step process to obtain the desired pyrrolo/indolo[1,2-*a*]-quinolines via intermediates **3** and **4** (Scheme 3).

RESULTS AND DISCUSSION

To probe the viability of the envisioned protocol (Scheme 3), we first carried out copper-catalyzed direct arylations of pyrrole/indole with *o*-dihalobenzenes per the protocol developed for different *N*-hetrocycles in our laboratory.[19e,f] The arylated substrates **1** and **2** were then treated with terminal alkynes to perform Sonogashira cross-coupling reaction[19c] with palladium complex $PdCl_2(PPh_3)_2$ (5 mol %) in the presence of CuI (1 mol %) as the cocatalyst using Et_3N (2 equiv) as the base in CH_3CN for 1−2 h at 60 °C under an inert atmosphere (Scheme 4). Though all the terminal alkynes coupled efficiently, it was found that the alkynes with electron-donating groups such as Me, OMe, Et, *t*-Bu, *n*-Bu, and NMe_2 coupled efficiently and afforded the coupling products in 74−92% yields.

With an effective protocol for *N*-arylations of pyrrole and Sonogashira coupling in hand, we then aimed to identify the optimal reaction conditions for electrophilic iodocyclization reaction. Several electrophiles and bases were examined along with variation in time and temperature for the electrophilic cyclization of 1-(2-(phenylethynyl)phenyl)-1*H*-pyrrole (**3a**). Interesting observations emerged from the data in Table 1. We first reacted

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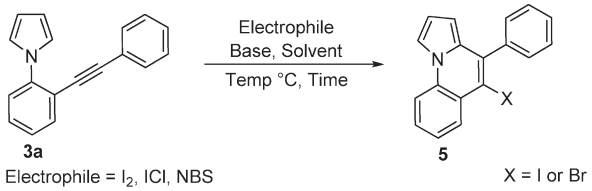
Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	E^+ (amt, equiv)	base (amt, equiv)	T (°C)	t (h)	yield[b] (%)
1	CH_2Cl_2	I_2 (1.2)	$NaHCO_3$ (2.0)	25	1	26
2	CH_2Cl_2	I_2 (2.0)	$NaHCO_3$ (2.0)	25	1	48
3	CH_2Cl_2	I_2 (2.0)	$NaHCO_3$ (2.0)	25	2	[c]
4	CH_2Cl_2	ICl (2.0)	$NaHCO_3$ (2.0)	25	1	[c]
5	CH_2Cl_2	NBS (2.0)	$NaHCO_3$ (2.0)	25	1	35
6	CH_2Cl_2	I_2 (2.0)	$NaHCO_3$ (2.0)	0	1	43
7	CH_2Cl_2	I_2 (2.0)	$NaHCO_3$(2.0)	0	2	82
8	CH_2Cl_2	ICl (2.0)	$NaHCO_3$ (2.0)	0	1	35
9	CH_2Cl_2	ICl (2.0)	$NaHCO_3$ (2.0)	0	2	[c]
10	CH_2Cl_2	ICl (2.0)	$NaHCO_3$ (2.0)	−78	2	74
11	CH_2Cl_2	I_2 (2.0)	KO*t*Bu (2.0)	0	2	22
12	CH_2Cl_2	I_2 (2.0)	Cs_2CO_3 (2.0)	0	2	28
13	CH_2Cl_2	I_2 (2.0)	K_3PO_4 (2.0)	0	2	12
14	CH_2Cl_2	I_2 (2.0)	K_2CO_3 (2.0)	0	2	47
15	CH_3CN	I_2 (2.0)	$NaHCO_3$ (2.0)	0	2	69
16	1,4-dioxane	I_2 (2.0)	$NaHCO_3$ (2.0)	0	2	trace
17	CH_2Cl_2	I_2 (2.0)	$NaHCO_3$ (2.0)	0	4	[c]
18	CH_2Cl_2	I_2 (2.0)	$NaHCO_3$ (3.0)	0	2	82

[a] All reactions were performed using 0.5 mmol of the alkyne **3a**, base, and 3.0 mL of solvent under inert conditions. [b] Isolated yields. [c] An inseparable mixture of products was obtained.

3a (0.5 mmol) with 1.2 equiv of I_2 and 2.0 equiv of $NaHCO_3$ in 3.0 mL of CH_2Cl_2 at 25 °C for 1 h, and the iodocyclized product **5** was obtained in only 26% yield (Table 1, entry 1). However, increasing the amount of I_2 from 1.2 to 2.0 equiv afforded product **5** in 48% yield (entry 2). When the reaction was allowed to stir for 2 h, an inseparable mixture of products was obtained (entry 3). When 2.0 equiv of ICl was taken instead of I_2 and the reaction was stirred for 1 h, an inseparable complex mixture of products was obtained (entry 4). When **3a** with 2.0 equiv of *N*-bromosuccinimide (NBS) and 2.0 equiv of $NaHCO_3$ in CH_2Cl_2 was stirred for 1 h, the desired cyclized product **5** was obtained in 35% yield (entry 5). When **3a** reacted with 2.0 equiv of I_2 and 2.0 equiv of $NaHCO_3$ in CH_2Cl_2 for 1 h at 0 °C, the corresponding iodocyclized product **5** was obtained in 43% yield, leaving behind 51% of the starting material (entry 6). Interestingly, when the reaction was continued for 2 h, it afforded the iodocyclized product **5** in 82% yield (entry 7). When **3a** with 2.0 equiv of ICl and 2.0 equiv of $NaHCO_3$ in CH_2Cl_2 was stirred for 1 h at 0 °C, the desired cyclized product **5** was obtained in 35% yield (entry 8). When the reaction was allowed to stir for 2 h, an inseparable mixture of products was obtained (entry 9). However, when the reaction was stirred for 2 h at −78 °C, the corresponding iodocyclized product **5** was obtained in 74% yield (entry 10). Among different bases tested in this reaction system, $NaHCO_3$ proved to be the most effective (entries 7 and 11−14). Also, among different solvents screened, CH_2Cl_2 proved to be more suitable for electrophilic cyclization (entries 7, 15, and 16). It is noteworthy that when the reaction was continued for a longer time (4 h), it resulted in an inseparable mixture of products (entry 17). However, increasing the amount of base from 2.0 to 3.0 equiv had no significant effect on the yield of the desired product **5** (entry 18). It is evident from the Table 1 that temperature and time play a crucial role in the yield of the desired product **5**. The combination of I_2 (2.0 equiv) and $NaHCO_3$ (2.0 equiv) in CH_2Cl_2 (3.0 mL) at 0 °C was found to be the most appropriate for carrying out the desired electrophilic iodocyclization.

Employing the optimized protocol, the scope of electrophilic iodocyclization was then examined for alkynes bearing different substituents for the synthesis of pyrrolo[1,2-*a*]quinolines. 1-(2-(Substituted ethynyl)phenyl)-1*H*-pyrroles **3a**−**t** afforded the desired pyrrolo[1,2-*a*]quinolines **5a**−**t** in 71−93% yields (Table 2, entries 1−20).

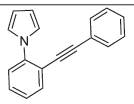
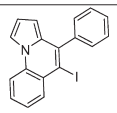
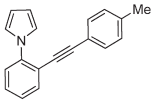
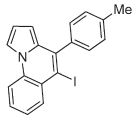
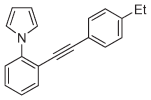
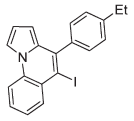
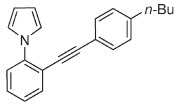
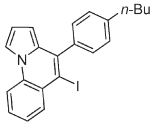
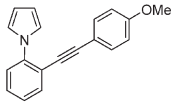
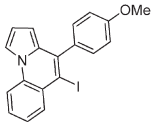
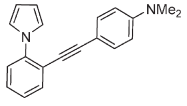
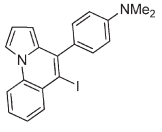
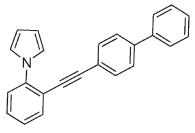
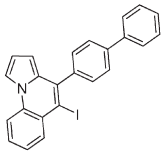
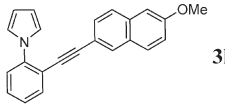
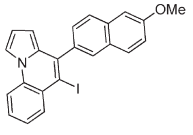
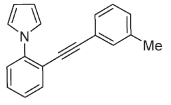
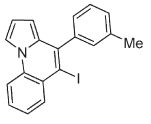
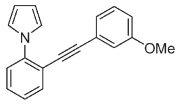
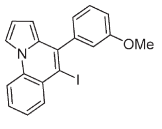
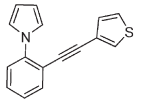
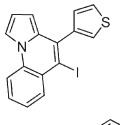
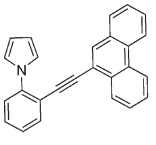
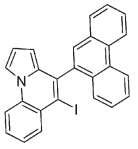
It is evident from Table 2 that substituents attached to the triple bond impart a major impact on the success of the regioselective cyclization as shown in compound **A** (Figure 1). The presence of an electron-donating group *para* to the triple bond increases the electron density on the distal end of the triple bond, which thereby favors 6-*endo*-*dig* cyclization. This in turn increased the efficiency of the reaction, and the cyclized products **5b**−**h** were obtained in good yields (Table 2, entries 2−8).

On the other hand, alkynes with substitution at the *meta* position, **3i,j**, afforded iodocyclized products **5i,j** in comparatively lower yield (Table 2, entries 9 and 10). Alkyne **3k** bearing an electron-rich heterocycle, i.e., thiophene, proved to be favorable for the reaction and afforded the desired product **5k** in 91% yield (entry 11). An alkyne bearing a polyaromatic phenanthrene group resulted in the corresponding iodocyclized product **5l** in 87% yield (entry 12). Alkynes **3m,n** having alkyl substituents, i.e., *n*-butyl and *tert*-butyl, gave the desired products **5m,n** in 71% and 73% yields, respectively (entries 13 and 14). Alkynes with cyclic alkyl substituents, **3o**−**q**, afforded the desired iodocyclized products **5o**−**q** in 77−79% yield (entries 15−17). Alkynes **3r**, **s** having propargylhydroxyl and propargylphenoxy as substituents gave regioselective 6-*endo*-*dig*-cyclized products **5r,s** in 74% and 76% yields, respectively (entries 18 and 19). However, the presence of an electron-withdrawing nitro group at the *para* position to the triple bond of **3t** provided an unidentified and inseparable complex mixture (entry 20).

