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ARTICLE

Gold(I)-Catalyzed Synthesis of 2-Substituted Indoles from 2-Alkynylnitroarenes with Diboron as Reductant

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An efficient method for the synthesis of 2-substituted indoles via a diboron/base promoted tandem reductive cyclization of o-alkynylnitroarene under Au catalysis conditions has been disclosed. This reaction is efficient and convenient, affording 2-substituted indoles with broad functional groups tolerance and excellent yields.

1. Introduction

The indole ring constitutes one of the most significant structural skeletons in pharmacologically and biologically active molecules.[1] Among them, 2-substituted indoles represent a subclass of biologically and synthetically useful scaffolds.[2] They are also present in medicinally-active compounds, such as Heterocombretastatin, CDK inhibitors and cytotoxic agents, etc.[3] (Figure 1). Traditional methods for the preparation of 2-substituted indoles are mainly based on the Fischer indole synthesis,[4] however, harsh reaction conditions sometimes limit the functional group tolerance. Thus, the development of efficient methods to construct these molecules has evoked considerable attention. Among the various indole syntheses, the metal- or base-catalyzed preparation of indoles starting from 2-alkynylanilines has been predominant.[5] However, the application of 2-nitroarylacetylenes to construct indoles via one step has been rarely reported in previous works.

In 2009, the Tokunaga group reported a two-step in one pot reaction by converting 1-ethynyl-2-nitrobenzene derivatives to 2-substituted indoles with nano-Au/Fe_2O_3 as catalyst in hydrogen atmosphere (Scheme 1a),[6] nevertheless, high temperature, high hydrogen pressure as well as special reaction apparatus limits the practical application in organic synthesis. Recently, we have reported the diborane-mediated deoxygenation of 2-nitrostyrenes to form indoles via reductive cyclization in good to high yields (Scheme 1b).[7] However, when 2-nitroarylacetylenes was subjected to the previous system, no desired indole was observed. As gold complexes have emerged as effective catalysts for the activation of C-C triple bonds,[8] we

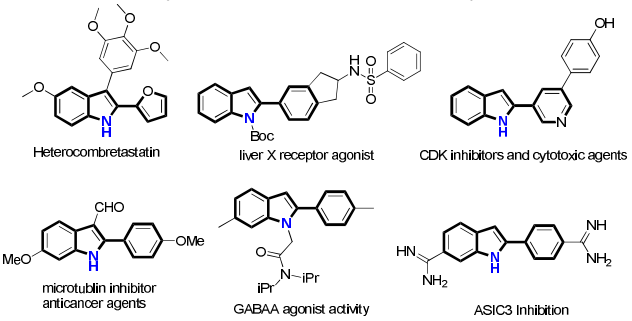
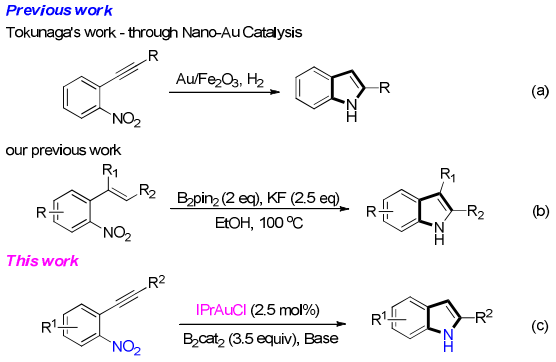


Figure 1 Several active molecules containing 2-substituted indoles.

examined their use in the reductive cyclization of 2-alkynylnitroarenes to form indoles. It is well-known that stoichiometric amount of metal reductants, such as Zn,[9] Ni,[10] In,[11] have been employed as reductant to reduce nitro group to amino group, however, the waste from these reductive agents cause the isolation of the aniline products troublesome from the reaction mixture. Despite the fact that diboron reagents have been widely used in organic synthesis as an efficient borylation agent,[12] their use as reductants[13] has rarely been reported in synthesis of indoles. As part of our



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Scheme 1 a, b) Recent important advance about indole synthesis. c) This study.

