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Palladium-Catalyzed Sonogashira-Coupling Conjoined C−H Activation: A Regioselective Tandem Strategy to Access Indolo- and Pyrrolo[1,2-*a*]quinolines

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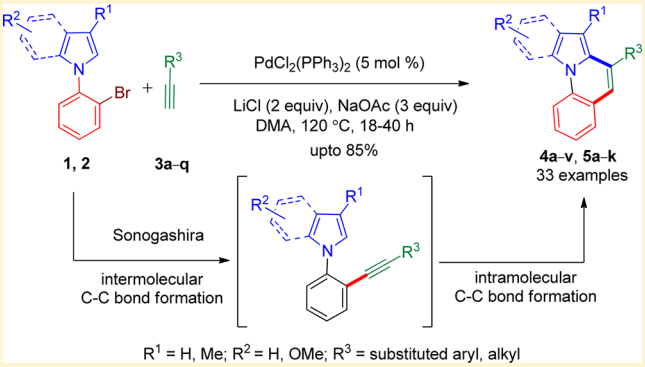
Supporting Information

ABSTRACT: An operationally simple approach for the regioselective tandem synthesis of indolo[1,2-*a*]quinolines **4a−v** and pyrrolo[1,2-*a*]quinolines **5a−k** from 1-(2-bromophenyl)-1*H*-indole/pyrrole/imidazole **1a−c**, **2a,b** by the palladium-catalyzed sequential C−C bond formation is described. The developed approach involves the palladium-catalyzed Sonogashira coupling followed by the intramolecular C−C bond formation via C−H activation, which leads to the formation of 6-*endo*-*dig* cyclized product. This synthetic methodology accommodates wide functional group variation on alkyne, which proves to be advantageous for the structural and biological activity assessments.



INTRODUCTION

In the past decade, transition-metal-catalyzed reactions have emerged as a powerful tool for the synthesis of heterocyclic compounds, natural-product-like scaffolds and fused carbocyclic compounds[1a−l] because of the intriguing selectivity, atom economy and excellent ability to trigger the π-systems, especially alkynes, toward intermolecular and intramolecular C−C and C−N bond formations. Tandem reactions have received a considerable interest because these reactions can swiftly assemble the complex molecules from simple starting material in an iterative manner[1m−o] and is ideally suited to access diverse skeletal complexity.[1p,q] Among the transition-metal-catalyzed reactions, palladium is extensively used for the synthesis of small molecules because of its exceptional reactivity, tolerance of many functional groups, low toxicity and attractiveness from the viewpoint of assembly efficiency.[2,3]

Indole and pyrrole fused heterocycles are known to exert significant biological activity in many active pharmaceutical ingredients.[4] Indolo- and pyrrolo[1,2-*a*]quinolines are such molecules that have unique nitrogen containing tricyclic and tetracyclic structures derived from indole and pyrrole, and their reduced and oxidized forms occur widely among natural products.[5] Along with antibacterial, antifungal[6] and apoptosis inducing[7] properties, these polycyclic compounds are also identified as rigid molecular platforms critical to advances in various areas of chemical research such as organic semiconductor chemistry,[8] host−guest chemistry,[9] liquid−crystal chemistry,[10] and even biochemical studies of synthetic peptides.[11]

Reported syntheses of these moieties include various protocols such as palladium-catalyzed reactions,[12] 1,2-alkyl migration,[13] DDQ-mediated intramolecular cyclization,[8a] flash vacuum pyrolysis,[14] and photosubstituted reactions.[15] Despite various synthetic protocols available for the synthesis of indolo- and pyrrolo[1,2-*a*]quinolines, a need for versatile methods for their efficient synthesis from simple and easily accessible starting material still attracts the interest of the synthetic chemist. Recently, Lautens and co-workers have reported an elegant approach for the synthesis of triazole fused indolo[1,2-*a*]quinolines from iodo-alkyne in one-pot by cycloaddition followed by palladium-catalyzed C−H functionalized cyclization. (Scheme 1, i).[16] Furthermore, Kim and co-workers reported the synthesis of indolo[1,2-*a*]quinolines from indoles by sequential Cu-mediated *N*-arylation of indole, followed by $Mn(OAc)_3$-mediated oxidative free radical cyclization, and NaI/O_2-assisted concomitant dealkoxycarbonylation/aerobic oxidation (Scheme 1, ii).[17]

In our preceding report during the synthesis of indolo[2,1-*a*]-isoquinolines,[18] the initial attempt was to synthesize indolo-[1,2-*a*]quinoline **4** in one-pot from *ortho*-haloarylalkynes **9** via *N*-arylation followed by the intramolecular electrophilic cyclization without isolating the *N*-arylated intermediate **6** (Scheme 2, i, path a). Interestingly, the reaction proceeded via the path b; i.e., hydroamination followed by the intramolecular C-2 arylation and afforded the indolo[2,1-*a*]isoquinolines **11**, a regioisomer of **4**, via the formation of enamine intermediate **10** (Scheme 2, i, path b). Alternatively, a two step protocol was designed for the synthesis of indolo/pyrrolo[1,2-*a*]quinolines **4**

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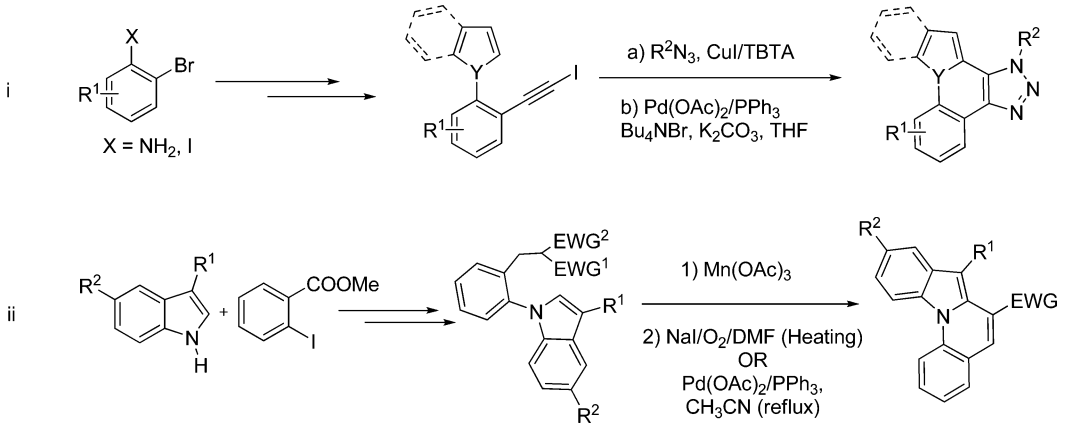
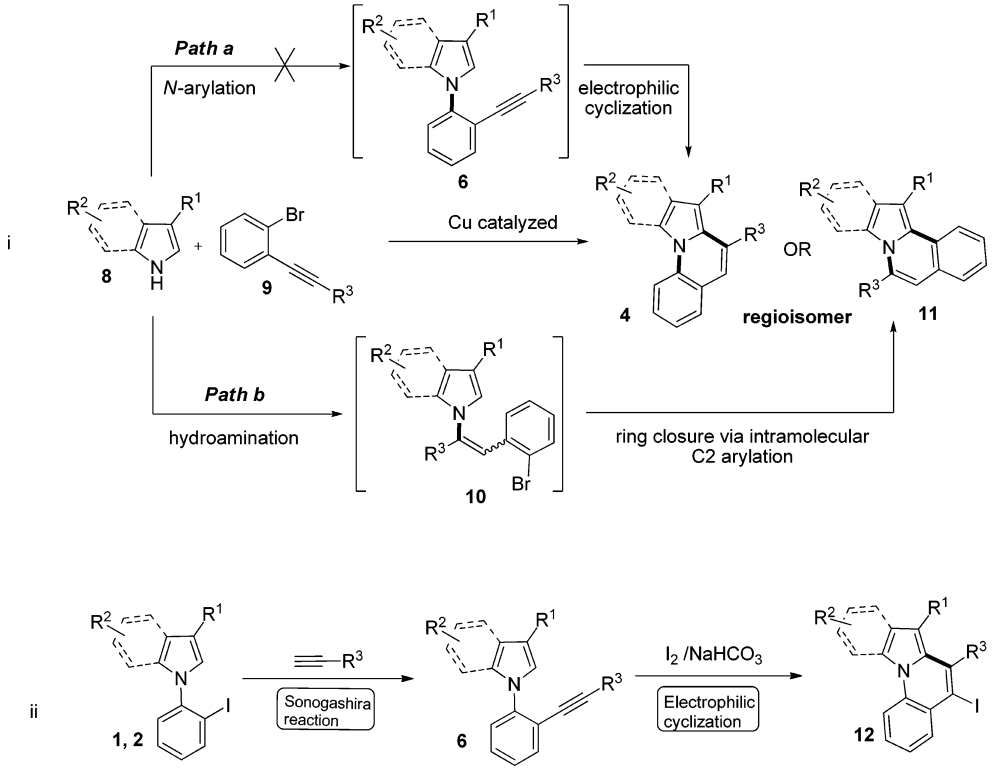
Scheme 1. Previous Approaches to Synthesize Indoloquinolines



