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Three-Component Ordered Annulation of Amines, Ketones and Nitrovinylarenes: Access to Fused Pyrroles and Substituted Indoles under Metal-Free Conditions

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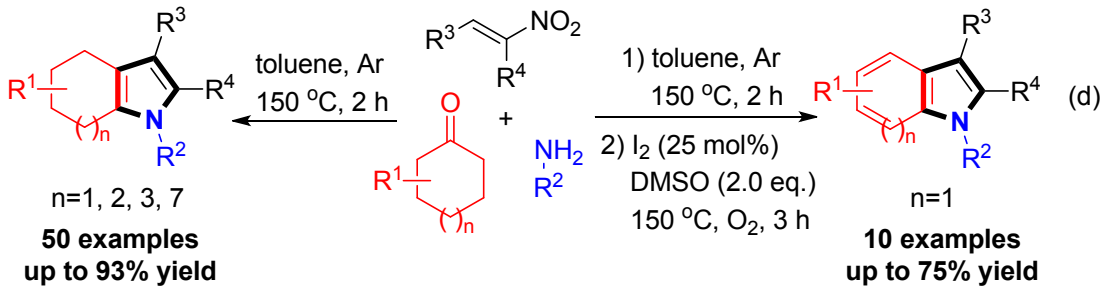


ABSTRACT: An efficient synthesis of pyrroles and indoles has been developed *via* three-component ordered annulation of amines, ketones and nitrovinylarenes. The reaction selectivity can be well controlled under metal-free conditions to afford the corresponding heterocyclic products in good yields.

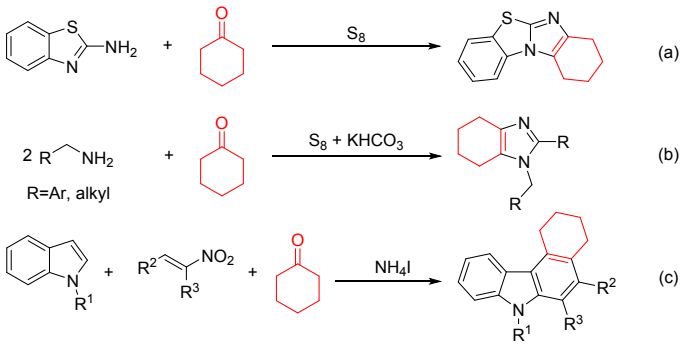
■ INTRODUCTION

Pyrroles and indoles both are privileged nitrogen-containing heterocycles and frequently found in biologically active natural products and pharmaceuticals. Some of them have antifungal, antitumor, anticancer, antibacterial, antiplasmodium, and anti-inflammortory properties.[1] Furthermore, pyrroles and indoles can be used as important building blocks in the synthesis of other nitrogen-containing biologically active chemicals and functional materials.[2] Accordingly, the development of efficient methods for the construction of pyrroles and indoles has attracted considerable interest and great progress has been made during the past several decades.[3]

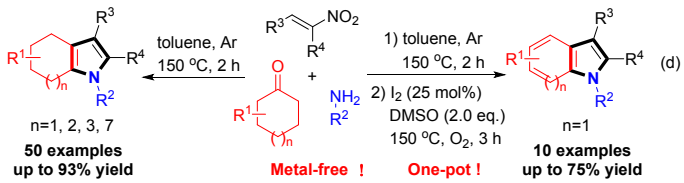
Cyclohexanones have received much attention because of the advantages of low-cost, stability and commercially available. In the past decade, cyclohexanones have been emerging as environmentally friendly and key reagents in organic synthesis. The versatility of cyclohexanones as aryl sources is reflected by the broad range of functionalized aromatic products they now provide, which includding phenols,[4] aromatic amines,[5] aromatic ethers,[6] biarenes,[7] and some kinds of benzoheterocycle.[8] Besides, cyclohexanones have been proved to be versatile building blocks for the construction of heterocycles without further dehydrogenative aromatization process. Our recent research revealed that cyclohexanones can couple with amines to permit 1,2-difunctionalization/C-N bond formation under sulfur-based aerobic conditions.[9] (Scheme 1a-b). In 2016, we developed a highly efficient method for carbazole formation through three-component assembly of indoles, ketones, and nitroalkenes under metal-free conditions (Scheme 1c).[10] However, cyclohexanone acts as the six-membered ring and dehydrogenative aromatization did not occur in these systems.

Scheme 1 Cyclohexanone involves heterocyclic compounds formation

Previous work (cyclohexanone as six-membered ring)



This work (cyclohexanone as both six-membered ring and aryl source)



As we know, enamines are important precursors for pyrrole synthesis. However, these important precursors are mainly rely on addition reaction of amines with alkynes which means aditional isolation process is usually required. The multicomponent reactions (MCRs) have been proved to be powerful protocol for the synthesis of pyrrole derivatives using simple

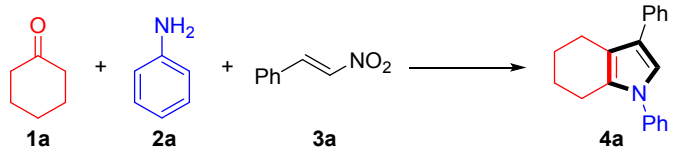
and readily available substrates.[11] Many MCRs pyrrole synthesis methods involve an enamine intermediate *in situ* generated from amines and alkynes or carbonyl compounds have been developed. The resulted enamines or enamides could subsequently cyclize with other substrates such as alkenes,[12] ketones,[13] aldehydes,[14] diketoesters[15] and diols[16]. In 2013, Davies and coworkers developed a strategy to convert cyclic ketones to 2,3-fused pyrroles *via* multi-step procedure. However, functionalized cyclohexenyl derivatives and Rh/Cu catalysts are required for the one-pot 2,3-fused pyrrole and substituted indole synthesis.[17] Other methods to convert fused pyrroles (tetrahydroindoles) into substituted indoles *via* dehydrogenation process usually use Pd/C or Pd/Al_2O_3 as catalyst at high temperatures.[18] Although these metal-catalyzed methods are very useful for the synthesis of pyrrole and indoles, critical issues remain regarding the presence of metal impurities in the final product, which may restrict their practical application. Therefore, efficient procedures for these nitrogen-containing heterocycles using readily available starting materials under metal-free conditions are still highly desirable. Although some efficient metal-free methods have been recently developed,[19] efficient method for both pyrrole and indole synthesis using the same starting materials is rare. As our continuing efforts on heterocycle formation under metal-free conditions,[20] herein we describe a general three-component reaction for fused pyrroles synthesis from readily available cyclic ketones, amines and nitrovinylarenes. Futhermore, substituted indoles could be obtained from the same starting materials when the reaction was carried out under oxidative conditions without the aid of metal-catalyst (Scheme 1d).

■ RESULTS AND DISCUSSION

Our study was initiated by using cyclohexanone (**1a**), aniline (**2a**) and (*E*)-(2-nitrovinyl)-benzene (**3a**) as the model reaction under an argon atmosphere to optimize the reaction conditions (Table 1). When the mixture in PhCl without any initiator was stirred at 150°C for 2 h, the desired product **4a** was obtained in 68% yield (entry 1). Encouraged by this result, various organic solvents were screened to find the suitable solvent (entries 2-7). To our delight, toluene showed the best efficiency to provide **4a** in 95% yield (entry 3). Other organic solvents such as mesitylene, DMSO, NMP and 1,1,2,2-tetrachloroethane were less effective (entries 4-7). Decreasing the amount of **2a** or the reaction temperature both did not enhance the reaction yields (entries 8 and 9). It should be noted that lower yield was obtained

when the reaction was run under air atmosphere (entry 10). Decreasing the amount of cyclohexanone and aniline decreased the reaction yield (entry 11). When three equiv. of **1a** and **2a** were used, the yield was not improved obviously (entry 12).

Table 1. Optimization of the reaction conditions[a]



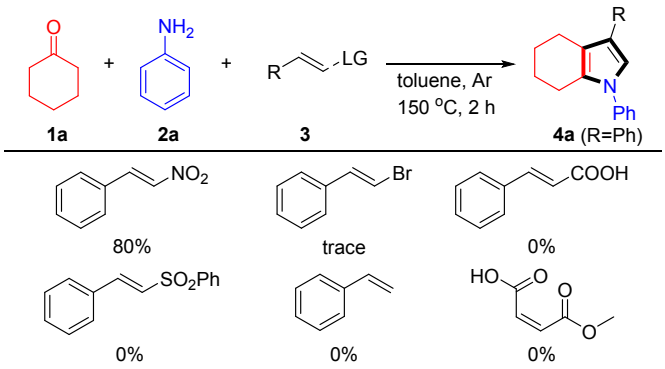
1a **2a** **3a** **4a**

entry	solvent	yield[b](%)
1	PhCl	68
2	*o*-xylene	85
3	toluene	95
4	mesitylene	57
5	DMSO	trace
6	NMP	60
7	$CHCl_2CHCl_2$	42
8[c]	toluene	75
9[d]	toluene	80
10[e]	toluene	85
11[f]	toluene	51
12[g]	toluene	96

[a] Conditions: **1a** (0.4 mmol), **2a** (0.4 mmol), **3a** (0.2 mmol), solvent (0.5 mL), 150 °C, 2 h, under argon unless otherwise noted. [b] GC yield. [c] **2a** (0.3 mmol). [d] 140 °C. [e] under air. [f] **1a** (0.2 mmol), **2a** (0.2 mmol). [g] **1a** (0.6 mmol), **2a** (0.6 mmol).