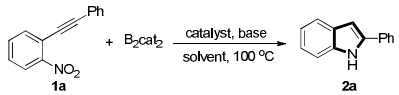
continuous interest in the development of new synthetic methods of new organoboron compound as well as discovery of new reactivity of diboron compounds, we envision that in the presence of both Au catalyst and diboron reagent, 2-alkynyl nitroarene could be smoothly transformed into 2-substituted indoles in suitable conditions (Scheme 1c). Herein, we report an indole synthesis via gold catalyzed reductive cyclization to convert 2-alkynylnitroarenes into 2-substituted indoles with diboron as reductant.

2. Results and discussion

We commenced our hypothesis by using 1-nitro-2-(phenylethynyl)benzene (**1a**) as the substrate and B_2cat_2 as reductant for the reaction optimization. The initial reaction was using commercially available 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene gold(I)chloride (IPrAuCl) as the catalyst and heated at 100 °C in THF (Table 1). As a result, the desired 2-phenyl-1H-indole (**2a**) was indeed formed in 29% yield (Table 1, entry 2) via a reductive cyclization in presence of 2.0 equiv of Na_2CO_3 and 2.0 equiv of B_2cat_2. Subsequently, we systematically investigated various bases and NaO*t*Bu demonstrated to be the optimal one (Table 1, entries 1-5). We also screened the solvent effect, which revealed that CH_3CN was superior to DCE and THF (Table 1, entries 6-7). To our delight, when the amount of B_2cat_2 was increased to 3.5 equiv, the desired product **2a** was obtained in 78% isolated yield (Table 1, entry 8). Interestingly, when B_2pin_2 was used instead of B_2cat_2, no amount of product **2a** was detected (Table 1, entry 9), which disclosed the specific reactivity of B_2cat_2 for this reaction. No corresponding product **2a** was observed when the reaction was performed under air (Table 1, entry 10). Whereas, an array of different gold sources and metal salts were tested and stagnant reactions were observed by using Ph_3PAuCl, Tf_2NAuCl, $FeCl_3$, $ZnCl_2$ and $NiCl_2$ as catalysts (Table 1, entries 11-15), which indicated remarkable catalytic performance of the IPrAuCl as Lewis acid. Notably, only marginal improvements were gained when the reaction temperature was reduced to 70°C and the reaction time was decreased to 6 h (Table 1, entries 16-17). Controlled experiment was carried out without IPrAuCl (Table 1, entry 18) no product **2a** was detected, and that conclusiveness of IPrAuCl as catalyst.