Further exploring the developed protocol for 3-methyl-1-(2-(substituted phenylethynyl)phenyl)-1*H*-indoles **4a**−**j** afforded the desired indolo[1,2-*a*]quinolines **6a**−**j** in 79−92% yields (Table 3, entries 1−10). However, 1-(2-(substituted phenylethynyl)phenyl)-1*H*-indoles **4k**−**n** afforded the respective iodocyclized products **6k**−**n** in lower yield (entries 11−14). The above observation could be explained as the effect of the substituent at the 3 position of indole. The presence of a methyl group at the 3 position of indole **B** (Figure 1) activates the indole ring system, which facilitates the intramolecular cyclization via formation of a tertiary carbocation, whereas in the case of unsubstituted indole **C** (Figure 1), decomposition occurred, which might be due to the proton loss or polymerization.[19a,d]

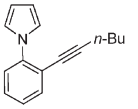
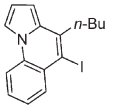
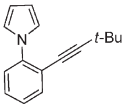
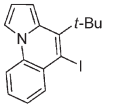
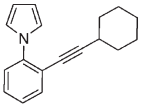
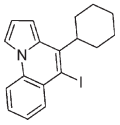
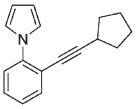
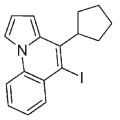
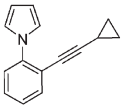
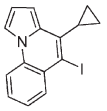
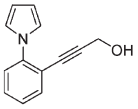
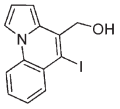
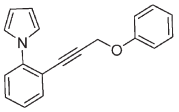
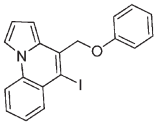
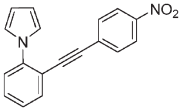
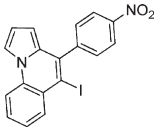
As discussed, the effect of an electron-donating group *para* to the triple bond imparts the same effect on the indole moiety; alkynes bearing an electron-donating group at the *para* position, **4b**−**g** and **4k**−**n**, afforded the corresponding iodocyclized products **6b**−**g** and **6k**−**n** in good yields (Table 3, entries 2−7 and 11−14). Substitution at the *meta* and *ortho* positions

Table 2. Synthesis of Pyrrolo[1,2-*a*]quinolines via I_2-Mediated Electrophilic Ring Closure[a]

Entry	Substrate		Product		*t* (h)	Yield (%)[b]
1.		**3a**		**5a**	2	82
2.		**3b**		**5b**	2	89
3.		**3c**		**5c**	2	87
4.		**3d**		**5d**	2	87
5.		**3e**		**5e**	1.5	93
6.		**3f**		**5f**	1.5	92
7.		**3g**		**5g**	1.5	89
8.		**3h**		**5h**	1.5	90
9.		**3i**		**5i**	2.5	82
10.		**3j**		**5j**	2.5	81
11.		**3k**		**5k**	1.5	91
12.		**3l**		**5l**	2	87

dx.doi.org/10.1021/jo200638k |*J. Org. Chem.* 2011, 76, 5670–5684

Table 2. Continued

13.		**3m**		**5m**	2.5	71
14.		**3n**		**5n**	2.5	73
15.		**3o**		**5o**	2.5	77
16.		**3p**		**5p**	2.5	77
17.		**3q**		**5q**	2	79
18.		**3r**		**5r**	2	74
19.		**3s**		**5s**	2	76
20.		**3t**		**5t**	2	-[c]

[a] All reactions were performed with 0.5 mmol of the alkynes **3a**−**t**, $NaHCO_3$ (2.0 equiv), and I_2 (2.0 equiv) in 3 mL of CH_2Cl_2 at 0 °C for 1.5−2.5 h under inert conditions. [b] Isolated yields. [c] An inseparable mixture of products.

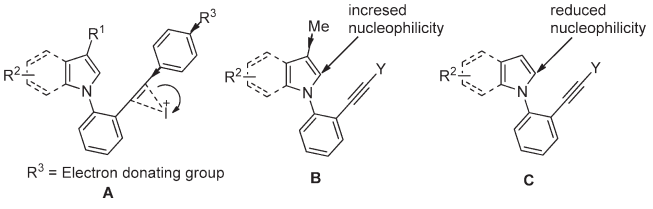


Figure 1. Effect of substituents on electrophilic cyclization.

afforded iodocyclized products **6h,i** in comparatively lower yields (entries 8 and 9). Electron-rich thiophene alkyne **4j** proved to be favorable for the reaction and afforded desired product **6j** in 92% yield (entry 10). However, the presence of a methoxy group at the 5 position of the indole ring provided an unidentified and inseparable complex mixture (entry 15).

Further studies include analysis of ^{1}H NMR, which on cyclization of alkynes into products showed a significant shift of the CH_3 peak of the indole ring (from ∼2.3 to ∼1.6 ppm), which could be attributed to the anisotropic effect of the phenyl ring, which is believed to be perpendicular to this methyl group. On the basis of the above observation, the regioisomers indolo[1,2-*a*]-quinoline **12** (obtained by the reduction of the iodo group of **6f**) and indolo[2,1-*a*]isoquinoline **13** (Figure 2) can be differentiated. The presence of a methyl peak at 1.89 ppm in the ^{1}H NMR spectrum of **12** is due to the anisotropic effect as the phenyl ring is perpendicular to the methyl group, whereas in indolo[2,1-*a*] isoquinoline **13** the CH_3 group attached to the indole ring appears at 2.88 ppm.

Furthermore, the disappearance of two characteristic peaks of the alkyne carbon (around ∼80−99 ppm) in ^{13}C NMR confirmed the formation of cyclized product. Formation of the desired regioselective 6-*endo*-*dig*-cyclized product was further confirmed by crystallographic analysis[20] of **5b** and **6f**.

On the basis of all the observations, an assumed pathway for the formation of iodocyclized products **5** and **6** is illustrated in Scheme 5. First, the Lewis acid (I_2) coordinates to an acetylene bond to form an iodonium complex, **14**, which then undergoes

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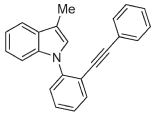
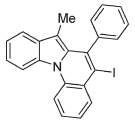
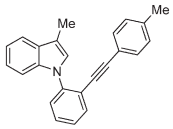
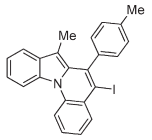
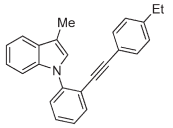
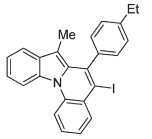
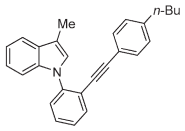
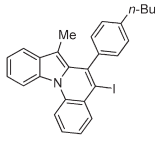
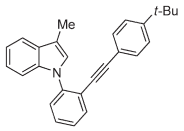
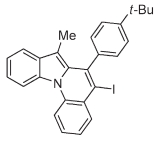
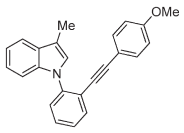
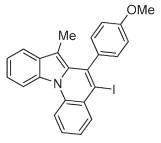
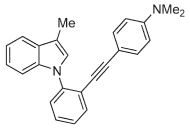
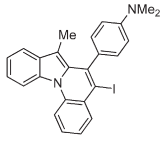
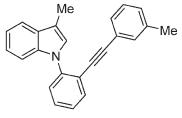
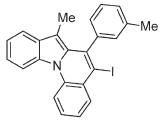
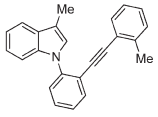
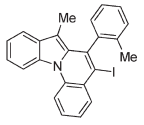
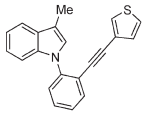
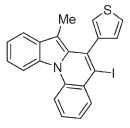
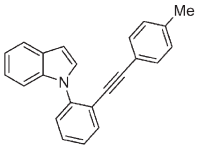
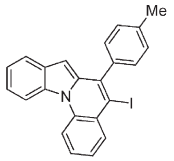
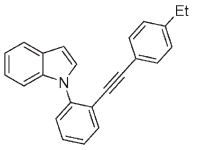
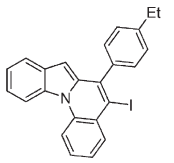
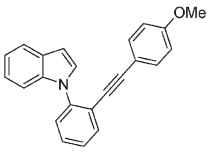
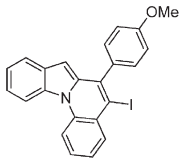
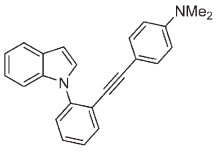
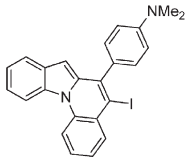
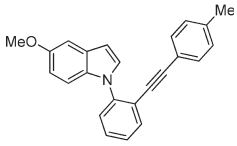
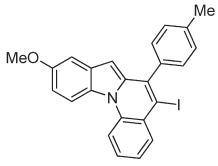
Table 3. Synthesis of Indolo[1,2-*a*]quinolines via I_2-Mediated Electrophilic Ring Closure[a]

Entry	Substrate		Product		*t* (h)	Yield (%)[b]
1.		**4a**		**6a**	2.5	82
2.		**4b**		**6b**	2	88
3.		**4c**		**6c**	2	86
4.		**4d**		**6d**	2	85
5.		**4e**		**6e**	1.5	88
6.		**4f**		**6f**	1.5	92
7.		**4g**		**6g**	1.5	92
8.		**4h**		**6h**	2.5	79
9.		**4i**		**6i**	2.5	80
10.		**4j**		**6j**	1.5	92

dx.doi.org/10.1021/jo200638k |*J. Org. Chem.* 2011, 76, 5670–5684

Table 3. Continued

11.		**4k**		**6k**	3.5	70
12.		**4l**		**6l**	3.5	71
13.		**4m**		**6m**	3	74
14.		**4n**		**6n**	3	75
15.		**4o**		**6o**	0.5	-[c]

[a] All reactions were performed with 0.5 mmol of the alkynes **4a**−**o**, $NaHCO_3$ (2.0 equiv), and I_2 (2.0 equiv) in 3 mL of CH_2Cl_2 at 0 °C for 1.5−3.5 h under inert conditions. [b] Isolated yields. [c] An inseparable mixture of products.

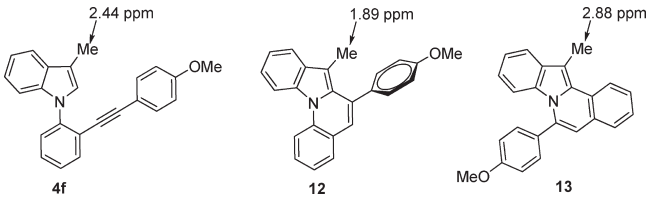


Figure 2. Study of the anisotropic effect in ^1H NMR.

intramolecular nucleophilic attack by the C2 of pyrrole and indole on the activated triple bond to form intermediate **15**. π-Electrocyclization and successive aromatization of **15** led to quinolines **5** and **6**. The presence of $NaHCO_3$ was crucial for a clean, high-yielding reaction. $NaHCO_3$ is presumed to neutralize the byproduct HI of the electrophilic cyclization.

An interesting feature of the electrophilic cyclization is the retention of the electrophile (I) on the polycyclic aromatic products, which could be further elaborated. Various palladium- and copper-catalyzed reactions can be performed for diversification of the quinoline moiety, and thereby, biological diversity can be introduced (Scheme 6).

In summary, the results of the above studies have demonstrated the feasible and efficient approach for the synthesis of pyrrolo- and indolo[1,2-*a*]quinolines. Diversified quinoline nuclei with different substituents were generated in moderate to excellent yields. In addition, the anisotropic observation of CH_3 was aimed at uncovering the unique orientation of the phenyl ring. The chemistry outlined here is extremely versatile and accommodates various functional groups, which makes it ideal for the generation of libraries. By further elaboration and diversification of the various functionally substituted scaffolds, a wide range of structurally and spatially diverse compounds can be produced. Also the iodine catalysis system will undoubtedly extend applications of electrophilic reactions where replacement of more expensive metal catalysts is desired.

