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Electrophilic Cyclization of Aryl Propargylic Alcohols: Synthesis of Dihalogenated 6,9-Dihydropyrido[1,2-*a*]indoles via a Cascade Iodocyclization

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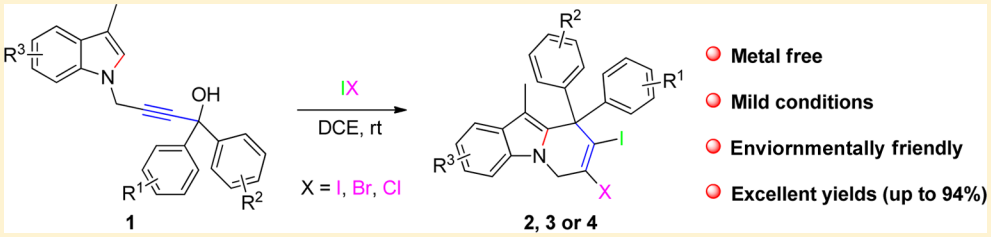
Supporting Information



ABSTRACT: A strategy for the synthesis of 6,9-dihydropyrido[1,2-*a*]indoles through a cascade iodocyclization of 4-(3-methyl-1*H*-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol derivatives is presented. This reaction was conducted under very mild conditions and in a short time. The reactions are metal-free, are environmentally friendly and give up to 94% yield. Moreover, the obtained halides allow functional group diversification by palladium-catalyzed coupling reactions, which could act as potential intermediates for the synthesis of valuable compounds.

INTRODUCTION

Nitrogen-containing heterocycles are ubiquitous structural units in significant natural products and biologically active molecules.[1] Synthesis of nitrogen-containing heterocycles has been the focus of considerable attention for a long time. Meanwhile, a variety of well-established methods have been reported.[2] Among multifarious N-heterocycles, indoles are well-known to exert biological activity in many medicinally important ingredients.[3] Furthermore, the pyridoindoles have unique nitrogen-containing tricyclic structures which are derived from indoles. The pyridoindoles are important heterocycles which essentially contribute to the biological activities.[4] As a result of the remarkable pharmacological activities, much attention has been paid to the exploration of mild and efficient preparative protocols for building pyridoindoles.[5] In recent years, electrophilic cyclization, especially iodocyclization, has been a prominent research objective in organic chemistry.[6] Many important carbocycles and heterocycles have been produced on the basis of the efficient iodocyclizations.[7] What is more, the iodocyclizations are considered to be mild, metal-free, and environmentally friendly.[8] Although great achievements have been made in iodocyclization, few examples of sequential cascade iodocyclizations to form pyridoindoles have been reported until now. Therefore, the search for alternative methods for the construction of 6,9-dihydropyrido[1,2-*a*]-indoles based on iodocyclization is indeed desirable.

Recently, methods involving iodonium-induced activation of propargylic alcohol substrates have offered the opportunity to construct diiodinated carbocycles by Yamamoto,[9] Wang,[10] and our group.[11] This reaction is generally believed to proceed through a cascade process. Initial activation of the propargyl hydroxyl group of **A** with a Lewis acidic iodine leads to the propargyl carbocation intermediate **B**, which could resonate with allene carbocation **C**. The intermediate **C** is reacted with an iodide anion to give **D**, which can be activated by an iodide cation. A subsequent intramolecular Friedel−Crafts type reaction of the aromatic ring with the activated allene forms the product **E** (Scheme 1a). Encouraged by these achievements and continuing our interest in the electrophilic cyclization of alkynols, we envisioned that the substrates **1** containing an indole moiety could undergo an identical isomerization process in the presence of electrophilic reagents and then cyclize to afford dihalogenated 6,9-dihydropyrido[1,2-*a*]indoles (Scheme 1b). Herein, we report an effective method for the synthesis of a variety of dihalogenated 6,9-dihydropyrido[1,2-*a*]indoles via sequential cascade iodocyclization under mild reaction conditions.

RESULTS AND DISCUSSION

At the onset of our investigation, we examined the reaction of 4-(3-methyl-1*H*-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol (**1a**) with 1.0 equiv of I_2 in 1,2-dichloroethane (DCE) at room

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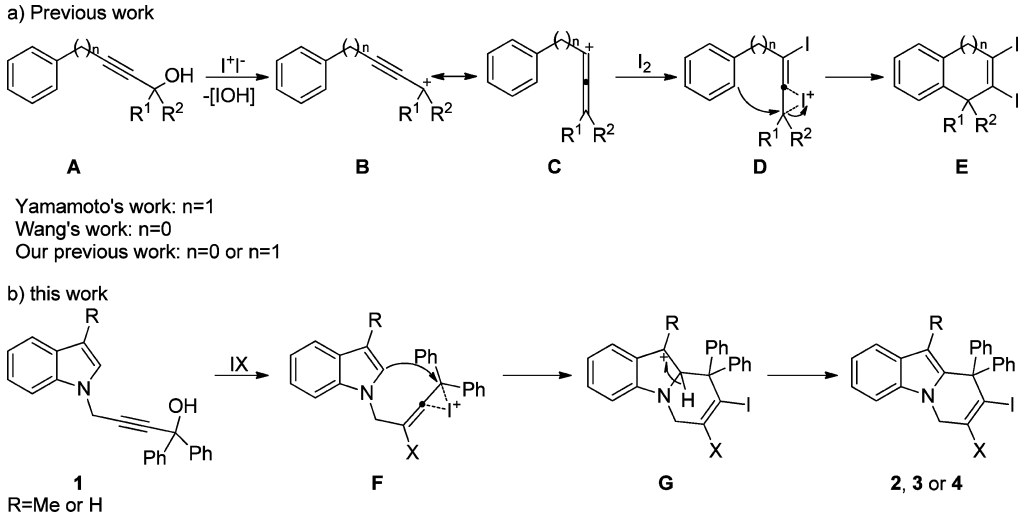
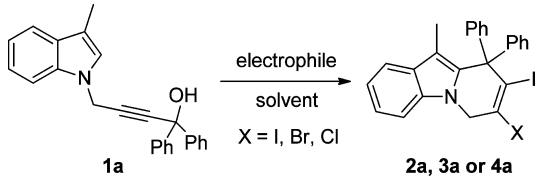
Scheme 1. Iodine-Promoted Cascade Carbocyclization



temperature. The desired product 7,8-diiodo-10-methyl-9,9-diphenyl-6,9-dihydropyrido[1,2-*a*]indole (**2a**) was isolated in 88% yield after 10 min (Table 1, entry 1). An increase in the amount of I_2 to 1.2 equiv afforded **2a** in 94% yield. The yield of **2a** equaled 94% on increasing the amount of I_2 to 1.5 equiv. After screening a series of solvents such as CH_2Cl_2, CH_3CN, CH_3NO_2, THF, Et_2O, CH_3COCH_3, MeOH, and toluene, we found that DCE was better than the other solvents (entries 2 and 4−11). However, an unsatisfactory yield of **2a** was obtained when the reaction was performed at 0 °C (entry 12). In addition, increasing the temperature to 40 °C could not give a superior yield (entry 13). The reactions of **1a** with IBr (1.2 equiv) gave the expected product 7-bromo-8-iodo-10-methyl-9,9-diphenyl-6,9-dihydropyrido[1,2-*a*]indole (**3a**) in 83% yield (entry 14). The desired product 7-chloro-8-iodo-10-methyl-9,9-diphenyl-6,9-dihydropyrido[1,2-*a*]indole (**4a**) was obtained in the presence of ICl (1.2 equiv) (entry 15). From the series of detailed investigations mentioned above, the combination of 1.0 equiv of **1a** and 1.2 equiv of electrophile in DCE at room temperature for 10 min was determined as the optimum reaction conditions.

Table 1. Optimization of Reaction Conditions for the Formation of 2a−4a with Different Electrophiles[a]



entry	solvent	electrophile (amt (equiv))	yield (%)[b]
1	DCE	I_2 (1.0)	88
2	**DCE**	**I_2 (1.2)**	**94**
3	DCE	I_2 (1.5)	94
4	CH_2Cl_2	I_2 (1.2)	92
5	CH_3CN	I_2 (1.2)	88
6	CH_3NO_2	I_2 (1.2)	83
7	THF	I_2 (1.2)	69
8	Et_2O	I_2 (1.2)	65
9	acetone	I_2 (1.2)	84
10	MeOH	I_2 (1.2)	80
11	toluene	I_2 (1.2)	88
12	DCE	I_2 (1.2)	83[c]
13	DCE	I_2 (1.2)	92[d]
14	DCE	IBr (1.2)	83
15	DCE	ICl (1.2)	81

[a]All reactions were run under the following conditions, unless otherwise indicated: 0.20 mmol of **1a** and 1.2 equiv of electrophile in 4 mL of solvent were stirred at room temperature for 10 min. [b]Yields of isolated products. [c]The reaction was run at 0 °C. [d]The reaction was run at 40 °C.

After having established the optimized conditions for the present reaction, various 4-(3-methyl-1*H*-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol derivatives were subjected to the above conditions, as summarized in Table 2. The structure of the representative product **2a** was determined by X-ray crystallographic analysis. The reactions of substrates **1b,c** bearing two electron-donating groups (R^1 and R^2) at the para positions of the aromatic rings resulted in the corresponding products **2b,c** in excellent yields. The yields of **2d,e** decreased with an increase in electronegativity on the substituent R^1 and R^2 groups. Subsequently, compounds **1f−n** with electron-donating or electron-withdrawing substituents (R^2) on different positions of the aromatic ring were designed. The corresponding products **2f−n** were obtained in good yields. In the meantime, the reactions also worked well with the substrates **1o,p** which had two substituents on the same aryl group, furnishing the expected products **2o,p** in good yields. Afterward, the substrate **1q** having huge steric hindrance with a 1-naphthyl group was attempted and afforded the product **2q** in 71% yield. It is noteworthy that the corresponding product **2r** was obtained in good yield when the substrate had a cyclic substituent. Substrate **1s** with both strongly electron rich and electron withdrawing substituent groups worked well and gave the product **2s** in a surprisingly high yield of 92%. The transformation proceeded smoothly for the substrate **1t** with a heterocyclic 2-thienyl group. Although the substrate **1y** with a secondary alcohol failed to afford the corresponding product **2y**, products **2u−x** with alkyl groups were obtained in good yields. This might be attributed to the fact that one aryl group could not adequately stabilize the allene carbocation generated by the propargylic alcohol substrate.[12] Substrate **1z** with a phenyl group at the 3-position of indole also worked well and afforded product **2z** in 86% yield. It is noteworthy that when