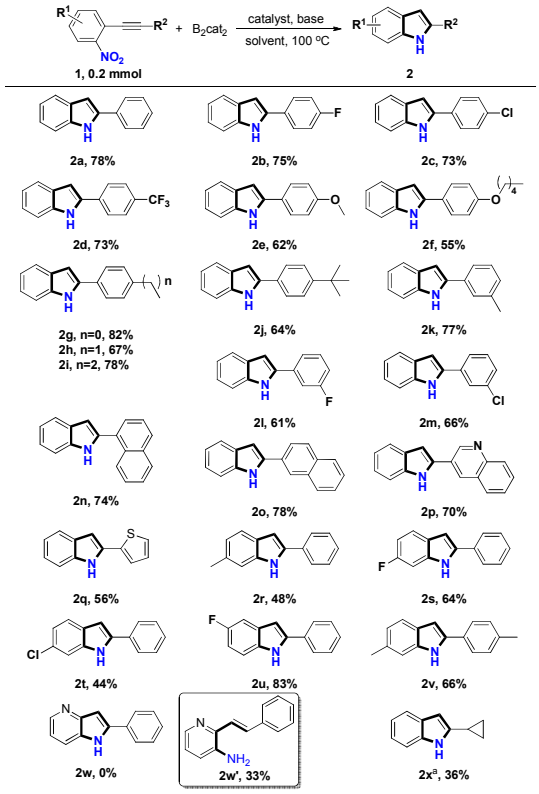
The optimal reaction conditions (entry 8, Table 1) were used to explore the scope and limitation of indole synthesis (Table 2). A number of functionalized 1-nitro-2-(phenylethynyl)benzene derivatives were inspected initially. It is noteworthy that electronic effects of substituents on the aromatic rings of 1-nitro-2-(phenylethynyl)benzene derivatives had no significant influence and corresponding indoles were obtained in good yields (**2a**-**2l**). When the sterically demanding ((2-nitrophenyl)ethynyl)naphthalenes (**1n** and **1o**) were submitted to the standard conditions, respectively, the corresponding products **2n** and **2o** were obtained in 74% and 78% yield. To our delight, 3-((2-nitrophenyl)ethynyl)quinoline **1p** and 2-(thiophen-2-yl)-1H-indole **1q** were also good candidates in this indole transformation, giving the corresponding desired products 2p and 2q in 70% and 56% yields respectively. In addition to the R2 groups, we also investigated the effect of R^1 groups on 1-nitro-2-(phenylethynyl)benzene derivatives (**1r**-**1v**). To our satisfaction,

Table 1 Optimization of the reaction for synthesis of 2-phenyl-1H-indole **2a**.



entry	base	B_2cat_2 (equiv)	solvent	cat.	yield of **2a** (%)[a]
1	CsOAc	2	THF	IPrAuCl	0
2	Na_2CO_3	2	THF	IPrAuCl	29
3	Cs_2CO_3	2	THF	IPrAuCl	9
4	NaO*t*Bu	2	THF	IPrAuCl	41
5	NaOMe	2	THF	IPrAuCl	37
6	NaO*t*Bu	2	CH_3CN	IPrAuCl	53
7	NaO*t*Bu	2	DCE	IPrAuCl	29
8	NaO*t*Bu	3.5	CH_3CN	IPrAuCl	78[b]
9[c]	NaO*t*Bu	3.5	CH_3CN	IPrAuCl	0
10[d]	NaO*t*Bu	3.5	CH_3CN	IPrAuCl	0
11	NaO*t*Bu	3.5	CH_3CN	Ph_3PAuCl	31
12	NaO*t*Bu	3.5	CH_3CN	Tf_2NAuCl	23
13[e]	NaO*t*Bu	3.5	CH_3CN	$FeCl_3$	0
14[e]	NaO*t*Bu	3.5	CH_3CN	$ZnCl_2$	0
15[e]	NaO*t*Bu	3.5	CH_3CN	$NiCl_2$	0
16[f]	NaO*t*Bu	3.5	CH_3CN	IPrAuCl	38
17[g]	NaO*t*Bu	3.5	CH_3CN	IPrAuCl	56
18	NaO*t*Bu	3.5	CH_3CN	none	0

Reaction condition: **1a** (0.2 mmol), base (2 equiv), IPrAuCl (2.5 mol%) and solvent (0.1 M), at 100 °C under N_2, 12 h. a) GC yield; b) isolated yield; c) B_2pin_2 instead of B_2cat_2; d) under air; e) catalyst (5 mol%); f) 70 °C; g) 6 h.



Reaction condition: **1** (0.2 mmol), NaO*t*Bu (2 equiv), IPrAuCl (2.5 mol%), B_2cat_2 (3.5 equiv) and CH_3CN (2 mL), at 100 °C under N_2, 12 h. a) NaOMe (2eq).