EXPERIMENTAL SECTION

General Method. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz or 400 and 100 MHz, respectively. Thin-layer chromatography was performed using commercially prepared 60 F_{254} silica gel plates, and visualization was effected with short-wavelength UV light (254 nm). All melting points are uncorrected. High-resolution mass spectra were recorded on a double-focusing magnetic sector mass spectrometer using EI at 70 eV. Anhydrous forms of all reagents such as ethyl ether, hexanes, ethyl acetate, molecular iodine, CH_2Cl_2, 3-methyl-1*H*-indole, 1*H*-indole, 1*H*-pyrrole, 5-methoxy-1*H*-indole, terminal alkynes,

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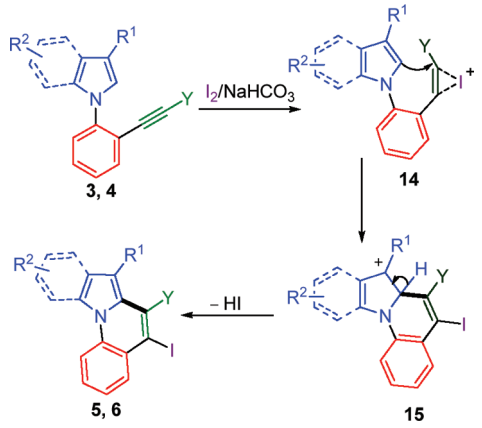
Scheme 5. Probable Mechanism



Et_3N, and the palladium salts were used directly as obtained commercially unless otherwise noted.

General Procedure for the Formation of the 1-(2-(Arylethynyl)phenyl)-1*H*-pyrroles 3a–t and 1-(2-(Arylethynyl)phenyl)-1*H*-indoles 4a–o. To a solution of 1.0 mmol of 1-(2-iodophenyl)-1*H*-indole/1-(2-iodophenyl)-1*H*-pyrrole and $PdCl_2(PPh_3)_2$ (5.0 mol %) in CH_3CN (5.0 mL) was added CuI (1.0 mol %). The reaction was flushed with N_2. To the reaction mixture were added Et_3N (2.0 equiv) and 1.2 equiv of the terminal alkyne. The reaction mixture was allowed to stir at 60 °C for 1–2 h. The disappearance of the starting material was determined by TLC. The resulting solution was filtered and washed with saturated aq NaCl solution and extracted with ethyl acetate (2 × 15 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent.

1-(2-(Phenylethynyl)phenyl)-1H-pyrrole (***3a***). The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.62 (m, 1H), 7.43–7.40 (m, 2H), 7.38–7.36 (m, 1H), 7.34–7.26 (m, 5H), 7.17 (t, J = 2.2 Hz, 2H), 6.35 (t, J = 2.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 1335, 131.4, 129.2, 128.4, 128.3, 126.2, 124.9, 122.9, 121.7, 118.0, 109.2, 93.7, 86.5; HRMS m/z calcd for $C_{18}H_{13}N$ 243.1048, found 243.1044.

1-(2-(p-Tolylethynyl)phenyl)-1H-pyrrole (***3b***). The product was obtained as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 9.1 Hz, 1H), 7.32–7.28 (m, 2H), 7.25–7.23 (m, 1H), 7.21–7.17 (m, 2H), 7.10–7.09 (m, 2H), 7.05–7.03 (m, 2H), 6.28–6.27 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 138.7, 133.5, 131.4, 129.1, 126.3, 124.9, 121.8, 120.0, 118.4, 109.1, 93.8, 85.9, 21.7; HRMS m/z calcd for $C_{19}H_{15}N$ 257.1204, found 257.1217.

1-(2-((4-Ethylphenyl)ethynyl)phenyl)-1H-pyrrole (***3c***). The product was obtained as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 1H), 7.33–7.28 (m, 3H), 7.27–7.26 (m, 1H), 7.20–7.18 (m, 1H), 7.10–7.07 (m, 4H), 6.28–6.27 (m, 2H), 2.57 (q, J = 7.3 Hz, 2H), 1.15 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 142.0, 133.6, 131.5, 129.1, 128.0, 126.3, 124.9, 121,8, 120.2, 118.4, 109.3, 94.2, 85.9, 28.9, 15.4; HRMS m/z calcd for $C_{20}H_{17}N$ 271.1361, found 271.1356.

1-(2-((4-Butylphenyl)ethynyl)phenyl)-1H-pyrrole (***3d***). The product was obtained as a white oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.9 Hz, 1H), 7.32–7.24 (m, 4H), 7.21–7.17 (m, 1H), 7.10–7.09 (m, 2H), 7.05 (d, J = 8.2 Hz, 2H), 6.27 (t, J = 2.3 Hz, 2H), 2.52 (t, J = 7.8 Hz, 2H), 1.50 (p, J = 7.7 Hz, 2H), 1.26 (st, J = 7.8 Hz, 2H), 0.84 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 142.0, 133.6, 131.4, 129.0, 128.5, 126.3, 124.9, 121.8, 120.1, 118.4, 109.2, 94.1, 85.9, 35.7, 33.4, 22.3, 14.01; HRMS m/z calcd for $C_{22}H_{21}N$ 299.1674, found 299.1681.

1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1H-pyrrole (***3e***). The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.4 Hz, 1H), 7.37–7.32 (m, 4H), 7.27–7.24 (m, 1H), 7.16 (t, J = 2.2 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.34 (t, J = 2.2 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 141.8, 133.3, 132.9, 128.8, 126.2, 124.8, 121.7, 118.4, 115.0, 114.0, 109.0, 93.9, 85.2, 55.3; HRMS m/z calcd for $C_{19}H_{15}NO$ 273.1154, found 273.1147.

4-((2-(1H-Pyrrol-1-yl)phenyl)ethynyl)-N,N-dimethylaniline (***3f***). The product was obtained as a white solid: mp 64–66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.4 Hz, 1H); 7.36–7.33 (m, 4H), 7.31–7.26 (m, 1H), 7.23 (t, J = 2.2 Hz, 2H), 6.66 (d, J = 9.5 Hz, 2H), 6.39 (t, J = 2.2 Hz, 2H), 3.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 141.5, 133.0 132.6, 128.2, 126.1, 124.7, 121.7, 118.9, 11.7, 109.7, 108.9, 95.3, 84.6, 40.1; HRMS m/z calcd for $C_{20}H_{18}N_2$ 286.1470, found 286.1474.

1-(2-(Biphenyl-4-ylethynyl)phenyl)-1H-pyrrole (***3g***). The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 1.5, 7.4 Hz, 1H), 7.60–7.54 (m, 4H), 7.50–7.47 (m, 2H), 7.46–7.33 (m, 5H), 7.31–7.27 (m, 1H), 7.19 (t, J = 2.2 Hz, 2H), 6.37 (t, J = 2.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 141.1, 140.3, 133.5, 131.8, 129.2, 128.8, 127.6, 126.9, 126.2, 124.9, 121.83, 121.76, 118.1, 109.2, 93.7, 87.2; HRMS m/z calcd for $C_{24}H_{17}N$ 319.1361, found 319.1355.

1-(2-((6-Methoxynaphthalen-2-yl)ethynyl)phenyl)-1H-pyrrole (***3h***). The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.62–7.57 (m, 4H), 7.37–7.21 (m, 3H), 7.14 (t, J = 2.2 Hz, 2H), 7.09–7.06 (m, 1H), 7.02 (d, J = 2.2 Hz, 1H), 6.31 (t, J = 2.6 Hz, 2H), 3,84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 141.9, 134.2, 133.5, 131.2, 129.4, 129.0, 128.7, 126.8, 126.2, 124.9, 121.8, 119.4, 118.3, 117.8, 109.2, 105.8, 94.4, 86.2, 55.3; HRMS m/z calcd for $C_{23}H_{17}NO$ 323.1310, found 323.1319.

1-(2-(m-Tolylethynyl)phenyl)-1H-pyrrole (***3i***). The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.60 (m, 1H), 7.39–7.31 (m, 3H), 7.28–7.19 (m, 4H), 7.17 (t, J = 2.2 Hz, 2H), 6.35 (t, J = 2.2 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 137.9, 133.6, 131.9, 129.4, 129.1, 128.5, 128.2, 126.2, 124.8, 122.7, 121.7, 118.1, 109.2, 93.9, 86.1, 21.2; HRMS m/z calcd for $C_{19}H_{15}N$ 257.1204, found 257.1211.

1-(2-((3-Methoxyphenyl)ethynyl)phenyl)-1H-pyrrole (***3j***). The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 1.5, 8.1 Hz, 1H), 7.41–7.34 (m, 2H), 7.30–7.19 (m, 2H), 7.17 (t, J = 2.2 Hz, 2H), 7.02 (d, J = 7.3 Hz, 1H), 6.95–6.94 (m, 1H), 6.87 (dd, J = 2.2, 7.32 Hz, 1H), 6.35 (t, J = 1.8 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 142.1, 133.5, 129.3, 129.2, 124.9, 123.9, 121.8, 118.0, 117.0, 116.1, 115.1, 109.2, 93.7, 86.3, 55.2; HRMS m/z calcd for $C_{19}H_{15}NO$ 273.1154, found 273.1164.

1-(2-(Thiophene-3-ylethynyl)phenyl)-1H-pyrrole (***3k***). The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 1.5, 8.0 Hz, 1H), 7.43 (d, J = 2.9 Hz, 1H), 7.40–7.32 (m, 3H), 7.27–7.24 (m, 1H), 7.15 (t, J = 2.2 Hz, 2H), 7.12–7.09 (m, 1H), 6.34 (t, J = 2.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 133.4, 129.6, 129.1, 128.9, 126.2, 125.3, 124.9, 122.0, 121.7, 118.0, 109.2, 89.1, 86.0; HRMS m/z calcd for $C_{16}H_{11}NS$ 249.0612, found 249.0608.

1-(2-(Phenanthren-9-ylethynyl)phenyl)-1H-pyrrole (***3l***). The product was obtained as a white solid: mp 80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (t, J = 8.8 Hz, 2H), 8.08 (dd, J = 1.5, 8.1 Hz, 1H), 7.91 (s, 1H), 7.76 (dd, J = 1.5, 8.1 Hz, 1H), 7.71 (dd, J = 1.4, 7.3 Hz, 1H), 7.61–7.48 (m, 4H), 7.35–7.25 (m, 3H), 7.16–7.14 (m, 2H), 6.36 (t, J = 2.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 133.8, 132.0, 131.1, 130.9, 130.3, 129.9, 128.6, 127.5, 127.26, 127.00, 126.90, 126.6, 125.4, 122.6, 121.9, 119.4, 118.8, 109.5, 92.2, 90.7; HRMS m/z calcd for $C_{26}H_{17}N$ 343.1361, found 343.1366.

