Article

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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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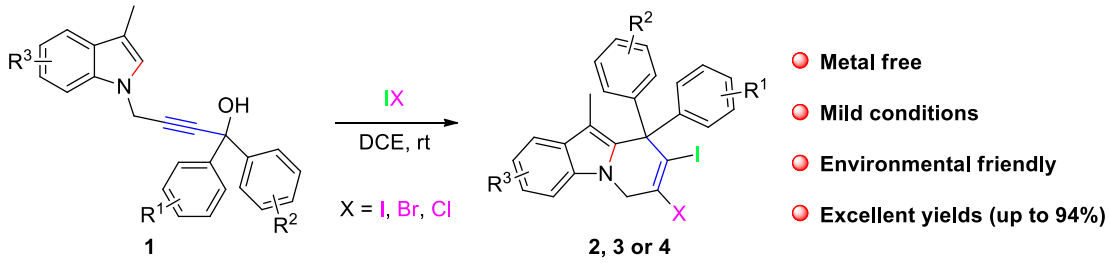
ABSTRACT



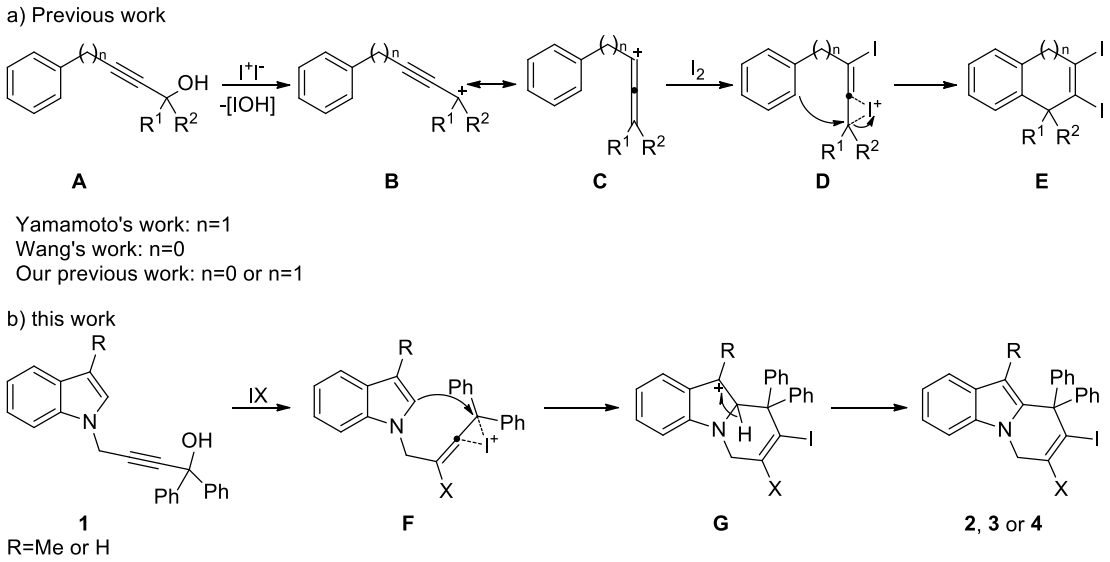
A strategy for the synthesis of 6,9-dihydropyrido[1,2-*a*]indoles through a cascade iodocyclization of 4-(3-methyl-1*H*-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol derivatives is presented. This reaction is conducted under very mild condition and in a short time. The reactions are metal-free, environmental friendly and 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 force 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 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 mild and efficient preparative protocols for building pyridoindoles.[5] In recent years, the electrophilic cyclization, especially iodocyclization, has been a prominent research objective in organic chemistry.[6] Many important carbocycles and heterocycles have been produced based on the efficient iodocyclizations.[7] What's more, the iodocyclizations are considered to be mild, metal-free and environmental friendly.[8] Although great achievements have been made to iodocyclization, few examples of sequential cascade iodocyclization to form pyridoindoles have been reported until now. Therefore, seeking alternative methods for the construction of 6,9-dihydropyrido[1,2-*a*]indoles based on iodocyclization is indeed desirable.