Scheme 2. Previous Work of Our Laboratory

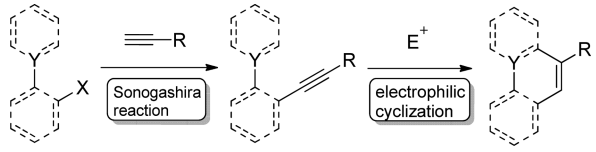


from 1-(2-iodophenyl)indole/pyrrole.[19] The key alkyne intermediate **6** was prepared by the Sonogashira coupling of the 1-(2-iodophenyl)indole/pyrrole, which upon electrophilic iodocyclization afforded the iodo-substituted indolo-, pyrrolo[1,2-*a*]-quinolines **12** (Scheme 2, ii).

In the past two decades, alkynyl substrates have been advantageously utilized in the syntheses of various heterocycles through electrophilic cyclization[20] and alkyne-annulation.[21] Literature survey revealed that most of the electrophilic cyclization of terminal alkynes generally utilize a two-step protocol; i.e., first, Sonogashira reaction is carried out, and the isolated product is then subjected to the electrophilic cyclization using various protocols (Scheme 3).

Encouraged by the above investigations and with our objective to develop parallel methodologies[22] capable of furnishing regioisomeric heterocyclic compounds starting from similar substrates,[18,19]

Scheme 3. General Synthetic Approach for the Electrophilic Cyclization of Terminal Alkynes



governed by various catalytic protocols, we herein report the regioselective tandem synthesis of indolo[1,2-*a*]quinolines **4a**–**v** and pyrrolo[1,2-*a*]quinolines **5a**–**k** directly from 1-(2-bromophenyl)-indole/pyrrole by the palladium-catalyzed sequential C–C bond formation via C–H activation. This tandem process is advantageous in improving the efficiency, atom economy, and modularity of the synthesis (Scheme 4).

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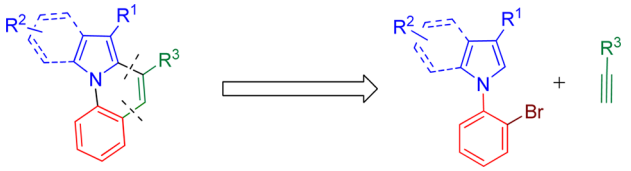
Scheme 4. Designed Retrosynthetic Approach for the Tandem Synthesis of Indolo-, Pyrrolo[1,2-*a*]quinolines



RESULTS AND DISCUSSION

Preparation of 1-(2-Bromophenyl)indole/pyrrole/imidazole. 1-(2-Bromophenyl)-1*H*-indoles **1a**−**d**, 1-(2-bromophenyl)-1*H*-pyrrole **2a** and 1-(2-bromophenyl)-1*H*-imidazole **2b**, required for the reaction, were prepared in good yields by the copper-catalyzed *N*-arylation of indoles/pyrrole and imidazole with *o*-dihalobenzenes using standard procedure developed for different *N*-hetrocycles in our laboratory (Scheme 5).[22g,h]

To probe the viability of the envisioned sequential protocol, we examined the reaction of 1-(2-bromophenyl)-3-methyl-1*H*-indole (**1a**) with ethynylbenzene (**3a**) using 5.0 mol % of $PdCl_2(PPh_3)_2$, 3.0 equiv of Et_3N in 2.0 mL of CH_3CN at 60 °C; the product **4a** was not observed, and an uncyclized product **6a** was obtained in 86% yield after 2 h (Table1, entry 1). Similar results were obtained when reaction was further allowed to stir for longer time (entries 2−4). Interestingly, when reaction was carried out at 120 °C in DMF for 12 h, the desired cyclized product **4a** was obtained in 21% yield along with 56% of **6a** (entry 5). The obtained results were encouraging, as the tandem synthesis protocol was working at elevated temperature. To further improve the yield of the cyclized product **4a**, different bases were screened to find an appropriate system for the proposed reaction. From entries 6−8 in Table 1, it is apparent that NaOAc was found to be suitable for the transformation, as product **4a** was obtained in improved yield. Using the above reaction conditions, product **4a** was obtained in 51 and 68% yields, respectively, after reaction was allowed to run for 18 and 28 h (entries 9−10). When reaction was further allowed to run for 36 h, no significant change in the yield of the cyclized product was observed (entry 11). Increasing the catalyst loading from 5 to 10 mol % made no significant improvement in the yield of the product **4a** (entry 12). Further efforts were made to come up with better conditions that could afford the product in good yield. Addition of 2.0 equiv of LiCl to the reaction afforded the desired product **4a** in 74% yield (entry 13). Other palladium catalysts such as $Pd(OAc)_2$, $PdCl_2$ and $Pd_2(dba)_3$ were found inferior for the reaction and afforded the desired products **4a** in 64, 58 and 50% yields, respectively, along with 10−12% of uncyclized intermediate **6a** (entries 14−16). After we found that $PdCl_2(PPh_3)_2$ is acting as the best among all the palladium catalysts tested for the reaction, some cocatalysts such as CuI, $Cu(OTf)_2$ and $Cu(OAc)_2$ were also screened along with palladium complex, but results were not impressive as Cu salts promotes dimerization of alkynes, thereby reducing the yield of the cyclized product **4a** (entries 17−19). Different solvents like DMA, DMSO and PEG_{400} were screened to find an appropriate solvent for the reaction (entries 20−22). It is clear from Table 1 that DMF and DMA at 120 °C were found to be suitable solvents for the tandem reaction (entries 13 and 20). The combination of 5.0 mol % of $PdCl_2(PPh_3)_2$, 3.0 equiv NaOAc, 2.0 equiv LiCl in 2.0 mL of DMA at 120 °C was found to be the standardized condition for tandem cyclization.

Synthesis of Indolo[1,2-*a*]quinolines. After optimizing the reaction condition, we examined the scope and generality of the reaction by employing a variety of alkynes **3a**−**m** and substituted 1-(2-bromophenyl)indoles **1a**−**d** (Table 2, entries 1−23). Electron-rich 1-(2-bromophenyl)-3-methyl-1*H*-indole (**1a**) and 1-(2-bromophenyl)-5-methoxy-1*H*-indole (**1c**) on reaction with substituted terminal alkynes afforded the desired indolo[1,2-*a*]-quinolines (**4a**−**j**, and **4r**−**v**) in good yield in comparison to 1-(2-bromophenyl)-1*H*-indole (**1b**) (entries 1−10, 18−22 vs 13−17). The terminal alkynes **3b**−**e** bearing electron-donating substituent such as Me, OMe, *n*-Bu and Ph groups at the *para* to the triple bond of the phenyl ring showed the capability to trigger the 6-*endo*-*dig* cyclization and afforded the respective cyclized products **4b**−**e** in good yields (entries 2−5). Reaction of **1a** with 2-ethynyl-6-methoxynaphthalene (**3f**) afforded the product **4f** in 78% yield (entry 6). Electron-rich heterocyclic alkyne, 3-ethynylthiophene (**3g**), proved to be favorable for the reaction and afforded the desired product **4g** in 80% yield (entry 7). Alkynes **3h**,**i** bearing substitution at *meta* position of the phenyl ring afforded the cyclized products **4h**,**i**, in comparatively lower yields (entries 8, 9). An alkyne **3j** having a methyl group at 2-position of the phenyl ring afforded the desired product **4j** in 73% yield (entry 10). Alkynes **3k**,**l** bearing a cyclopropyl and cyclohexyl group provided the desired products **4k**,**l** in 38 and 40% yields, respectively, along with uncyclized intermediate (entries 11, 12). Further, exploring the reaction using **1b** with a variety of terminal alkynes (**3b**, **3c**, **3m**, **3i** and **3g**) provided the desired cyclized products **4m**−**q** in 68−73% yields (entries 13−17). Substrate **1c** having methoxy group at 5-position of the indole on reaction with alkynes **3a**, **3b**, **3c**, **3m** and **3g** afforded the tandem cyclized products **4r**−**v** in 74−80% yields (entries 18−22). However, the presence of electron-withdrawing nitro group at 5 position of indole ring **1d** provided uncyclized intermediate **6w** in 42% yield (entry 23).