1-(2-(Hex-1-ynyl)phenyl)-1H-pyrrole (***3m***). The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49

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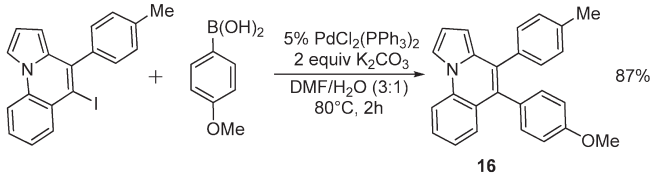
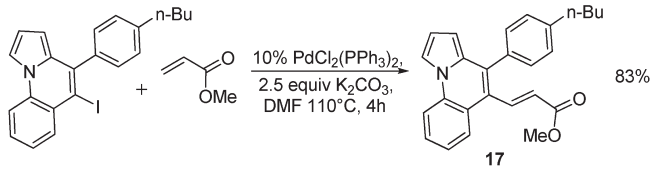
Scheme 6. Diversification of the Quinoline Nucleus[a]

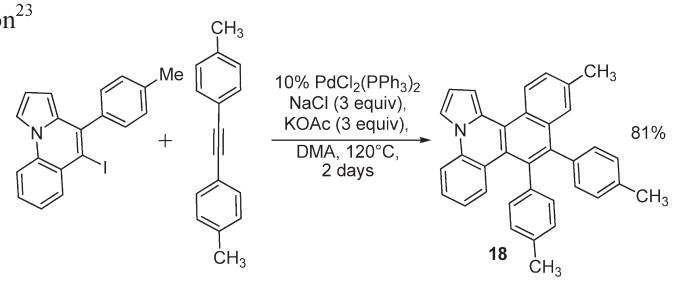
A. Suzuki reaction[21]



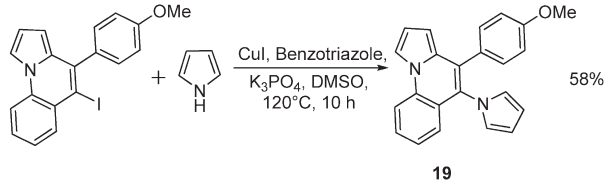
B. Heck reaction[22]



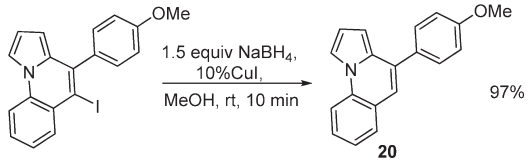
C. Alkyne annulation[23]



D. Ullmann type coupling[24, 19e–f]



E. Reduction of Iodine[25]



[a] Key: (A) Suzuki reaction,[21] (B) Heck reaction,[22] (C) alkyne annulation,[23] (D) Ullmann-type coupling,[24,19e,19f] (E) reduction of iodine.[25]

(d, J = 8.0 Hz, 1H), 7.33−7.19 (m, 3H), 7.09 (t, J = 2.2 Hz, 2H), 6.29 (t, J = 2.2 Hz, 2H), 2.34 (t, J = 6.6 Hz, 2H), 1.55−1.48 (m, 2H), 1.43−1.34 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 133.9, 128.4, 126.1, 124.8, 121.5, 118.8, 108.9, 95.3, 30.4, 21.9, 19.2, 13.6; HRMS m/z calcd for $C_{16}H_{17}N$ 223.1361, found 223.1359.

*1-(2-(3,3-Dimethylbut-1-ynyl)phenyl)-1H-pyrrole (**3n**).* The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 1.4, 7.8 Hz, 1H), 7.23−7.20 (m, 2H), 7.14−7.12 (m, 1H), 7.02 (t, J = 2.2 Hz, 2H), 6.21 (t, J = 2.2 Hz, 2H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 133.6, 128.4, 126.0, 124.7, 121.6, 118.7, 108.7, 103.0, 76.0, 30.5, 29.7; HRMS m/z calcd for $C_{16}H_{17}N$ 223.1361, found 223.1369.

*1-(2-(Cyclohexylethynyl)phenyl)-1H-pyrrole (**3o**).* The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 1.4, 7.8 Hz, 1H), 7.25−7.718 (m, 2H), 7.15−7.711 (m, 1H), 7.02 (t, J = 2.3 Hz, 2H), 6.22 (t, J = 1.8 Hz, 2H), 2.48−2.43 (m, 1H), 1.73−1.69 (m, 2H), 1.63−1.58 (m, 2H), 1.46−1.35 (m, 4H), 1.26−1.83 (m, 2H).); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 133.8, 128.3, 126.0, 124.7, 121.6, 118.8, 108.8, 99.2, 32.2, 29.7, 25.8, 24.7; HRMS m/z calcd for $C_{18}H_{19}N$ 249.1517, found 249.1522.

*1-(2-(Cyclopentylethynyl)phenyl)-1H-pyrrole (**3p**).* The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 1.5, 7.3 Hz, 1H), 7.25−7.17 (m, 2H), 7.15−7.10 (m, 1H), 7.02 (t, J = 2.2 Hz, 2H), 6.22 (t, J = 2.2 Hz, 2H), 2.73−2.66 (m, 1H), 1.84−1.79 (m, 2H), 1.65−1.54 (m, 4H), 1.53−1.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 133.7, 128.3, 126.0, 124.7, 121.5, 118.8, 108.8, 99.4, 33.4, 30.8, 24.9; HRMS m/z calcd for $C_{17}H_{17}N$ 235.1361, found 235.1359.

*1-(2-(Cyclopropylethynyl)phenyl)-1H-pyrrole (**3q**).* The product was obtained as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 1.44, 7.3 Hz, 1H), 7.32−7.17 (m, 3H), 7.06 (t, J = 2.6 Hz, 2H), 6.29 (t, J = 2.6 Hz, 2H), 1.39−1.33 (m, 1H), 0,83−0.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 133.3, 127.9, 125.7, 124.4, 121.2, 118.4, 108.5, 97.9, 72.1, 8.1, 0.0; HRMS m/z calcd for $C_{15}H_{13}N$ 207.2700, found 207.2698.

*3-(2-(1H-Pyrrol-1-yl)phenyl)prop-2-yn-1-ol (**3r**).* The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 1.5, 7.3 Hz, 1H), 7.40−7.36 (m, 1H), 7.31−7.23 (m, 2H), 7.07 (t, J = 2.2 Hz, 2H), 6.31 (t, J = 2.2 Hz, 2H), 4.39 (s, 2H), 1.77 (s, 1H); ^{13}C

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NMR (100 MHz, $CDCl_3$) δ 142.1, 133.8, 129.4, 126.3, 125.0, 121.7, 117.5, 109.2, 91.8, 82.6, 51.6; HRMS calcd for $C_{13}H_{11}NO$ 197.0841, found 197.0844.

*1-(2-(3-Phenoxyprop-1-ynyl)phenyl)-1H-pyrrole (**3s**).* The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 1.5, 8.1 Hz, 1H), 7.40−7.36 (m, 1H), 7.32−7.21 (m, 4H), 7.04 (t, J = 2.2 Hz, 2H), 7.01−6.95 (m, 3H), 6.30 (t, J = 2.2 Hz, 2H), 4.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 142.3, 134.3, 129.7, 129.4, 126.2, 124.9, 121.4, 116.9, 114.9, 109.4, 88.5, 84.0, 56.4; HRMS m/z calcd for $C_{19}H_{15}NO$ 273.1154, found 273.1147.

*3-Methyl-1-(2-(phenylethynyl)phenyl)-1H-indole (**4a**).* The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.6, 1.6 Hz, 1H), 7.68−7.66 (m, 1H), 7.52−7.45 (m, 2H), 7.40−7.36 (m, 2H), 7.30 (d, J = 1.6 Hz, 1H), 7.25−7.19 (m, 5H), 7.12−7.09 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 136.8, 133.6, 131.5, 129.5, 129.3, 128.5, 128.3, 126.96, 126.87, 126.81, 123.0, 122.2, 120.6, 119.7, 119.1, 112.1, 111.2, 94.7, 86.8, 9.9; HRMS m/z calcd for $C_{23}H_{17}N$ 307.1361, found 307.1356.

*3-Methyl-1-(2-(p-tolylethynyl)phenyl)-1H-indole (**4b**).* The product was obtained as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.55 (m, 2H), 7.40−7.32 (m, 2H), 7.28−7.20 (m, 3H), 7.15−7.07 (m, 2H), 6.96−6.88 (m, 4H), 2.33 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 138.5, 136.6, 133.2, 131.2, 128.9, 126.6, 121.9, 120.6, 119.7, 119.5, 118.8, 111.8, 110.9, 94.7, 85.9, 21.5, 9.7; HRMS m/z calcd for $C_{24}H_{19}N$ 321.1517, found 321.1525.

*1-(2-((4-Ethylphenyl)ethynyl)phenyl)-3-methyl-1H-indole (**4c**).* The product was obtained as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62−7.56 (m, 2H), 7.42−7.36 (m, 2H), 7.30−7.27 (m, 2H), 7.21−7.07 (m, 3H), 6.99−6.92 (m, 4H), 2.51 (q, J = 7.5 Hz, 2H), 2.34 (s, 3H), 1.11 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 140.8, 136.6, 133.3, 131.4, 129.4, 128.9, 127.8, 126.7, 121.9, 120.7, 120.0, 119.5, 118.5, 111.8, 111.0, 94.8, 85.9, 28.8, 15.3, 9.7; HRMS m/z calcd for $C_{25}H_{21}N$ 335.1674, found 335.1666.

*1-(2-((4-Butylphenyl)ethynyl)phenyl)-3-methyl-1H-indole (**4d**).* The product was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68−7.64 (m, 2H), 7.48−7.42 (m, 2H), 7.36−7.27 (m, 3H), 7.23−7.17 (m, 2H), 7.10−6.83 (m, 4H), 2.54 (t, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.53 (p, J = 6.9 Hz, 2H), 1.30 (st, J = 7.2 Hz, 2H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 140.8, 136.6, 133.3, 131.3, 129.3, 128.8, 128.3, 126.77, 126.69, 121.9, 120.7, 120.0, 119.5, 118.9, 111.8, 111.0, 94.8, 85.9, 35.6, 33.3, 22.3, 13.9, 9.7; HRMS m/z calcd for $C_{27}H_{25}N$ 363.1987, found 363.1981.

*1-(2-((4-tert-Butylphenyl)ethynyl)phenyl)-3-methyl-1H-indole (**4e**).* The product was obtained as a white oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66−7.63 (m, 2H), 7.46−7.33 (m, 5H), 7.25−7.17 (m, 4H), 7.03 (d, J = 8.4 Hz, 2H), 2.42(s, 3H), 1.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 140.8, 136.6, 133.3, 131.1, 129.0, 128.8, 126.74, 126.64, 125.1, 121.9, 120.7, 119.8, 119.5, 118.8, 111.8, 111.0, 94.6, 85.9, 34.7, 31.3, 9.7; HRMS m/z calcd for $C_{27}H_{25}N$ 363.1987, found 363.1988.