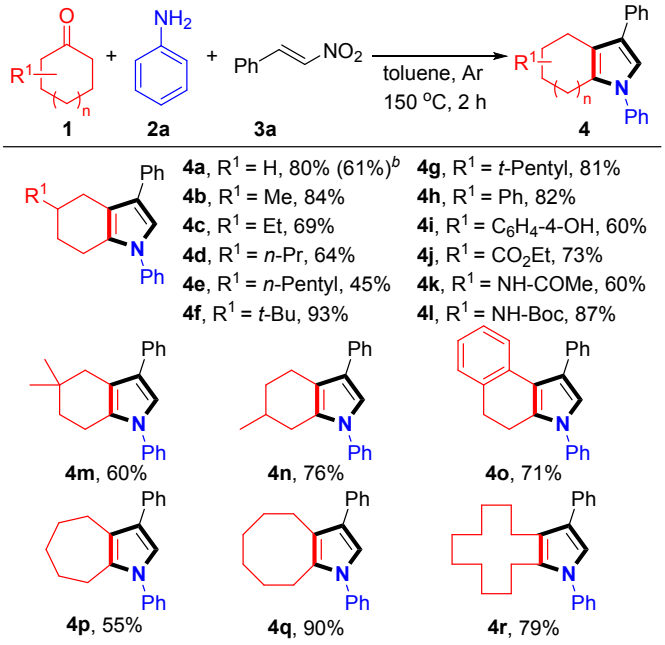
Besides (*E*)-(2-nitrovinyl)-benzene, several other alkenes were also investigated to provide two-carbon source for the present three-component reaction (Scheme 2). However, all of them were found to be unfruitful for the pyrrole formation. These results show the unique feature of nitrovinylarenes in this reaction system.

Scheme 2. Screening Different Alkenes for the Pyrrole Formation[a]



[a] Conditions: **1a** (0.4 mmol), **2a** (0.4 mmol), **3** (0.2 mmol), toluene (0.5 mL), 150 °C, 2 h, under Ar. Isolated yields based on **3**.

Scheme 3. Scope of Cyclic Ketones[a]

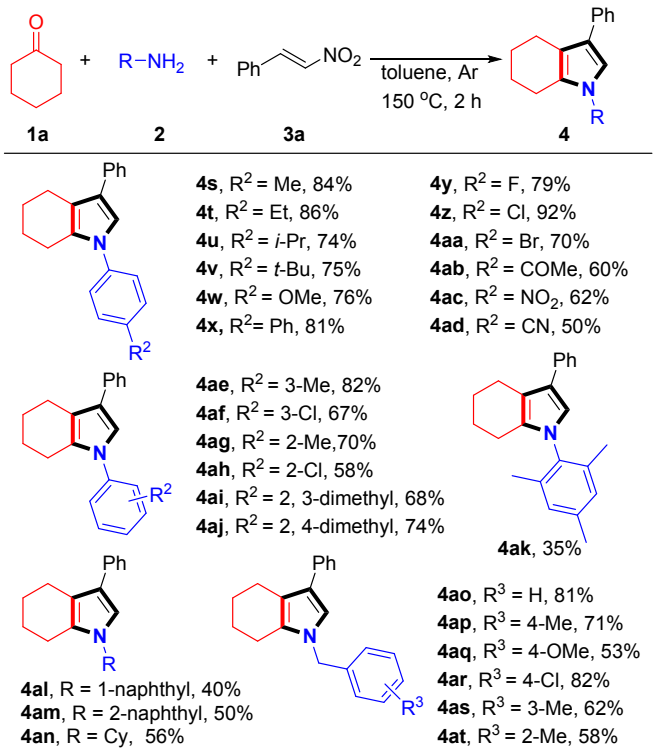


[a] Conditions: **1** (0.4 mmol), **2a** (0.4 mmol), **3a** (0.2 mmol), toluene (0.5 mL), 150 °C, 2 h, under Ar. Isolated yields based on **3a**. [b] Yield from 5 mmol scale reaction.

Under the optimized reaction conditions, the scope and generality of the three-component reaction was explored by using various cyclic ketones (Scheme 3). Moderate to good to high yields were obtained when electron-donating substituents presented at the *para* position in cyclohexanones (**4b-4g**). The reaction yields decreased with the linear alkyl substituents prolonged. When 4-*tert*-butylcyclohexanone was used as the substrate, the desired product **4f** was obtained in 93% yield. The desired product **4h** was obtained in 82% yield when 4-phenylcyclohexanone was used as the substrate. Good yield could be achieved when a free

hydroxy group was presented at the phenyl ring of 4-phenylcyclohexanone (**4i**). We delightedly found that functional groups such as ester and amide also could be survived to give the desired product **4j** and **4k** in good yield. Furthermore, 4-NH-Boc substituted cyclohexanones also smoothly reacted in this reaction to provide the corresponding products **4l** in 87% yield. When 4,4-dimethylcyclohexanone was used as the substrate, the desired product **4m** was obtained in 60% yield. The substituent position slightly affected the reaction yield and 76% yield was gained when a methyl group was located at the *meta* position of cyclohexanone (**4n**). When *β*-tetralone was employed as the substrate, **4o** was obtained in 71% yield. Besides cyclohexanones, other cyclic ketones such as cycloheptanone, cyclooctanone, cyclododecanone were also successfully participated in the reaction, delivering the corresponding products **4p, 4q** and **4r** in 55%, 90% and 79% yield, respectively. Whereas the use of non-cyclic ketones and acetophenones as reaction partners only provided the corresponding products in trace amounts.

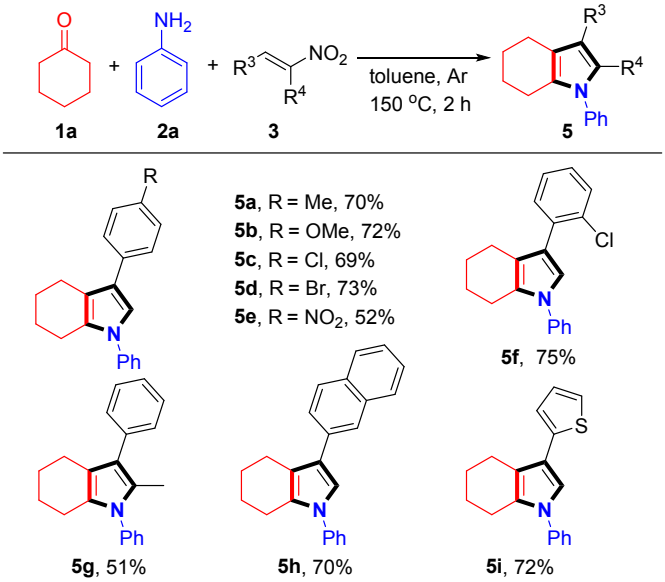
Scheme 4. Scope of Amines[a]



[a] Conditions: **1a** (0.4 mmol), **2** (0.4 mmol), **3a** (0.2 mmol), toluene (0.5 mL), 150 °C, 2 h, under Ar. Isolated yields based on **3a**.

To further investigate the scope and limitation of this three-component system, various amines were examined under the optimized reaction conditions (Scheme 4). Anilines bearing alkyl substituents at the *para* position proceeded smoothly to give the corresponding substituted pyrrole products in good to high yields (**4s-4v**). *p*-Anisidine and 4-phenylaniline reacted smoothly to produce the desired products in 76% and 81% yields, respectively (**4w-4x**). Halogen substituents such as fluoro, chloro and bromo were all well tolerated under the optimized reaction conditions (**4y-4aa**). When substrates with electron-withdrawing groups were employed, lower yields were obtained (**4ac-4ad**). The position of the substituent on the benzene ring (*ortho* or *meta*) slightly affected the reaction yields (**4ae-4aj**). For example, when the methyl group was located at the *meta* or *ortho* position on the benzene ring, the corresponding products **4ae** and **4ag** were obtained in 82% and 70% yields, respectively. Anilines with two functional groups were also found to be suitable substrates to give the corresponding products in good yields (**4ai-4aj**). The reaction yield decreased dramatically when 2,4,6-trimethylaniline was used as the substrate (**4ak**). Moderate yield was observed when naphthylamine were used as the substrate (**4al-4am**). Interestingly, aliphatic cyclohexylamine and benzylamines also could smoothly react with **1a** and **2a** to give the corresponding products in moderate to good yields (**4an-4at**).

Scheme 5. Scope of Nitrovinylarenes[a]

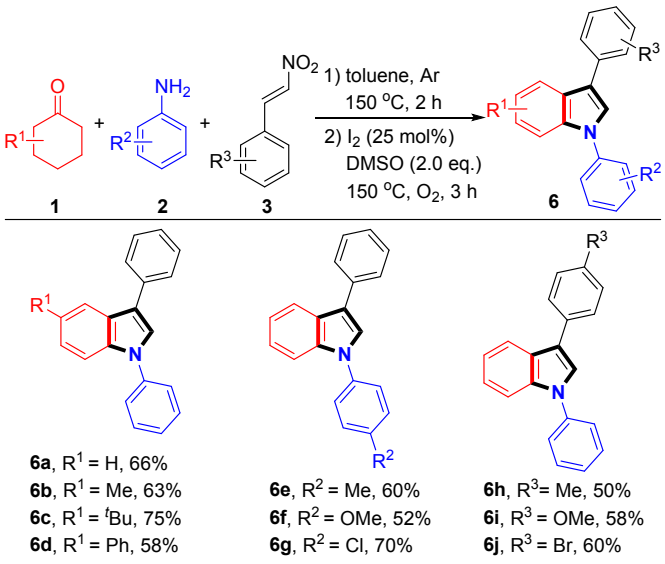


[a] Conditions: **1a** (0.4 mmol), **2a** (0.4 mmol), **3** (0.2 mmol), toluene (0.5 mL), 150 °C, 2 h, under Ar. Isolated yields based on **3**.