Scheme 1. Iodine-promoted Cascade Carbocyclization

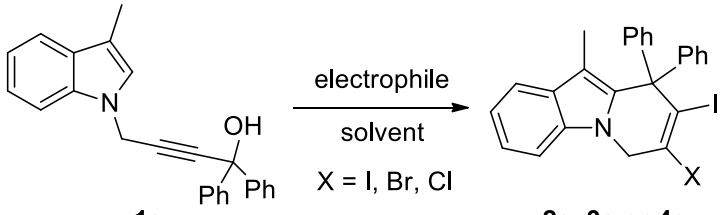


Recently, methods involving iodonium-induced activation of propargylic alcohol substrates have offered the opportunity to construct diiodinated carbocycles by Yamamoto,[9] Wang,[10] and our group.[11] This reaction is generally believed to proceed through a cascade process. Initial activation of the 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. Subsequent intramolecular Friedel–Craft type reaction of the aromatic ring with the activated allene forms the product **E** (Scheme 1a). Encouraged by these achievements and in continuing our interest in the electrophilic cyclization of alkynols, we envisioned that the substrates **1** containing an indole moiety could undergo the 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

Table 1. Optimization of Reaction Conditions for the Formation of 2a, 3a or 4a with different electrophiles[a]



1a **2a, 3a or 4a**

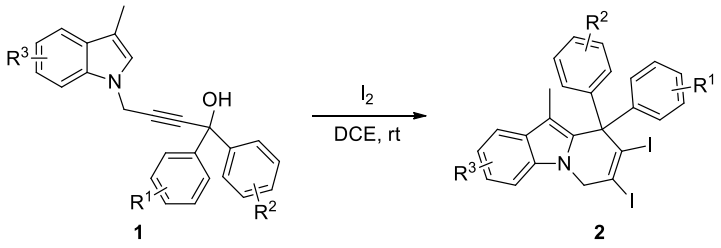
entry	solvent	electrophile (equiv)	yield (%)[b]
1	DCE	I_2 (1.0)	88
2	**DCE**	**I_2 (1.2)**	**94**
3	DCE	I_2 (1.5)	94
4	CH_2Cl_2	I_2 (1.2)	92
5	CH_3CN	I_2 (1.2)	88
6	CH_3NO_2	I_2 (1.2)	83
7	THF	I_2 (1.2)	69
8	Et_2O	I_2 (1.2)	65
9	acetone	I_2 (1.2)	84
10	MeOH	I_2 (1.2)	80
11	toluene	I_2 (1.2)	88
12	DCE	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**, 1.2 equiv of electrophile in 4 mL of solvent were

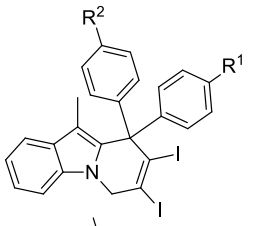
stirred at room temperature for 10 min. [b]Yields of isolated products. [c]The reaction was run at 0 °C. [d]The reaction was run at 40 °C.

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 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 to 94% by 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 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 a series of detailed investigations mentioned above, the combination of 1.0 equiv of **1a**, 1.2 equiv of electrophile in DCE at room temperature for 10 min was determined as the optimum reaction conditions.

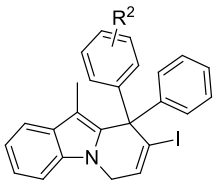
Table 2. Electrophilic Iodocyclization for the Formation of 2[a]



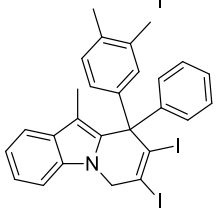
1 **2**



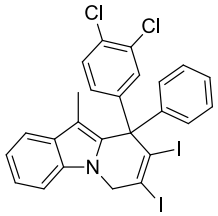
2a, $R^1 = R^2$ = H, 94%
2b, $R^1 = R^2$ = Me, 92%
2c, $R^1 = R^2$ = OMe, 87%
2d, $R^1 = R^2$ = F, 66%
2e, $R^1 = R^2$ = Cl, 73%



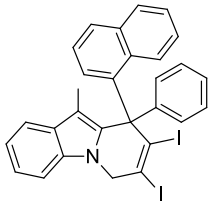
2f, R^2 = *o*-Me, 89%
2g, R^2 = *m*-Me, 82%
2h, R^2 = *p*-Me, 88%
2i, R^2 = *p*-OMe, 88%
2j, R^2 = *o*-Cl, 78%
2k, R^2 = *m*-Cl, 85%
2l, R^2 = *p*-Cl, 84%
2m, R^2 = *p*-F, 87%
2n, R^2 = *p*-Ph, 90%