*1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-3-methyl-1H-indole (**4f**).* The product was obtained as a viscous yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.65 (m, 2H), 7.50−7.42 (m, 2H), 7.38−7.36 (m, 2H), 7.30 (s, 1H), 7.22−7.19 (m, 2H), 7.03 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 140.8, 136.8, 133.2, 133.0, 129.5, 128.8, 126.92, 126.86, 126.83, 122.1, 121.0, 119.7, 119.0, 115.1, 114.0, 111.9, 111.3, 94.8, 85.6, 55.5, 9.9; HRMS m/z calcd for $C_{24}H_{19}NO$ 337.1467, found 337.1471.

*N,N-Dimethyl-4-((2-(3-methyl-1H-indol-1-yl)phenyl)ethynyl)aniline (**4g**).* The product was obtained as a white solid: mp 57−58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.68 (m, 2H), 7.50 (d, J = 7.6 Hz, 1H), 7.42−7.40 (m, 2H), 7.38−7.34 (m, 2H), 7.27−7.21 (m, 2H), 7.03 (d, J = 8.8 Hz, 2H), 6.56 (d, J = 8.8 Hz, 2H), 2.96 (s, 6H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 140.5, 136.8, 133.0, 132.6, 129.5, 128.2, 126.9, 126.8, 122.0, 121.5, 119.5, 118.9, 111.8, 111.3, 109.7, 96.2, 84.9, 40.3, 9.9; HRMS m/z calcd for $C_{25}H_{22}N_2$ 350.1783, found 350.1790.

*3-Methyl-1-(2-(m-tolylethynyl)phenyl)-1H-indole (**4h**).* The product was obtained as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69−7.64 (m, 1H), 7.47−7.41 (m, 2H), 7.37−7.32 (m, 2H), 7.28 (s, 1H), 7.24−7.20 (m, 3H), 7.18−7.06 (m, 2H), 6.96−6.90 (m, 1H), 6.85 (s, 1H), 2.42 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 137.8, 136.6, 133.2, 132.1, 130.0, 129.3, 128.9, 128.2, 128.0, 127.2, 126.6, 122.6, 121.9, 120.5, 119.5, 118.8, 115.9, 111.8, 111.6, 94.7, 86.2, 21.3, 9.6; HRMS m/z calcd for $C_{24}H_{19}N$ 321.1517, found 321.1526.

*3-Methyl-1-(2-(o-tolylethynyl)phenyl)-1H-indole (**4i**).* The product was obtained as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70−7.55 (m, 2H), 7.40−7.34 (m, 2H), 7.31−7.28 (m, 2H), 7.23 (s, 1H), 7.20−7.06 (m, 2H), 6.95−6.86 (m, 4H), 2.38 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 137.9, 136.6, 133.2, 132.2, 130.0, 129.6, 128.9, 128.2, 128.0, 127.2, 126.6, 122.2, 121.9, 120.5, 119.5, 118.2, 115.7, 111.8, 111.6, 94.7, 86.2, 21.4, 9.6; HRMS m/z calcd for $C_{24}H_{19}N$ 321.1517, found 321.1509.

*3-Methyl-1-(2-(thiophene-3-ylethynyl)phenyl)-1H-indole (**4j**).* The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.66 (m, 2H), 7.49−7.44 (m, 2H), 7.39−7.35 (m, 2H), 7.27 (d, J = 5.0 Hz, 1H), 7.23−7.21 (m, 2H), 7.19 (dd, J = 2.0, 3.2 Hz, 1H), 7.11 (d, J = 3.2 Hz, 1H), 6.79 (d, J = 5.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 136.8, 133.3, 129.7, 129.5, 129.2, 129.0, 126.9, 126.8, 126.7, 125.3, 122.1, 120.6, 119.7, 119.1, 111.3, 111.1, 90.0, 86.3, 9.9; HRMS m/z calcd for $C_{21}H_{15}NS$ 313.0925, found 313.0919.

*1-(2-(p-Tolylethynyl)phenyl)-1H-indole (**4k**).* The product was obtained as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72−7.68 (m, 2H), 7.52−7.46 (m, 3H), 7.43−7.36 (m, 2H), 7.22−7.16 (m, 2H), 7.12−7.03 (m, 2H), 6.91−6.89 (m, 1H), 6.82 (s, 1H), 6.70 (d, J = 3.3 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 137.8, 136.4, 133.3, 132.0, 129.3, 129.1, 129.0, 128.3, 128.0, 127.1, 126.9, 122.4, 122.0, 120.8, 120.1, 111.1, 102.8, 94.7, 85.8, 21.1; HRMS m/z calcd for $C_{23}H_{17}N$ 307.1361, found 307.1369.

*1-(2-((4-Ethylphenyl)ethynyl)phenyl)-1H-indole (**4l**).* The product was obtained as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71−7.66 (m, 2H), 7.50−7.34 (m, 5H), 7.21−7.13 (m, 2H), 7.04−6.97 (m, 4H), 6.69 (d, J = 3.0, 1H), 2.56 (q, J = 7.8, 2H), 1.16 (t, J = 7.5, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 140.6, 136.5, 133.3, 131.4, 129.1, 128.9, 127.8, 127.1, 127.0, 122.0, 121.1, 120.8, 120.1, 119.9, 114.7, 111.1, 102.8, 94.8, 85.6, 28.8, 15.5; HRMS m/z calcd for $C_{24}H_{19}N$ 321.1517, found 321.1525.

*1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1H-indole (**4m**).* The product was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.70 (m, 2H), 7.53−7.51 (m, 2H), 7.46 (dd, J = 2.0, 7.2 Hz, 1H), 7.42−7.38 (m, 2H), 7.21−7.18 (m, 2H), 7.02 (dd, J = 2.0, 4.8 Hz, 2H), 6.77−6.73 (m, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 140.6, 136.6, 133.2, 133.1, 129.3, 128.9, 128.8, 127.3, 127.1, 122.1, 121.4, 120.9, 120.3, 114.9, 114.0, 111.3, 102.9, 94.9, 85.2, 55.4; HRMS m/z calcd for $C_{23}H_{17}NO$ 323.1310, found 323.1305.

*4-((2-(1H-Indol-1-yl)phenyl)ethynyl)-N,N-dimethylaniline (**4n**).* The product was obtained as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68−7.64 (m, 2H), 7.51−7.46 (m, 2H), 7.42−7.35 (m, 3H), 7.21−7.15 (m, 3H), 6.95 (d, J = 9.0 Hz, 2H), 6.51 (d, J = 9.0 Hz, 2H), 2.92 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 140.1, 136.5, 132.8, 132.6, 129.3, 128.8, 128.1, 127.0, 126.9, 121.9, 121.8, 120.7, 120.0, 111.6, 111.2, 109.5, 102.5, 96.1, 84.4, 40.1; HRMS m/z calcd for $C_{24}H_{20}N_2$ 336.1626, found 336.1620.

*5-Methoxy-1-(2-(p-tolylethynyl)phenyl)-1H-indole (**4o**).* The product was obtained as a brown liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 1H), 7.49−7.42 (m, 1H), 7.40−7.31 (m, 3H), 7.28−7.25 (m, 1H), 7.19−7.12 (m, 2H), 7.08 (d, J = 2.3 Hz, 1H), 7.01−6.99 (m, 1H), 6.81−6.75 (m, 2H), 6.53 (d, J = 3.2 Hz, 1H), 3.79 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 140.6, 138.5, 133.3,

131.2, 129.6, 128.9, 127.1, 126.7, 120.7, 119.6, 114.1, 112.0, 111.8, 108.6, 102.6, 102.4, 101.8, 94.6, 85.6, 55.9, 21.4; HRMS *m*/*z* calcd for $C_{24}H_{19}NO$ 337.1467, found 337.1460.

General Procedure for the Synthesis of 5-Iodopyrrplo[1,2-*a*]quinolines 5a−t and 5-Iodoindolo[1,2-*a*]quinolines 6a−o. To a solution of 0.5 mmol of 1-(2-(arylethynyl)phenyl)-1*H*-pyrroles/1-(2-(arylethynyl)phenyl)-1*H*-indoles in a 5.0 mL round-bottom flask in 2.0 mL of CH_2Cl_2 was added 2 equiv of $NaHCO_3$. This was followed by dropwise addition of I_2 solution (2 equiv of I_2 in 1 mL of CH_2Cl_2). The reaction mixture was allowed to stir at 0 °C for 1.5−3.5 h under inert conditions. The disappearance of the starting material was determined by TLC. The reaction mixture was then quenched with saturated aq sodium thiosulfate solution. The resulting solution was extracted with ethyl acetate (2 × 10 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography on silica gel (100−200 mesh) using hexane as the eluent.

*5-Iodo-4-phenylpyrrolo[1,2-a]quinoline (**5a**).* The product was obtained as a brown viscous oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.35−8.34 (m, 1H), 8.24 (d, *J* = 8.1 Hz, 1H), 8.06−8.03 (m, 1H), 7.65−7.61 (m, 1H), 7.54−7.44 (m, 4H), 7.33−7.31 (m, 2H), 6.68 (t, *J* = 3.3 Hz, 1H), 5.85 (dd, *J* = 1.4, 3.7 Hz, 1H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 141.7, 138.5, 133.6, 132.0, 131.2, 129.2, 129.0, 128.5, 128.2, 124.9, 123.9, 115.0, 114.3, 113.1, 104.7, 93.0; HRMS *m*/*z* calcd for $C_{18}H_{12}IN$ 369.0014, found 369.0009.

*5-Iodo-4-p-tolylpyrrolo[1,2-a]quinoline (**5b**).* The product was obtained as a brown solid: mp 122−127 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.35−8.34 (m, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 6.8 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 3.7 Hz, 1H), 5.89−5.88 (m, 1H), 2.39 (s, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 139.1, 138.7, 137.4, 133.5, 132.1, 131.3, 129.0, 124.9, 124.0, 115.1, 114.2, 113.2, 104.7, 93.2, 20.9; HRMS *m*/*z* calcd for $C_{19}H_{14}IN$ 383.0171, found 383.0177.

Compound **5b** crystallized in the triclinic crystal system with space group $P\bar{1}$. The single-crystal X-ray data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved using SIR-92 and refined by the full matrix least-squares technique on F^2 using the SHELXL-97[26] program within the WinGX v 1.80.05 software package. All hydrogen atoms were fixed at the calculated positions with isotropic thermal parameters, and all non-hydrogen atoms were refined anisotropically. Crystal data for **5b**: $C_{19}H_{14}IN$, *M* = 383.21, triclinic, space group $P\bar{1}$, *a* = 9.435(8) Å, *b* = 9.792(8) Å, *c* = 9.984(8) Å, α = 110.441(8)°, β = 114.906(8)°, γ = 93.239(7)°, *V* = 761.22(11) Å^3, *Z* = 2, *T* = 150 K, d_{calcd} = 1.672 Mg/m^3, *R*(int) = 0.0269, R1 = 0.0353, wR2 = 0.0913 [$I > 2\sigma(I)$], R1 = 0.0380, wR2 = 0.0928 (all data), GOF = 1.062. For further details on the crystal structure of compound **5b**, see the CIF file (Supporting Information).