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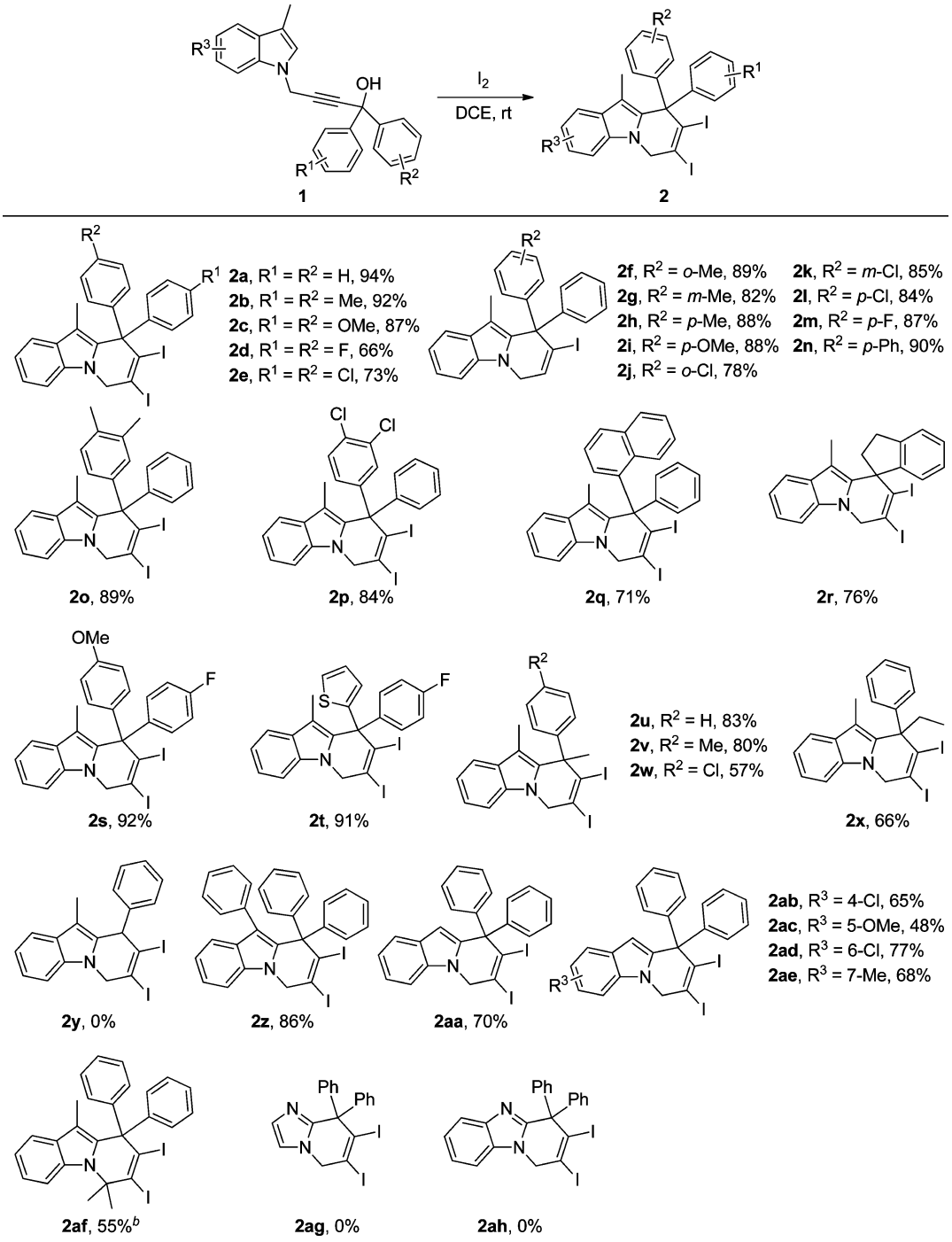
Table 2. Electrophilic Iodocyclization for the Formation of 2[a]



[a]All reactions were run under the following conditions, unless otherwise indicated: 0.20 mmol of **1** and 1.2 equiv of I_2 in 4 mL of DCE were stirred at room temperature for 10 min. [b]The reaction was run for 30 min. Yields are given for isolated products.

the methyl group was absent from the 3-position of the indole ring, the yield of **2aa** was significantly reduced. This might be due to the presence of a methyl group at the 3-position of indole, which activated the indole ring system, facilitating the intramolecular cyclization.[13] Meanwhile, substrates with substituents on different positions of the indole rings gave the products **2ab**−**2ae** in moderate to good yields. Due to the fact that the electron cloud of indole could be influenced by the substituents on it, the subsequent cyclization process was potentially affected. As a strongly electron donating group, a methoxy group showed a more remarkable influence on the product yield. In particular, the substrate **1af** with two methyl groups instead of hydrogens on the methylene was attempted under the standard conditions. In this reaction, more reaction time was needed for a full conversion of the substrate. A relatively lower yield was obtained due to steric effects. Neither the substrate **1ag** with imidazole nor substrate **1af** with benzimidazole gave the desired products, in line with our expectation.

To explore the scope of the iodine-containing electrophiles and the mechanism of this electrophilic cyclization, the reactions of 4-(3-methyl-1*H*-indol-1-yl)-1,1-diphenylbut-2-yn-

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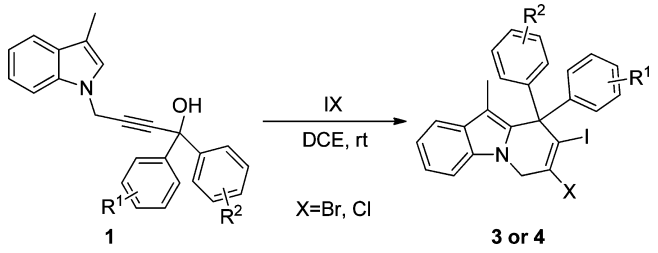
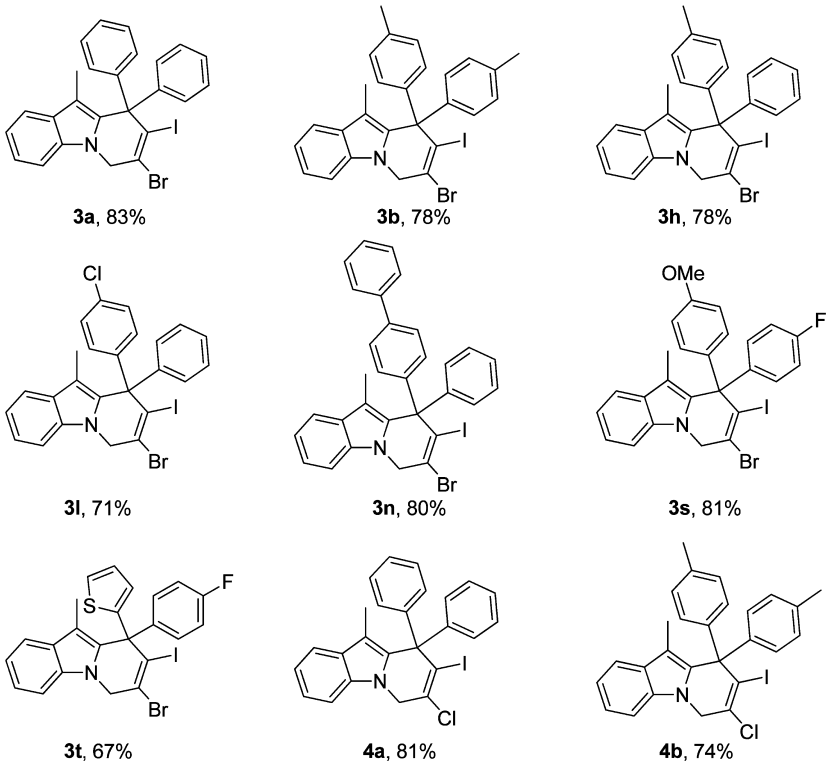
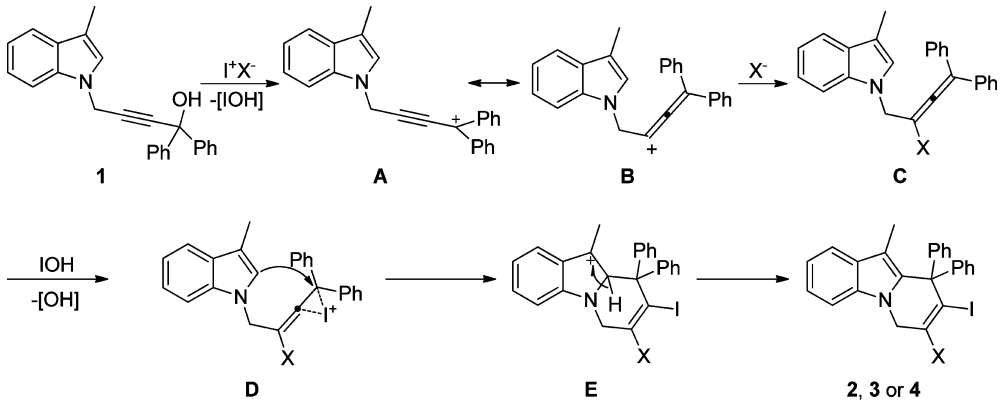
Table 3. Synthesis of Dihalogenated 6,9-dihydropyrido[1,2-*a*]indoles with IBr and ICl[a]





[a]All reactions were run under the following conditions, unless otherwise indicated: 0.20 mmol of **1** and 1.2 equiv of IBr or ICl in 4 mL of DCE were stirred at room temperature for 10 min. Yields are given for isolated products.

Scheme 2. Proposed Reaction Mechanism



1-ol derivatives with IBr and ICl were tested, as depicted in Table 3. The product **3a** was achieved in 83% yield. The structure of the representative product **3a** was determined by X-ray crystallographic analysis. Similarly, other typical substrates also gave the corresponding bromine-containing products in good yields. Meanwhile, in the presence of ICl, the desired products **4a**,**b** were gained in good yields. With an increasing electronegativity of halogen anion, the yields of **3a** and **4a** were progressively decreased in comparison with **2a** due to the unstable intermediate **C**.

On the basis of the above observations, a plausible mechanism is proposed in Scheme 2. First, in the presence of Lewis acidic iodine, propargylic alcohol **1** was converted to the intermediate **A** along with the unstable hypoiodous acid (HOI)

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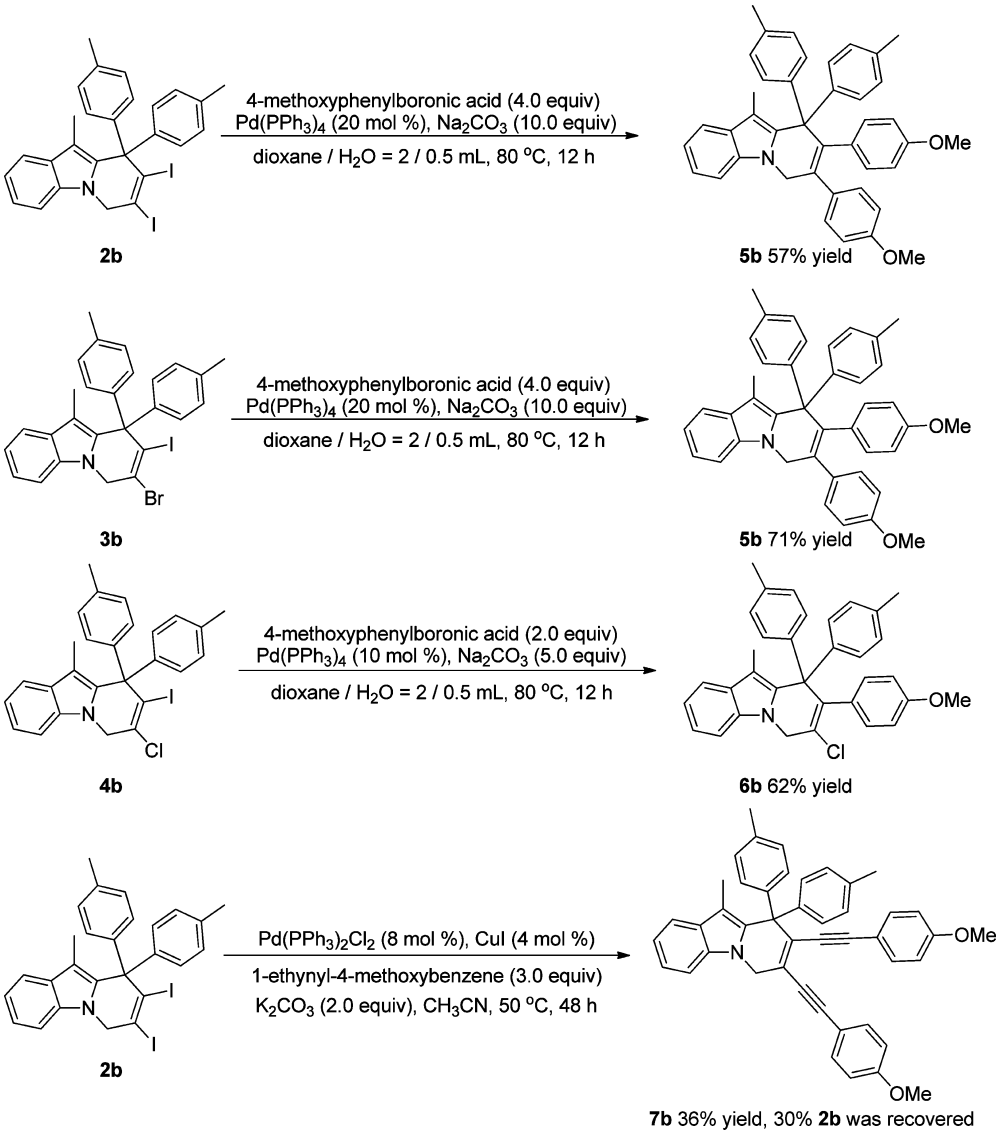
Scheme 3. Palladium-Catalyzed Coupling Reactions



and an iodine anion. The rapid tautomerization of **A** formed intermediate allene carbocation **B**. At the same time, the halogen anion captured the allene carbocation to give the halogenated intermediate **C**, which reacted with hypoiodous acid to form the iodonium intermediate **D**. Subsequently, the activated allene intermediate **D** was attacked by the 2-position of the indole ring to give the intermediate **E**, which delivered the products **2**–**4** by deprotonation.[13]

As shown in Scheme 3, the compounds **2b**–**4b** can be further elaborated by using various palladium-catalyzed processes. The Suzuki coupling[14] of **2b** and **3b** afforded the same product **5b** in 57% and 71% yields, respectively. In the meantime, the Suzuki coupling of **4b** furnished the product **6b** in 62% yield. The Sonagashira coupling[15] of **2b** gave the corresponding product **7b** in 36% yield, and 30% of **2b** was recovered.