Subsequently, a range of nitrovinylarenes were subjected to the optimized reaction conditions (Scheme 5). When electron-donating substituents and halogen were present at the *para* position, moderate to good yields of the desired adducts were generally obtained (**5a-5d**). However, **5e** was obtained in low yield when a strong electron-withdrawing nitro group was located in *para* position. Slightly higher yield was obtained when the chloro substituent was presented at the *ortho* position (**5f**). Notably, (*Z*)-(2-nitroprop-1-en-1-yl)-benzene reacted well to afford the 2-methyl-1,3-diphenyl-4,5,6,7-tetrahydro-1*H*-indole **5g** in moderate yield. (*E*)-2-(2-nitrovinyl)naphthalene and (*E*)-2-(2-nitrovinyl)thiophene were also suitable substrates to afford **5h** and **5i** in good yields.

To obtain the corresponding indoles from the same starting materials, we further optimized the reaction conditions *via* an one-pot, two-step process. After systematic investigation of the reaction conditions, we found that the combination use of I_2/DMSO could smoothly convert the fused pyrroles into the corresponding indole products (Scheme 6). The desired products (**6a-6j**) were obtained in moderate yields when the substituents were located at the *para* position of cyclohexanones, anilines and nitrovinylarenes. Under the given reaction conditions, halogen functional groups such as chloro and bromo were survived to give the desired products in good yields.

Scheme 6. One-Pot Synthesis of Indoles[a]

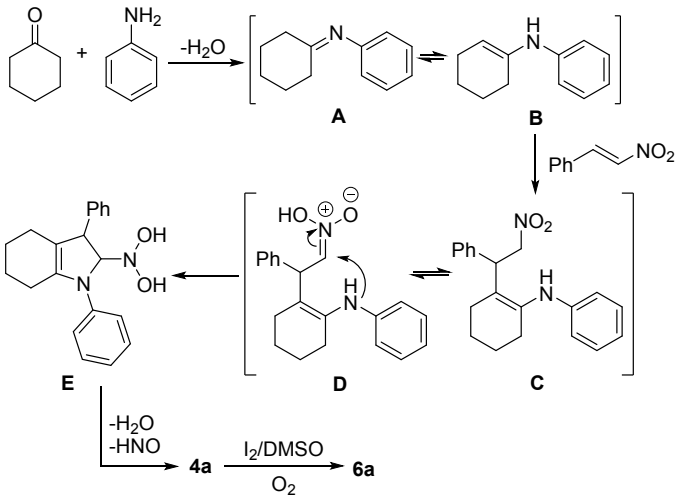


[a] Conditions: **1** (0.4 mmol), **2** (0.4 mmol), **3** (0.2 mmol), toluene (0.5 mL), 150 °C, 2 h, under Ar. Then I_2

(0.05 mmol), DMSO (0.4 mmol) was added and the mixture was further stirred under O_2 at 150 °C for 3 h. Isolated yields based on **3**.

Based on the observations and the literature,[10, 21] a plausible mechanism is outlined in Scheme 7. Condensation of the amino group with the carbonyl group in cyclohexanones generates an imine intermediate **A** which can be transformed into intermediate **B** *via* isomerization process. Subsequent addition of nitrovinylarene **3a** to the intermediate **B** affords intermediate **C**, which tautomerizes into the intermediate **D**. Then the desired cyclo intermediate **E** is obtained by the cyclization of intermediate **D**. Finally, the elimination of water and nitroxyl molecules affords the desired product **4a**.[21] Treatment of **4a** with I_2/DMSO provides the final product **6a** *via* dehydrogenative aromatization process.

Scheme 7. Proposed Mechanism



■ CONCLUSIONS

In summary, we have disclosed a general three-component reaction for fused pyrroles synthesis from readily available cyclic ketones, amines and nitrovinylarenes under metal- and additive free conditions. Active substituents such as halogens, nitro, hydroxy, ester and *N*-boc groups all survived under the current reaction systems. Substituted indoles were selectively formed from the same starting materials when the reaction was carried out under oxidative conditions without the aid of metal-catalyst. This controllable process provides new routes to functionalized pyrroles and indoles under metal-free conditions.

■ EXPERIMENTAL SECTION

General Information. All experiments were carried out under the standard conditions. Flash

column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to TMS, chloroform signals. MS analyses were performed on Agilent 5975 GC-MS instrument (EI). HRMS was conducted using electrospraying ionization (ESI) and was performed on a Thermo Scientific LTQ Orbitrap XL at Keecloud (Shanghai) Biotechnology co. LTD. Melting points were measured with a BÜ CHI B-545 melting point instrument. The new compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS, and HRMS. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR, and MS data with those of literature. All ketones and amines were used as received from commercial sources without further purification. The nitroolefins obtained by the published methods,[22] and all nitroolefins are known compounds. The ^{1}H and ^{13}C NMR spectra of the nitroolefins are copied in the Supporting Information.

General Procedure for the Synthesis of Pyrroles. A oven-dried reaction vessel was charged with nitrovinylarenes (0.2 mmol), ketones (0.4 mmol), anilines (0.4 mmol) and toluene (0.5 mL). The reaction vessel was sealed under argon and stirred at 150 ^{o}C for 2 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel to give the pure product.

General Procedure for the Synthesis of Pyrroles in 5 mmol Scale. To a 25 mL pressure tube with Teflon cover was added (*E*)-(2-nitrovinyl)-benzene (747.5mg, 5 mmol), cyclohexanone (1.03 mL, 10 mmol), aniline (0.91 mL, 10 mmol) and toluene (12.5 mL). The reaction vessel was sealed under argon and stirred at 150 ^{o}C for 2 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to give the desired product **4a** as yellow solid (831 mg, 61% yield).

General Procedure for the One-Pot Synthesis of Indoles. A oven-dried reaction vessel was charged with nitrovinylarenes (0.2 mmol), ketones (0.4 mmol), anilines (0.4 mmol) and toluene (0.5 mL). The reaction vessel was sealed under argon and stirred at 150 ^{o}C for 2 h. After cooling to room temperature, I_2 (12.7 mg, 25 mol%) , DMSO (28.4 μL, 0.4 mmol) was added and the resulting solution was sealed under oxygen. The reaction vessel was stirred at 150 ^{o}C for 3 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel to give the pure product.

1,3-diphenyl-4,5,6,7-tetrahydro-1H-indole (4a). Yellow solid (43.8 mg, yield 80%, petroleum ether), mp 55-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.39-7.30 (m, 6H), 7.22 (t, *J* = 8.0 Hz, 1H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.63 (t, *J* = 6.0 Hz, 2H), 1.85-1.82 (m, 4H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) 139.9, 136.1, 129.2, 129.1, 128.4, 126.9, 126.3, 125.3, 124.6, 123.7, 117.6, 117.1, 23.6, 23.5, 23.5, 23.2. HRMS (ESI, *m/z*): calcd for: $C_{20}H_{20}N^+$ $[M+H]^+$, 274.1590; found 274.1591.

5-methyl-1,3-diphenyl-4,5,6,7-tetrahydro-1H-indole (4b). Yellow solid (48.3 mg, yield 84%, petroleum ether), mp 92-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 4H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 2.85 (dd, *J* = 15.5, 5.0 Hz, 1H), 2.75-2.58 (m, 2H), 2.39 (dd, *J* = 15.6, 9.9 Hz, 1H), 1.93-1.89 (m, 2H), 1.52-1.42 (m, 1H), 1.12 (d, *J* = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 140.0, 136.1, 129.1, 128.9, 128.4, 126.9, 126.3, 125.3, 124.5, 123.6, 117.8, 117.2, 32.1, 31.5, 29.9, 23.3, 21.9. HRMS (ESI) m/z calcd for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747, found 288.1745.

5-ethyl-1,3-diphenyl-4,5,6,7-tetrahydro-1H-indole (4c). Yellow solid (41.4 mg, yield 69%, petroleum ether), mp 63-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.40-7.35 (m, 4H), 7.31 (t, *J* = 6.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 2.88 (dd, *J* = 15.4, 5.0 Hz, 1H), 2.74-2.59 (m, 2H), 2.39 (dd, *J* = 15.5, 10.0 Hz, 1H), 1.97 (d, *J* = 12.0 Hz, 1H), 1.69-1.60 (m, 1H), 1.46 (p, *J* = 8.0 Hz, 3H), 0.99 (t, *J* = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 140.0, 136.1, 129.2, 129.1, 128.4, 127.0, 126.3, 125.3, 124.5, 123.7, 117.8, 117.1, 36.7, 29.7, 29.3, 29.1, 23.4, 11.8. HRMS (ESI) m/z calcd for $C_{22}H_{24}N^+$ $[M+H]^+$ 302.1903, found 302.1908.

1,3-diphenyl-5-propyl-4,5,6,7-tetrahydro-1H-indole (4d). Yellow solid (40.6 mg, yield 64%, petroleum ether), mp 52-54 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.40-7.36 (m, 4H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 2.88 (dd, *J* = 15.5, 5.0 Hz, 1H), 2.74-2.58 (m, 2H), 2.42-2.36 (m, 1H), 1.98-1.93 (m, 1H), 1.77-1.73 (m, 1H), 1.49-1.38 (m, 5H), 0.94 (t, *J* = 6.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 140.0, 136.1, 129.2, 129.1, 128.4, 126.9, 126.2, 125.3, 124.5, 123.7, 117.8, 117.1, 38.7, 34.6, 30.0, 29.7, 23.4, 20.2, 14.3. HRMS (ESI) m/z calcd for $C_{23}H_{26}N^+$ $[M+H]^+$ 316.2060, found 316.2058.