*4-(4-Ethylphenyl)-5-iodopyrrolo[1,2-a]quinoline (**5c**).* The product was obtained as a brown solid: mp 103−106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.86−7.79 (m, 2H), 7.54−7.49 (m, 1H), 7.39−7.22 (m, 5H), 6.68−6.66 (m, 1H), 6.07−6.06 (m, 1H), 2.76 (q, *J* = 7.5 Hz, 2H), 1.32 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 139.6, 139.2, 134.4, 132.4, 132.3, 129.2, 128.5, 127.7, 124.8, 124.4, 114.0, 112.9, 112.5, 105.1, 93.3, 28.7, 15.3; HRMS *m*/*z* calcd for $C_{20}H_{16}IN$ 397.0327, found 397.0334.

*4-(4-Butylphenyl)-5-iodopyrrolo[1,2-a]quinoline (**5d**).* The product was obtained as a gray solid: mp 80−81 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.33 (s, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 10.5 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 6.8 Hz, 2H), 7.23 (d, *J* = 5.9 Hz, 2H), 6.68 (t, *J* = 4.1 Hz, 1H), 5.88 (d, *J* = 4.1 Hz, 1H), 2.66 (t, *J* = 8.2 Hz, 2H), 1.62 (p, *J* = 6.8 Hz, 2H), 1.35 (st, *J* = 8.2 Hz, 2H), 0.91 (t, *J* = 8.2 Hz, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 142.3, 139.1, 138.5, 133.6, 131.9, 131.3, 129.1, 128.9, 128.2, 124.8, 124.0, 114.9, 114.2, 113.0, 104.7, 93.1, 34.6, 33.0, 21.7, 13.7; HRMS *m*/*z* calcd for $C_{22}H_{20}IN$ 425.0640, found 425.0635.

*5-Iodo-4-(4-methoxyphenyl)pyrrolo[1,2-a]quinoline (**5e**).* The product was obtained as a brown solid: mp 127−130 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.34−8.33 (m, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.68 (t, *J* = 3.6 Hz, 1H), 5.91 (dd, *J* = 1.5, 3.7 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 159.0, 138.3, 134.1, 133.7, 131.9, 131.4, 130.4, 129.1, 124.9, 124.0, 115.0, 114.3, 113.8, 113.1, 104.8, 93.6, 55.1; HRMS *m*/*z* calcd for $C_{19}H_{14}INO$ 399.0120, found 399.0131.

*4-(5-Iodopyrrolo[1,2-a]quinolin-4-yl)-N,N-dimethylaniline (**5f**).* The product was obtained as a brown solid: mp 142−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 1.4, 8.0 Hz, 1H), 7.88−7.87 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.55−7.51 (m, 1H), 7.40−7.36 (m, 1H), 7.28−7.25 (m, 2H), 6.84−6.81 (m, 2H), 6.69 (t, *J* = 3.3 Hz, 1H), 6.15 (dd, *J* = 1.5, 3.7 Hz, 1H), 3.05 (s, 6H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 149.9, 133.6, 131.7, 129.9, 128.9, 128.6, 127.9, 124.8, 124.2, 123.1, 114.9, 114.1, 113.0, 111.6, 104.9, 93.6, 39.9; HRMS *m*/*z* calcd for $C_{20}H_{17}IN_2$ 412.0436, found 412.0429.

*4-(Biphenyl-4-yl)-5-iodopyrrolo[1,2-a]quinoline (**5g**).* The product was obtained as a brown oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.37 (d, 1H, *J* = 2.2 Hz), 8.26 (d, 1H, *J* = 8.0 Hz), 8.07 (dd, 1H, *J* = 1.5, 8.1 Hz), 7.83 (d, 2H, *J* = 8.0 Hz), 7.79 (d, 2H, *J* = 6.6 Hz), 7.66 (t, 1H, *J* = 7.3 Hz), 7.51−7.48 (m, 4H), 7.44−7.39 (m, 2H), 6.71 (t, 1H, *J* = 3.3 Hz), 5.95 (dd, 1H, *J* = 1.5, 4.9 Hz); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 140.9, 139.6. 139.6, 138.2, 133.7, 132.0, 131.1, 129.8, 129.3, 129.0, 127.7, 126.7, 124.9, 123.9, 115.0, 114.4, 113.2, 104.8, 93.1; HRMS *m*/*z* calcd for $C_{24}H_{16}IN$ 445.0327, found 445.0342.

*5-Iodo-4-(6-methoxynaphthalen-2-yl)pyrrolo[1,2-a]quinoline (**5h**).* The product was obtained as a brown solid: mp 152−155 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.34−8.33 (m, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 8.05 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.80 (m, 1H), 7.65−7.60 (m, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.39−7.36 (m, 2H), 7.18 (dd, *J* = 2.9, 8.8 Hz, 1H), 6.66 (t, *J* = 3.8 Hz1H), 5.88 (dd, *J* = 1,5, 3.8 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 157.8, 138.6, 136.9, 134.0, 133.6, 132.0, 131.4, 129.6, 129.3, 128.2, 127.9, 127.6, 126.9, 124.9, 124.0, 118.9, 115.0, 114.3, 113.2, 106.0, 104.9, 93.5, 55.3; HRMS *m*/*z* calcd for $C_{23}H_{16}INO$ 449.0277, found 449.0259.

*5-Iodo-4-m-tolylpyrrolo[1,2-a]quinoline (**5i**).* The product was obtained as a brown solid: mp 89−91 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.35−8.33 (m, 1H), 8.24 (d, *J* = 7.4 Hz, 1H), 8.05 (dd, *J* = 1.4, 8.0 Hz, 1H), 7.64 (dt, *J* = 1.5, 7.4 Hz, 1H), 7.49−7.39 (m, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.14−7.10 (m, 2H), 6.68 (t, *J* = 2.9 Hz, 1H), 5.88 (dd, *J* = 1.5, 3.7 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 141.7, 138.6, 137.6, 133.6, 132.0, 131.2, 129.5, 129.2, 128.9,128.2, 126.2, 124.9, 123.9, 115.0, 114.3, 113.1, 104.8, 92.9, 21.1; HRMS *m*/*z* calcd for $C_{19}H_{14}IN$ 383.0171, found 383.0164.

*5-Iodo-4-(3-methoxyphenyl)pyrrolo[1,2-a]quinoline (**5j**).* The product was obtained as a brown solid: mp 109−112 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.35−8.34 (m, 1H), 8.24 (d, *J* = 3.2 Hz, 1H), 8.06 (dd, *J* = 1.5, 8.8 Hz, 1H), 7.66−7.62 (m, 1H), 7.49−7.42 (m, 2H), 7.06−7.03 (m, 1H), 6.90−6.88 (m, 2H), 6.69 (t, *J* = 2.9 Hz, 1H), 5.93−5.92 (m, 1H), 3.78 (s, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 159.1, 143.0, 138.4, 133.6, 132.0, 131.0, 129.7, 129.3, 124.9, 123.9, 121.3, 115.0, 114.8, 114.3, 113.6, 113.1, 104.7, 92.9, 55.1; HRMS *m*/*z* calcd for $C_{19}H_{14}INO$ 399.0120, found 399.0111.

*5-Iodo-4-(thiophene-3-yl)pyrrolo[1,2-a]quinoline (**5k**).* The product was obtained as a brown solid: mp 127−130 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.35−8.34 (m, 1H), 8.24 (d, *J* = 8.1 Hz, 1H), 8.05 (dd, *J* = 1.4, 8.0 Hz, 1H), 7.72−7.62 (m, 3H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.21−7.19 (m, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.04−6.03 (m, 1H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 141.2, 134.2, 133.7, 131.9, 131.0, 129.3,

128.7, 126.0, 125.5, 124.9, 123.9, 115.0, 114.3, 113.1, 104.6, 93.4; HRMS m/z calcd for $C_{16}H_{10}INS$ 374.9579, found 374.9568.

*5-Iodo-4-(phenanthren-9-yl)pyrrolo[1,2-a]quinoline (**5l**).* The product was obtained as a yellow solid: mp 208−210 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$ + $CDCl_3$} δ 7.98 (t, J = 8.4 Hz, 2H), 7.34−7.24 (m, 3H), 7.10 (d, J = 7.3 Hz, 1H), 6.89−6.86 (m, 2H), 6.82−6.77 (m, 3H), 6.69 (d, J = 8.1 Hz, 1H), 6.62−6.56 (m, 2H), 5.73 (t, J = 2.9 Hz, 1H), 4.94 (dd, J = 1.5, 3.7 Hz, 1H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$ + $CDCl_3$} δ 136.5, 135.2, 131.9, 130.7, 130.0, 129.5, 128.5, 128.3, 127.8, 127.5, 127.1, 126.1, 125.5 125.2, 125.1, 124.2, 122.9, 122.3, 121.3, 120.9, 113.1, 111.9, 111.4, 103.2, 93.3; HRMS m/z calcd for $C_{26}H_{16}IN$ 469.0320, found 469.0327.

*4-Butyl-5-iodopyrrolo[1,2-a]quinoline (**5m**).* The product was obtained as a gray oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 7.46−7.35 (m, 3H), 7.21−7.13 (m, 1H), 6.90−6.87 (m, 2H), 6,59 (t, J = 2.2 Hz, 1H), 2.81−2.77 (m, 2H), 1.51−1.47 (m, 2H), 1.37−1.33 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 141.6, 137.3, 130.5, 129.2, 127.1, 125.7, 121.6, 119.3, 109.2, 108.7, 97.2, 94.3, 48.7, 29.7, 20.9, 13.9; HRMS m/z calcd for $C_{16}H_{16}IN$ 349.0327, found 349.0315.

*4-tert-Butyl-5-iodopyrrolo[1,2-a]quinoline (**5n**).* The product was obtained as a brown oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.34 (dd, J = 1.5, 2.9 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 8.1 Hz, 1H), 7.40 (t, J = 8.1 Hz, 1H), 6.76 (t, J = 8.4 Hz, 1H), 6,59 (dd, J = 1.5, 3.6 Hz, 1H), 1,16 (s, 9H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 141.2, 135.6, 133.3, 129.1, 126.4, 124.7, 121.3, 117.2, 114.2, 108.9, 102.8, 100.3, 34.8, 30.2; HRMS m/z calcd for $C_{16}H_{16}IN$ 349.0327, found 349.0333.

*4-Cyclohexyl-5-iodopyrrolo[1,2-a]quinoline (**5o**).* The product was obtained as a brown oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.27 (d, J = 2.2 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 8.05 (d, J = 7.4 Hz, 1H), 7.56 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 3.6 Hz, 1H), 6.77 (t, J = 2.9 Hz, 1H), 3.57−3.51 (m, 1H), 2.23 (m, 2H), 1.88−1.86 (m, 2H), 1.73−1.67 (m, 2H), 1.46−1.38 (m, 4H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 139.9, 134.3, 131.7, 128.6, 127.9, 124.7, 114.7, 113.4, 112.6, 104.4, 94.4, 93.4, 52.7, 29.5, 26.7, 25.3; HRMS m/z calcd for $C_{18}H_{18}IN$ 375.0484, found 375.0491.