CONCLUSION

In conclusion, a new and mild protocol for the synthesis of dihalogenated 6,9-dihydropyrido[1,2-*a*]indoles has been established. This method adds interest to this clean process and also relates to the incorporation of iodine, which opens broad perspectives for future research. It is worth noting that the resulting halogenated 6,9-dihydropyrido[1,2-*a*]indoles are readily elaborated to more products by using known organopalladium chemistry, which may be essential intermediates for building delicate and sophisticated natural products. Further studies on expanding this strategy are in progress in our laboratory.

EXPERIMENTAL SECTION

General Procedure for Synthesis of 4-(3-Methyl-1*H*-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol Derivatives 1a–1ae. To a solution of the indole derivative (100 mmol) in DMF (250 mL) was added NaH (60%, 2.0 equiv) slowly at 0 °C. The resulting solution was stirred for 1 h at 0 °C. Then, the propargylic bromide (2.0 equiv) was added dropwise through a syringe. The reaction mixture was stirred at room temperature for another 2 h. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched with water (200 mL) and extracted with ethyl acetate (3 × 150 mL). The combined organic layers were dried over anhydrous Na_2SO_4, Na_2SO_4 was removed by decantation, and the organic phase was concentrated under reduced pressure and purified by silica gel flash column chromatography (petroleum ether/EtOAc 30/1) in 70–90%

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yields.[16] A solution of the above 1-(prop-2-yn-1-yl)-1*H*-indole derivative (5 mmol) in THF (20 mL) with Ar was cooled to −40 °C, and *n*-BuLi (2.4 mol/L in THF, 1.1 equiv) was added dropwise. After the mixture was stirred for 30 min at −40 °C, a solution of ketone (1.5 equiv) in THF (5 mL) was added to the reaction via syringe and the resulting mixture was removed to room temperature. After 2 h, the mixture was quenched with water and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were washed with water and brine and dried over Na_2SO_4, Na_2SO_4 was removed by decantation, and the organic phase was concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc 10/1) in 65−85% yields to give the substrate **1**.[17]

Synthesis of 1af. To a solution of 3-methyl-1*H*-indole (30 mmol) in DMF (100 mL) was added NaH (60%, 2.0 equiv) slowly at 0 °C. The resulting solution was stirred for 2 h at 0 °C. Then, 3-chloro-3-methylbut-1-yne (2.0 equiv) was added dropwise through a syringe. The reaction mixture was stirred at room temperature for another 12 h. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched with water and extracted with ethyl acetate (3 × 60 mL). The combined organic layers were dried over anhydrous Na_2SO_4, Na_2SO_4 was removed by decantation, and the organic phase was concentrated under reduced pressure and purified by silica gel flash column chromatography (petroleum ether/EtOAc 30/1) in 15% yield (887 mg) to provide the desired product 3-methyl-1-(2-methylbut-3-yn-2-yl)-1*H*-indole.[18] The substrate **1af** was synthesized from 3-methyl-1-(2-methylbut-3-yn-2-yl)-1*H*-indole according to the general procedure as mentioned above.

Synthesis of 1ag,ah. To a solution of imidazole (28.0 mmol) in THF (30 mL) was added NaOH (28.0 mmol). The resulting mixture was stirred at 50 °C for 1 h before it was cooled to room temperature. Subsenquently, 3-bromopropyne (30.8 mmol, 1.1 equiv) was added and the solution was stirred for another 12 h. After filtration, the resulting solution was concentrated under reduced pressure and purified by silica gel flash column chromatography (petroleum ether/EtOAc 2/1) in 70% yield to provide 1-(prop-2-yn-1-yl)-1*H*-imidazole.[19] The substrate **1ag** was synthesized from 1-(prop-2-yn-1-yl)-1*H*-imidazole according to the general procedure as mentioned above. The substrate **1ah** was synthesized from benzimidazole similarly to the general procedure for the synthesis of substrate **1ag**.

General Procedure for Synthesis of Halogenated 6,9-Dihydropyrido[1,2-*a*]indoles. To a solution of **1** (0.20 mmol) in DCE (4.0 mL) was added I_2, IBr, or ICl (0.24 mmol, 1.2 equiv) at room temperature. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was quenched by the addition of saturated aqueous sodium thiosulfate, diluted with ethyl acetate (3 × 15 mL), washed with water and saturated brine, and dried over Na_2SO_4; Na_2SO_4 was removed by decantation, and the organic phase was concentrated under reduced pressure. The residue was purified by chromatography on silica gel (petroleum ether/EtOAc 30/1) to afford the corresponding halogenated 6,9-dihydropyrido[1,2-*a*]indole derivatives **2**−**4**.

To a solution of **1af** (0.20 mmol) in DCE (4.0 mL) was added I_2 (0.24 mmol, 1.2 equiv) at room temperature. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (petroleum ether/EtOAc 30/1) to afford the corresponding product **2af**.

*Typical Procedure for **5b** (Synthesis from **2b**).* To a solution of 7,8-diiodo-10-methyl-9,9-di-*p*-tolyl-6,9-dihydropyrido[1,2-*a*]indole (**2b**; 123.0 mg, 0.20 mmol) in dioxane/H_2O (2/0.5 mL) were added 4-methoxyphenylboronic acid (121.6 mg, 4.0 equiv), $Pd(PPh_3)_4$ (46.2 mg, 20 mol %), and Na_2CO_3 (212 mg, 10.0 equiv). The reaction vial was flushed with Ar, and the reaction mixture was stirred at 80 °C for 12 h. On completion of the reaction, the reaction mixture was quenched with H_2O (10 mL) and extracted with ethyl ether (3 × 10 mL). The combined organic layers were washed with water and brine and dried over Na_2SO_4, Na_2SO_4 was removed by decantation, and the organic phase was concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc 20/1) to give **5b**.[14a]

*Typical Procedure for **5b** (Synthesis from **3b**).* To a solution of 7-bromo-8-iodo-10-methyl-9,9-di-*p*-tolyl-6,9-dihydropyrido[1,2-*a*]indole (**3b**; 113.6 mg, 0.20 mmol) in dioxane/H_2O (2/0.5 mL) were added 4-methoxyphenylboronic acid (121.6 mg, 4.0 equiv), $Pd(PPh_3)_4$ (46.2 mg, 20 mol %), and Na_2CO_3 (212 mg, 10.0 equiv). The reaction vial was flushed with Ar, and the reaction mixture was stirred at 80 °C for 12 h. On completion of the reaction, the reaction mixture was quenched with H_2O (10 mL) and extracted with ethyl ether (3 × 10 mL). The combined organic layers were washed with water and brine and dried over Na_2SO_4, Na_2SO_4 was removed by decantation, and the organic phase was concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc 20/1) to give **5b**.[14a]

*Typical Procedure for **6b**.* To a solution of 7-chloro-8-iodo-10-methyl-9,9-di-*p*-tolyl-6,9-dihydropyrido[1,2-*a*]indole (**4b**; 104.7 mg, 0.20 mmol) in dioxane/H_2O (2:0.5 mL) were added 4-methoxyphenylboronic acid (60.8 mg, 2.0 equiv), $Pd(PPh_3)_4$ (23.1 mg, 10 mol %), and Na_2CO_3 (106 mg, 5.0 equiv). The reaction vial was flushed with Ar, and the reaction mixture was stirred at 80 °C for 12 h. On completion of the reaction, the reaction mixture was quenched with H_2O (10 mL) and extracted with ethyl ether (3 × 10 mL). The combined organic layers were washed with water and brine and dried over Na_2SO_4, Na_2SO_4 was removed by decantation, and the organic phase was concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc 20/1) to give **6b**.[14a]

*Typical Procedure for **7b**.* To a soluton of **2b** (123.0 mg, 0.2 mmol) in anhydrous CH_3CN (4 mL) were added K_2CO_3 (55.2 mg, 2.0 equiv), $PdCl_2(PPh_3)_2$ (11.2 mg, 8 mol %), CuI (1.5 mg, 4 mol %), and 1-ethynyl-4-methoxybenzene (79.2 mg, 3.0 equiv). The reaction vial was flushed with Ar, and the reaction mixture was stirred for 48 h at 50 °C. Then, the mixture was quenched slowly by addition of aqueous 1 M HCl (4 mL) and extracted with ethyl ether (3 × 20 mL). The combined organic layers were washed with water and brine and dried over Na_2SO_4, Na_2SO_4 was removed by decantation, and the organic phase was concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc 20/1) to give **7b**.[15c]

Characterization Data of 1a−1ah. *4-(3-Methyl-1H-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol (**1a**).* Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.55 (d, J = 8.0 Hz, 1H), 7.50−7.47 (m, 4H), 7.33 (d, J = 8.0 Hz, 1H), 7.26−7.18 (m, 7H), 7.12 (t, J = 8.0 Hz, 1H), 6.89 (s, 1H), 4.83 (s, 2H), 2.81 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.4, 136.1, 129.2, 128.2, 127.7, 125.9, 124.9, 121.7, 119.1, 111.2, 109.3, 87.5, 81.8, 74.3, 35.9, 9.6.

*4-(3-Methyl-1H-indol-1-yl)-1,1-di-p-tolylbut-2-yn-1-ol (**1b**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.56 (d, J = 7.6 Hz, 1H), 7.39−7.34 (m, 5H), 7.22 (t, J = 7.6 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 8.0 Hz, 4H), 6.93 (s, 1H), 4.88 (s, 2H), 2.70 (s, 1H), 2.30 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 141.8, 137.4, 136.1, 129.1, 128.9, 125.8, 124.9, 121.7, 119.1, 111.1, 109.3, 87.8, 81.4, 74.1, 35.9, 21.0, 9.6.

*1,1-Bis(4-methoxyphenyl)-4-(3-methyl-1H-indol-1-yl)but-2-yn-1-ol (**1c**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.55 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.8 Hz, 4H), 7.33 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.90 (s, 1H), 6.76 (d, J = 8.8 Hz, 4H), 4.84 (s, 2H), 3.71 (s, 6H), 2.88 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 158.9, 137.0, 136.1, 129.1, 127.2, 124.9, 121.7, 119.1, 113.4, 111.1, 109.3, 87.9, 81.3, 73.6, 55.2, 35.9, 9.6.

*1,1-Bis(4-fluorophenyl)-4-(3-methyl-1H-indol-1-yl)but-2-yn-1-ol (**1d**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.56 (d, J = 8.0 Hz, 1H), 7.41−7.38 (m, 4H), 7.31 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 6.92 (t, J = 8.4 Hz, 4H), 6.88 (s, 1H), 4.87 (s, 2H), 2.82 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 162.2 (d, $^1J_{C-F}$ = 245 Hz), 140.1, 136.1, 129.2, 127.7 (d, $^3J_{C-F}$ = 8 Hz), 124.9, 121.8, 119.2, 115.1 (d, $^2J_{C-F}$ = 21 Hz), 111.4, 190.2, 87.0, 82.3, 73.4, 35.8, 9.5.

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*1,1-Bis(4-chlorophenyl)-4-(3-methyl-1H-indol-1-yl)but-2-yn-1-ol (**1e**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.54 (d, J = 8.0 Hz, 1H), 7.32−7.29 (m, 5H), 7.19−7.15 (m, 5H), 7.13−7.09 (m, 1H), 6.84 (s, 1H), 4.82 (s, 2H), 2.86 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 142.5, 136.0, 133.8, 129.2, 128.4, 127.3, 124.9, 121.8, 119.2, 111.4, 109.2, 86.4, 82.6, 73.4, 35.8, 9.5.