Synthesis of Pyrrolo[1,2-*a*]quinolines. Pyrrolo[1,2-*a*]-quinolines exhibit interesting biological activities and have always been an area of interest for synthetic chemists and biologists. To ascertain the generality and scope of the developed chemistry, we designed the direct synthesis of pyrrolo[1,2-*a*] quinolines from simple and readily accessible starting material 1-(2-bromophenyl)-pyrrole (**2a**). Using the above optimized reaction conditions, scope and limitation of this palladium-catalyzed tandem process were next explored by employing variety of terminal alkynes with substrate **2a** (Table 3, entries 1−11). As observed in the synthesis

Scheme 5. Preparation of 1-(2-Bromophenyl)indole/pyrrole/imidazole

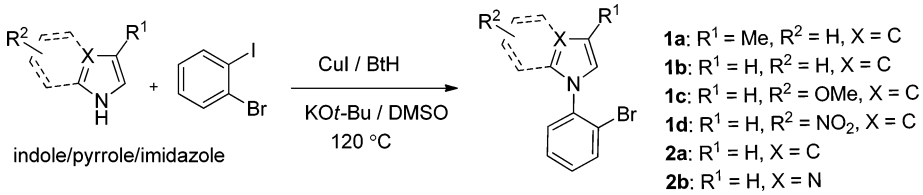


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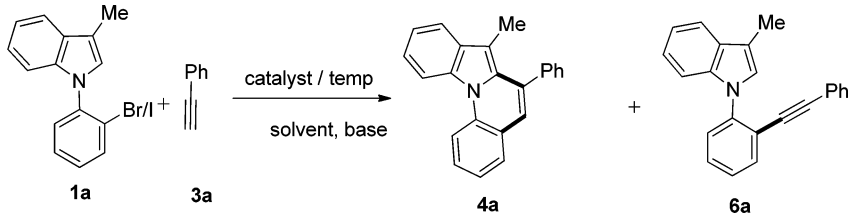
Table 1. Optimization of the Reaction Conditions for the Tandem Synthesis of Indolo-, Pyrrolo[1,2-*a*]quinolines[a]



entry	catalyst	additives[b]	solvent	base	T (°C)	time (h)	yield 4a	yield 6a
1	$PdCl_2(PPh_3)_2$		CH_3CN	Et_3N	60	2	0	86
2	$PdCl_2(PPh_3)_2$		CH_3CN	Et_3N	60	10	0	86
3	$PdCl_2(PPh_3)_2$		CH_3CN	Et_3N	60	24	0	86
4	$PdCl_2(PPh_3)_2$		CH_3CN	Et_3N	60	36	0	85
5	$PdCl_2(PPh_3)_2$		DMF	Et_3N	120	12	21	56
6	$PdCl_2(PPh_3)_2$		DMF	KO*t*Bu	120	12	29	37
7	$PdCl_2(PPh_3)_2$		DMF	K_3PO_4	120	12	27	38
8	$PdCl_2(PPh_3)_2$		DMF	NaOAc	120	12	37	43
9	$PdCl_2(PPh_3)_2$		DMF	NaOAc	120	18	51	21
10	$PdCl_2(PPh_3)_2$		DMF	NaOAc	120	28	68	
11	$PdCl_2(PPh_3)_2$		DMF	NaOAc	120	36	68	
12[c]	$PdCl_2(PPh_3)_2$		DMF	NaOAc	120	28	68	
13	$PdCl_2(PPh_3)_2$	LiCl	DMF	NaOAc	120	28	74	
14	$Pd(OAc)_2$	LiCl	DMF	NaOAc	120	28	64	10
15	$PdCl_2$	LiCl	DMF	NaOAc	120	28	58	12
16	$Pd_2(dba)_3$	LiCl	DMF	NaOAc	120	28	50	12
17	$PdCl_2(PPh_3)_2$	LiCl + CuI (5 mol %)	DMF	NaOAc	120	28	71	
18	$PdCl_2(PPh_3)_2$	LiCl + $Cu(OTf)_2$ (5 mol %)	DMF	NaOAc	120	28	73	
19	$PdCl_2(PPh_3)_2$	LiCl + $Cu(OAc)_2$ (5 mol %)	DMF	NaOAc	120	28	70	
20	$PdCl_2(PPh_3)_2$	LiCl	DMA	NaOAc	120	28	76	
21	$PdCl_2(PPh_3)_2$	LiCl	DMSO	NaOAc	120	28	24	27
22	$PdCl_2(PPh_3)_2$	LiCl	PEG_{400}	NaOAc	120	28	17	25

[a]The reactions were performed using **1a** (0.5 mmol), with ethynylbenzene **3a** (1.2 equiv), base (3.0 equiv) in 2.0 mL of solvent under inert conditions. [b]2.0 equiv of LiCl was used. [c]10.0 mol % of $PdCl_2(PPh_3)_2$ was used.

of indolo[1,2-*a*]quinolines, alkynes bearing the electron-donating group *para* to triple bond afforded the desired pyrrolo[1,2-*a*]-quinolines **5a−h** in good yields. Alkynes **3b−e** and **3m,n** bearing electron-donating group at *para* position afforded the corresponding cyclized products **5a−f** in 79−84% yields (Table 3, entries 1−6). Alkyne **3i** with methyl substitution at *meta* position afforded the desired cyclized products **5g** in 78% yield (entry 7). Electron-rich thiophene substituted alkyne **3g** afforded the desired product **5h** in 83% yield (entry 8). However, alkynes **3o,p** bearing cyclopentyl and *n*-butyl substituents, provided the corresponding desired products **5i,j** in 44 and 41% yields, respectively, along with uncyclized intermediate (entries 9−10). Alkyne **3q** bearing an electron-withdrawing CF_3 group at *para*-position of the phenyl ring the was found to be unfavorable for the reaction, as the desired product **5k** was obtained only in 31% yield (entry 11).

Substrate 1-(2-bromophenyl)indoles/pyrrole **1a−c** and **2a** on reaction with various alkynes afforded the desired cyclized products **4a−v** and **5a−k**; however, reaction of 1-(2-bromophenyl)-1*H*-imidazole (**2b**) with alkyne **3b** provided an inseparable mixture of unidentifiable compounds, which might be the result of the reduced nucleophilicity of the imidazole ring or the formation of a relatively unstable intermediate (Table 3, entry 12).

It is evident from Tables 2 and 3 that reactions were faster with alkynes bearing electron-rich substituent attached to the triple bond, as respective products were obtained in good yields, whereas slower or incomplete reactions were observed with electron-deficient or electron-neutral (alkyl substituent) substituents (Scheme 6).

A plausible catalytic cycle for the above transformation based on the palladium chemistry reported by Larock and co-workers[23] is shown in Scheme 7. The oxidative addition of the 1-(2-bromophenyl)indole/pyrrole **1**, **2** to Pd(0) gives the intermediate **P**, which on subsequent complexation with the alkyne results in palladium alkyne complex **Q**. Palladium complex **Q** is susceptible to attack by the nucleophile. The intramolecular attack of the C-2 position of indole/pyrrole on the vinylpalladium intermediate forms intermediate **S** (path b). Elimination of HX from intermediate **S** generates the palladacyclic complex **T**, which upon reductive elimination results in the formation of the product **4**, **5** and regenerates the Pd(0). The palladacyclic complex **T** can also be obtained from intermediate **R**, which could be obtained by the oxidative addition of the vinylpalladium **Q** to the C−H bond of the indole/pyrrole (path a). No products of multiple alkyne insertion have been observed.