5-pentyl-1,3-diphenyl-4,5,6,7-tetrahydro-1H-indole (4e). Yellow solid (31.0 mg, yield

45%, petroleum ether), mp 44-46 °C.^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.40-7.35 (m, 4H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 2.87 (dd, *J* = 15.3, 4.8 Hz, 1H), 2.73-2.58 (m, 2H), 2.38 (dd, *J* = 15.3, 10.1 Hz, 1H), 1.96 (d, *J* = 12.0 Hz, 1H), 1.73 (s, 1H), 1.50-1.27 (m, 9H), 0.89 (t, *J* = 6.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 140.0, 136.1, 129.2, 129.1, 128.4, 127.0, 126.3, 125.4, 124.5, 123.7, 117.8, 117.2, 36.4, 35.0, 32.2, 30.1, 29.7, 26.9, 23.4, 22.7, 14.2. HRMS (ESI) m/z calcd for $C_{25}H_{30}N^+$ $[M+H]^+$ 344.2373, found 344.2373.

5-(tert-butyl)-1,3-diphenyl-4,5,6,7-tetrahydro-1H-indole (4f). Yellow solid (61.0 mg, yield 93%, petroleum ether), mp 51-53 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.46-7.29 (m, 8H), 7.23 (t, *J* = 8.0 Hz, 1H), 2.81 (dd, *J* = 15.2, 4.3 Hz, 1H), 2.70-2.62 (m, 2H), 2.53 (t, *J* = 12.0 Hz,1H), 2.06 (d, *J* = 11.6 Hz, 1H), 1.53-1.35 (m, 2H), 0.97 (s, 9H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 140.0, 136.1, 129.3, 129.1, 128.5, 127.0, 126.2, 125.4, 124.4, 123.9, 117.8, 117.6, 45.57, 32.53, 27.5, 24.8, 24.7, 24.5. HRMS (ESI, *m/z*): calcd for: $C_{24}H_{28}N^+$ $[M+H]^+$ 330.2216, found 330.2218.

5-(tert-pentyl)-1,3-diphenyl-4,5,6,7-tetrahydro-1H-indole (4g). Yellow solid (55.8 mg, yield 81%, petroleum ether), mp 36-37 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.46-7.29 (m, 8H), 7.23 (t, *J* = 8.0 Hz, 1H), 2.77-2.51 (m, 4H), 2.01 (d, *J* = 12.0 Hz, 1H), 1.65-1.61 (m, 1H), 1.45-1.32 (m, 3H), 0.91 (d, *J* = 4.0 Hz, 6H), 0.83 (t, *J* = 8.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 140.0, 136.1, 129.3, 129.1, 128.4, 127.0, 126.2, 125.4, 124.4, 123.9, 117.8, 117.7, 42.9, 34.8, 32.7, 24.5, 24.3, 24.3, 24.2, 24.1, 8.2. HRMS (ESI) m/z calcd for $C_{25}H_{30}N^+$ $[M+H]^+$ 344.2372, found 344.2373.

1,3,5-triphenyl-4,5,6,7-tetrahydro-1H-indole (4h). Yellow solid (57.5 mg, yield 82%, petroleum ether). mp 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50-7.45 (m, 4H), 7.39 (d, *J* = 4.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 7H), 7.25-7.23 (m, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 3.11-3.00 (m, 2H), 2.93-2.83 (m, 2H), 2.76-2.71 (m, 1H), 2.19-2.16 (m, 1H), 2.07 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 146.8, 139.9, 135.75, 129.2, 128.8, 128. 4, 128.4, 127.0, 127.0, 126.5, 126.2, 125.5, 124.6, 123.6, 118.0, 117.2, 41.6, 32.4, 30.0, 23.9. HRMS (ESI) m/z calcd for $C_{26}H_{24}N^+$ $[M+H]^+$ 350.1903, found 350.1906.

4-(1,3-diphenyl-4,5,6,7-tetrahydro-1H-indol-5-yl)phenol (4i). Yellow solid (45.1 mg, yield 62%, petroleum ether/ethyl acetate = 5:1), mp 119-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ

7.49-7.44 (m, 5H), 7.39-7.32 (m, 6H), 7.19 (d, J = 8.0 Hz, 3H), 6.81 (d, J = 8.0 Hz, 2H), 3.05 (dd, J = 14.6, 4.5 Hz, 1H), 2.99-2.93 (m, 1H), 2.87-2.81 (m, 2H), 2.74-2.69 (m, 1H), 2.15-2.11 (m, 1H), 2.05-1.95 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 153.8, 139.9, 139.1, 135.8, 129.2, 128.8, 128.4, 128.0, 126.9, 126.4, 125.4, 124.6, 123.5, 118.0, 117.2, 115.2, 40.69, 32.5, 30.3, 23.8. HRMS (ESI) m/z calcd for $C_{26}H_{24}NO^+$ $[M+H]^+$ 366.1852, found 366.1857.

Ethyl 1,3-diphenyl-4,5,6,7-tetrahydro-1H-indole-5-carboxylate (4j). Yellow solid (50.4 mg, yield 73%, petroleum ether/ethyl acetate = 20:1), mp 70-71 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46 (q, J = 8.0, 4H), 7.39-7.31 (m, 5H), 7.22 (t, J = 6.0 Hz, 1H), 6.99 (s, 1H), 4.18 (q, J =6.7 Hz, 2H), 3.08-2.95 (m, 2H), 2.78-2.67 (m, 3H), 2.27-2.23 (m, 1H), 1.96-1.85 (m, 1H), 1.28 (t, J = 6.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 175.6, 139.7, 135.6, 129.1, 128.4, 128.1, 126.9, 126.5, 125.5, 124.5, 123.7, 118.1, 115.5, 60.4, 40.7, 26.1, 25.9, 22.7, 14.2. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO_2^+$ $[M+H]^+$ 346.1802, found 346.1805.

***N*-(1,3-diphenyl-4,5,6,7-tetrahydro-1H-indol-5-yl)acetamide (4k).** Yellow solid (39.8 mg, yield 60%, petroleum ether/ethyl acetate = 1:1), mp 140-142 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46 (t, J = 8.0 Hz, 4H), 7.38-7.32 (m, 5H), 7.22 (t, J = 8.0 Hz, 1H), 7.01 (s, 1H), 5.68 (d, J = 4.0 Hz, 1H), 4.43-4.36 (m, 1H), 3.15 (dd, J = 15.5, 5.2 Hz, 1H), 2.80-2.73 (m, 1H), 2.69-2.62 (m, 2H), 2.04-1.88 (m, 5H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 169.6, 139.6, 135.5, 129.2, 128.5, 127.8, 126.8, 126.6, 125.6, 124.5, 123.8, 118.4, 114.3, 45.3, 30.0, 28.0, 23.5, 20.6. HRMS (ESI) m/z calcd for $C_{22}H_{23}N_2O^+$ $[M+H]^+$ 331.1805, found 331.1803.

Tert-butyl (1,3-diphenyl-4,5,6,7-tetrahydro-1H-indol-5-yl)carbamate (4l). Yellow solid (67.5 mg, yield 87%, petroleum ether/ethyl acetate = 10:1), mp 133-135 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (d, J = 8.0 Hz, 4H), 7.38-7.31 (m, 5H), 7.22 (t, J = 8.0 Hz, 1H), 6.99 (s, 1H), 4.73 (d, J = 4.0 Hz, 1H), 4.11-4.04 (m, 1H), 3.13 (dd, J = 15.5, 5.2 Hz, 1H), 2.76-2.62 (m, 3H), 2.07-2.00 (m, 1H), 1.91-1.82 (m, 1H), 1.45 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 155.3, 139.7, 135.6, 129.2, 128.5, 127.8, 126.9, 126.6, 125.6, 124.6, 123.9, 118.4, 114.6, 79.1, 46.4, 30.4, 28.6, 28.4, 20.8. HRMS (ESI) m/z calcd for $C_{25}H_{29}N_2O_2^+$ $[M+H]^+$ 389.2224, found 389.2220.

5,5-dimethyl-1,3-diphenyl-4,5,6,7-tetrahydro-1H-indole (4m). Yellow solid (36.3 mg, yield 60%, petroleum ether), mp 67-69 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50-7.43 (m, 4H), 7.39-7.35 (m, 4H), 7.31 (t, J = 6.0 Hz, 1H), 7.21 (t, J = 6.0 Hz, 1H), 7.01 (s, 1H), 2.62 (t, J = 8.0

Hz, 2H), 2.58 (s, 2H), 1.60 (t, *J* = 6.0 Hz, 2H), 1.05 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 140.1, 136.2, 129.1, 128.4, 127.8, 127.0, 126.2, 125.3, 124.5, 123.9, 118.0, 116.7, 37.4, 36.0, 30.1, 28.1, 20.8. HRMS (ESI) m/z calcd for $C_{22}H_{24}N^+$ $[M+H]^+$ 302.1903, found 302.1904.