*4-(3-Methyl-1H-indol-1-yl)-1-phenyl-1-(o-tolyl)but-2-yn-1-ol (**1f**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.86−7.84 (m, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.4 Hz, 1H), 7.25−7.18 (m, 6H), 7.12 (t, J = 7.6 Hz, 1H), 7.08−7.06 (m, 1H), 6.89 (s, 1H), 4.85 (s, 2H), 2.68 (s, 1H), 2.30 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 143.5, 141.0, 136.2, 136.1, 132.0, 129.1, 128.3, 128.1, 127.9, 126.3, 126.0, 125.5, 124.9, 121.7, 119.1, 111.2, 109.2, 86.6, 82.2, 74.0, 35.9, 20.9, 9.6.

*4-(3-Methyl-1H-indol-1-yl)-1-phenyl-1-(m-tolyl)but-2-yn-1-ol (**1g**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.57−7.55 (m, 1H), 7.51−7.48 (m, 2H), 7.36−7.31 (m, 2H), 7.27−7.21 (m, 5H), 7.14−7.11 (m, 2H), 7.02 (d, J = 6.8 Hz, 1H), 6.91 (s, 1H), 4.85 (s, 2H), 2.83 (s, 1H), 2.29 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.5, 144.4, 137.9, 136.1, 129.1, 128.5, 128.2, 128.1, 127.7, 126.5, 125.9, 124.9, 123.0, 121.7, 119.1, 111.1, 109.3, 87.6, 81.7, 74.3, 35.9, 21.4, 9.6.

*4-(3-Methyl-1H-indol-1-yl)-1-phenyl-1-(p-tolyl)but-2-yn-1-ol (**1h**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.56 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.38−7.33 (m, 3H), 7.27−7.19 (m, 4H), 7.15−7.10 (m, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.91 (s, 1H), 4.85 (s, 2H), 2.81 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.6, 141.6, 137.5, 136.1, 129.1, 128.9, 128.2, 127.6, 125.8, 124.9, 121.7, 119.1, 111.1, 109.3, 87.6, 81.6, 74.2, 35.8, 21.0, 9.6.

*1-(4-Methoxyphenyl)-4-(3-methyl-1H-indol-1-yl)-1-phenylbut-2-yn-1-ol (**1i**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.54 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 1H), 7.26−7.17 (m, 4H), 7.14−7.09 (m, 1H), 6.88 (s, 1H), 6.73 (d, J = 8.8 Hz, 2H), 4.82 (s, 2H), 3.67 (s, 3H), 2.87 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 159.0, 144.7, 136.8, 136.1, 129.2, 128.1, 127.6, 127.3, 125.9, 124.9, 121.7, 119.1, 113.5, 111.1, 109.3, 87.8, 81.5, 74.0, 55.1, 35.8, 9.5.

*1-(2-Chlorophenyl)-4-(3-methyl-1H-indol-1-yl)-1-phenylbut-2-yn-1-ol (**1j**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.83 (d, J = 7.2 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.40 (s, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.29−7.17 (m, 7H), 7.11 (t, J = 6.8 Hz, 1H), 6.92 (s, 1H), 4.84 (s, 2H), 3.17 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 142.7, 140.3, 136.1, 132.3, 131.1, 129.3, 129.1, 128.2, 128.0, 127.9, 126.6, 126.5, 125.0, 121.7, 119.0, 111.0, 109.3, 85.5, 82.1, 73.7, 35.9, 9.6.

*1-(3-Chlorophenyl)-4-(3-methyl-1H-indol-1-yl)-1-phenylbut-2-yn-1-ol (**1k**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.56−7.53 (m, 2H), 7.46 (d, J = 6.8 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.26−7.20 (m, 4H), 7.18−7.10 (m, 3H), 6.89 (s, 1H), 4.87 (s, 2H), 2.82 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 146.4, 143.8, 136.1, 134.1, 129.5, 129.2, 128.4, 128.0, 127.9, 126.1, 125.8, 124.9, 124.1, 121.9, 119.2, 111.3, 109.2, 86.8, 82.3, 73.9, 35.8, 9.6.

*1-(4-Chlorophenyl)-4-(3-methyl-1H-indol-1-yl)-1-phenylbut-2-yn-1-ol (**1l**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.55 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 6.8 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.27−7.18 (m, 6H), 7.12 (t, J = 8.0 Hz, 1H), 6.88 (s, 1H), 4.86 (s, 2H), 2.82 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.0, 143.0, 136.1, 133.6, 129.2, 128.3, 128.3, 128.0, 127.4, 125.8, 124.9, 121.8, 119.2, 111.3, 109.2, 86.9, 82.2, 73.9, 35.8, 9.6.

*1-(4-Fluorophenyl)-4-(3-methyl-1H-indol-1-yl)-1-phenylbut-2-yn-1-ol (**1m**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.55 (d, J = 8.0 Hz, 1H), 7.46−7.40 (m, 4H), 7.33 (d, J = 8.0 Hz, 1H), 7.27−7.18 (m, 4H), 7.15−7.10 (m, 1H), 6.92−6.88 (m, 3H), 4.85 (s, 2H), 2.81 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 162.1 (d, $^1J_{C-F}$ = 245 Hz), 144.3, 140.3, 136.1, 129.2, 128.8, 127.9, 127.8, 127.8, 125.8, 124.9, 121.8, 119.2, 115.0 (d, $^2J_{C-F}$ = 22 Hz), 111.3, 109.2, 87.2, 82.0, 73.9, 35.8, 9.6.

*1-([1,1′-Biphenyl]-4-yl)-4-(3-methyl-1H-indol-1-yl)-1-phenylbut-2-yn-1-ol (**1n**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.56−7.50 (m, 7H), 7.46 (d, J = 8.0 Hz, 2H), 7.39−7.34 (m, 3H), 7.31−7.19 (m, 5H), 7.14−7.11 (m, 1H), 6.90 (s, 1H), 4.85 (s, 2H), 2.82 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.3, 143.4, 140.6, 140.4, 136.1, 129.2, 128.7, 128.3, 127.8, 127.3, 127.0, 126.9, 126.4, 125.9, 124.9, 121.8, 119.1, 111.2, 109.3, 87.4, 81.9, 74.2, 35.9, 9.6.

*1-(3,4-Dimethylphenyl)-4-(3-methyl-1H-indol-1-yl)-1-phenylbut-2-yn-1-ol (**1o**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.56−7.51 (m, 3H), 7.35 (s, 1H), 7.25−7.21 (m, 6H), 7.13−7.12 (m, 1H), 7.01 (s, 1H), 6.91 (s, 1H), 4.83 (s, 2H), 2.80 (s, 1H), 2.31 (s, 3H), 2.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.6, 142.0, 136.4, 136.2, 136.1, 129.4, 129.2, 128.2, 127.6, 127.1, 125.9, 124.9, 123.3, 121.7, 119.1, 111.1, 109.3, 87.8, 81.5, 74.2, 35.9, 19.8, 19.4, 9.6.

*1-(3,4-Dichlorophenyl)-4-(3-methyl-1H-indol-1-yl)-1-phenylbut-2-yn-1-ol (**1p**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.60 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.45−7.43 (m, 2H), 7.34 (d, J = 8.4 Hz, 1H), 7.29−7.19 (m, 6H), 7.13 (t, J = 8.0 Hz, 1H), 6.89 (s, 1H), 4.89 (s, 2H), 2.83 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.7, 143.5, 136.1, 132.3, 131.8, 130.1, 129.2, 128.5, 128.2, 127.9, 125.8, 125.4, 124.9, 121.9, 119.2, 111.5, 109.2, 86.4, 82.6, 73.5, 35.8, 9.6.

*4-(3-Methyl-1H-indol-1-yl)-1-(naphthalen-1-yl)-1-phenylbut-2-yn-1-ol (**1q**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.00−7.94 (m, 2H), 7.80−7.77 (m, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.45−7.39 (m, 3H), 7.34 (t, J = 7.6 Hz, 1H), 7.26−7.15 (m, 6H), 7.10 (t, J = 7.6 Hz, 1H), 6.79 (s, 1H), 4.77 (s, 2H), 2.89 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.1, 138.3, 136.2, 134.5, 129.8, 129.5, 129.2, 128.6, 128.4, 128.0, 126.6, 126.3, 125.5, 125.3, 125.0, 124.6, 124.5, 121.7, 119.1, 119.1, 111.1, 109.2, 87.5, 82.9, 74.4, 35.9, 9.5.

*1-(3-(3-Methyl-1H-indol-1-yl)prop-1-yn-1-yl)-2,3-dihydro-1H-inden-1-ol (**1r**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.52 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 6.4 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.22−7.16 (m, 4H), 7.11−7.08 (m, 1H), 6.86 (s, 1H), 4.73 (s, 2H), 3.02−2.95 (m, 1H), 2.80 (s, 1H), 2.46−2.39 (m, 2H), 2.31−2.29 (m, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 145.2, 142.8, 136.0, 129.0, 128.9, 127.0, 124.9, 124.8, 123.1, 121.6, 119.0, 119.0, 110.9, 109.2, 86.9, 79.2, 76.1, 42.9, 35.7, 29.4, 9.5.

*1-(4-Fluorophenyl)-1-(4-methoxyphenyl)-4-(3-methyl-1H-indol-1-yl)but-2-yn-1-ol (**1s**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.55 (d, J = 8.0 Hz, 1H), 7.43−7.39 (m, 2H), 7.35−7.31 (m, 3H), 7.20 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.93−6.87 (m, 3H), 6.74 (d, J = 8.0 Hz, 2H), 4.83 (s, 2H), 3.69 (s, 3H), 3.04 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 162.0 (d, $^1J_{C-F}$ = 245 Hz), 159.0, 140.5, 136.6, 136.0, 129.1, 127.7 (d, $^3J_{C-F}$ = 8 Hz), 127.2, 124.9, 121.7, 119.1, 114.9 (d, $^2J_{C-F}$ = 21 Hz), 111.2, 109.2, 87.4, 81.7, 73.4, 55.1, 35.8, 9.5.

*1-(4-Fluorophenyl)-4-(3-methyl-1H-indol-1-yl)-1-(thiophen-2-yl)-but-2-yn-1-ol (**1t**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.57−7.51 (m, 3H), 7.34 (d, J = 8.4 Hz, 1H), 7.23−7.19 (m, 2H), 7.13 (t, J = 7.6 Hz, 1H), 6.98−6.91 (m, 4H), 6.85−6.83 (m, 1H), 4.88 (s, 2H), 3.00 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 162.4 (d, $^1J_{C-F}$ = 246 Hz), 149.4, 139.5, 136.1, 129.1, 127.6 (d, $^3J_{C-F}$ = 9 Hz), 126.5, 126.1, 125.5, 124.9, 121.8, 119.2, 115.0 (d, $^2J_{C-F}$ = 21 Hz), 111.3, 109.2, 86.6, 81.4, 71.3, 35.8, 9.6.

*5-(3-Methyl-1H-indol-1-yl)-2-phenylpent-3-yn-2-ol (**1u**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.54−7.51 (m, 3H), 7.32−7.18 (m, 5H), 7.10 (t, J = 7.6 Hz, 1H), 6.88 (s, 1H), 4.78 (s, 2H), 2.54 (s, 1H), 2.28 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 145.1, 136.1, 129.1, 128.2, 127.7, 124.8, 124.8, 121.7, 119.1, 119.0, 111.0, 109.2, 88.2, 79.2, 69.8, 35.7, 33.0, 9.5.

*5-(3-Methyl-1H-indol-1-yl)-2-(p-tolyl)pent-3-yn-2-ol (**1v**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.55 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.15−7.09 (m, 3H), 6.91 (s, 1H), 4.81 (s, 2H), 2.51 (s, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 142.2, 137.4, 136.0, 129.0, 128.9, 124.8, 124.7, 121.7, 119.1, 119.0, 111.0, 109.2, 88.3, 79.0, 69.7, 35.7, 32.9, 21.0, 9.6.

*2-(4-Chlorophenyl)-5-(3-methyl-1H-indol-1-yl)pent-3-yn-2-ol (**1w**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.54 (d, J

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= 7.6 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.24−7.18 (m, 3H), 7.11 (t, J = 7.6 Hz, 1H), 6.88 (s, 1H), 4.81 (s, 2H), 2.56 (s, 1H), 2.29 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 143.5, 136.0, 133.4, 129.0, 128.3, 126.3, 124.8, 121.7, 119.2, 119.1, 111.2, 109.1, 87.6, 79.6, 69.4, 35.7, 33.0, 9.6.