CONCLUSION

In summary, the results of the above studies have demonstrated the feasible and efficient one-pot approach for the synthesis of indolo[1,2-*a*]quinolines and pyrrolo[1,2-*a*]quinolines. Diversified fused quinolines with different substituents were generated in moderate to good yields. The palladium-catalyzed Sonogashira

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Table 2. Synthesis of Indolo[1,2-*a*]quinolines[a]

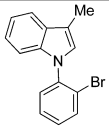
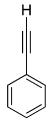
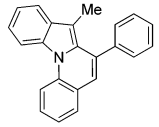
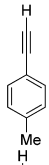
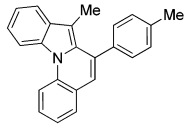
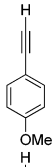
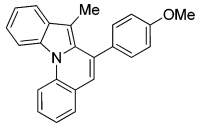
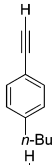
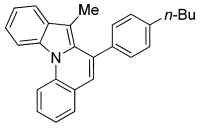
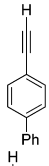
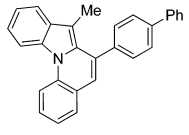
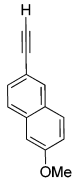
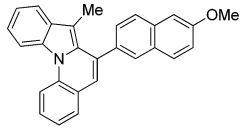
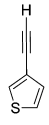
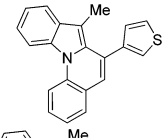
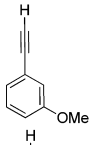
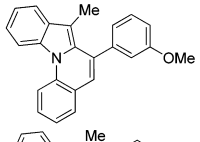
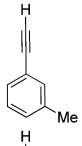
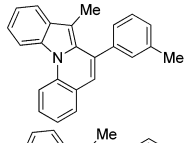
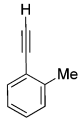
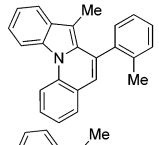
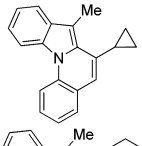
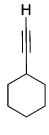
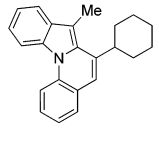
entry	substrate	alkyne	Product	time (h)	yield (%)
1.	 **1a**	 **3a**	 **4a**	28	76
2.	**1a**	 **3b**	 **4b**	23	78
3.	**1a**	 **3c**	 **4c**	18	80
4.	**1a**	 **3d**	 **4d**	23	77
5.	**1a**	 **3e**	 **4e**	25	76
6.	**1a**	 **3f**	 **4f**	23	78
7.	**1a**	 **3g**	 **4g**	18	80
8.	**1a**	 **3h**	 **4h**	30	70
9.	**1a**	 **3i**	 **4i**	28	74
10.	**1a**	 **3j**	 **4j**	28	73
11.	**1a**	 **3k**	 **4k**	40	38[b]
12.	**1a**	 **3l**	 **4l**	40	40[c]

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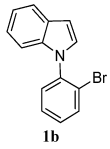
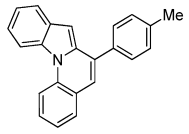
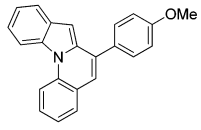
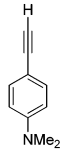
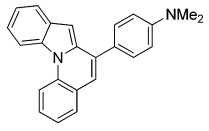
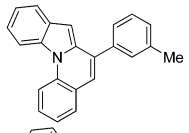
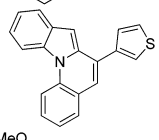
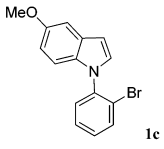
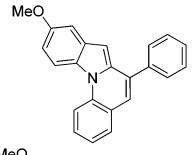
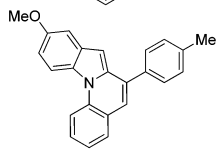
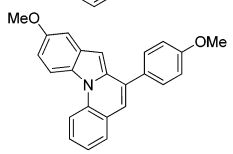
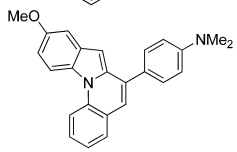
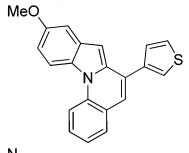
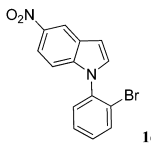
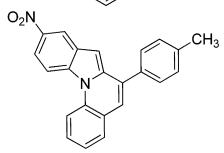
Table 2. continued

entry	substrate	alkyne	Product	time (h)	yield (%)
13.	 **1b**	**3b**		**4m** 28	70
14.	**1b**	**3c**		**4n** 24	72
15.	**1b**	 **3m**		**4o** 24	72
16	**1b**	**3i**		**4p** 30	68
17	**1b**	**3g**		**4q** 24	73
18	 **1c**	**3a**		**4r** 28	74
19	**1c**	**3b**		**4s** 25	74
20	**1c**	**3c**		**4t** 20	78
21	**1c**	**3m**		**4u** 20	79
22	**1c**	**3g**		**4v** 20	80
23	 **1d**	**3b**		**4w** 40	-[d]

[a]The reactions were performed using 0.5 mmol of the indole **1a–d**, $PdCl_2(PPh_3)_2$ (5.0 mol %), LiCl (2.0 equiv) and NaOAc (3.0 equiv) in 2.0 mL of DMA at 120 °C for 18–40 h under inert conditions. [b]28% of uncyclized intermediate was obtained. [c]24% of uncyclized intermediate was obtained. [d]42% of uncyclized intermediate was obtained.

coupling followed by C–H activation protocol achieving the regioselective 6-*endo-dig* C–C bond formation is advantageous in improving the efficiency, atom economy, and modularity of the synthesis. The chemistry outlined here is extremely versatile, as it accommodates various functional groups, which makes it ideal for the generation of various functionally substituted scaffolds, and a wide range of structurally and spatially diverse compounds can be produced.

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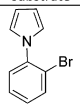
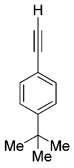
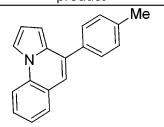
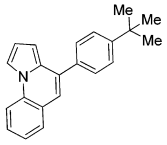
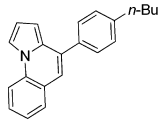
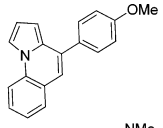
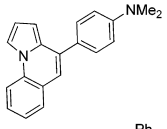
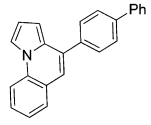
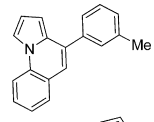
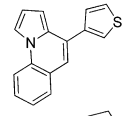
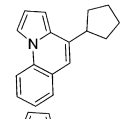
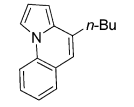
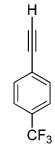
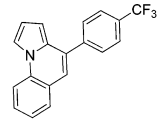
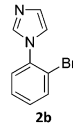
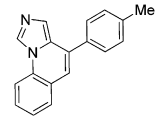
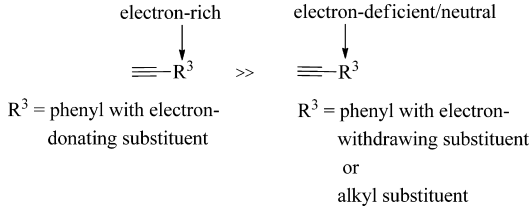
Table 3. Synthesis of Pyrrolo[1,2-*a*]quinolines[a]