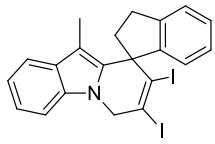
2o, 89%



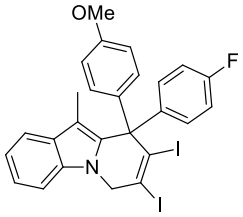
2p, 84%



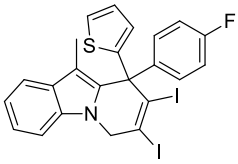
2q, 71%



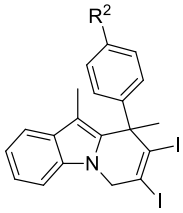
2r, 76%



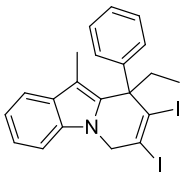
2s, 92%



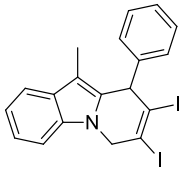
2t, 91%



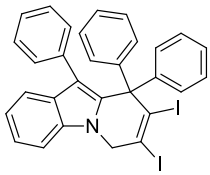
2u, R^2 = H, 83%
2v, R^2 = Me, 80%
2w, R^2 = Cl, 57%



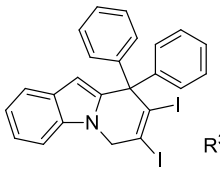
2x, 66%



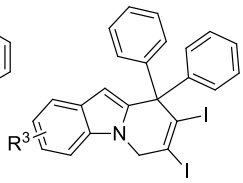
2y, 0%



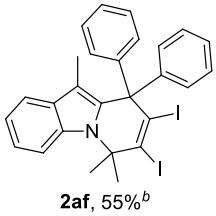
2z, 86%



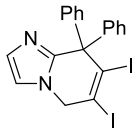
2aa, 70%



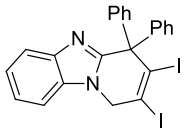
2ab, R^3 = 4-Cl, 65%
2ac, R^3 = 5-OMe, 48%
2ad, R^3 = 6-Cl, 77%
2ae, R^3 = 7-Me, 68%



2af, 55%[b]



2ag, 0%



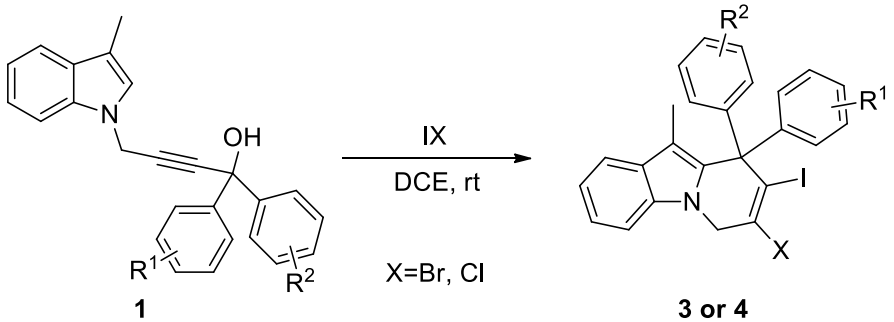
2ah, 0%

[a]All reactions were run under the following conditions, unless otherwise indicated: 0.20 mmol of **1**, 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.

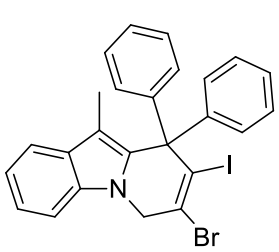
After having established the optimized conditions for the present reaction, various 4-(3-methyl-1*H*-indol-1-yl)-1,1-diphenylbut-2-yn-1-ol derivatives were subjected to the above conditions, as summarized in Table 2. The structure of the representative product **2a** was determined by X-ray crystallographic analysis. The reactions of substrates **1b** and **1c** bearing double electron-donating groups (R^1 and R^2) on the *para*-position of the aromatic ring resulted in the corresponding products **2b** and **2c** in excellent yields. The yields of **2d** and **2e** decreased with the increase of electronegativity on the substituent R^1 and R^2 groups. Subsequently, compounds **1f**-**1n** with electron-donating or electron-withdrawing substituents (R^2) on different positions of the aromatic ring were designed. The corresponding products **2f**-**2n** were obtained in good yields. In the meantime, the reactions also worked well with the substrates **1o** and **1p** which had two substituents on the same aryl group, furnishing the expected products **2o** and **2p** in good yields. Afterwards, the huge steric hindrance substrate **1q** with the 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 strong 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 secondary alcohol failed to afford the corresponding product **2y**, products