*6-(3-Methyl-1H-indol-1-yl)-3-phenylhex-4-yn-3-ol (**1x**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.56 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 7.2 Hz, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.31−7.19 (m, 4H), 7.13 (t, J = 7.2 Hz, 1H), 6.95 (s, 1H), 4.87 (s, 2H), 2.46 (s, 1H), 2.31 (s, 3H), 1.96−1.82 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 143.9, 136.0, 129.1, 128.1, 127.6, 125.4, 124.9, 121.7, 119.1, 119.0, 111.1, 109.2, 87.1, 80.3, 73.8, 38.11, 35.7, 9.6, 9.0.

*4-(3-Methyl-1H-indol-1-yl)-1-phenylbut-2-yn-1-ol (**1y**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.54 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 6.4 Hz, 2H), 7.31−7.26 (m, 4H), 7.21−7.18 (m, 1H), 7.14−7.09 (m, 1H), 6.86 (s, 1H), 5.30 (s, 1H), 4.75 (s, 2H), 2.50 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 140.1, 136.0, 129.1, 128.5, 128.3, 126.5, 124.9, 121.7, 119.1, 119.1, 111.1, 109.2, 84.5, 81.0, 64.3, 35.6, 9.5.

*1,1-Diphenyl-4-(3-phenyl-1H-indol-1-yl)but-2-yn-1-ol (**1z**).* Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.93 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.51−7.49 (m, 4H), 7.42−7.38 (m, 3H), 7.29 (s, 1H), 7.27−7.17 (m, 9H), 4.89 (s, 2H), 2.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.4, 136.6, 135.2, 128.7, 128.3, 127.8, 127.3, 126.7, 125.9, 125.9, 124.9, 122.3, 120.4, 120.1, 117.6, 109.7, 88.3, 81.2, 74.4, 36.2.

*4-(1H-Indol-1-yl)-1,1-diphenylbut-2-yn-1-ol (**1aa**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.60 (d, J = 7.6 Hz, 1H), 7.48−7.46 (m, 4H), 7.35 (d, J = 8.0 Hz, 1H), 7.25−7.17 (m, 7H), 7.12−7.08 (m, 2H), 7.47 (d, J = 3.2 Hz, 1H), 4.84 (s, 2H), 2.83 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.4, 135.7, 128.8, 128.2, 127.7, 127.2, 125.9, 121.8, 121.0, 119.8, 109.4, 101.9, 87.9, 81.4, 74.3, 36.1.

*4-(4-Chloro-1H-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol (**1ab**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49−7.47 (m, 4H), 7.27−7.20 (m, 7H), 7.16 (d, J = 3.2 Hz, 1H), 7.13−7.07 (m, 2H), 6.60 (s, 1H), 4.88 (s, 2H), 2.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.3, 136.5, 128.3, 127.8, 127.6, 126.2, 125.9, 122.4, 119.6, 108.2, 100.7, 88.3, 80.9, 74.4, 36.5.

*4-(5-Methoxy-1H-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol (**1ac**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, J = 7.2 Hz, 4H), 7.26−7.16 (m, 7H), 7.09 (d, J = 2.8 Hz, 1H), 7.05 (s, 1H), 6.85 (d, J = 8.8 Hz, 1H), 6.39 (s, 1H), 4.83 (s, 2H), 3.77 (s, 3H), 3.01 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 15.42, 144.5, 131.1, 129.3, 128.2, 127.8, 127.7, 125.9, 112.1, 110.2, 102.8, 101.5, 87.9, 81.4, 74.3, 55.8, 36.3.

*4-(6-Chloro-1H-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol (**1ad**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49−7.47 (m, 5H), 7.40 (s, 1H), 7.28−7.19 (m, 6H), 7.09−7.07 (m, 2H), 6.43 (d, J = 3.2 Hz, 1H), 4.80 (s, 2H), 2.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.3, 136.1, 128.3, 128.1, 127.8, 127.4, 125.9, 121.9, 120.6, 109.6, 102.1, 88.4, 80.8, 74.4, 36.3.

*4-(7-Methyl-1H-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol (**1ae**).* Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.44−7.41 (m, 5H), 7.23−7.16 (m, 6H), 7.04 (d, J = 3.2 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.45 (d, J = 2.8 Hz, 1H), 5.10 (s, 2H), 2.76 (s, 1H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.4, 134.8, 130.0, 129.0, 128.2, 127.7, 125.8, 124.8, 120.9, 120.2, 119.2, 102.6, 88.4, 82.9, 74.3, 38.8, 19.4.

*4-Methyl-4-(3-methyl-1H-indol-1-yl)-1,1-diphenylpent-2-yn-1-ol (**1af**).* Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.75 (s,1H), 7.54−7.52 (m, 5H), 7.28−7.22 (m, 6H), 7.09−7.05 (m, 3H), 2.78 (s, 1H), 2.29 (s, 3H), 1.95 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.6, 135.2, 130.1, 128.2, 127.7, 126.0, 121.9, 121.1, 119.0, 118.8, 112.9, 110.0, 89.9, 86.2, 74.4, 52.0, 30.0, 9.6.

*4-(1H-Imidazol-1-yl)-1,1-diphenylbut-2-yn-1-ol (**1ag**).* White solid. ^{1}H NMR (400 MHz, DMSO) 7.75 (s, 1H), 7.55 (d, J = 7.2 Hz, 4H), 7.32 (t, J = 7.2 Hz, 4H), 7.28 (s, 1H), 7.23 (d, J = 7.2 Hz, 2H), 6.96 (s, 2H), 5.12 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ ppm 146.0, 137.0, 128.7, 128.0, 127.1, 125.6, 119.3, 88.7, 80.4, 72.8, 35.8.

*4-(1H-Benzo[d]imidazol-1-yl)-1,1-diphenylbut-2-yn-1-ol (**1ah**).* White solid. ^{1}H NMR (400 MHz, DMSO) 8.36 (s, 1H), 7.78−7.71 (m, 2H), 7.54 (d, J = 6.8 Hz, 4H), 7.29−7.21 (m, 8H), 6.95 (s, 1H), 5.42 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ ppm 146.0, 143.5, 143.5, 133.5, 128.0, 127.2, 125.6, 122.6, 121.9, 119.6, 110.9, 88.8, 80.1, 72.9, 34.3.

Characterization Data of Products 2−4. *7,8-Diiodo-10-methyl-9,9-diphenyl-6,9-dihydropyrido[1,2-a]indole (**2a**).* Yellow solid (110.4 mg, 94%). Mp: 198−200 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, J = 7.6 Hz, 1H), 7.30−7.28 (m, 10H), 7.20−7.18 (m, 2H), 7.14−7.09 (m, 1H), 4.89 (s, 2H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.2, 134.5, 133.8, 129.4, 129.1, 128.0, 127.4, 125.1, 121.8, 119.6, 118.7, 108.3, 107.4, 105.7, 61.4, 55.0, 10.1. IR (neat, cm^{-1}): 2919, 1491, 1466, 1443, 1239, 808, 761, 701. HRMS (ESI): m/z calcd for $C_{25}H_{20}I_2N$ $[M + H]^+$ 587.9680, found 587.9675.

*7,8-Diiodo-10-methyl-9,9-di-p-tolyl-6,9-dihydropyrido[1,2-a]indole (**2b**).* Yellow solid (113.2 mg, 92%). Mp: 100−102 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.47 (d, J = 8.0 Hz, 1H), 7.20−7.18 (m, 6H), 7.10−7.08 (m, 5H), 4.89 (s, 2H), 2.33 (s, 6H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 137.0, 134.7, 133.8, 130.2, 129.3, 129.3, 128.7, 125.9, 121.7, 119.5, 118.7, 108.3, 107.3, 105.1, 61.0, 55.0, 21.1, 10.1. IR (neat, cm^{-1}): 2917, 1508, 1467, 1448, 1236, 813, 738, 671. HRMS (ESI): m/z calcd for $C_{27}H_{24}I_2N$ $[M + H]^+$ 615.9993, found 615.9997.

*7,8-Diiodo-9,9-bis(4-methoxyphenyl)-10-methyl-6,9-dihydropyrido[1,2-a]indole (**2c**).* White solid (112.6 mg, 87%). Mp: 102−104 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, J = 8.0 Hz, 1H), 7.21−7.16 (m, 6H), 7.13−7.09 (m, 1H), 6.82 (d, J = 7.2 Hz, 4H), 4.88 (s, 2H), 3.79 (s, 6H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 158.5, 136.7, 134.8, 133.8, 130.5, 129.2, 126.5, 121.7, 119.5, 118.7, 113.2, 108.3, 107.1, 104.9, 60.3, 55.2, 54.9, 10.1. IR (neat, cm^{-1}): 2928, 1606, 1508, 1466, 1251, 826, 789, 739. HRMS (ESI): m/z calcd for $C_{27}H_{24}I_2NO_2$ $[M + H]^+$ 647.9891, found 647.9886.

*9,9-Bis(4-fluorophenyl)-7,8-diiodo-10-methyl-6,9-dihydropyrido-[1,2-a]indole (**2d**).* Yellow solid (82.2 mg, 66%). Mp: 86−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.50 (d, J = 8.0 Hz, 1H), 7.27−7.22 (m, 6H), 7.16−7.11 (m, 1H), 7.00 (t, J = 8.4 Hz, 4H), 4.90 (s, 2H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 161.9 (d, $^1J_{C-F}$ = 246 Hz), 140.0 (d, $^4J_{C-F}$ = 3 Hz), 134.1, 133.8, 131.0 (d, $^3J_{C-F}$ = 8 Hz), 129.0, 124.8, 122.1, 119.8, 118.9, 115.0 (d, $^2J_{C-F}$ = 22 Hz), 108.4, 107.3, 106.1, 60.3, 55.0, 10.1. IR (neat, cm^{-1}): 2920, 1601, 1504, 1467, 1232, 829, 806, 740. HRMS (ESI): m/z calcd for $C_{25}H_{18}F_2I_2N$ $[M + H]^+$ 623.9491, found 623.9487.

*9,9-Bis(4-chlorophenyl)-7,8-diiodo-10-methyl-6,9-dihydropyrido-[1,2-a]indole (**2e**).* Yellow solid (95.6 mg, 73%). Mp: 102−104 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.48 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.4 Hz, 4H), 7.22−7.20 (m, 6H), 7.14−7.10 (m, 1H), 4.89 (s, 2H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 142.4, 133.9, 133.6, 133.5, 130.7, 129.1, 128.4, 123.8, 122.2, 119.9, 118.9, 108.5, 107.6, 106.4, 60.5, 55.1, 10.3. IR (neat, cm^{-1}): 2918, 1488, 1467, 1094, 1013, 820, 739, 663. HRMS (ESI): m/z calcd for $C_{25}H_{17}Cl_2I_2N$ $[M + H]^+$ 654.8822, found 654.8822.

*7,8-Diiodo-10-methyl-9-phenyl-9-(o-tolyl)-6,9-dihydropyrido[1,2-a]indole (**2f**).* Pale yellow solid (107.0 mg, 89%). Mp: 216−218 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.51 (d, J = 8.0 Hz, 1H), 7.41 (s, 2H), 7.30−7.22 (m, 4H), 7.20−7.17 (m, 3H), 7.14−7.06 (m, 2H), 6.77 (d, J = 7.6 Hz, 1H), 5.26 (d, J = 17.2 Hz, 1H), 4.33 (d, J = 16.8 Hz, 1H), 1.94 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 146.7, 141.6, 139.4, 133.8, 132.8, 132.1, 129.2, 129.0, 128.4, 128.1, 127.3, 125.1, 124.8, 121.6, 119.4, 118.9, 108.3, 107.0, 105.3, 60.8, 54.8, 21.5, 9.2. IR (neat, cm^{-1}): 2920, 1466, 1448, 1373, 1084, 808, 736, 704. HRMS (ESI): m/z calcd for $C_{26}H_{22}I_2N$ $[M + H]^+$ 601.9836, found 601.9838.

*7,8-Diiodo-10-methyl-9-phenyl-9-(m-tolyl)-6,9-dihydropyrido-[1,2-a]indole (**2g**).* Pale yellow solid (98.6 mg, 82%). Mp: 88−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, J = 7.6 Hz, 1H), 7.32−7.26 (m, 5H), 7.20−7.16 (m, 3H), 7.13−7.05 (m, 4H), 4.92 (d, J = 17.2 Hz, 1H), 4.86 (d, J = 17.2 Hz, 1H), 2.29 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.3, 144.2, 137.5, 134.7,

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133.8, 130.3, 129.5, 129.2, 128.2, 128.0, 127.8, 127.3, 126.5, 125.4, 121.7, 119.5, 118.8, 108.3, 107.4, 105.6, 61.5, 55.0, 21.8, 10.1. IR (neat, cm^{-1}): 2915, 1601, 1467, 1445, 1237, 786, 738, 701. HRMS (ESI): *m/z* calcd for $C_{26}H_{22}I_2N$ $[M + H]^+$ 601.9836, found 601.9838.