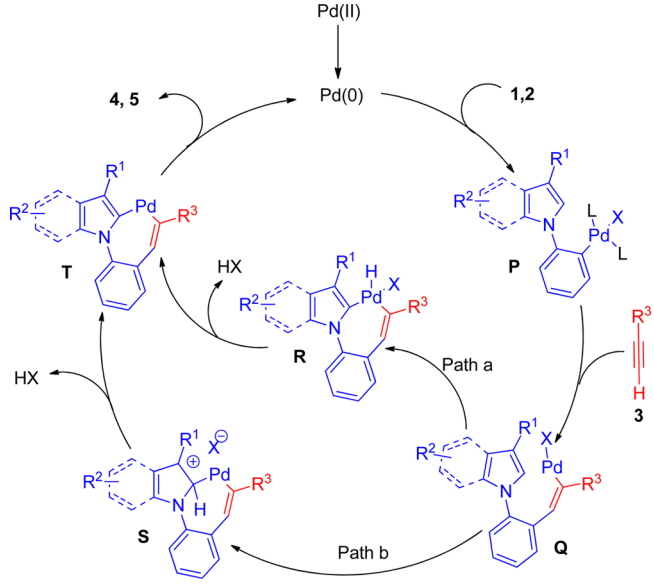
entry	substrate	alkyne	product	time (h)	yield (%)
1.	 **2a**	 **3b**	 **5a**	22	79
2.	**2a**	**3n**	 **5b**	22	82
3.	**2a**	**3d**	 **5c**	22	80
4.	**2a**	**3c**	 **5d**	18	84
5.	**2a**	**3m**	 **5e**	18	82
6.	**2a**	**3e**	 **5f**	25	84
7.	**2a**	**3i**	 **5g**	28	78
8.	**2a**	**3g**	 **5h**	18	83
9.	**2a**	 **3o**	 **5i**	40	44[b]
10.	**2a**	 **3p**	 **5j**	40	41[c]
11.	**2a**	 **3q**	 **5k**	40	31
12.	 **2b**	**3b**	 **5l**	40	[d]

[a]All reactions were performed with 0.5 mmol of the pyrrole/imidazole **2a,b**, $PdCl_2(PPh_3)_2$ (5.0 mol %), LiCl (2.0 equiv) and NaOAc (3.0 equiv) in 2.0 mL of DMA at 120 °C for 18−40 h under inert conditions. [b]20% of uncyclized intermediate was obtained. [c]23% of uncyclized intermediate was obtained. [d]Inseparable complex mixture.

Scheme 6. Substituent Effect on Alkynes



Scheme 7. Probable Mechanism



EXPERIMENTAL SECTION

General Method. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$. Chemical shifts for protons are reported in ppm from tetramethylsilane with the residual $CHCl_3$ resonance as internal reference. Chemical shifts for carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constants in Hertz, and integration. High-resolution mass spectra were recorded on QqTOF mass analyzer. TLC analysis was performed on commercially prepared 60 F_{254} silica gel plates and visualized by either UV irradiation or by staining with I_2. Anhydrous forms of all reagents such as ethyl ether, hexanes, ethyl acetate, DMA, DMF, 3-methyl-1*H*-indole, 1*H*-indole, 1*H*-pyrrole, 5-methoxy-1*H*-indole, 1*H*-imidazole, terminal alkynes, 1-bromo-2-iodobenzene, 1,2-diiodobenzene, Et_3N, palladium salts and copper salts were used directly as obtained commercially unless otherwise noted.

General Procedure for the Synthesis of Indolo[1,2-*a*]-quinolones/pyrrolo[1,2-*a*]quinolines (4a−v and 5a−k). To a solution of 0.5 mmol of 1-(2-bromophenyl)-1*H*-indole/1-(2-bromophenyl)-1*H*-pyrrole in 2.0 mL of DMA was added 2.0 equiv of LiCl followed by 5.0 mol % of $PdCl_2(PPh_3)_2$ and 3.0 equiv of NaOAc. The reaction was flushed with N_2, and 1.2 equiv of terminal alkyne **3** was added to the reaction mixture. The reaction mixture was allowed to stir at 120 °C for 18−40 h under inert conditions. The disappearance of the starting material was determined by TLC. The reaction mixture was then washed with brine solution and was extracted with ethyl acetate (2 × 10 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under a vacuum to yield the crude product. The crude product was purified by column chromatography on silica gel using hexane as the eluent.

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7-Methyl-6-phenylindolo[1,2-*a*]quinoline (4a). The product was obtained as a brown colored viscous oil (116.7 mg, 76% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.0 Hz, 1H), 8.49 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.64−7.63 (m, 1H), 7.42−7.38 (m, 3H), 7.31−7.27 (m, 2H), 7.21−7.16 (m, 3H), 7.10−7.08 (m, 1H), 7.03 (s, 1H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.9, 133.9, 129.6, 129.1, 128.9, 128.2, 127.9, 126.2, 123.7, 122.5, 122.1, 121.7, 119.6, 119.1, 119.0, 115.0, 114.0, 112.3, 110.5, 9.6; HRMS calcd for $C_{23}H_{18}N$ ($[M+H]^+$) 308.1439, found 308.1440.

7-Methyl-6-(*p*-tolyl)indolo[1,2-*a*]quinoline (4b). The product was obtained as yellow needle crystals (125.2 mg, 78% yield): mp 101−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 8.0 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.3 Hz, 1H), 7.50−7.44 (m, 2H), 7.35−7.31 (m, 2H), 7.30−7.26 (m, 2H), 7.23−7.17 (m, 3H), 6.79 (s, 1H), 2.37 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 136.7, 136.4, 133.8, 132.2, 131.2, 129.5, 129.2, 129.0, 128.8, 124.2, 123.8, 122.5, 122.1, 121.2, 119.1, 115.0, 114.0, 21.3, 10.7; HRMS calcd for $C_{24}H_{20}N$ ($[M+H]^+$) 322.1596, found 322.1597.

6-(4-Methoxyphenyl)-7-methylindolo[1,2-*a*]quinoline (4c). The product was obtained as yellow needles (134.8 mg, 80% yield): 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), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 136.4, 133.5, 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 calcd for $C_{24}H_{20}NO$ ($[M+H]^+$) 338.1545, found 338.1546.

6-(4-Butylphenyl)-7-methylindolo[1,2-*a*]quinoline (4d). The product was obtained as yellow needles (139.8 mg, 77% yield): mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 8.8 Hz, 1H), 8.38 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 7.3 Hz, 1H), 7.50−7.43 (m, 2H), 7.37−7.26 (m, 4H), 7.19−7.14 (m, 3H), 6.80 (s, 1H), 2.62 (t, J = 7.2 Hz, 2H), 1.84 (s, 3H), 1.61−1.55 (m, 2H), 1.37−1.28 (m, 2H), 0.89 (t, J = 7.0 Hz, 3H); ^{13} C NMR (100 MHz, $CDCl_3$) δ 142.5, 136.9, 136.4, 133.9, 132.2, 131.9, 131.3, 129.0, 128.4, 128.1, 124.2, 123.8, 122.5, 122.1, 121.2, 119.1, 115.0, 114.0, 105.8, 35.4, 33.7, 22.4, 14.0, 10.6; HRMS calcd for $C_{27}H_{26}N$ ($[M+H]^+$) 364.2065, found 364.2066.

6-([1,1′-Biphenyl]-4-yl)-7-methylindolo[1,2-*a*]quinoline (4e). The product was obtained as yellow needles (145.6 mg, 76% yield): mp 82−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 8.8 Hz, 1H), 8.58 (d, J = 8.7 Hz, 1H), 8.00−7.95 (m, 2H), 7.69 (s, 1H), 7.35−7.34 (m, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 6.89−6.86 (m, 2H), 6.82−6.77 (m, 4H), 6.69 (d, J = 8.1 Hz, 1H), 6.62−6.56 (m, 2H), 1.77 (s, 3H); ^{13} C NMR (100 MHz, $CDCl_3$) δ 140.0, 136.5, 135.3, 131.9, 130.7, 130.1, 129.5, 128.5, 128.3, 127.8, 127.5, 127.1, 126.1, 125.5, 125.2, 125.1, 124.2, 122.9, 121.3, 121.0, 113.1, 111.9, 111.4, 103.2, 9.9; HRMS calcd for $C_{29}H_{22}N$ ($[M+H]^+$) 384.1752, found 384.1753.