6-methyl-1,3-diphenyl-4,5,6,7-tetrahydro-1H-indole (4n). Yellow solid (43.6 mg, yield 76%, petroleum ether), mp 118-120 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.39-7.31 (m, 5H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 2.88-2.76 (m, 2H), 2.64 (dd, *J* = 15.7, 5.0 Hz, 1H), 2.33-2.27 (m, 1H), 1.95-1.92 (m, 2H), 1.50-1.40 (m, 1H), 1.09 (d, *J* = 8.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 139.9, 136.1, 129.2, 129.1, 128.4, 126.9, 126.3, 125.3, 124.7, 123.5, 117.8, 116.9, 32.0, 32.0, 29.7, 23.2, 21.9. HRMS (ESI) m/z calcd for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747, found 288.1745.

1,3-diphenyl-4,5-dihydro-3H-benzo[*e*]indole (4o). Brown solid (45.6 mg, yield 71%, petroleum ether), mp 155-157 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.55 (d, *J* = 4.0 Hz, 2H), 7.48 (t, *J* = 6.0 Hz, 2H), 7.42-7.30 (m, 6H), 7.22 (t, *J* = 6.0 Hz, 2H), 7.02 (t, *J* = 6.0 Hz, 2H), 6.89 (s, 1H), 3.00 (t, *J* = 6.0 Hz, 2H), 2.81 (t, *J* = 6.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 139.1, 136.1, 134.1, 133.2, 131.8, 129.2, 128.8, 128.3, 127.8, 126.7, 126.2, 126.2, 124.5, 124.4, 123.3, 123.2, 120.2, 117.2, 30.4, 21.8. HRMS (ESI) m/z calcd for $C_{24}H_{20}N^+$ $[M+H]^+$ 322.1590, found 322.1592.

1,3-diphenyl-1,4,5,6,7,8-hexahydrocyclohepta[*b*]pyrrole (4p). Yellow solid (31.8 mg, yield 55%, petroleum ether), mp 82-84 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45-7.33 (m, 7H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 6.0 Hz, 1H), 6.72 (s, 1H), 2.76 (t, *J* = 6.0 Hz, 2H), 2.69 (t, *J* = 6.0 Hz, 2H), 1.88-1.83 (m, 2H), 1.73-1.64 (m 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 140.1, 136.3, 132.8, 128.9, 128.6, 128.2, 126.7, 126.1, 125.5, 124.9, 121.6, 117.5, 32.1, 28.5, 27.3, 26.8, 25.7. HRMS (ESI) m/z calcd for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747, found 288.1745.

1,3-diphenyl-4,5,6,7,8,9-hexahydro-1H-cycloocta[*b*]pyrrole (4q). Yellow solid (54.2 mg, yield 90%, petroleum ether), mp 62-64 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (t, *J* = 8.0 Hz, 4H), 7.39-7.34 (m, 5H), 7.23 (t, *J* = 8.0 Hz, 1H), 6.83 (s, 1H), 2.74 (t, *J* = 6.0 Hz, 2H), 2.67 ((t, *J* = 6.0 Hz, 2H), 1.79-1.71 (m, 2H), 1.60-1.49 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 140.3, 136.5, 131.2, 129.0, 128.3, 128.0, 126.9, 126.2, 125.4, 124.4, 119.2, 118.4, 31.2, 30.3, 26.1, 26.0, 23.4, 23.4. HRMS (ESI) m/z calcd for $C_{22}H_{24}N^+$ $[M+H]^+$ 302.1903, found 302.1906.

1,3-diphenyl-4,5,6,7,8,9,10,11,12,13-decahydro-1H-cyclododeca[*b*]pyrrole (4r). Yellow

solid (56.2 mg, yield 79%, petroleum ether), mp 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.39-7.34 (m, 5H), 7.22 (t, *J* = 6.0 Hz, 1H), 6.78 (s, 1H), 2.72-2.66 (m, 4H), 1.51-1.42 (m, 6H), 1.35 (s, 4H), 1.26-1.19 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 141.0, 137.1, 131.5, 129.0, 128.2, 127.6, 126.9, 126.1, 125.4, 124.2, 120.3, 119.9, 28.2, 27.2, 25.5, 25.4, 24.9, 24.9, 22.6, 22.5, 22.3, 21.5. HRMS (ESI) m/z calcd for $C_{26}H_{32}N^+$ $[M+H]^+$ 358.2529, found 358.2524.

3-phenyl-1-(p-tolyl)-4,5,6,7-tetrahydro-1H-indole (4s) Yellow solid (48.2 mg, yield 84%, petroleum ether), mp 87-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.25 (s, 5H), 7.21 (t, *J* = 8.0 Hz, 1H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.61 (t, *J* = 6.0 Hz, 2H), 2.41 (s, 3H), 1.85-1.82 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 137.4, 136.2, 136.1, 129.7, 129.2, 128.4, 126.9, 125.2, 124.6, 123.4, 117.6, 116.8, 23.6, 23.5, 23.2, 21.0. HRMS (ESI) m/z calcd for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747, found 288.1745.

1-(4-ethylphenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4t). Yellow solid (51.6 mg, yield 86%, petroleum ether), mp 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 6.0 Hz, 2H), 7.27 (s, 5H), 7.21 (t, *J* = 8.0 Hz, 1H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.71 (q, *J* = 8.0Hz, 2H), 2.61 (t, *J* = 6.0 Hz, 2H), 1.85-1.81 (m, 4H) (s, 4H), 1.29 (t, *J* = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 142.4, 137.5, 136.1, 129.2, 128.4, 128.4, 126.9, 125.2, 124.6, 123.4, 117.6, 116.8, 28.3, 23.6, 23.5, 23.2, 15.5. HRMS (ESI) m/z calcd for $C_{22}H_{24}N^+$ $[M+H]^+$ 302.1903, found 302.1908.

1-(4-isopropylphenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4u). Yellow solid (46.6 mg, yield 74%, petroleum ether), mp 67-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.29 (s, 5H), 7.21 (t, *J* = 8.0 Hz, 1H), 3.00-2.93 (m, 1H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.62 (t, *J* = 6.0 Hz, 2H), 1.85-1.82 (m, 4H), 1.30 (d, *J* = 8.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 147.0, 137.6, 136.2, 129.3, 128.4, 127.0, 126.9, 125.2, 124.6, 123.4, 117.7, 116.8, 33.7, 24.0, 23.6, 23.5, 23.5, 23.2. HRMS (ESI) m/z calcd for $C_{23}H_{26}N^+$ $[M+H]^+$ 316.2060, found 316.2059.

1-(4-(tert-butyl)phenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4v). Yellow solid (49.3 mg, yield 75%, petroleum ether), mp 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 3H), 7.21 (t, *J* = 8.0 Hz, 1H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.62 (t, *J* = 6.0 Hz, 2H), 1.85-1.82 (m, 4H), 1.37 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 149.3, 137.3, 136.2, 129.3, 128.4, 126.9, 126.0, 125.2, 124.2, 123.4, 117.6, 116.8, 34.5, 31.4, 23.6, 23.6, 23.5, 23.2. HRMS (ESI, *m/z*): calcd for: $C_{24}H_{28}N^+$ $[M+H]^+$ 330.2216, found 330.2218.

1-(4-methoxyphenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4w). Yellow solid (46.1 mg, yield 76%, petroleum ether/ethyl acetate = 100:1), mp 74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 12.0 Hz, 2H), 3.86 (s, 3H), 2.80-2.77 (t, *J* = 6.0 Hz, 2H), 2.58-2.55 (t, *J* = 6.0 Hz, 2H), 1.85-1.81 (m, 4H).$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 158.1, 136.2, 133.0, 129.4, 128.4, 126.9, 126.1, 125.2, 123.2, 117.8, 116.5, 114.2, 55.5, 23.6, 23.5, 23.3, 23.2. HRMS (ESI) m/z calcd for $C_{21}H_{22}NO^+$ $[M+H]^+$ 304.1696, found 304.1698.

1-([1,1'-biphenyl]-4-yl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4x). Yellow solid (56.8 mg, yield 81%, petroleum ether/ethyl acetate = 100:1), mp 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.65 (q, *J* = 8.0 Hz, 4H), 7.53-7.36 (m, 10H), 7.23 (t, *J* = 8.0 Hz, 1H), 2.80 (t, *J* =6.0 Hz, 2H), 2.69 (t, *J* = 6.0 Hz, 2H), 1.87-1.84 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 140.2, 139.2, 139.1, 136.0, 129.2, 128.8, 128.4, 127.8, 127.4, 127.0, 127.0, 125.4, 124.8, 123.9, 117.5, 117.3, 23.7, 23.5, 23.5, 23.2. HRMS (ESI) m/z calcd for $C_{26}H_{24}N^+$ $[M+H]^+$ 350.1903, found 350.1906.

1-(4-fluorophenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4y). Yellow solid (45.8 mg, yield 79%, petroleum ether), mp 69-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.49 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.32 (q, *J* = 4.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 2H), 6.93 (s, 1H), 2.77 (t, *J* = 6.0 Hz, 2H), 2.57 (t, *J* = 6.0 Hz, 2H), 1.85-1.80 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 161.1(d, *J* = 245 Hz), 136.0(d, *J* = 3 Hz), 135.9, 129.3, 128.4, 126.9, 126.4(d, *J* = 9 Hz), 125.4, 123.8, 117.7, 117.1, 115.9(d, *J* = 23 Hz), 23.5, 23.4, 23.4, 23.2. HRMS (ESI) m/z calcd for $C_{21}H_{19}FN^+$ $[M+H]^+$ 292.1496, found 292.1494.