*4-Cyclopentyl-5-iodopyrrolo[1,2-a]quinoline (**5p**).* The product was obtained as a brown oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.28 (d, J = 2.9 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.04−8.02 (m,1H), 7.57−7.53 (m, 1H), 7.42−7.38 (m, 1H), 6.75 (t, J = 4.0 Hz, 1H), 6.59 (dd, J = 1.4, 3.6 Hz, 1H), 3.96−3.86 (m, 1H), 2.13−2.05 (m, 2H), 1.98−1.86 (m, 2H), 1.79−1.74 (m, 2H), 1.64−1.50 (m, 2H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 138.8, 134.2, 131.9, 128.6, 127.7, 124.1, 114.8, 113.7, 112.7, 103.1, 94.8, 52.0, 30.0, 26.7; HRMS m/z calcd for $C_{17}H_{16}IN$ 361.0327, found 361.0318.

*4-Cyclopropyl-5-iodopyrrolo[1,2-a]quinoline (**5q**).* The product was obtained as a brown oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.22−8.21 (m, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.99 (dd, J = 1.4, 8.0 Hz, 1H), 7.55−7.51 (m, 1H), 7.39−7.36 (m, 1H), 6.75−6.71 (m, 2H), 1.98−1.91 (m, 1H), 1.21−1.18 (m, 4H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 136.1 132.9, 131.8, 131.5, 128.9, 124.8, 124.2, 114.9, 114.0, 112.8, 103.0, 96.1, 19.8, 9.8; HRMS m/z calcd for $C_{15}H_{12}IN$ 333.0014, found 333.0022.

*(5-Iodopyrrolo[1,2-a]quinolin-4-yl)methanol (**5r**).* The product was obtained as a brown oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.29 (t, J = 2.2 Hz, 1H), 8.20 (d, J = 2.2 Hz, 1H), 8.05 (dd, J = 1.5, 8.1 Hz, 1H), 7.61 (td, J = 1.5, 7.3 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 2.2 Hz, 1H), 6.77 (t, J = 2.9 Hz, 1H), 4.87 (s, 2H), 3.74 (br s, 1H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 140.8, 137.1, 130.4, 129.7, 126.9, 125.5, 121.6, 112.1, 109.5, 103.4, 92.8, 73.0; HRMS m/z calcd for $C_{13}H_{10}INO$ 322.9807, found 322.9801.

*5-Iodo-4-(phenoxymethyl)pyrrolo[1,2-a]quinoline (**5s**).* The product was obtained as a brown oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 7.48−7.44 (m, 2H), 7.33−7.29 (m, 1H), 7.25−7.23 (m, 1H), 7.13−7.06 (m, 2H), 6.98−6.94 (m, 1H), 6.84−6.78 (m, 2H), 6.42 (dd, J = 1.5, 8.1 Hz, 1H), 6.03 (t, J = 2.2 Hz, 2H), 5.40 (s, 2H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 158.5, 152.3, 138.8, 133.7, 131.5, 129.92, 129.80, 127.2, 125.5, 125.0, 121.6, 121.2, 115.8, 115.1, 109.3, 103.2, 73.8; HRMS m/z calcd for $C_{19}H_{14}INO$ 399.0120, found 399.0133.

*5-Iodo-7-methyl-6-phenylindolo[1,2-a]quinoline (**6a**).* The product was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45−8.42 (m, 2H), 8.14 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 7.2 Hz, 1H), 7.60 (t, J = 6.6 Hz, 1H), 7.50−7.19 (m, 7H), 7.04 (d, J = 4.5 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 136.1, 134.6, 131.5, 129.5, 129.3, 125.7, 124.9, 123.2, 122.9, 121.8, 119.7, 115.1, 114.2, 106.8, 9.4; HRMS m/z calcd for $C_{23}H_{16}IN$ 433.0327, found 433.0332.

*5-Iodo-7-methyl-6-p-tolylindolo[1,2-a]quinoline (**6b**).* The product was obtained as a yellow solid: mp 150−152 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.59 (t, J = 8.8 Hz, 2H), 8.10 (dd, J = 1.5, 8.1 Hz, 1H), 7.75 (d, J = 7.3 Hz, 1H), 7.72−7.67 (m, 1H), 7.48−7.35 (m, 5H), 7.18 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H), 1.56 (s, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 140.5, 139.7, 137.6, 135.0, 134.0, 131.17, 131.08, 130.5, 130.1, 129.4, 129.1, 124.0, 123.7, 123.3, 121.9, 119.5, 115.3, 114.4, 106.0, 101.6, 21.0, 9.8; HRMS m/z calcd for $C_{24}H_{18}IN$ 447.0483, found 447.0498.

*6-(4-Ethylphenyl)-5-iodo-7-methylindolo[1,2-a]quinoline (**6c**).* The product was obtained as a yellow solid: mp 155−157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (dd, J = 8.4, 4.2 Hz, 2H), 8.09 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.40−7.23 (m, 5H), 7.15 (t, J = 8.5 Hz, 2H), 2.71 (q, J = 7.5 Hz, 2H), 1.55 (s, 3H), 1.27 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5, 141.2, 140.3, 135.9, 134.5, 131.9, 131.1, 129.6, 129.2, 127.9, 124.8, 123.1, 122.8, 121.6, 119.6, 115.0, 114.1, 106.9, 101.2, 28.8, 15.5, 9.8; HRMS m/z calcd for $C_{25}H_{20}IN$ 461.0640, found 461.0631.

*6-(4-Butylphenyl)-5-iodo-7-methylindolo[1,2-a]quinoline (**6d**).* The product was obtained as a yellow solid: mp 144−147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46−8.39 (m, 2H), 8.15 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.60−7.55 (m,1H), 7.46−7.28 (m, 5H), 7.28−7.17 (m, 2H), 2.74 (t, J = 7.5 Hz, 2H), 1.75−1.68 (m, 2H), 1.62 (s, 3H), 1.47−1.35 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 141.1, 140.3, 135.9, 134.4, 131.8, 131.1, 129.5, 129.1, 128.4, 124.8, 123.1, 122.8, 121.6, 119.5, 115.0, 114.1, 106.9, 101.1, 35.5, 33.5, 22.3,14.9, 9.8; HRMS m/z calcd for $C_{27}H_{24}IN$ 489.0953, found 489.0941.

*6-(4-tert-Butylphenyl)-5-iodo-7-methylindolo[1,2-a]quinoline (**6e**).* The product was obtained as a yellow solid: mp 192−194 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47−8.40 (m, 2H), 8.16 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.61−7.50 (m, 3H), 7.46−7.29 (m, 3H), 7.24−7.19 (m, 2H), 1.60 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 140.8, 140.3, 135.9, 134.4, 131.9, 131.1, 129.2, 125.2, 124.8, 123.1, 122.8, 121.6, 119.6, 115.1, 114.8, 106.9, 101.9, 101.0, 34.7, 31.4, 9.7; HRMS m/z calcd for $C_{27}H_{24}IN$ 489.0953, found 489.0966.

*5-Iodo-6-(4-methoxyphenyl)-7-methylindolo[1,2-a]quinoline (**6f**).* The product was obtained as a yellow solid: mp 156−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 8.6 Hz, 1H), 8.44 (d, J = 8.5 Hz, 1H), 8.17 (dd, J = 6.0, 1.2 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.22 (t, J = 7.2 Hz, 2H), 7.06 (t, J = 8.2 Hz, 2H), 3.91 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 140.1, 136.7, 136.2, 134.7, 132.3, 132.1, 131.3, 131.1, 129.4, 125.0, 123.4, 123.1, 121.8, 119.8, 115.2, 114.3, 114.0, 107.1, 102.1, 55.5, 10.4; HRMS m/z calcd for $C_{24}H_{18}INO$ 463.0433, found 463.0448.

Compound **6f** crystallized with twin structures in the triclinic crystal system with space group $P\bar{1}$. The single-crystal X-ray data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved using SIR-92 and refined by the full matrix least-squares technique on F^2 using the SHELXL-97 program within the WinGX v 1.80.05 software package. All hydrogen atoms were fixed at the calculated positions with isotropic thermal parameters, and all

non-hydrogen atoms were refined anisotropically. Crystal data for **6f**: $C_{24}H_{18}INO$, M = 463.29, triclinic, space group $P\bar{1}$, a = 10.733(5) Å, b = 11.104(5) Å, c = 18.129(5) Å, α = 89.215(5)°, β = 81.700(5)°, γ = 61.836(5)°, V = 1881.2(13) Å^3, Z = 4, T = 296 K, d_{calcd} = 1.636 Mg/m^3, R(int) = 0.0325, R1 = 0.0523, wR2 = 0.1219 [$I > 2\sigma(I)$], R1 = 0.0627, wR2 = 0.1271 (all data), GOF = 1.058. For further details on the crystal structure of compound **6f**, see the CIF file (Supporting Information).

*4-(5-Iodo-7-methylindolo[1,2-a]quinolin-6-yl)-N,N-dimethylaniline (**6g**).* The product was obtained as a yellow solid: mp 158−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, J = 8.4, 6.8 Hz, 2H), 8.17 (dd, J = 6.8, 1.2 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.59 (dt, J = 6.4, 1.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 6.4 Hz, 1H), 7.31−7.27 (m, 1H), 7.16−7.13 (m, 2H), 6.86 (d, J = 8.8 Hz, 2H), 3.08 (s, 6H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 140.6, 136.0, 135.4, 134.5, 131.1, 130.4, 129.0, 126.8, 126.6, 123.1, 122.7, 121.8, 119.9, 118.8, 115.0, 114.1, 111.8, 107.1, 40.5, 10.2; HRMS m/z calcd for $C_{25}H_{21}IN_2$ 476.0749, found 476.0737.

*5-Iodo-7-methyl-6-m-tolylindolo[1,2-a]quinoline (**6h**).* The product was obtained as a yellow solid: mp 118−120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49−8.42 (m, 2H), 8.17 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.63−7.58 (m, 1H), 7.48−7.31 (m, 5H), 7.12−7.10 (m, 2H), 2.44 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 140.2, 138.1, 135.9, 134.4, 131.8, 131.1, 130.3, 129.2, 128.3, 126.8, 124.7, 123.1, 122.8, 121.6, 119.5, 115.0, 114.1, 106.8, 100.8, 21.5, 9.9; HRMS m/z calcd for $C_{24}H_{18}IN$ 447.0484, found 447.0496.

*5-Iodo-7-methyl-6-o-tolylindolo[1,2-a]quinoline (**6i**).* The product was obtained as a yellow solid: mp 126−129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 1H), 8.44 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.64−7.59 (m, 1H), 7.48−7.31 (m, 6H), 7.18 (d, J = 7.8 Hz, 1H), 2.13 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 139.7, 136.6, 136.0, 134.4, 132.0, 131.8, 130.1, 129.8, 129.3, 128.7, 126.1, 124.6, 123.2, 122.9, 121.7, 119.6, 115.1, 114.2, 106.7, 19.4, 9.7; HRMS m/z calcd for $C_{24}H_{18}IN$ 447.0484, found 447.0489.