6-(6-Methoxynaphthalen-2-yl)-7-methylindolo[1,2-*a*]-quinoline (4f). The product was obtained as yellow needles (151.4 mg, 78% yield): mp 115−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 8.8 Hz, 1H), 8.58 (d, J = 8.8 Hz, 1H), 8.34−8.33 (m, 1H), 8.23 (d, J = 8.0 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 (s, 1H), 7.65−7.60 (m, 1H), 7.45 (t, J = 7.9 Hz, 1H), 7.39 (d, J = 1.5 Hz, 1H), 7.36 (d, J = 2.2 Hz, 1H), 7.18 (dd, J = 3.0, 8.8 Hz, 1H), 7.00 (s, 1H), 6.87 (s, 1H), 3.88 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ155.1, 138.6, 137.0, 135.4, 134.0, 133.6, 132.1, 131.4, 129.6, 129.3, 128.2, 127.7, 126.9, 124.9, 124.1, 122.1, 120.7, 119.0, 115.1, 114.4, 113.2, 110.1, 106.0, 104.9, 55.3, 10.7; HRMS calcd for $C_{28}H_{22}NO$ ($[M+H]^+$) 388.1701, found 388.1702.

7-Methyl-6-(thiophen-3-yl)indolo[1,2-*a*]quinoline (4g). The product was obtained as a yellow colored viscous oil (125.6 mg, 80% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60−8.56 (m, 2H), 8.07 (d, J = 8.2 Hz, 1H), 7.79−7.75 (m, 2H), 7.71−7.67 (m, 1H), 7.57−7.56 (m, 1H), 7.54−7.51 (m, 1H), 7.47−7.35 (m, 2H), 7.14−7.11 (m,1H), 7.00 (s, 1H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ142.8, 135.4, 135.1, 134.0, 131.1, 130.5, 130.2, 129.8, 129.2, 126.6, 125.4, 124.0, 123.7, 123.3, 121.9, 119.5, 115.3, 114.4, 110.1, 106.0, 9.0; HRMS calcd for $C_{21}H_{16}NS$ ($[M+H]^+$) 314.1003, found 314.1004.

6-(3-Methoxyphenyl)-7-methylindolo[1,2-*a*]quinoline (4h). The product was obtained as yellow semisolid (118.0 mg, 70% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 8.0 Hz, 1H), 8.59 (d, J = 8.0 Hz, 1H), 8.35−8.34 (m, 1H), 8.24 (d, J = 7.3 Hz, 1H), 8.07−8.04 (m, 1H), 7.82 (s, 1H), 7.66−7.62 (m, 1H), 7.49−7.42 (m, 2H), 7.22 (s, 1H), 7.05 (s, 1H), 6.90−6.88 (m, 2H), 3.78 (s, 3H), 1.83 (s, 3H); ^{13} C NMR (100 MHz, $CDCl_3$) δ 159.2, 143.0, 138.4, 135.4, 133.6, 132.0, 131.0, 129.7, 129.3, 127.8, 126.3, 124.9, 123.9, 121.3, 118.9, 115.0, 114.8, 114.3, 113.7, 113.2, 109.8, 104.7, 55.1, 9.7; HRMS calcd for $C_{24}H_{20}NO$ ($[M+H]^+$) 338.1545, found 338.1545.

7-Methyl-6-(*m*-tolyl)indolo[1,2-*a*]quinoline (4i). The product was obtained as a yellow semisolid (118.8 mg, 74% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 8.0 Hz, 1H), 8.67 (d, J = 8.0 Hz, 1H), 835−8.33 (m, 1H), 8.24 (d, J = 7.4 Hz, 1H), 8.05 (dd, J = 1.5, 8.1 Hz, 1H), 7.83 (s, 1H), 7.64 (dt, J = 1.5, 7.4 Hz, 1H), 7.49−7.44 (m, 1H), 7.41 (t, J = 7.3 Hz, 1H), 7.28 (d, J = 7.3 Hz, 1H), 7.14−7.10 (m, 2H), 7.00 (s, 1H), 2.37 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 138.6, 137.6, 135.2, 133.6, 132.0, 131.2, 129.5, 129.2, 128.9, 128.4, 126.2, 124.9, 124.0, 121.5, 117.7, 115.0, 114.3, 113.1, 112.2, 107.9, 104.8, 21.1, 9.4; HRMS calcd for $C_{24}H_{20}N$ ($[M+H]^+$) 322.1596, found 322.1598.

7-Methyl-6-(*o*-tolyl)indolo[1,2-*a*]quinoline (4j). The product was obtained as a yellow semisolid (117.2 mg, 73% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.0 Hz, 1H), 8.49 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.65−7.63 (m, 1H), 7.42−7.38 (m, 3H), 7.31−7.27 (m, 2H), 7.20−7.16 (m, 2H), 7.10−7.08 (m, 1H), 7.03 (s, 1H), 2.41 (s, 3H), 1.66 (s, 3H); ^{13} C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.9, 133.9, 132.3, 129.6, 129.1, 128.8, 128.4, 128.2, 128.0, 126.2, 123.7, 122.5, 122.2, 121.7, 119.6, 119.1, 119.0, 115.0, 114.0, 112.3, 110.5, 21.6, 9.7; HRMS calcd for $C_{24}H_{20}N$ ($[M+H]^+$) 322.1596, found 322.1597.

6-Cyclopropyl-7-methylindolo[1,2-*a*]quinoline (4k). The product was obtained as a yellow semisolid (51.5 mg, 38% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 7.2 Hz, 1H), 8.47 (d, J = 8.7 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.86−7.78 (m, 1H), 7.51−7.47 (m, 2H), 7.41−7.36 (m, 2H), 6.78 (s, 1H), 2.50 (s, 3H), 1.58 −1.55 (m, 1H), 1.05−1.02 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.3, 137.0, 133.9, 130.9, 129.5, 128.2, 127.8, 125.8, 123.9, 121.8, 121.1, 119.1, 118.8, 115.0, 113.9, 110.3, 22.7, 14.1, 10.5; HRMS calcd for $C_{20}H_{18}N$ ($[M+H]^+$) 272.1439, found 272.1440.

6-Cyclohexyl-7-methylindolo[1,2-*a*]quinoline (4l). The product was obtained as a yellow semisolid (62.6 mg, 40% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.0 Hz, 1H), 8.44 (d, J = 7.4 Hz, 1H), 7.86−7.84 (m, 1H), 7.58−7.55 (m, 2H), 7.51−7.47 (m, 2H), 7.42−7.37 (m, 1H), 6.92 (s, 1H), 3.31−3.26 (m, 1H), 2.58 (s, 3H), 2.13−2.10 (m, 2H), 1.96−1.93 (m, 2H), 1.88−1.84 (m, 2H), 1.66−1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 139.0, 137.3, 133.4, 132.1, 131.3, 129.5, 127.4, 126.4, 125.8, 125.4, 123.9, 121.1, 115.0, 114.0, 110.3, 52.2, 29.7, 26.2, 22.7, 10.9; HRMS calcd for $C_{23}H_{24}N$ ($[M+H]^+$) 314.1909, found 314.1909.

6-(*p*-Tolyl)indolo[1,2-*a*]quinoline (4m). The product was obtained as a yellow semisolid (107.8 mg, 70% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61−8.57 (m, 2H), 8.09 (dd, J = 1.5, 8.1 Hz, 1H), 7.76 (d, J = 7.3 Hz, 1H), 7.72−7.67 (m, 1H), 7.48−7.42 (m, 2H), 7.40−7.35 (m, 3H), 7.18 (d, J = 8.1 Hz, 2H), 7.00 (s, 1H), 6.31 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 139.7, 137.6, 135.1, 134.0, 131.2, 131.1, 130.5, 130.1, 129.4, 129.2, 124.1, 123.7, 123.3, 121.9, 119.4, 115.3, 114.4, 106.0, 104.1, 21.0; HRMS calcd for $C_{23}H_{18}N$ ($[M+H]^+$) 308.1439, found 308.1440.

6-(4-Methoxyphenyl)indolo[1,2-*a*]quinoline (4n). The product was obtained as a brown color oil (116.3 mg, 72% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68−8.58 (m, 2H), 8.35−8.34 (m, 1H), 8.24 (d, J = 7.3 Hz, 1H), 8.06 (dd, J = 1.5, 8.1 Hz, 1H), 7.64−7.62 (m, 2H), 7.49−7.42 (m, 3H), 7.06−7.03 (m, 1H), 6.90−6.88 (m, 2H), 6.51 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 138.6, 137.0, 134.0, 133.6, 132.1, 131.4, 129.7, 129.3, 128.2, 127.9, 127.7, 126.9, 124.9, 124.1, 118.9, 114.4, 113.2, 106.0, 104.9, 55.3; HRMS calcd for $C_{23}H_{18}NO$ ($[M+H]^+$) 324.1388, found 324.1390.