1-(4-chlorophenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4z). Yellow solid (56.5 mg, yield 92%, petroleum ether), mp 137-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.48 (d, *J* = 4.0 Hz, 2H), 7.42-7.35 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 2.76 (t, *J* = 6.0 Hz, 2H), 2.59 (t, *J* = 4.0 Hz, 2H), 1.86-1.79 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 138.4, 135.8, 131.9, 129.2, 129.1, 128.4, 126.9, 125.7, 125.5, 124.2, 117.6, 117.4, 23.5, 23.4, 23.4, 23.2. HRMS (ESI) m/z calcd for $C_{20}H_{19}ClN^+$ $[M+H]^+$ 308.1201, found 308.1203.

1-(4-bromophenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4aa). Yellow solid (48.8 mg, yield 70%, petroleum ether), mp 108-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 4H), 2.76 (t, *J* = 6.0 Hz, 2H), 2.59 (t, *J* = 4.0 Hz, 2H), 1.86-1.79 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 138.9, 135.8, 132.2, 129.0, 128.4, 126.9, 126.0, 125.5, 124.2, 119.7, 117.6, 117.3, 23.6, 23.4, 23.4, 23.2. HRMS (ESI) m/z calcd for $C_{20}H_{19}BrN^+$ $[M+H]^+$ 352.0695, found 352.0697.

1-(4-(3-phenyl-4,5,6,7-tetrahydro-1H-indol-1-yl)phenyl) ethan-1-one (4ab). Yellow solid (37.5 mg, yield 60%, petroleum ether/ethyl acetate = 10:1) mp 136-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 12.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 2.77 (t, *J* = 4.0 Hz, 2H), 2.68 (t, *J* = 6.0 Hz, 2H), 2.64 (s, 3H), 1.85-1.83 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 197.0, 143.8, 135.6, 134.4, 129.6, 129.0, 128.4, 127.0, 125.7, 124.9, 123.6, 118.6, 117.2, 26.6, 24.0, 23.4, 23.3, 23.2. HRMS (ESI) m/z calcd for $C_{22}H_{22}NO^+$ $[M+H]^+$ 316.1696, found 316.1697.

1-(4-nitrophenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4ac). Yellow solid (39.5mg, yield 62%, petroleum ether/ethyl acetate = 50:1), mp 89-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.33 (d, *J* = 8.9 Hz, 2H), 7.49 (dd, *J* = 8.0, 5.7 Hz, 4H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.03 (s, 1H), 2.76 (t, *J* = 4.0 Hz, 2H), 2.69 (t, *J* = 6.0 Hz, 2H), 1.87-1.83 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 145.2, 145.0, 135.2, 129.1, 128.5, 127.1, 126.0, 125.8, 125.0, 123.6, 119.6, 117.1, 24.2, 23.4, 23.2, 23.2. HRMS (ESI) m/z calcd for $C_{20}H_{19}N_2O_2^+$ $[M+H]^+$ 319.1441, found 319.1441.

4-(3-phenyl-4,5,6,7-tetrahydro-1H-indol-1-yl)benzonitrile (4ad). Yellow solid (29.7 mg, yield 50%, petroleum ether/ethyl acetate = 50:1), mp 126-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.2 Hz, 4H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.25 (t, *J* = 6.0 Hz, 1H), 6.99 (s, 1H), 2.76 (t, *J* =6.0 Hz, 2H), 2.66 (t, *J* =6.0 Hz, 2H), 1.85-1.82 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 143.5, 135.3, 133.3, 129.0, 128.5, 127.0, 125.9, 125.5, 124.1, 119.1, 118.5, 117.0, 109.2, 24.0, 23.4, 23.2, 23.2. HRMS (ESI) m/z calcd for $C_{21}H_{19}N_2^+$ $[M+H]^+$ 299.1543, found 299.1542.

3-phenyl-1-(m-tolyl)-4,5,6,7-tetrahydro-1H-indole (4ae). Yellow liquid (47.2 mg, yield 82%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.39-7.31 (m, 3H), 7.23-7.13 (m, 4H), 6.98 (s, 1H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.62 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H),

1.85-1.82 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 139.8, 139.0, 136.2, 129.1, 128.8, 128.3, 127.1, 126.9, 125.3, 125.2, 123.6, 121.7, 117.6, 117.0, 23.6, 23.6, 23.5, 23.2, 21.4. HRMS (ESI) m/z calcd for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747, found 288.1745.

1-(3-chlorophenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4af). Yellow solid (41.4 mg, yield 67%, petroleum ether), mp 82-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.49 (d, J = 7.1 Hz, 2H), 7.37 (t, J = 7.8 Hz, 4H), 7.30-7.21 (m, 3H), 6.96 (s, 1H), 2.77 (t, J = 4.6 Hz, 2H), 2.63 (t, J = 4.7 Hz, 2H), 1.87-1.80 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 141.0, 135.8, 134.7, 130.1, 129.1, 128.4, 127.0, 126.3, 125.5, 124.7, 124.3, 122.6, 117.8, 117.4, 23.6, 23.4, 23.2. HRMS (ESI) m/z calcd for $C_{20}H_{19}ClN^+$ $[M+H]^+$ 308.1201, found 308.1203.

3-phenyl-1-(o-tolyl)-4,5,6,7-tetrahydro-1H-indole (4ag). Yellow solid (40.4 mg, yield 70%, petroleum ether), mp 78-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, J = 7.8 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.30 (d, J = 3.2 Hz, 2H), 7.25 (t, J = 3.3 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 6.80 (s, 1H), 2.79 (t, J = 4.0 Hz, 2H), 2.43-2.26 (m, 2H), 2.11 (s, 3H), 1.82-1.78 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 139.0, 136.5, 135.9, 130.7, 130.0, 128.4, 128.0, 128.0, 126.7, 126.3, 125.0, 122.7, 117.8, 115.5, 23.8, 23.6, 23.0, 22.5, 17.5. HRMS (ESI) m/z calcd for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747, found 288.1745.

1-(2-chlorophenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4ah). Yellow solid (35.4 mg, yield 58%, petroleum ether), mp 42-43 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.54-7.50 (m, 3H), 7.37-7.33 (m, 5H), 7.19 (t, J = 7.4 Hz, 1H), 6.86 (s, 1H), 2.79 (d, J = 4.0 Hz, 2H), 2.38 (t, J = 6.0 Hz, 2H), 1.83-1.80 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 137.6, 136.1, 132.1, 130.4, 130.3, 129.6, 129.0, 128.3, 127.3, 126.8, 125.2, 123.4, 118.1, 116.0, 23.7, 23.5, 22.9, 22.4. HRMS (ESI) m/z calcd for $C_{20}H_{19}ClN^+$ $[M+H]^+$ 308.1201, found 308.1203.

1-(2,3-dimethylphenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4ai). Yellow solid (40.7 mg, yield 68%, petroleum ether), mp 82-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, J = 8.1 Hz, 2H), 7.35 (t, J = 7.7 Hz, 2H), 7.21-7.16 (m, 3H), 7.13 (t, J = 6.3 Hz, 1H), 6.80 (s, 1H), 2.80 (t, J = 4.9 Hz, 2H), 2.34 (s, 4H), 2.21-2.17 (m, 1H), 1.96 (s, 3H), 1.83-1.79 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 139.0, 138.0, 136.5, 134.7, 130.3, 129.5, 128.4, 126.6, 125.6, 125.0, 122.6, 118.1, 115.3, 23.9, 23.6, 23.0, 22.5, 20.4, 14.2. HRMS (ESI) m/z calcd for $C_{22}H_{24}N^+$ $[M+H]^+$ 302.1903, found 302.1907.

1-(2,4-dimethylphenyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4aj). Yellow liquid (44.8

mg, yield 74%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.20-7.12 (m, 3H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.79 (s, 1H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.38 (s, 3H), 2.33-2.19 (m, 2H), 2.07 (s, 3H), 1.82-1.79 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 137.8, 136.5, 136.4, 135.5, 131.3, 130.0, 128.3, 127.7, 126.9, 126.6, 124.9, 122.6, 117.9, 115.3, 23.8, 23.6, 23.0, 22.5, 21.0, 17.4. HRMS (ESI) m/z calcd for $C_{22}H_{24}N^+$ $[M+H]^+$ 302.1903, found 302.1907.

1-mesityl-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4ak). Yellow liquid (22.2 mg, yield 35%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 7.1 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.95 (s, 2H), 6.69 (s, 1H), 2.82-2.78 (m, 2H), 2.34 (s, 3H), 2.17-2.13 (m, 2H), 1.99 (s, 6H), 1.81-1.78 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 137.7, 136.8, 136.4, 135.6, 129.3, 128.5, 128.4, 126.4, 124.8, 122.7, 116.6, 115.2, 24.0, 23.8, 23.0, 22.2, 21.0, 17.5. HRMS (ESI) m/z calcd for $C_{23}H_{26}N^+$ $[M+H]^+$ 316.2060, found 316.2058.

1-(naphthalen-1-yl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4al). Brown solid (25.9 mg, yield 40%, petroleum ether), mp 72-73 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.92 (t, *J* = 7.7 Hz, 2H), 7.57-7.52 (m, 5H), 7.50-7.47 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.01 (s, 1H), 2.86 (t, *J* = 4.0 Hz, 2H), 2.41-2.34 (m, 1H), 2.22-2.16 (m, 1H), 1.88-1.75 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 136.6, 136.3, 134.1, 131.2, 131.0, 128.4, 128.2, 128.0, 127.0, 126.7, 126.5, 125.2, 125.1, 124.9, 123.7, 122.9, 119.4, 115.8, 23.8, 23.6, 23.0, 22.5. HRMS (ESI) m/z calcd for $C_{24}H_{22}N^+$ $[M+H]^+$ 324.1747, found 324.1756.