2u-**2x** with alkyl groups were gained 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 on the 3-position of indole also worked well and afforded product **2z** in 86% yield. It is noteworthy that when the methyl group was absent from the 3-position of 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, the 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 strong electron-donating group, a methoxy group showed more remarkable influence on the product yield. In particular, the substrate **1af** with two methyl groups instead of the 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 relative lower yield was obatined due to steric effect. Neither the substrate **1ag** with imidazole nor substrate **1af** with benzimidazole gave the desired products as our expectation.

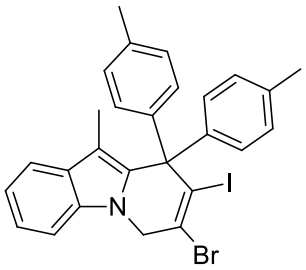
Table 3. Synthesis of Dihalogenated 6,9-dihydropyrido[1,2-*a*]indoles with IBr and ICl[a]



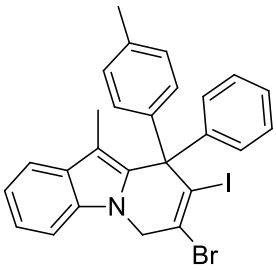
1 **3 or 4**



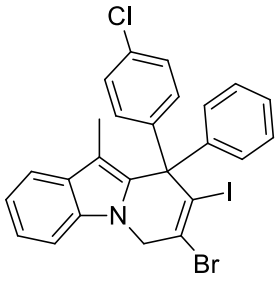
3a, 83%



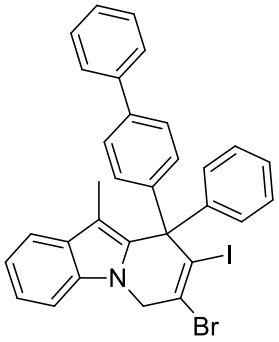
3b, 78%



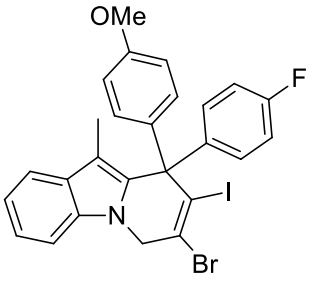
3h, 78%



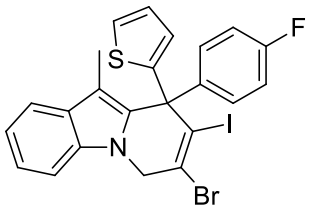
3l, 71%



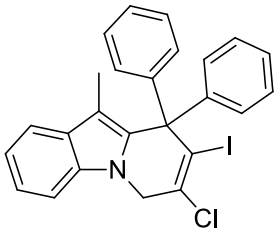
3n, 80%



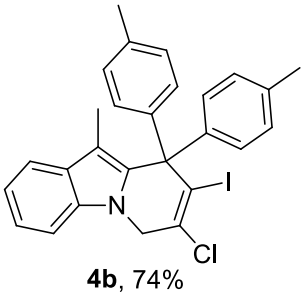
3s, 81%



3t, 67%



4a, 81%

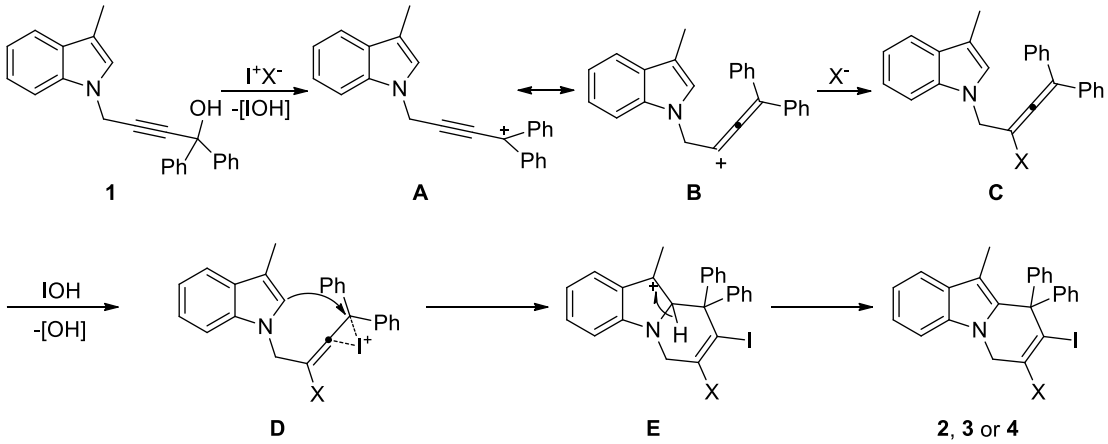


4b, 74%

[a]All reactions were run under the following conditions, unless otherwise indicated: 0.20 mmol of **1**, 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.

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-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** and **4b** were gained in good yields. For an increasing electronegativity of halogen anion, the yields of **3a** and **4a** were progressively decreased due to an unstable intermediate **C** compared with **2a**.