*5-Iodo-7-methyl-6-(thiophene-3-yl)indolo[1,2-a]quinoline (**6j**).* The product was obtained as a yellow oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.58 (t, J = 8.2 Hz, 2H), 8.07 (d, J = 8.2 Hz, 1H), 7.79−7.75 (m, 2H), 7.71−7.67 (m, 1H), 7.56−7.51 (m, 2H), 7.47−7.35 (m, 2H), 7.14−7.11 (m,1H), 1.66 (s, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 142.8, 135.4, 135.1, 134.0, 131.1, 130.5, 130.2, 129.2, 126.6, 125.3, 123.9, 123.7, 123.3, 121.9, 119.5, 115.3, 114.4, 110.1, 106.0, 102.2, 9.0; HRMS m/z calcd for $C_{21}H_{14}INS$ 438.9892, found 438.9905.

*5-Iodo-6-p-tolylindolo[1,2-a]quinoline (**6k**).* The product was obtained as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75−7.62 (m, 3H), 7.53−7.47 (m, 1H), 7.38−7.14 (m, 5H), 7.04−6.73 (m, 2H), 6.70−6.68 (m, 1H), 6.39−6.32 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 138.1, 135.9, 134.4, 131.8, 131.7, 131.1, 130.3, 129.2, 128.9, 128.3, 126.8, 124.7, 123.1, 122.8, 121.6, 119.5, 114.1, 106.8, 100.8, 21.6; HRMS m/z calcd for $C_{23}H_{16}NI$ 433.0327, found 433.0319.

*6-(4-Ethylphenyl)-5-iodoindolo[1,2-a]quinoline (**6l**).* The product was obtained as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74−7.76 (m, 2H), 7.63−7.60 (m, 1H), 7.51−7.46 (m, 2H), 7.37−7.22 (m, 5H), 7.18−7.03 (m, 1H), 6.72−6.67 (m, 1H), 6.39−636 (m, 1H), 2.77 (q, J = 8.2 Hz, 2H), 1.31 (t, J = 8.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 132.5 132.0, 131.6, 130.8, 130.5, 130.1, 129.3, 129.0, 128.4, 128.1, 127.5, 124.7, 124.0, 122.7, 122.0, 110.7, 110.2, 102.5, 96.6, 28.7, 15.3; HRMS m/z calcd for $C_{24}H_{18}IN$ 447.0484, found 447.0491.

*5-Iodo-6-(4-methoxyphenyl)indolo[1,2-a]quinoline (**6m**).* The product was obtained as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.2 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.42 (m, 2H), 7.28 (d, J = Hz, 3H), 7.00 (dd, J = 2.0 Hz, 1H), 6.28 (dd, J = 6.4,2.0 Hz, 1H), 5.90 (dd, J = 5.6, 2.8 Hz, 1H), 5.53 (dd, J = 5.6, 2.8 Hz, 1H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 139.7, 135.7, 135.3, 134.8, 134.3, 131.9, 131.6, 130.2, 130.0, 129.5, 125.3, 123.3, 122.8, 122.2, 121.2, 115.2, 114.1, 112.3, 105.5, 102.8, 54.6; HRMS m/z calcd for $C_{23}H_{16}NIO$ 449.0276, found 449.0268.

*4-(5-Iodoindolo[1,2-a]quinolin-6-yl)-N,N-dimethylaniline (**6n**).* The product was obtained as a yellow solid: mp 146−148 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.69−8.62 (m, 2H), 8.15 (d, J = 8.2 Hz, 1H), 7.80−7.71 (m, 2H), 7.49−7.41 (m, 2H), 7.37−7.33 (m, 1H), 7.21 (d, J = 9.6 Hz, 2H), 6.87 (d, J = 9.2 Hz, 2H), 6.29 (s, 1H), 3.01 (s, 6H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 150.0, 139.4, 136.8, 134.2, 132.3, 130.0, 129.9, 129.5, 129.3, 124.4, 123.9, 122.7, 122.3, 121.4, 115.4, 114.6, 111.8, 100.6, 99.3, 40.1; HRMS m/z calcd for $C_{24}H_{19}IN_2$ 462.0593, found 462.0597.

6-(4-Methoxyphenyl)-7-methylindolo[1,2-*a*]quinoline (12). The compound was synthesized by a reported procedure[24] with a slight modification. To a solution of **6f** (0.25 mmol) in 5.0 mL of MeOH was added CuI (10 mol %) followed by $NaBH_4$ (1.5 equiv). The reaction mixture was allowed to stir for 10 min at 25 °C under inert conditions. The product was obtained as a yellow solid: mp 160−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 9.2 Hz, 1H), 8.38 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.51−7.44 (m, 2H), 7.38−7.29 (m, 4H), 7.18 (t, J = 9.2 Hz, 1H), 6.92 (d, J = 5.0 Hz, 2H), 6.79 (s 1H), 3.81 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 136.4, 135.5, 132.3, 132.1, 131.3, 130.3, 128.3, 128.1, 124.2, 123.8, 122.5, 122.1, 121.2, 119.1, 115.0, 114.0, 113.5, 105.8, 55.3, 10.7; HRMS m/z calcd for $C_{24}H_{19}NO$ 337.1467, found 337.1455.

6-(4-Methoxyphenyl)-12-methylindolo[2,1-*a*]isoquinoline (13). The compound was synthesized by a reported procedure.[18a] The product was obtained as a yellow solid: mp 156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.52−7.39 (m, 5H), 7.27−7.24 (m, 1H), 7.05 (d, J = 8.4 Hz, 2H), 6.92 (t, J = 7.6 Hz, 1H), 6.48 (d, J = 8.4 Hz, 1H), 6.42 (s, 1H), 3.93 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 138.3, 131.5, 130.5, 130.4, 130.2, 130.1, 129.3, 127.3, 126.7, 126.6, 126.2, 124.4, 121.0, 120.3, 118.1, 114.6, 114.4, 110.9, 105.5, 55.5, 11.9; HRMS m/z calcd for $C_{24}H_{19}NO$ 337.1467, found 337.1465.

5-(4-Methoxyphenyl)-4-*p*-tolylpyrrolo[1,2-*a*]quinoline (16). The compound was synthesized by a reported procedure.[20] The product was obtained as a pale yellow solid: mp 160−164 °C; ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.33−8.29 (m, 2H), 7.58−7.50 (m, 2H), 7.28−7.20 (m, 2H), 7.11−7.04 (m, 4H), 6.97 (d, J = 8.7 Hz, 1H), 6.83 (d, J = 8.6 Hz, 2H), 6.74−6.72 (m, 1H), 6.02−6.00 (m, 1H), 3.71 (s, 3H), 2.24 (s, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 158.8, 136.5, 135.0, 132.6, 131.7, 130.8, 130.2, 129.7, 129.0, 128.4, 127.8, 127.7, 124.8, 124.2, 115.2, 114.7, 114.1, 113.8, 113.3, 104.3, 55.6, 21.3; HRMS m/z calcd for $C_{26}H_{21}NO$ 363.1623, found 363.1626.

Methyl 3-(4-(4-Butylphenyl)pyrrolo[1,2-*a*]quinolin-5-yl)acrylate (17). The compound was synthesized by a reported procedure.[21] The product was obtained as a yellow oil: ^{1}H NMR {400 MHz, $(CD_3)_2SO$} δ 8.37 (s, 1H), 8.30 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.68−7.59 (m, 2H), 7.43−7.39 (m, 1H), 7.30−7.22 (m, 4H), 6.74 (t, J = 3.4 Hz, 1H), 6.08 (d, J = 3.7 Hz, 1H), 5.93 (d, J = 16.4 Hz, 1H), 3.62 (s, 3H), 2.63 (t, J = 7.8 Hz, 2H), 1.59 (p, J = 7.3 Hz, 2H), 1.30 (st, J = 7.3 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR {100 MHz, $(CD_3)_2SO$} δ 166.1, 142.3, 140.6, 133.67, 132.8, 133.1, 130.6, 129.4, 128.3, 125.9, 124.2, 123.2, 121.4, 119.6, 115.3, 115.1, 113.65, 106.4, 51.4, 34.5, 32.9, 21.6, 13.8; HRMS m/z calcd for $C_{26}H_{25}NO_2$ 383.1885, found 383.1895.

12-Methyl-9,10-di-*p*-tolylbenzo[*i*]pyrrolo[1,2-*f*]phenanthridine (18). The compound was synthesized by a reported procedure[22] with a slight modification. To a solution of **5b** (0.25 mmol) in 5.0 mL of DMA were added $PdCl_2(PPh_3)_2$ (10 mol %) and 1,2-di-*p*-tolylethyne (1.3 equiv) followed by addition of 3.0 equiv of NaCl and 3.0 equiv of KOAc. The reaction mixture was allowed to stir for 2 days at 110 °C under inert conditions. The product was obtained as a yellow solid: mp

246−248 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 1.4 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.35−7.31 (m, 3H), 7.23−7.15 (m, 2H), 6.97 (d, J = 7.3 Hz, 2H), 6.90−6.88 (m, 2H), 6.86−6.82 (3H), 6.80−6.78 (m, 2H), 6,69 (t, J = 8.8 Hz, 1H), 2.33 (s, 3H), 2.26 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 137.0, 136.52, 136.22, 136.01, 135.5, 133.3, 132.8, 131.3, 131.2, 130.1, 128.55, 128.45, 128.18, 127.2, 126.46, 126.28, 126.15, 124.9, 123.2, 122.32, 122.17, 115.0, 113.5, 112.8, 107.4, 29.7, 21.78, 21.27; HRMS m/z calcd for $C_{35}H_{27}N$ 461.2143, found 461.2149.

4-(4-Methoxyphenyl)-5-(1*H*-pyrrol-1-yl)pyrrolo[1,2-*a*]quinoline (19). The compound was synthesized by a reported procedure.[18e,f] The product was obtained as a brown solid: mp 152−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.85 (m, 2H), 7.48−7.44 (m, 1H), 7.21−7.18 (m, 3H), 7.10−7.08 (m, 1H), 6.78−6.72 (m, 3H), 6.58 (d, J = 2.2 Hz, 2H), 6.33 (dd, J = 1.4, 3.6 Hz, 1H), 6.11 (t, J = 2.2 Hz, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 132.5, 131.2, 129.9, 128.2, 127.0, 126.4, 125.0, 124.1, 123.8, 123.2, 113.94, 113.48, 113.32, 113.02, 108.5, 105.7, 55.1; HRMS m/z calcd for $C_{23}H_{18}N_2O$ 338.1419, found 338.1422.

4-(4-Methoxyphenyl)pyrrolo[1,2-*a*]quinoline (20). The synthesis procedure was the same as that for **12**. The product was obtained as a brown solid: mp 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.80 (m, 2H), 7.59−7.57 (m, 3H), 7.42−7.38 (m, 1H), 7.26−7.22 (m, 1H), 6.94 (dd, J = 2.2, 6.6 Hz, 2H), 6.72 (t, J = 3.3 Hz, 2H), 6.54 (dd, J = 1.5, 3.7 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 132.5, 132.3, 131.4, 131.0, 129.4, 128.5, 127.3, 124.3, 123.6, 117.5, 114.0, 113.9, 112.7, 112.5, 103.2, 55.3; HRMS m/z calcd for $C_{19}H_{15}NO$ 273.1154, found 273.1149.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data of compounds **5b** and **6f** in CIF format and copies of NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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