1-(naphthalen-2-yl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4am). Brown solid (32.4 mg, yield 50%, petroleum ether), mp 55-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.88 (m, 3H), 7.79 (s, 1H), 7.56-7.49 (m, 5H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 2.81 (s, 2H), 2.70 (s, 2H), 1.87-1.84 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 137.4, 136.1, 133.5, 131.7, 129.4, 129.0, 128.4, 127.7, 127.7, 127.0, 126.8, 126.0, 125.4, 124.0, 123.6, 122.2, 117.8, 117.4, 23.7, 23.6, 23.5, 23.3. HRMS (ESI) m/z calcd for $C_{24}H_{22}N^+$ $[M+H]^+$ 324.1747, found 324.1756.

1-cyclohexyl-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4an). Yellow solid (31.3 mg, yield 56%, petroleum ether), mp 78-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (d, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.85 (s, 1H), 3.80-3.72 (m, 1H), 2.72 (t, *J* = 5.7 Hz, 2H), 2.61 (t, *J* = 6.0 Hz, 2H), 2.06 (d, *J* = 12.0 Hz, 2H), 1.92-1.87 (m, 4H), 1.81-1.74 (m, 3H),

1.64 (q, *J* = 12.0 Hz, 2H), 1.42 (q, *J* = 12.0 Hz, 2H), 1.26 (t, *J* = 14.0 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 136.7, 128.2, 126.6, 124.7, 121.8, 114.8, 112.9, 54.8, 34.3, 25.9, 25.5, 23.9, 23.4, 23.0, 22.1. HRMS (ESI) m/z calcd for $C_{20}H_{26}N^+$ $[M+H]^+$ 280.2060, found 280.2058

1-benzyl-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4ao). Yellow liquid (46.3 mg, yield 81%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 5H), 7.28 (d, *J* = 8.8 Hz 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 5.01 (s, 2H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.47 (t, *J* = 6.0 Hz, 2H), 1.84-1.80 (m, 2H), 1.78-1.74 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 138.1, 136.5, 129.1, 128.7, 128.3, 127.3, 126.7, 126.6, 124. 9, 122.2, 117.3, 115.8, 50.0, 23.7, 23.5, 22.9, 21.9. HRMS (ESI) m/z calcd for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747, found 288.1741.

1-(4-methylbenzyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4ap). Yellow liquid (42.6 mg, yield 71%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.17-7.12 (m, 3H), 7.00 (d, J = 7.8 Hz, 2H), 6.78 (s, 1H), 4.95 (s, 2H), 2.72 (t, J = 6.0 Hz, 2H), 2.48 (t, J = 6.2 Hz, 2H), 2.33 (s, 3H), 1.85-1.81 (m, 2H), 1.77-1.72 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 137.0, 136.6, 135.0, 129.3, 129.1, 128.3, 126.8, 126.6, 124.8, 122.2, 117.2, 115.8, 49.8, 23.7, 23.5, 22.9, 22.0, 21.0. HRMS (ESI) m/z calcd for $C_{22}H_{24}N^+$ $[M+H]^+$ 302.1903, found 302.1904.

1-(4-methoxybenzyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4aq). Yellow liquid (33.8 mg, yield 53%, petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 7.06 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 6.77 (s, 1H), 4.93 (s, 2H), 3.80 (s, 3H), 2.72 (t, J = 5.9 Hz, 2H), 2.50 (t, J = 6.0 Hz, 2H), 1.87-1.81 (m, 2H), 1.78-1.72 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 158.9, 136.6, 130.0, 129.0, 128.3, 128.1, 126.6, 124.8, 122.1, 117.1, 115.8, 114.0, 55.2, 49.5, 23.7, 23.5, 22.9, 22.0. HRMS (ESI) m/z calcd for $C_{22}H_{24}NO^+$ $[M+H]^+$ 318.1853, found 318.1855.

1-(4-chlorobenzyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4ar). Yellow liquid (52.7 mg, yield 82%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (d, J = 7.4 Hz, 2H), 7.35-7.27 (m, 4H), 7.17 (t, J = 7.3 Hz, 1H), 7.01 (d, J = 8.2 Hz, 2H), 6.77 (s, 1H), 4.96 (s, 2H), 2.72 (t, J = 6.0 Hz, 2H), 2.44 (t, J = 6.2 Hz, 2H), 1.85-1.79 (m, 2H), 1.77-1.72 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 136.7, 136.3, 133.1, 128.8, 128.5, 128.3, 128.0, 126.6, 125.0, 122.5, 117.2, 116.1, 49.4, 23.7, 23.5, 22.9, 21.9. HRMS (ESI) m/z calcd for $C_{21}H_{21}ClN^+$ $[M+H]^+$

322.1357, found 322.1358.

1-(3-methylbenzyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4as). Yellow liquid (37.0 mg, yield 62%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.96 (s, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.79 (s, 1H), 4.96 (s, 2H), 2.73 (t, J = 5.9 Hz, 2H), 2.50 (t, J = 6.0 Hz, 2H), 2.34 (s, 3H), 1.86-1.81 (m, 2H), 1.79-1.73 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 138.3, 138.0, 136.6, 129.1, 128.6, 128.3, 128.1, 127.5, 126.6, 124.8, 123.9, 122.2, 117.3, 115.7, 50.0, 23.7, 23.5, 22.9, 22.0, 21.4. HRMS (ESI) m/z calcd for $C_{22}H_{24}N^+$ $[M+H]^+$ 302.1903, found 302.1904.

1-(2-methylbenzyl)-3-phenyl-4,5,6,7-tetrahydro-1H-indole (4at). Yellow liquid (34.7 mg, yield 58%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.7 Hz, 2H), 7.20-7.13 (m, 4H), 6.71 (d, J = 5.3 Hz, 2H), 4.95 (s, 2H), 2.75 (t, J = 5.9 Hz, 2H), 2.48 (t, J = 5.9 Hz, 2H), 2.33 (s, 3H), 1.87-1.82 (m, 2H), 1.80-1.75 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 136.6, 136.1, 135.1, 130.1, 129.3, 128.3, 127.3, 126.9, 126.6, 126.4, 124.8, 122.2, 117.2, 115.7, 47.9, 23.8, 23.6, 22.9, 21.9, 19.0. HRMS (ESI) m/z calcd for $C_{22}H_{24}N^+$ $[M+H]^+$ 302.1903, found 302.1904.

1-phenyl-3-(p-tolyl)-4,5,6,7-tetrahydro-1H-indole (5a). Yellow solid (40.1 mg, yield 70%, petroleum ether), mp 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46-7.35 (m, 7H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 2.77 (t, *J* = 6.0 Hz, 2H), 2.63 (t, *J* = 5.7 Hz, 2H), 2.37 (s, 3H), 1.84-1.81 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 139.9, 134.9, 133.1, 129.1, 129.1, 129.0, 126.9, 126.2, 124.6, 123.7, 117.3, 117.1, 23.6, 23.5, 23.4, 23.2, 21.1. HRMS (ESI) m/z calcd for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747, found 288.1745.

3-(4-methoxyphenyl)-1-phenyl-4,5,6,7-tetrahydro-1H-indole (5b). Yellow solid (43.4 mg, yield 72%, petroleum ether), mp 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.44 (t, *J* = 8.6 Hz, 4H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 4.0 Hz, 3H), 3.84 (s, 3H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.63 (t, *J* = 6.0 Hz, 2H), 1.84-1.81 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 157.5, 139.9, 129.1, 128.9, 128.6, 128.0, 126.1, 124.5, 123.4, 117.0, 116.9, 113.8, 55.2, 23.6, 23.5, 23.4, 23.2. HRMS (ESI) m/z calcd for $C_{21}H_{22}NO^+$ $[M+H]^+$ 304.1696, found 304.1698.

3-(4-chlorophenyl)-1-phenyl-4,5,6,7-tetrahydro-1H-indole (5c). Yellow solid (42.3 mg,

yield 69%, petroleum ether), mp 100-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.47-7.42 (m, 4H), 7.36-7.32 (m, 5H), 6.98 (s, 1H), 2.75 (s, 2H), 2.62 (s, 2H), 1.86-1.81 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 139.7, 134.6, 130.8, 129.4, 129.1, 128.5, 128.0, 126.4, 124.6, 122.5, 117.6, 116.9, 23.5, 23.4, 23.4, 23.1. HRMS (ESI) m/z calcd for $C_{20}H_{19}ClN^+$ $[M+H]^+$ 308.1201, found 308.1203.

3-(4-bromophenyl)-1-phenyl-4,5,6,7-tetrahydro-1H-indole (5d). Yellow solid (51.3 mg, yield 73%, petroleum ether), mp 81-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50-7.41 (m, 4H), 7.37-7.31 (m, 5H), 6.98 (s, 1H), 2.74 (t, *J* = 6.0 Hz, 2H), 2.60 (t, *J* = 6.0 Hz, 2H), 1.84-1.81 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 139.7, 135.0, 131.4, 129.5, 129.1, 128.4, 126.5, 124.6, 122.5, 118.9, 117.6, 116.9, 23.5, 23.5, 23.4, 23.1. HRMS (ESI) m/z calcd for $C_{20}H_{19}BrN^+$ $[M+H]^+$ 352.0695, found 352.0697.