4-(Indolo[1,2-*a*]quinolin-6-yl)-*N*,*N*-dimethylaniline (4o). The product was obtained as yellow needles (121.0 mg, 72% yield): mp 73−75 °C; ^{1}H NMR (400 MHz, $CHCl_3$) δ 8.68 (d, J = 8.2 Hz, 1H), 8.63 (d, J = 8.7 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.76−7.71 (m, 1H), 7.49−7.41 (m, 2H), 7.37−7.33 (m, 1H), 7.21 (d, J = 8.6 Hz, 2H), 7.04 (s, 1H), 6.87 (d, J = 8.7 Hz, 2H), 6.29 (s, 1H),

2.99 (s, 6H); ^{13}C NMR (100 MHz, $CHCl_3$) δ 150.0, 139.5, 136.8, 134.8, 134.2, 132.3, 130.0, 129.9, 129.5, 129.3, 127.2, 124.5, 123.9, 122.7, 122.3, 121.5, 118.6, 115.4, 114.6, 111.8, 99.3, 40.1; HRMS calcd for $C_{24}H_{21}N_2$ ([M + H]$^+$) 337.1705, found 337.1706.

6-(*m*-Tolyl)indolo[1,2-*a*]quinoline (4p). The product was obtained as a brown color oil (104.4 mg, 68% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.01 (m, 2H), 7.62−7.58 (m, 2H), 7.39−7.35 (m, 2H), 7.28−7.25 (m, 1H), 7.18−7.10 (m, 4H), 6.96−6.94 (m, 2H), 6.63 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.9, 133.8, 129.8, 129.6, 129.1, 128.8, 128.4, 128.2, 128.0, 126.2, 123.7, 122.5, 122.2, 121.7, 119.6, 119.1, 119.0, 114.0, 112.3, 110.5, 105.7, 21.5 ; HRMS calcd for $C_{23}H_{18}N$ ([M + H]$^+$) 308.1439, found 308.1439.

6-(Thiophen-3-yl)indolo[1,2-*a*]quinoline (4q). The product was obtained as a brown yellow oil (109.2 mg, 73% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.0 Hz, 1H), 8.52 (d, J = 7.2 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.65−7.63 (m, 1H), 7.42−7.38 (m, 2H), 7.31−7.27 (m, 2H), 7.21−7.16 (m, 2H), 7.10−7.08 (m, 1H), 7.02 (s, 1H), 6.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.9, 133.9, 129.6, 129.1, 128.8, 128.3, 128.2, 126.2, 123.7, 122.5, 121.7, 119.6, 119.0, 115.0, 114.0, 112.3, 110.5, 102.1; HRMS calcd for $C_{20}H_{14}NS$ ([M + H]$^+$) 300.0847, found 300.0849.

9-Methoxy-6-phenylindolo[1,2-*a*]quinoline (4r). The product was obtained as a brown color oil (119.5 mg, 74% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.82 (m, 1H), 7.74−7.72 (m, 2H), 7.65−7.59 (m, 5H), 7.52 (m, 1H), 7.45−7.36 (m, 2H), 7.32−7.24 (m, 1H), 6.97 (s, 1H), 6.61 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 140.6, 138.6, 133.3, 131.3, 131.0, 129.6, 129.0, 128.9, 128.8, 127.1, 126.9, 126.7, 123.7, 120.7, 119.6, 112.0, 111.8, 108.6, 102.6, 102.4, 55.9; HRMS calcd for $C_{23}H_{18}NO$ ([M + H]$^+$) 324.1388, found 324.1389.

9-Methoxy-6-(*p*-tolyl)indolo[1,2-*a*]quinoline (4s). The product was obtained as a brown color oil (124.7 mg, 74% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 1H), 7.48−7.42 (m, 1H), 7.40−7.37 (m, 2H), 7.34−7.29 (m, 2H), 7.28−7.25 (m, 1H), 7,18 (d, J = 8.7 Hz, 1H), 7.16−7.12 (m, 1H), 7.01−6.99 (m, 1H), 6.81 (s, 1H), 6.79−6.75 (m, 1H), 6.54 (s, 1H), 3.79 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 140.6, 138.6, 133.3, 131.2, 129.6, 129.0, 128.9, 128.8, 127.1, 126.9, 126.7, 120.7, 119.6, 114.1, 112.0, 111.8, 108.6, 102.6, 102.4, 55.9, 21.5; HRMS calcd for $C_{24}H_{20}NO$ ([M + H]$^+$) 338.1545, found 338.1544.

9-Methoxy-6-(4-methoxyphenyl)indolo[1,2-*a*]quinoline (4t). The product was obtained as a colorless oil (137.7 mg, 78% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61−8.57 (m, 2H), 8.09 (dd, J = 1.5, 8.1 Hz, 1H), 7.76 (d, J = 7.3 Hz, 1H), 7.72−7.67 (m, 1H), 7.48−7.42 (m, 2H), 7.40−7.35 (m, 2H), 7.19−7.17(m, 2H), 6.97 (s, 1H), 6.45 (s, 1H), 3.88 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ159.3, 155.4, 140.5, 139.7, 137.6, 135.1, 134.0, 131.2, 130.5, 130.1, 129.2, 124.1, 123.7, 123.3, 121.9, 119.5, 115.3, 114.4, 106.0, 101.6, 55.6, 55.0; HRMS calcd for $C_{24}H_{20}NO_2$ ([M + H]$^+$) 354.1494, found 354.1497.

4-(9-Methoxyindolo[1,2-*a*]quinolin-6-yl)-*N*,*N*-dimethylaniline (4u). The product was obtained as a yellow semisolid (144.6 mg, 79% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 1.5, 8.1 Hz, 1H), 7.47−7.41 (m, 3H), 7.35 (dt, J = 1.5, 7.3 Hz, 1H), 7.26 (d, J = 8.7 Hz, 1H), 7.16−7.14 (m, 3H), 7.00 (s, 1H), 6.85 (dd, J = 2.2, 8.8 Hz, 1H), 6.82−6.80 (m, 1H), 6.60 (s, 1H), 3.87 (s, 3H), 3.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 140.7, 138.7, 136.5, 133.1, 131.7, 129.5, 129.6, 129.2, 128.97, 128.90, 126.9, 126.7, 125.2, 121.7, 120.5, 116.7, 112.0, 111.8, 102.5, 55.9, 40.3; HRMS calcd for $C_{25}H_{23}N_2O$ ([M + H]$^+$) 367.1810, found 367.1811.

9-Methoxy-6-(thiophen-3-yl)indolo[1,2-*a*]quinoline (4v). The product was obtained as a yellow semisolid (131.6 mg, 80% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.8 Hz, 1H), 7.51 (s, 1H), 7.49−7.44 (m, 3H), 7.34−7.32 (m, 2H), 7.24−7.23 (m, 1H), 7.18−7.17 (m, 1H), 7.03 (d, J = 8.8 Hz, 1H), 6.88 (dd, J = 2.2, 8.8 Hz, 1H), 6.65 (s, 1H), 3.89 (s, 3H); ^{13}C NMR 100 MHz, $CDCl_3$) δ 154.5, 138.5, 133.9, 131.9, 129.6, 129.5, 129.3, 129.2, 128.7, 128.2, 126.2, 123.9, 123.5, 121.8, 115.8, 112.4, 111.35, 111.28, 102.7, 102.5, 55.8; HRMS calcd for $C_{21}H_{16}NOS$ ([M + H]$^+$) 330.0953, found 330.0954.