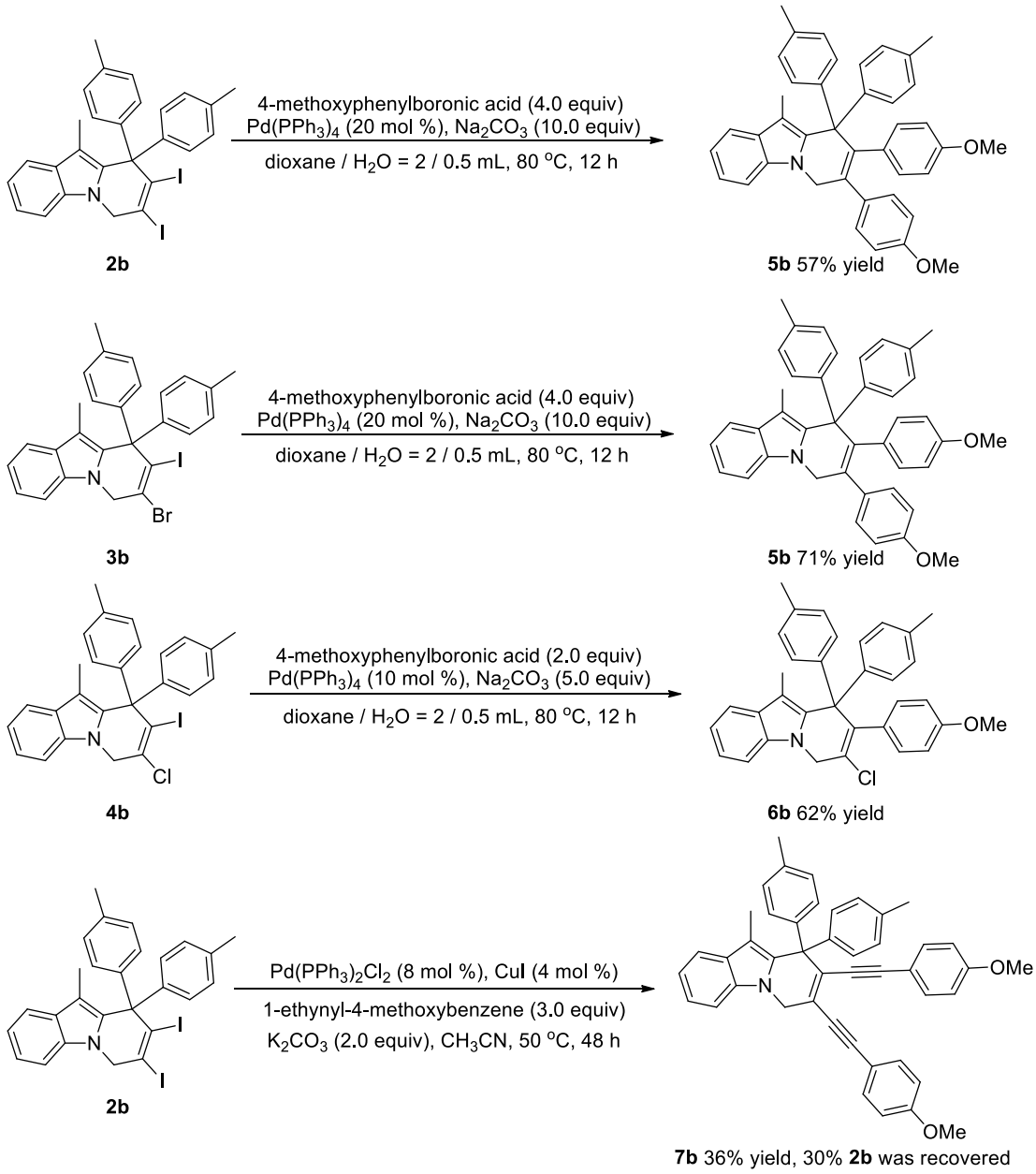
Scheme 2. Proposed Reaction Mechanism



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 an unstable hypoiodous acid (HOI) 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 an 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**, **3** or **4** by deprotonation.[13]

Scheme 3. Palladium-Catalyzed Coupling Reactions



As shown in Scheme 3, the compounds **2b**, **3b**, and **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. Noteworthily, 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 indole derivatives (100 mmol) in DMF (250 mL) was added NaH (60%, 2.0 equiv) slowly at 0 ^{o}C, The resulting solution was stirred 1h at 0 ^{o}C, Then, the propargylic bromide (2.0 equiv) was added dropwise through a syringe. The reaction mixture was stirred at room temperature for

another 2h. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched by water (200 mL) and extracted by ethyl acetate (3 x 150 mL). The combined organic layer was dried over anhydrous Na_2SO_4, the 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% yields.[16] A solution of the above 1-(prop-2-yn-1-yl)-1*H*-indole derivatives (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 stirring 30 minutes at −40 ^{o}C, the solution of ketone **C** (1.5 equiv) in THF (5 mL) was added to the reaction via syringe and the resulting mixture was removed to room temperature. After 2h, the mixture was quenched by water, and extracted with ethyl acetate (3 x 40 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4, the 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 ^{o}C, The resulting solution was stirred 2h at 0 ^{o}C, Then, the 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 12h. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched by water and extracted by ethyl acetate (3 x 60 mL). The combined organic layer was dried over anhydrous Na_2SO_4, the 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 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 general procedure as mentioned above.

Synthesis of 1ag and 1ah