7,8-Diiodo-10-methyl-9-phenyl-9-(p-tolyl)-6,9-dihydropyrido[1,2-a]indole (**2h**). Pale yellow solid (105.8 mg, 88%). Mp: 98−100 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.48 (d, *J* = 8.0 Hz, 1H), 7.30−7.28 (m, 5H), 7.19 (d, *J* = 7.2 Hz, 4H), 7.12−7.10 (m, 3H), 4.93 (d, *J* = 16.8 Hz, 1H), 4.87 (d, *J* = 17.2 Hz, 1H), 2.34 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.5, 141.0, 137.1, 134.6, 133.8, 129.5, 129.3, 129.2, 128.7, 128.0, 127.3, 125.5, 121.7, 119.5, 118.7, 108.3, 107.3, 105.4, 61.2, 55.0, 21.1, 10,1. IR (neat, cm^{-1}): 2916, 1509, 1467, 1445, 1236, 815, 738, 700. HRMS (ESI): *m/z* calcd for $C_{26}H_{22}I_2N$ $[M + H]^+$ 601.9836, found 601.9834.

7,8-Diiodo-9-(4-methoxyphenyl)-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**2i**). Pale yellow solid (108.6 mg, 88%). Mp: 94−96 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, *J* = 7.6 Hz, 1H), 7.30−7.28 (m, 5H), 7.23−7.19 (m, 4H), 7.13−7.09 (m, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.92 (d, *J* = 17.2 Hz, 1H), 4.87 (d, *J* = 17.2 Hz, 1H), 3.80 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 158.7, 144.4, 136.6, 134.7, 133.8, 130.7, 129.4, 129.2, 128.0, 127.3, 125.9, 121.8, 119.6, 118.8, 113.2, 108.4, 107.3, 105.3, 60.9, 55.2, 55.0, 10.1. IR (neat, cm^{-1}): 2922, 1606, 1508, 1466, 1251, 827, 740, 701. HRMS (ESI): *m/z* calcd for $C_{26}H_{22}I_2NO$ $[M + H]^+$ 617.9785, found 617.9781.

9-(2-Chlorophenyl)-7,8-diiodo-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**2j**). Pale yellow solid (96.9 mg, 78%). Mp: 208−210 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.51 (d, *J* = 8.0 Hz, 1H), 7.44−7.41 (m, 3H), 7.33−7.27 (m, 4H), 7.20−7.16 (m, 3H), 7.14−7.10 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.26 (d, *J* = 17.2 Hz, 1H), 4.38 (d, *J* = 17.2 Hz, 1H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 145.2, 140.6, 136.9, 133.7, 132.1, 131.3, 130.8, 129.4, 129.1, 129.0, 128.6, 127.5, 126.0, 122.2, 121.5, 119.3, 118.8, 108.3, 106.5, 105.4, 60.4, 54.7, 9.1. IR (neat, cm^{-1}): 2920, 1466, 1445, 1372, 1238, 808, 737, 702. HRMS (ESI): *m/z* calcd for $C_{25}H_{19}ClI_2N$ $[M + H]^+$ 621.9290, found 621.9295.

9-(3-Chlorophenyl)-7,8-diiodo-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**2k**). Pale yellow solid (105.6 mg, 85%). Mp: 88−90 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.50 (d, *J* = 7.6 Hz, 1H), 7.32−7.25 (m, 7H), 7.24−7.21 (m, 3H), 7.18−7.12 (m, 2H), 4.96 (d, *J* = 17.2 Hz, 1H), 4.85 (d, *J* = 17.2 Hz, 1H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 146.7, 143.2, 134.0, 133.9, 133.9, 129.6, 129.2, 129.2, 129.1, 128.2, 127.7, 127.7, 127.6, 124.0, 122.0, 119.7, 118.9, 108.4, 107.5, 106.3, 61.1, 55.0, 10.2. IR (neat, cm^{-1}): 2917, 1590, 1467, 1445, 1236, 811, 738, 699. HRMS (ESI): *m/z* calcd for $C_{25}H_{19}ClI_2N$ $[M + H]^+$ 621.9290, found 621.9287.

9-(4-Chlorophenyl)-7,8-diiodo-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**2l**). Yellow solid (104.3 mg, 84%). Mp: 96−98 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, *J* = 8.0 Hz, 1H), 7.31−7.27 (m, 7H), 7.25−7.21 (m, 4H), 7.14−7.10 (m, 1H), 4.93 (d, *J* = 17.2 Hz, 1H), 4.87 (d, *J* = 17.2 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 143.6, 142.9, 134.0, 133.8, 133.4, 130.9, 129.2, 129.1, 128.2, 127.6, 124.4, 122.0, 119.7, 118.8, 108.4, 107.4, 106.1, 55.0, 10.2. IR (neat, cm^{-1}): 2918, 1489, 1467, 1446, 1237, 1013, 740, 700. HRMS (ESI): *m/z* calcd for $C_{25}H_{19}ClI_2N$ $[M + H]^+$ 621.9290, found 621.9283.

9-(4-Fluorophenyl)-7,8-diiodo-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**2m**). Pale yellow solid (105.3 mg, 87%). Mp: 190−192 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, *J* = 8.0 Hz, 1H), 7.30−7.24 (m, 7H), 7.21−7.20 (m, 2H), 7.14−7.10 (m, 1H), 6.99 (t, *J* = 8.8 Hz, 2H), 4.93 (d, *J* = 17.2 Hz, 1H), 4.85 (d, *J* = 17.2 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 161.9 (d, $^1J_{C-F}$ = 246 Hz), 143.8, 140.5, 140.4, 134.3, 133.9, 131.3 (d, $^3J_{C-F}$ = 8 Hz), 129.2, 129.2, 128.2, 127.5, 125.0, 122.0, 119.7, 118.8, 114.9 (d, $^2J_{C-F}$ = 21 Hz), 108.4, 107.4, 105.9, 60.9, 55.0, 10.1. IR (neat, cm^{-1}): 2918, 1601, 1505, 1467, 1446, 1233, 740, 700. HRMS (ESI): *m/z* calcd for $C_{25}H_{19}FI_2N$ $[M + H]^+$ 605.9585, found 605.9598.

9-([1,1′-Biphenyl]-4-yl)-7,8-diiodo-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**2n**). Pale yellow solid (119.3 mg, 90%). Mp: 108−110 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.59 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42−7.37 (m, 4H), 7.35−7.28 (m, 6H), 7.20−7.17 (m, 2H), 7.13−7.09 (m, 1H), 4.95 (d, *J* = 17.2 Hz, 1H), 4.88 (d, *J* = 17.2 Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.5, 142.8, 140.3, 140.0, 134.5, 133.9, 129.8, 129.5, 129.2, 128.8, 128.1, 127.5, 127.4, 127.0, 126.6, 125.0, 121.9, 119.7, 118.8, 108.4, 107.5, 105.7, 61.3, 55.1, 10.2. IR (neat, cm^{-1}): 2916, 1486, 1466, 1445, 1236, 832, 738, 698. HRMS (ESI): *m/z* calcd for $C_{31}H_{24}I_2N$ $[M + H]^+$ 663.9993, found 663.9987.

9-(3,4-Dimethylphenyl)-7,8-diiodo-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**2o**). Pale yellow solid (109.5 mg, 89%). Mp: 94−96 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.48 (d, *J* = 8.0 Hz, 1H), 7.31−7.27 (m, 5H), 7.21−7.18 (m, 2H), 7.12−7.08 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.00−6.97 (m, 1H), 4.92 (d, *J* = 16.8 Hz, 1H), 4.87 (d, *J* = 17.2 Hz, 1H), 2,25 (s, 3H), 2.20 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.7, 141.4, 136.1, 135.8, 134.8, 133.9, 130.7, 130.0, 129.3, 129.2, 127.9, 127.3, 126.7, 125.7, 121.7, 119.5, 118.7, 108.3, 107.4, 105.3, 61.3, 55.0, 20.2, 19.4, 10.1. IR (neat, cm^{-1}): 2916, 1493, 1467, 1445, 1236, 818, 738, 700. HRMS (ESI): *m/z* calcd for $C_{27}H_{24}I_2N$ $[M + H]^+$ 615.9993, found 615.9995.

9-(3,4-Dichlorophenyl)-7,8-diiodo-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**2p**). Pale yellow solid (110.0 mg, 84%). Mp: 108−110 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.50 (d, *J* = 7.6 Hz, 1H), 7.42−7.30 (m, 7H), 7.22 (s, 2H), 7.13−7.11 (m, 2H), 4.98 (d, *J* = 17.2 Hz, 1H), 4.85 (d, *J* = 17.2 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.9, 142.8, 133.9, 133.4, 132.2, 131.7, 131.4, 129.9, 129.0, 129.0, 128.4, 127.8, 123.4, 122.2, 119.8, 118.9, 108.5, 107.5, 106.6, 60.7, 55.0, 10.3. IR (neat, cm^{-1}): 2917, 1468, 1445, 1374, 1237, 820, 738, 701. HRMS (ESI): *m/z* calcd for $C_{25}H_{18}Cl_2I_2N$ $[M + H]^+$ 655.8900, found 655.8903.

7,8-Diiodo-10-methyl-9-(naphthalen-1-yl)-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**2q**). Pale yellow solid (90.5 mg, 71%). Mp: 138−140 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.83 (t, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.39−7.27 (m, 7H), 7.23−7.13 (m, 4H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 5.39 (d, *J* = 16.8 Hz, 1H), 4.31 (d, *J* = 16.8 Hz, 1H), 1.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.5, 141.6, 134.0, 133.8, 133.5, 133.3, 129.5, 129.2, 128.7, 128.6, 127.5, 127.4, 125.7, 125.5, 125.5, 125.4, 124.3, 121.7, 119.3, 118.9, 108.2, 107.8, 105.5, 60.7, 54.9, 8.9. IR (neat, cm^{-1}): 2918, 1466, 1444, 1237, 1030, 777, 737, 698. HRMS (ESI): *m/z* calcd for $C_{29}H_{22}I_2N$ $[M + H]^+$ 637.9836, found 637.9827.

7′,8′-Diiodo-10′-methyl-2,3-dihydro-6′H-spiro[indene-1,9′-pyrido[1,2-a]indole] (**2r**). Yellow solid (81.6 mg, 76%). Mp: 84−86 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.45 (d, *J* = 7.6 Hz, 1H), 7.26−7.24 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.14−7.10 (m, 2H), 6.81 (d, *J* = 7.6 Hz, 1H), 5.12 (d, *J* = 17.2 Hz, 1H), 4.95 (d, *J* = 17.2 Hz, 1H), 3.42−3.33 (m, 1H), 3.16−3.09 (m, 1H), 2.72−2.61 (m, 2H), 1.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 148.9, 143.1, 135.0, 133.2, 128.9, 128.1, 127.2, 125.3, 124.8, 124.2, 121.4, 119.8, 118.1, 108.5, 106.1, 101.3, 60.6, 54.7, 42.0, 31.8, 8.4. IR (neat, cm^{-1}): 2913, 1467, 1452, 1368, 1233, 811, 763, 738. HRMS (ESI): *m/z* calcd for $C_{21}H_{18}I_2N$ $[M + H]^+$ 537.9523, found 537.9514.

9-(4-Fluorophenyl)-7,8-diiodo-9-(4-methoxyphenyl)-10-methyl-6,9-dihydropyrido[1,2-a]indole (**2s**). White solid (116.8 mg, 92%). Mp: 96−98 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, *J* = 7.6 Hz, 1H), 7.27−7.13 (m, 7H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.94−4.84 (m, 3H), 3.79 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 161.8 (d, $^1J_{C-F}$ = 246 Hz), 158.7, 140.6, 136.1, 134.5, 133.8, 131.1 (d, $^3J_{C-F}$ = 8 Hz), 130.4, 129.8, 125.7, 121.9, 119.6, 118.8, 114.8 (d, $^2J_{C-F}$ = 21 Hz), 113.3, 108.4, 107.2, 105.5, 60.3, 55.2, 54.9, 10.1. IR (neat, cm^{-1}): 2928, 1603, 1505, 1467, 1252, 1034, 827, 739. HRMS (ESI): *m/z* calcd for $C_{26}H_{21}FI_2NO$ $[M + H]^+$ 635.9691, found 635.9684.