4-(*p*-Tolyl)pyrrolo[1,2-*a*]quinoline (5a). The product was obtained as a yellow semisolid (101.5 mg, 79% yield): ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.87 (m, 2H), 7.66−7.64 (m, 1H), 7.60 (d, J = 8.1 Hz, 2H), 7.50−7.45 (m, 1H), 7.32−7.30 (m, 1H), 7.29−7.27 (m, 2H), 6.96 (s, 1H), 6.79−6.78 (m, 1H), 6.61−6.60 (m, 1H), 2.43 (s, 3H); ^{13} C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.1, 132.64, 132.59, 130.9, 129.2, 128.6, 128.2, 127.4, 124.3, 123.6, 117.7, 114.0, 112.7, 112.5, 103.3, 21.3; HRMS calcd for $C_{19}H_{16}N$ ([M + H]$^+$) 258.1283, found 258.1284.

4-(4-(*tert*-Butyl)phenyl)pyrrolo[1,2-*a*]quinoline (5b). The product was obtained as a yellow semisolid (122.6 mg, 82% yield): ^{1}H NMR (400 MHz, $CDCl_3$) 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), 7.00 (s, 1H), 6.68 (t, J = 3.7 Hz, 1H), 5.89−5.88 (m, 1H), 1.38 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ142.0, 140.0, 133.6, 132.3, 130.2, 128.3, 126.0, 124.7, 123.2, 121.6, 118.7, 116.9, 111.7, 110.4, 108.7, 103.0, 34.2, 30.5; HRMS calcd for $C_{22}H_{22}N$ ([M + H]$^+$) 300.1752, found 300.1752.

4-(4-Butylphenyl)pyrrolo[1,2-*a*]quinoline (5c). The product was obtained as a yellow semisolid (119.6 mg, 80% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34−8.33 (m, 1H), 8.23 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.33 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 7.00 (s, 1H), 6.68 (t, J = 3.7 Hz, 1H), 5.88−5.87 (m, 1H), 2.66 (t, J = 8.2 Hz, 2H), 1.6−1.58 (m, 2H), 1.40−1.30 (m, 2H), 0.91 (t, J = 8.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 139.1, 138.5, 133.6, 131.9, 131.3, 129.1, 128.9, 128.2, 124.8, 124.0, 120.0, 114.9, 114.2, 113.0, 104.7, 34.6, 33.0, 21.7, 13.8; HRMS calcd for $C_{22}H_{22}N$ ([M + H]$^+$) 300.1752, found 300.1752.

4-(4-Methoxyphenyl)pyrrolo[1,2-*a*]quinoline (5d). The product was obtained as yellow needles (115.1 mg, 84% yield): 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), 6.87 (s, 1H), 6.72 (t, J = 3.3 Hz, 1H), 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 calcd for $C_{19}H_{16}NO$ ([M + H]$^+$) 274.1232, found 274.1233.

***N*,*N*-Dimethyl-4-(pyrrolo[1,2-*a*]quinolin-4-yl)aniline (5e).** The product was obtained as a yellow semisolid (117.3 mg, 82% yield): ^{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), 7.53 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.28−7.25 (m, 2H), 7.01 (s, 1H), 6.83 (d, J = 8.8 Hz, 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, $CDCl_3$) δ 150.2, 141.5, 133.0, 132.6, 130.2, 128.2, 126.1, 124.7, 121.7, 118.9, 116.5, 111.7, 109.7, 108.9, 105.9, 40.1; HRMS calcd for $C_{20}H_{19}N_2$ ([M + H]$^+$) 287.1548, found 287.1549.

4-([1,1′-Biphenyl]-4-yl)pyrrolo[1,2-*a*]quinoline (5f). The product was obtained as a yellow semisolid (134.0 mg, 84% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 2.2 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.07 (dd, J = 1.5, 8.1 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 6.6 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.51−7.48 (m, 3H), 7.44−7.37 (m, 3H), 6.97 (s, 1H), 6.71 (t, J = 3.3 Hz, 1H), 5.95 (dd, J = 1.5, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.9, 139.5, 138.2, 133.7, 132.1, 131.2, 129.9, 129.4, 129.1, 127.3, 126.8, 125.0, 124.0, 120.0, 115.1, 114.4, 113.2, 104.8 HRMS calcd for $C_{24}H_{18}N$ ([M + H]$^+$) 320.1439, found 320.1440.

4-(*m*-Tolyl)pyrrolo[1,2-*a*]quinoline (5g). The product was obtained as a yellow oil (100.2 mg, 78% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35−8.33 (m, 1H), 8.24 (d, J = 7.4 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 8.7 Hz, 1H), 7.41 (t, J = 7.3 Hz, 1H), 7.28 (d, J = 7.3 Hz, 1H), 7.14−7.10 (m, 2H), 6.92 (s, 1H), 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, $CDCl_3$) 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, 120.1, 118.1, 110.2, 109.2, 108.3, 103.8, 21.2; HRMS calcd for $C_{19}H_{16}N$ ([M + H]$^+$) 258.1283, found 258.1282.

4-(Thiophen-3-yl)pyrrolo[1,2-*a*]quinoline (5h). The product was obtained as a yellow oil (103.3 mg, 83% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35−8.34 (m, 1H), 8.24 (d, J = 8.1 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.72−7.70 (m, 1H), 7.68−7.66 (m, 1H), 7.65−7.62 (m, 1H), 7.47 (t, J = 7.3 Hz, 1H), 7.21−7.19 (m, 1H), 7.01 (s,1H), 6.71 (t, J = 7.3 Hz, 1H), 6.04−6.03 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 141.9, 133.4, 129.6, 129.1, 128.9, 127.4, 126.2, 125.3, 124.9, 122.0, 121.7, 118.0, 111.0,

109.2, 108.1, 104.2; HRMS calcd for $C_{16}H_{12}NS$ ($[M + H]^+$) 250.0690, found 250.0689.

4-Cyclopentylpyrrolo[1,2-*a*]quinoline (5i). The product was obtained as a yellow oil (51.7 mg, 44% yield): ^{1}H NMR (400 MHz, $CDCl_3$) 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), 7.01 (s, 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, $CDCl_3$) δ 138.8, 134.2, 131.9, 128.6, 127.5, 124.7, 118.0, 114.8, 113.7, 112.7, 103.1, 52.0, 30.0, 26.7; HRMS calcd for $C_{17}H_{18}N$ ($[M + H]^+$) 236.1439, found 236.1440.

4-Butylpyrrolo[1,2-*a*]quinoline (5j). The product was obtained as a yellow oil (45.7 mg, 41% yield): ^{1}H NMR (400 MHz, $CDCl_3$) 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), 7.04 (s, 1H), 6.90 (d, J = 3.6 Hz, 1H), 6.77 (t, J = 2.9 Hz, 1H), 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 141.8, 138.2, 133.8, 128.4, 126.1, 124.8, 121.5, 118.8, 115.7, 111.5, 110.8, 108.9, 40.2, 30.4, 21.9, 13.6; HRMS calcd for $C_{16}H_{18}N$ ($[M + H]^+$) 224.1439, found 224.1439.

4-(4-(Trifluoromethyl)phenyl)pyrrolo[1,2-*a*]quinoline (5k). The product was obtained as a yellow semisolid (48.3 mg, 31% yield): ^{1}H NMR (400 MHz, $CDCl_3$) 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), 7.02 (s, 1H), 6.68 (t, J = 3.7 Hz, 1H), 5.89−5.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ139.1, 138.7, 137.4, 133.5, 132.1, 131.3, 130.4, 129.2, 129.0, 124.9, 124.0, 120.3, 115.1, 114.2, 113.2, 104.7; HRMS calcd for $C_{19}H_{13}F_3N$ ($[M + H]^+$) 312.1000, found 312.1002.

5-Nitro-1-(2-(*p*-tolylethynyl)phenyl)-1*H*-indole (6w). The product was obtained as a yellow semisolid (74.0 mg, 42% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55−8.54 (m, 1H), 8.09−8.07 (m, 1H), 7.60−7.58 (m, 1H), 7.48−7.44 (m, 1H), 7.40−7.33 (m, 1H), 7.29−7.25 (m, 1H), 7.19−7.17 (m, 2H), 7.15−7.12 (m, 1H), 7.01−6.99 (m, 1H), 6.81−6.75 (m, 2H), 6.54−6.53 (m, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ140.6, 138.6, 133.3, 131.3, 129.6, 128.9, 128.8, 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, 21.5; HRMS calcd for $C_{23}H_{17}N_2O_2$ ($[M + H]^+$) 353.1290, found 353.1293.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C NMR spectra and HRMS. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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