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 ^{o}C for 1h before it was coold to room temperature. Subsenquently, 3-bromopropyne (30.8 mmol, 1.1 equiv) was added and the solution stirred for another 12h. 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 general procedure as mentioned above. The substrate **1ah** which was synthesized from benzimidazole was similar to 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 addition of saturated aqueous sodium thiosulfate and diluted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na_2SO_4, the 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 corresponding halogenated 6,9-dihydropyrido[1,2-*a*]indoles derivatives **2**, **3** or **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 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) was added 4-Methoxyphenylboronic acid (121.6 mg, 4.0 equiv), $Pd(PPh_3)_4$ (46.2 mg, 20 mol %), 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 12h. On completion, the reaction mixture was quenched with H_2O (10 mL) and extracted with ethyl ether (3 x 10 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4, the 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) was added 4-Methoxyphenylboronic acid (121.6 mg, 4.0 equiv), $Pd(PPh_3)_4$ (46.2 mg, 20 mol %), 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 12h. On completion, the reaction mixture was quenched with H_2O (10 mL) and extracted with ethyl ether (3 x 10 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4, the 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) was added

4-Methoxyphenylboronic acid (60.8 mg, 2.0 equiv), $Pd(PPh_3)_4$ (23.1 mg, 10 mol %), 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 12h. On completion, the reaction mixture was quenched with H_2O (10 mL) and extracted with ethyl ether (3 x 10 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4, the 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) was 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 48h at 50°C. Then, the mixture was quenched slowly by addition of aqueous 1M HCl (4 mL) and extracted with ethyl ether (3 x 20 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4, the 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, $^1J_{C\text{-}F}$ = 245 Hz), 140.1, 136.1, 129.2, 127.7 (d, $^3J_{C\text{-}F}$ = 8 Hz), 124.9, 121.8, 119.2, 115.1 (d, $^2J_{C\text{-}F}$ = 21 Hz), 111.4, 190.2, 87.0, 82.3, 73.4, 35.8, 9.5.