3-(4-nitrophenyl)-1-phenyl-4,5,6,7-tetrahydro-1H-indole (5e). Yellow solid (32.8 mg, yield 52%, petroleum ether), mp 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.13 (s, 1H), 2.81 (t, *J* = 6.0 Hz, 2H), 2.59 (t, *J* = 6.0 Hz, 2H), 1.86-1.83 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 145.0, 143.4, 139.3, 130.5, 129.3, 127.1, 126.4, 124.8, 124.1, 121.6, 119.4, 117.2, 23.8, 23.4, 23.4, 22.9. HRMS (ESI) m/z calcd for $C_{20}H_{19}N_2O_2^+$ $[M+H]^+$ 319.1441, found 319.1441.

3-(2-chlorophenyl)-1-phenyl-4,5,6,7-tetrahydro-1H-indole (5f). Yellow liquid (46.1 mg, yield 75%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46-7.40 (m, 4H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 2.64 (t, *J* = 5.6 Hz, 2H), 2.58 (t, *J* = 5.6 Hz, 2H), 1.83-1.77 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 139.8, 134.7, 133.0, 131.6, 129.8, 129.0, 128.0, 127.1, 126.3, 126.2, 124.5, 120.6, 119.8, 118.5, 23.5, 23.4, 23.3, 22.9. HRMS (ESI) m/z calcd for $C_{20}H_{19}ClN^+$ $[M+H]^+$ 308.1201, found 308.1203.

2-methyl-1,3-diphenyl-4,5,6,7-tetrahydro-1H-indole (5g). Yellow solid (29.2 mg, yield 51%, petroleum ether), mp 86-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.48 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 4.5 Hz, 5H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 8.0, 1H), 2.62 (t, *J* = 5.2 Hz, 2H), 2.41 (t, *J* = 5.1 Hz, 2H), 2.15 (s, 3H), 1.82-1.77 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 138.5, 136.5, 129.4, 129.0, 128.0, 128.0, 127.8, 127.3, 125.1, 124.8, 120.2, 115.8, 23.9, 23.4,

22.9, 22.7, 11.5. HRMS (ESI) m/z calcd for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747, found 288.1745.

3-(naphthalen-2-yl)-1-phenyl-4,5,6,7-tetrahydro-1H-indole (5h). Yellow solid (45.1 mg, yield 70%, petroleum ether), mp 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.93 (s, 1H), 7.83 (t, *J* = 6.4 Hz, 3H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 4H), 7.40 (t, *J* = 6.4 Hz, 3H), 7.34 (t, *J* = 7.3 Hz, 1H), 2.90 (s, 2H), 2.66 (s, 2H), 1.88-1.86 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 139.8, 133.8, 133.6, 131.6, 129.4, 129.1, 127.9, 127.7, 127.6, 126.4, 126.2, 125.9, 124.9, 124.7, 124.5, 123.6, 118.1, 117.3, 23.7, 23.6, 23.6, 23.2. HRMS (ESI) m/z calcd for $C_{24}H_{22}N^+$ $[M+H]^+$ 324.1747, found 324.1747.

1-phenyl-3-(thiophen-2-yl)-4,5,6,7-tetrahydro-1H-indole (5i). Yellow liquid (45.1 mg, yield 72%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (t, *J* = 7.7 Hz, 2H), 7.36-7.31 (m, 3H), 7.14 (d, *J* = 4.9 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 3H), 2.79 (t, *J* = 6.1 Hz, 2H), 2.60 (t, *J* = 4.0 Hz, 2H), 1.89-1.79 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 139.6, 138.6, 129.3, 129.1, 127.3, 126.4, 124.5, 121.8, 121.8, 117.4, 117.2, 117.0, 23.5, 23.3, 23.2, 23.1. HRMS (ESI) m/z calcd for $C_{18}H_{18}NS^+$ $[M+H]^+$ 280.1155, found 280.1156.

1,3-diphenyl-1H-indole (6a, CAS: 20538-11-8)[23]. Yellow solid (35.5 mg, yield 66%, petroleum ether), mp 102-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 6.5 Hz, 4H), 7.51 (s, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.41–7.36 (m, 1H), 7.34–7.24 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 139.4, 136.6, 135.0, 129.6, 128.8, 127.6, 127.1, 126.6, 126.2, 125.5, 124.4, 122.8, 120.8, 120.1, 119.0, 110.8.

5-methyl-1,3-diphenyl-1H-indole (6b). Yellow solid (35.7 mg, yield 63%, petroleum ether), mp 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.57–7.46 (m, 8H), 7.39-7.31 (m, 2H), 7.11 (d, *J* = 8.3 Hz, 1H), 2.51 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 139.6, 135.2, 134.9, 130.2, 129.6, 128.8, 127.6, 127.3, 126.4, 126.1, 125.5, 124.3, 124.2, 119.7, 118.6, 110.5, 21.5. HRMS (ESI) m/z calcd for $C_{21}H_{18}N^+$ $[M+H]^+$ 284.1434, found 284.1436

5-(tert-butyl)-1,3-diphenyl-1H-indole (6c). White solid (48.8 mg, yield 75%, petroleum ether), mp 168-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.59–7.49(m, 8H), 7.40-7.33 (m, 3H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 143.9, 139.6, 135.3, 134.7, 129.6, 128.8, 127.6, 126.9, 126.4, 126.1, 125.6, 124.1, 121.0, 119.2,

115.7, 110.4, 34.7, 31.9. HRMS (ESI) m/z calcd for $C_{24}H_{24}N^+$ $[M+H]^+$ 326.1903, found 326.1905.

1,3,5-triphenyl-1H-indole (6d). Yellow solid (40.2 mg, yield 58%, petroleum ether), mp 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.18 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 3H), 7.61–7.45 (m, 10H), 7.41 (t, *J* = 6.7 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 142.3, 139.4, 136.0, 134. 9, 134.5, 129.7, 128.9, 128.7, 127.7, 127.6, 127.5, 126.7, 126.5, 126.3, 126.1, 124.3, 122.6, 119.4, 118.6, 111.1. HRMS (ESI) m/z calcd for $C_{26}H_{20}N^+$ $[M+H]^+$ 346.1590, found 346.1592.

3-phenyl-1-(p-tolyl)-1H-indole (6e). Yellow liquid (33.9 mg, yield 60%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.46 (dd, *J* = 15.9, 7.4 Hz, 5H), 7.35–7.29 (m, 3H), 7.25 (t, *J* = 6.0 Hz, 2H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 136.9, 136.7, 136.5, 135.1, 130.2, 128.8, 127.5, 126.9, 126.1, 125.6, 124.4, 122.6, 120.7, 120.0, 118.7, 110.8, 21.1. HRMS (ESI) m/z calcd for $C_{21}H_{18}N^+$ $[M+H]^+$ 284.1434, found 284.1436.

1-(4-methoxyphenyl)-3-phenyl-1H-indole (6f, CAS: 1423744-14-2)[24]. Yellow liquid (31.3 mg, yield 52%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.51–7.44 (m, 6H), 7.33-7.21 (m, 3H), 7.05 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 158.3, 137.0, 135.2, 132.4, 128.8, 127.5, 126.6, 126.0, 126.0, 125.9, 122.6, 120.6, 120.0, 118.4, 114.7, 110.7, 55.5.

1-(4-chlorophenyl)-3-phenyl-1H-indole (6g). Yellow solid (42.5 mg, yield 70%, petroleum ether), mp 95-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.51-7.46 (m, 7H), 7.35–7.28 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 138.0, 136.4, 134.7, 132.1, 129.8, 128.8, 127.6, 127.1, 126.4, 125.5, 125.1, 123.0, 121.1, 120.2, 119.5, 110.5. HRMS (ESI) m/z calcd for $C_{20}H_{15}ClN^+$ $[M+H]^+$ 304.0888, found 304.0884.

1-phenyl-3-(p-tolyl)-1H-indole (6h)[25]. Yellow liquid (28.5 mg, yield 50%, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 3H), 7.54 (q, *J* = 8.0 Hz, 4H), 7.48 (s, 1H), 7.37 (t, *J* = 6.4 Hz, 1H), 7.30-7.22 (m, 4H), 2.42 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 139.5, 136.5, 135.8, 132.0, 129.6, 129.5, 127.5, 127.1, 126.5, 125.2, 124.4, 122.7, 120.7, 120.1, 119.0, 110.7, 21.2.

3-(4-methoxyphenyl)-1-phenyl-1H-indole (6i, CAS: 1379825-88-3)[25]. Yellow solid (34.8

mg, yield 58%, petroleum ether), mp 83-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 8.6 Hz, 3H), 7.54 (q, *J* = 8.0 Hz, 4H), 7.45 (s, 1H), 7.40–7.35 (m, 1H), 7.29–7.22 (m, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 158.2, 139.5, 136.4, 129.6, 128.7, 127.5, 127.2, 126.5, 124.9, 124.3, 122.7, 120.7, 120.0, 118.7, 114.3, 110.7, 55.3.

3-(4-bromophenyl)-1-phenyl-1H-indole (6j, CAS: 1379825-86-1)[25]. Yellow solid (41.9 mg, yield 60%, petroleum ether), mp 120-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.59 (s, 5H), 7.55 (d, *J* = 4.3 Hz, 4H), 7.51 (s, 1H), 7.42-7.38 (m, 1H), 7.32–7.26 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 139.3, 136.6, 134.0, 131.9, 129.7, 129.0, 126.8, 126.7, 125.6, 124.5, 122.9, 121.0, 119.8, 117.8, 110.9.

■ ASSOCIATED CONTENT

Supporting Information

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^{1}H and ^{13}C NMR spectra for the products.

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