9-(4-Fluorophenyl)-7,8-diiodo-10-methyl-9-(thiophen-2-yl)-6,9-dihydropyrido[1,2-a]indole (**2t**). Pale yellow solid (111.2 mg, 91%). Mp: 90−92 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.51 (d, *J* = 7.6 Hz, 1H), 7.22−7.09 (m, 7H), 7.01−6.93 (m, 3H), 5.18 (d, *J* = 17.2 Hz, 1H), 4.72 (d, *J* = 17.2 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 161.9 (d, $^1J_{C-F}$ = 246 Hz), 146.1, 143.2, 143.2, 134.1, 133.6, 130.8 (d, $^3J_{C-F}$ = 8 Hz), 128.8, 127.3, 126.6, 125.9, 123.7,

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122.2, 119.8, 119.0, 114.8 (d, $^2J_{C-F}$ = 21 Hz), 108.5, 107.8, 106.1, 57.8, 54.7, 9.8. IR (neat, cm^{-1}): 2915, 1602, 1504, 1467, 1234, 830, 740, 703. HRMS (ESI): *m/z* calcd for $C_{23}H_{17}FI_2NS$ [M + H]$^+$ 611.9150, found 611.9144.

*7,8-Diiodo-9,10-dimethyl-9-phenyl-6,9-dihydropyrido[1,2-a]-indole (**2u**).* Yellow solid (87.2 mg, 83%). Mp: 84−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.45 (d, *J* = 7.6 Hz, 1H), 7.30−7.20 (m, 7H), 7.13 (t, *J* = 7.6 Hz, 1H), 5.18 (d, *J* = 17.2 Hz, 1H), 4.98 (d, *J* = 17.2 Hz, 1H), 1.98 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 146.2, 133.5, 133.2, 128.9, 127.9, 127.6, 127.0, 126.7, 121.4, 119.8, 118.1, 108.6, 106.3, 101.9, 54.6, 51.9, 27.4, 9.1. IR (neat, cm^{-1}): 2917, 1467, 1455, 1369, 1232, 769, 739, 697. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}I_2N$ [M + H]$^+$ 525.9523, found 525.9518.

*7,8-Diiodo-9,10-dimethyl-9-(p-tolyl)-6,9-dihydropyrido[1,2-a]-indole (**2v**).* Yellow solid (86.2 mg, 80%). Mp: 90−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.45 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.22−7.19 (m, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.08 (s, 3H), 5.16 (d, *J* = 17.2 Hz, 1H), 4.97 (d, *J* = 17.2 Hz, 1H), 2.32 (s, 3H), 1.95 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 143.2, 136.6, 133.6, 133.1, 128.9, 128.6, 127.4, 127.2, 121.3, 119.8, 118.1, 108.6, 106.2, 101.6, 54.6, 51.6, 27.4, 21.1, 9.1. IR (neat, cm^{-1}): 2916, 1510, 1468, 1454, 1369, 1234, 813, 739. HRMS (ESI): *m/z* calcd for $C_{21}H_{20}I_2N$ [M + H]$^+$ 539.9680, found 539.9685.

*9-(4-Chlorophenyl)-7,8-diiodo-9,10-dimethyl-6,9-dihydropyrido-[1,2-a]indole (**2w**).* Pale yellow solid (63.7 mg, 57%). Mp: 94−96 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.47 (d, *J* = 8.0 Hz, 1H), 7.30−7.27 (m, 2H), 7.25−7.23 (m, 2H), 7.16−7.13 (m, 3H), 5.17 (d, *J* = 17.2 Hz, 1H), 4.97 (d, *J* = 17.2 Hz, 1H), 1.96 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 144.8, 133.2, 132.9, 132.8, 129.0, 128.8, 128.1, 125.9, 121.6, 120.0, 118.2, 108.6, 106.4, 102.3, 54.6, 51.5, 27.4, 9.2. IR (neat, cm^{-1}): 2920, 1488, 1467, 1454, 1234, 1012, 821, 740. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}ClI_2N$ [M + H]$^+$ 559.9133, found 559.9135.

*9-Ethyl-7,8-diiodo-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]-indole (**2x**).* Yellow solid (71.1 mg, 66%). Mp: 80−82 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.45 (d, *J* = 8.0 Hz, 1H), 7.29−7.20 (m, 7H), 7.12 (t, *J* = 7.6 Hz, 1H), 5.17 (d, *J* = 17.6 Hz, 1H), 4.96 (d, *J* = 17.6 Hz, 1H), 2.67−2.58 (m, 1H), 2.47−2.38 (m, 1H), 1.66 (s, 3H), 0.67 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 146.4, 133.3, 131.9, 129.0, 127.9, 127.8, 126.9, 125.4, 121.2, 119.8, 118.1, 108.5, 106.1, 102.6, 56.9, 55.0, 31.5, 9.1, 8.7. IR (neat, cm^{-1}): 2928, 1467, 1452, 1369, 1231, 766, 738, 696. HRMS (ESI): *m/z* calcd for $C_{21}H_{20}I_2N$ [M + H]$^+$ 539.9680, found 539.9672.

*7,8-Diiodo-9,9,10-triphenyl-6,9-dihydropyrido[1,2-a]indole (**2z**).* Yellow solid (111.6 mg, 86%). Mp: 210−212 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.37 (d, *J* = 8.4 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.14−7.06 (m, 11H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 2H), 6.48 (d, *J* = 7.2 Hz, 2H), 5.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 143.1, 134.6, 133.9, 133.1, 130.8, 129.8, 129.4, 127.4, 127.2, 127.1, 126.3, 125.8, 122.2, 120.5, 119.8, 115.6, 108.5, 104.3, 61.2, 54.8. IR (neat, cm^{-1}): 3052, 1490, 1466, 1448, 1375, 907, 740, 701. HRMS (ESI): *m/z* calcd for $C_{30}H_{22}I_2N$ [M + H]$^+$ 649.9836, found 649.9853.

*7,8-Diiodo-9,9-diphenyl-6,9-dihydropyrido[1,2-a]indole (**2aa**).* Yellow solid (80.2 mg, 70%). Mp: 96−98 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.47 (d, *J* = 8.0 Hz, 1H), 7.28−7.26 (m, 10H), 7.24−7.15 (m, 2H), 7.11−7.07 (m, 1H), 5.91 (s, 1H), 4.92 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 144.6, 140.0, 134.7, 129.7, 128.0, 127.8, 127.4, 123.6, 121.5, 120.7, 120.3, 108.7, 106.1, 101.9, 61.4, 55.0. IR (neat, cm^{-1}): 3054, 1491, 1465, 1445, 1360, 1034, 745, 699. HRMS (ESI): *m/z* calcd for $C_{24}H_{18}I_2N$ [M + H]$^+$ 573.9523, found 573.9515.

*1-Chloro-7,8-diiodo-9,9-diphenyl-6,9-dihydropyrido[1,2-a]indole (**2ab**).* White solid (78.9 mg, 65%). Mp: 100−102 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.32−7.26 (m, 10H), 7.13−7.04 (m, 3H), 6.05 (s, 1H), 4.90 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 144.3, 140.6, 135.3, 129.6, 127.9, 127.6, 126.8, 126.0, 123.6, 122.1, 120.2, 107.4, 105.4, 100.3, 61.4, 55.1. IR (neat, cm^{-1}): 3056, 1492, 1433, 1351, 1273, 1035, 761, 698. HRMS (ESI): *m/z* calcd for $C_{24}H_{17}ClI_2N$ [M + H]$^+$ 607.9133, found 607.9121.

*7,8-Diiodo-2-methoxy-9,9-diphenyl-6,9-dihydropyrido[1,2-a]-indole (**2ac**).* White solid (57.9 mg, 48%). Mp: 92−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.29−7.24 (m, 10H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.86−6.83 (m, 1H), 5.83 (s, 1H), 4.92 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 154.6, 144.6, 140.5, 130.0, 129.7, 128.4, 127.8, 127.4, 123.5, 111.7, 109.5, 106.1, 102.5, 101.5, 61.4, 55.8, 55.1. IR (neat, cm^{-1}): 3055, 1619, 1478, 1445, 1209, 1034, 820, 701. HRMS (ESI): *m/z* calcd for $C_{25}H_{20}I_2NO$ [M + H]$^+$ 603.9629, found 603.9620.

*3-Chloro-7,8-diiodo-9,9-diphenyl-6,9-dihydropyrido[1,2-a]indole (**2ad**).* Yellow solid (93.4 mg, 77%). Mp: 102−104 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.35 (d, *J* = 8.0 Hz, 1H), 7.30−7.24 (m, 10H), 7.21 (d, *J* = 6.0 Hz, 1H), 7.05−7.03 (m, 1H), 5.88 (s, 1H), 4.86 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 144.4, 140.7, 135.1, 129.6, 127.9, 127.5, 127.4, 126.4, 123.5, 121.5, 121.0, 108.9, 105.6, 101.9, 61.3, 54.9. IR (neat, cm^{-1}): 3056, 1491, 1469, 1446, 1340, 811, 731, 700. HRMS (ESI): *m/z* calcd for $C_{24}H_{17}ClI_2N$ [M + H]$^+$ 607.9133, found 607.9125.

*7,8-Diiodo-4-methyl-9,9-diphenyl-6,9-dihydropyrido[1,2-a]indole (**2ae**).* Pale yellow solid (79.8 mg, 68%). Mp: 94−96 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.30−7.25 (m, 11H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 6.8 Hz, 1H), 5.86 (s, 1H), 5.30 (s, 2H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 144.7, 140.3, 134.6, 129.7, 128.7, 127.8, 127.4, 124.5, 123.1, 120.6, 120.4, 118.8, 107.2, 102.9, 61.2, 58.0, 19.8. IR (neat, cm^{-1}): 3051, 1596, 1490, 1444, 1318, 795, 740, 698. HRMS (ESI): *m/z* calcd for $C_{25}H_{20}I_2N$ [M + H]$^+$ 587.9680, found 587.9675.

*7,8-Diiodo-6,6,10-trimethyl-9,9-diphenyl-6,9-dihydropyrido[1,2-a]indole (**2af**).* Pale yellow solid (67.7 mg, 55%). Mp: 230−232 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.51 (d, *J* = 8.4 Hz, 1H), 7.47−7.43 (m, 5H), 7.32−7.23 (m, 6H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 2.17 (s, 6H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 144.0, 135.4, 134.0, 130.7, 129.5, 127.8, 127.1, 126.7, 126.7, 121.0, 119.3, 118.8, 113.8, 107.5, 64.5, 61.7, 30.8, 10.9. IR (neat, cm^{-1}): 2919, 1489, 1454, 1318, 1201, 761, 741, 696. HRMS (ESI): *m/z* calcd for $C_{27}H_{24}I_2N$ [M + H]$^+$ 615.9993, found 615.9987.

*7-Bromo-8-iodo-10-methyl-9,9-diphenyl-6,9-dihydropyrido[1,2-a]indole (**3a**).* Pale yellow solid (89.5 mg, 83%). Mp: 180−182 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.51−7.49 (m, 1H), 7.33−7.30 (m, 10H), 7.22 (s, 2H), 7.14−7.12 (m, 1H), 4.90 (s, 2H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 143.7, 134.6, 134.0, 129.5, 129.3, 128.0, 127.4, 126.1, 121.9, 119.7, 118.8, 116.9, 108.4, 107.5, 60.8, 50.3, 10.1. IR (neat, cm^{-1}): 2918, 1492, 1467, 1445, 1237, 811, 741, 700. HRMS (ESI): *m/z* calcd for $C_{25}H_{20}BrIN$ [M + H]$^+$ 539.9818, found 539.9808.

*7-Bromo-8-iodo-10-methyl-9,9-di-p-tolyl-6,9-dihydropyrido[1,2-a]indole (**3b**).* Yellow solid (88.5 mg, 78%). Mp: 88−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.48 (d, *J* = 7.6 Hz, 1H), 7.21−7.18 (m, 6H), 7.13−7.09 (m, 5H), 4.89 (s, 2H), 2.33 (s, 6H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 140.9, 137.0, 134.9, 134.0, 129.4, 128.7, 125.5, 121.7, 119.6, 118.7, 117.7, 108.4, 107.4, 60.4, 50.3, 21.0, 10.1. IR (neat, cm^{-1}): 2917, 1508, 1468, 1449, 1236, 813, 738, 678. HRMS (ESI): *m/z* calcd for $C_{27}H_{24}BrIN$ [M + H]$^+$ 568.0131, found 568.0124.