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, $^{1}J_{C\text{-}F}$ = 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, $^{2}J_{C\text{-}F}$ = 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, $^1J_{C\text{-}F}$ = 245 Hz), 159.0, 140.5, 136.6, 136.0, 129.1, 127.7 (d, $^3J_{C\text{-}F}$ = 8 Hz), 127.2, 124.9, 121.7, 119.1, 114.9 (d, $^2J_{C\text{-}F}$ = 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, $^{1}J_{C\text{-}F}$ = 246 Hz), 149.4, 139.5, 136.1, 129.1, 127.6 (d, $^{3}J_{C\text{-}F}$ = 9 Hz), 126.5, 126.1, 125.5, 124.9, 121.8, 119.2, 115.0 (d, $^{2}J_{C\text{-}F}$ = 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* = 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, 3, and 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]ind

ole (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, $^{1}J_{C\text{-}F}$ = 246 Hz), 140.0 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 134.1, 133.8, 131.0 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 129.0, 124.8, 122.1, 119.8, 118.9, 115.0 (d, $^{2}J_{C\text{-}F}$ = 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 $C_{25}H_{17}Cl_2I_2N$: $[M]^+$ = 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, ^1H 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, 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, ^{1}H 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, ^{1}H 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, ^{1}H 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, ^{1}H 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, ^{1}H 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, $^1J_{C\text{-}F}$ = 246 Hz), 143.8, 140.5, 140.4, 134.3, 133.9, 131.3 (d, $^3J_{C\text{-}F}$ = 8 Hz), 129.2, 129.2, 128.2, 127.5, 125.0, 122.0, 119.7, 118.8, 114.9 (d, $^2J_{C\text{-}F}$ = 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, ^{1}H 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, ^{1}H 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, ^{1}H 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, ^{1}H 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, ^{1}H 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, ^{1}H 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, $^1J_{C\text{-}F}$ = 246 Hz), 158.7, 140.6, 136.1, 134.5, 133.8, 131.1 (d, $^3J_{C\text{-}F}$ = 8 Hz), 130.4, 129.8, 125.7, 121.9, 119.6, 118.8, 114.8 (d, $^2J_{C\text{-}F}$ = 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, ^{1}H 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, $^1J_{C\text{-}F}$ = 246 Hz), 146.1, 143.2, 143.2, 134.1, 133.6, 130.8 (d, $^3J_{C\text{-}F}$ = 8 Hz), 128.8, 127.3, 126.6, 125.9, 123.7,

122.2, 119.8, 119.0, 114.8 (d, $^{2}J_{C\text{-}F}$ = 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, ^1H 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, ^1H 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, ^1H 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, ^1H 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, ^1H 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, ^1H 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]in

dole (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, 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, ^{1}H 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, ^{1}H 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, $^1J_{C\text{-}F}$ = 246 Hz), 158.7, 140.2, 140.2, 135.6, 134.6, 134.0, 131.2 (d, $^3J_{C\text{-}F}$ = 8 Hz), 130.5, 129.3, 125.9, 122.0, 119.7, 118.8, 117.4, 114.8 (d, $^2J_{C\text{-}F}$ = 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, ^{1}H 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, $^1J_{C\text{-}F}$ = 246 Hz), 146.2, 142.4, 142.4, 134.3,

133.9, 130.9 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 129.1, 127.4, 126.6, 126.3, 125.9, 122.3, 119.9, 119.0, 115.7, 114.6 (d, $^{2}J_{C\text{-}F}$ = 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 $C_{23}H_{16}BrFINS$: $[M]^{+}$ = 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, ^{1}H 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, ^{1}H 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, 6b, and 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. ^{1}H 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. ^{1}H 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. ^{1}H 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, ^{1}H 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.

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ASSOCIATED CONTENT

Supporting Information

Spectral data for all new compounds are provided. This Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Crystallographic file of **2a** (CIF)

Crystallographic file of **3a** (CIF)

Copies of ^{1}H NMR, ^{13}C NMR spectra. (PDF)

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Notes

The authors declare no competing financial interest.

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