*7-Bromo-8-iodo-10-methyl-9-phenyl-9-(p-tolyl)-6,9-dihydropyrido[1,2-a]indole (**3h**).* Pale yellow solid (86.4 mg, 78%). Mp: 84−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.48 (d, *J* = 8.0 Hz, 1H), 7.33−7.27 (m, 5H), 7.22−7.19 (m, 4H), 7.13−7.09 (m, 3H), 4.91 (d, *J* = 17.2 Hz, 1H), 4.86 (d, *J* = 16.8 Hz, 1H), 2.32 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 144.1, 140.6, 137.1, 134.7, 134.0, 129.5, 129.3, 128.7, 128.0, 127.3, 125.8, 121.8, 119.6, 118.8, 117.3, 108.4, 107.4, 60.6, 50.3, 21.1, 10.1. IR (neat, cm^{-1}): 2917, 1509, 1467, 1446, 1236, 816, 739, 701. HRMS (ESI): *m/z* calcd for $C_{26}H_{22}BrIN$ [M + H]$^+$ 553.9975, found 553.9969.

*7-Bromo-9-(4-chlorophenyl)-8-iodo-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**3l**).* Pale yellow solid (81.4 mg, 71%). Mp: 78−80 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.50 (d, *J* = 8.0 Hz, 1H), 7.30−7.26 (m, 8H), 7.25−7.22 (m, 3H), 7.17−7.11 (m, 1H), 4.92 (d, *J* = 16.8 Hz, 1H), 4.87 (d, *J* = 17.2 Hz, 1H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 143.2, 142.5, 134.1, 134.1, 133.4,

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131.0, 129.3, 128.2, 127.6. 126.4, 122.1, 119.8, 118.9, 116.3, 108.4, 107.6, 60.4, 50.3, 10.2. IR (neat, cm^{-1}): 2929, 1489, 1467, 1446, 1094, 823, 740, 700. HRMS (ESI): *m/z* calcd for $C_{25}H_{19}BrClIN$ $[M + H]^+$ 573.9429, found 573.9419.

*9-([1,1′-Biphenyl]-4-yl)-7-bromo-8-iodo-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (**3n**).* Pale yellow solid (98.4 mg, 80%). Mp: 106−108 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.58 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.42−7.39 (m, 4H), 7.37−7.34 (m, 2H), 7.32−7.28 (m, 4H), 7.21−7.20 (m, 2H), 7.15−7.10 (m, 1H), 4.93 (d, *J* = 16.8 Hz, 1H), 4.88 (d, *J* = 16.8 Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.0, 142.4, 140.2, 140.0, 134.5, 134.0, 129.8, 129.6, 129.4, 128.8, 128.0, 127.4, 127.4, 126.9, 126.6, 126.1, 121.9, 119.7, 118.8, 116.8, 108.4, 107.5, 60.6, 50.3, 10.2. IR (neat, cm^{-1}): 2918, 1599, 1486, 1467, 1447, 762, 738, 699. HRMS (ESI): *m/z* calcd for $C_{31}H_{24}BrIN$ $[M + H]^+$ 616.0131, found 616.0121.

*7-Bromo-9-(4-fluorophenyl)-8-iodo-9-(4-methoxyphenyl)-10-methyl-6,9-dihydropyrido[1,2-a]indole (**3s**).* White solid (95.1 mg, 81%). Mp: 88−90 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, *J* = 8.0 Hz, 1H), 7.29−7.26 (m, 2H), 7.22−7.19 (m, 4H), 7.14−7.10 (m, 1H), 6.98 (t, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.91 (d, *J* = 17.2 Hz, 1H), 4.85 (d, *J* = 17.2 Hz, 1H), 3.78 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 161.2 (d, $^1J_{C-F}$ = 246 Hz), 158.7, 140.2, 140.2, 135.6, 134.6, 134.0, 131.2 (d, $^3J_{C-F}$ = 8 Hz), 130.5, 129.3, 125.9, 122.0, 119.7, 118.8, 117.4, 114.8 (d, $^2J_{C-F}$ = 22 Hz), 113.4, 108.4, 107.3, 59.7, 55.2, 50.2, 10.1. IR (neat, cm^{-1}): 2928, 1603, 1505, 1467, 1252, 1034, 828, 740. HRMS (ESI): *m/z* calcd for $C_{26}H_{21}BrFINO$ $[M + H]^+$ 587.9830, found 587.9822.

*7-Bromo-9-(4-fluorophenyl)-8-iodo-10-methyl-9-(thiophen-2-yl)-6,9-dihydropyrido[1,2-a]indole (**3t**).* Pale yellow solid (75.4 mg, 67%). Mp: 172−174 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.51 (d, *J* = 7.6 Hz, 1H), 7.26−7.23 (m, 4H), 7.20−7.18 (m, 1H), 7.16−7.10 (m, 2H), 6.99 (t, *J* = 8.8 Hz, 2H), 6.94−6.92 (m, 1H), 5.08 (d, *J* = 17.2 Hz, 1H), 4.77 (d, *J* = 17.2 Hz, 1H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 162.0 (d, $^1J_{C-F}$ = 246 Hz), 146.2, 142.4, 142.4, 134.3, 133.9, 130.9 (d, $^3J_{C-F}$ = 8 Hz), 129.1, 127.4, 126.6, 126.3, 125.9, 122.3, 119.9, 119.0, 115.7, 114.6 (d, $^2J_{C-F}$ = 21 Hz), 108.5, 107.9, 57.5, 50.1, 9.8. IR (neat, cm^{-1}): 2918, 1602, 1505, 1467, 1233, 832, 738, 708. HRMS (ESI): *m/z* calcd for $C_{23}H_{16}BrFINS$ $[M + H]^+$ 562.9210, found 562.9203.

*7-Chloro-8-iodo-10-methyl-9,9-diphenyl-6,9-dihydropyrido[1,2-a]indole (**4a**).* Pale yellow solid (80.2 mg, 81%). Mp: 190−192 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, *J* = 7.6 Hz, 1H), 7.34−7.30 (m, 5H), 7.29−7.26 (m, 5H), 7.21−7.20 (m, 2H), 7.13−7.09 (m, 1H), 4.81 (s, 2H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 143.7, 134.8, 134.2, 133.8, 129.5, 128.7, 128.0, 127.4, 121.9, 119.7, 118.8, 113.0, 108.4, 107.6, 59.9, 48.1, 10.1. IR (neat, cm^{-1}): 2917, 1614, 1469, 1443, 1239, 747, 707, 695. HRMS (ESI): *m/z* calcd for $C_{25}H_{20}ClIN$ $[M + H]^+$ 496.0323, found 496.0316.

*7-Chloro-8-iodo-10-methyl-9,9-di-p-tolyl-6,9-dihydropyrido[1,2-a]indole (**4b**).* Pale yellow solid (77.4 mg, 74%). Mp: 84−86 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.48 (d, *J* = 7.6 Hz, 1H), 7.22−7.18 (m, 6H), 7.10−7.08 (m, 5H), 4.81 (s, 2H), 2.32 (s, 6H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 140.8, 137.0, 135.0, 134.1, 133.2, 129.4, 128.9, 128.7, 121.7, 119.6, 118.7, 113.7, 108.4, 107.4, 59.4, 48.0, 21.0, 10.1. IR (neat, cm^{-1}): 2918, 1610, 1509, 1469, 1452, 1384, 815, 738. HRMS (ESI): *m/z* calcd for $C_{27}H_{24}ClIN$ $[M + H]^+$ 524.0636, found 524.0630.

Characterization Data of 5b−7b. *7,8-Bis(4-methoxyphenyl)-10-methyl-9,9-di-p-tolyl-6,9-dihydropyrido[1,2-a]indole (**5b**, Synthesis from **2b**).* White solid (65.6 mg, 57%). Mp: 112−114 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 4H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.11−7.07 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 4H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.37 (d, *J* = 8.4 Hz, 2H), 6.28 (d, *J* = 8.4 Hz, 2H), 4.97 (s, 2H), 3.70 (s, 3H), 3.57 (s, 3H), 2.26 (s, 6H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 158.1, 157.3, 139.8, 139.6, 138.8, 135.6, 134.2, 132.6, 132.5, 132.0, 131.7, 130.5, 129.9, 129.7, 128.2, 120.6, 119.0, 118.3, 113.4, 112.0, 108.5, 105.2, 56.6, 55.1, 54.8, 47.3, 20.9, 10.1. IR (neat, cm^{-1}): 2920, 1606, 1510, 1469, 1248, 1179, 809, 739. HRMS (ESI): *m/z* calcd for $C_{41}H_{38}NO_2$ $[M + H]^+$ 576.2897, found 576.2886.

*7,8-Bis(4-methoxyphenyl)-10-methyl-9,9-di-p-tolyl-6,9-dihydropyrido[1,2-a]indole (**5b**, Synthesis from **3b**).* White solid (81.7 mg, 71%). Mp: 112−114 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.49 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 4H), 7.18 (s, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 4H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.37 (d, *J* = 8.8 Hz, 2H), 6.28 (d, *J* = 9.2 Hz, 2H), 4.97 (s, 2H), 3.69 (s, 3H), 3.56 (s, 3H), 2.26 (s, 6H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 158.1, 157.3, 139.8, 139.6, 138.8, 135.6, 134.2, 132.6, 132.5, 132.0, 131.7, 130.5, 129.9, 129.7, 128.2, 120.6, 119.0, 118.3, 113.4, 112.0, 108.5, 105.2, 56.5, 55.1, 54.8, 47.3, 20.9, 10.1. IR (neat, cm^{-1}): 2920, 1606, 1510, 1469, 1248, 1179, 809, 739. HRMS (ESI): *m/z* calcd for $C_{41}H_{38}NO_2$ $[M + H]^+$ 576.2897, found 576.2886.

*7-Chloro-8-(4-methoxyphenyl)-10-methyl-9,9-di-p-tolyl-6,9-dihydropyrido[1,2-a]indole (**6b**).* Pale yellow solid (62.4 mg, 62%). Mp: 208−210 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.47 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.23−7.20 (m, 1H), 7.14−7.11 (m, 5H), 6.97 (d, *J* = 7.6 Hz, 4H), 6.57−6.54 (m, 2H), 6.46−6.43 (m, 2H), 5.05 (s, 2H), 3.70 (s, 3H), 2.28 (s, 6H), 1.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 158.5, 139.2, 138.0, 136.7, 136.1, 134.1, 131.4, 129.9, 129.7, 129.6, 128.2, 124.3, 121.1, 119.6, 118.3, 112.6, 108.6, 106.4, 57.5, 55.0, 47.8, 20.9, 10.1. IR (neat, cm^{-1}): 2918, 1608, 1510, 1470, 1244, 1034, 816, 738. HRMS (ESI): *m/z* calcd for $C_{34}H_{31}ClNO$ $[M + H]^+$ 504.2089, found 504.2081.

*7,8-Bis((4-methoxyphenyl)ethynyl)-10-methyl-9,9-di-p-tolyl-6,9-dihydropyrido[1,2-a]indole (**7b**).* Pale yellow solid (44.9 mg, 36%). Mp: 102−104 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.54 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.22−7.19 (m, 5H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 4H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.77 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 2.34 (s, 6H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 160.0, 159.7, 140.4, 136.3, 135.5, 134.4, 134.1, 133.1, 133.0, 129.5, 129.4, 128.6, 121.7, 121.3, 119.1, 118.6, 115.5, 115.1, 114.1, 113.8, 108.6, 107.6, 99.9, 96.7, 88.6, 86.6, 55.4, 55.3, 55.3, 44.9, 21.0, 9.6. IR (neat, cm^{-1}): 2918, 1606, 1508, 1468, 1249, 1031, 830, 739. HRMS (ESI): *m/z* calcd for $C_{45}H_{38}NO_2$ $[M + H]^+$ 624.2897, found 624.2888.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02013.

Crystallographic data for **2a** (CIF)
Crystallographic data for **3a** (CIF)
Spectral data for all new compounds and crystal data for **2a** and **3a** (PDF)

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Notes

The authors declare no competing financial interest.

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