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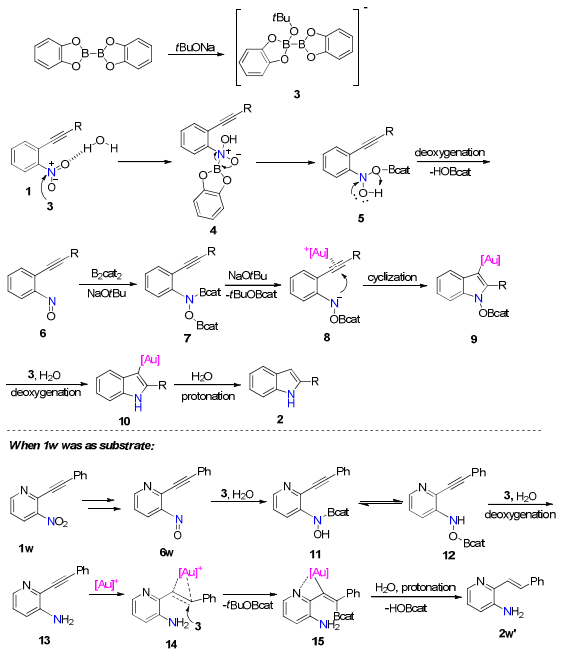
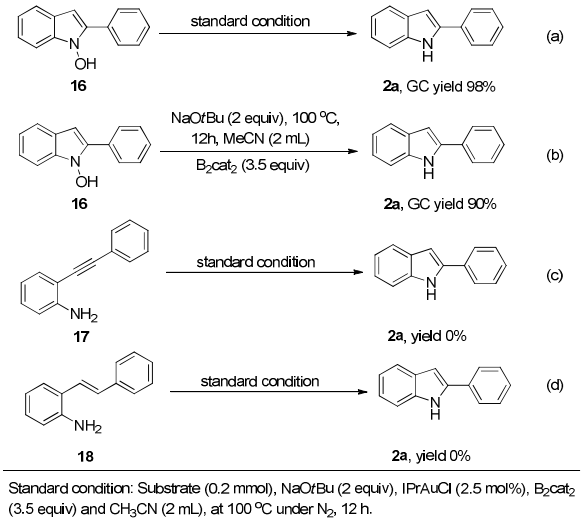
Scheme 2 Synthesis of 2-substituted indoles through 2-alkynyl nitroarenes.

the desired 2-substituted indoles were achieved in moderate to good yields (**2r**-**2v**). Of note, when the 3-nitro-2-(phenylethynyl)pyridine **1w** was used as substrate, no corresponding indole product **2w** was observed, instead, reduced product (E)-2-styrylpyridin-3-amine **2w'** was obtained in 33% yield. Probably due to the strong coordination of pyridine ring, which lead to the undesired reduction of **1w**. Whereas **2p** containing a 3-quinoline framework was obtained in good yield owing to the weaker coordination of quinoline than pyridine. In addition to the aromatic substituents of R^2 group, the substrate **1x** bearing the cyclopropyl substituent was also amenable to this reaction, albeit low yield of **2x** was obtained.



Scheme 3 Plausible Mechanism

On the basis of previous report,[7,14] the plausible reaction mechanism for the formation of indoles is described in Scheme 3. Initially, base activate diboron to generate the anionic sp^2-sp^3 diborane reagents **3** $[B_2cat_2tBuO]^-$.[14b] With the help of water, the nucleophile **3** attaches **1** to engender the intermediate **4**.[14b,15] Rearrangement of **4** and diborane-mediated deoxygenation[14] of **5** produces the nitroso species **6**,[14b] which is further transformed into species **7** with B_2cat_2.[7] Afterwards, base-mediated deboronation of **7** generates the borate-nitroso anion **8**,[7,16] which attacks the carbon-carbon triple bond in the presence of IPrAuCl to render the intermediate **9** via a 6π-electron-5-atom electrocyclization.[7] Subsequently, once again B_2cat_2-mediated deoxygenation of species **9** and protonation of **10** deliver the 2-substituted indoles **2**. Especially, when **1w** was used as substrate, 3-nitroso-pyridine species **6w** was formed as the represented path in the top of Scheme 3. In the presence of **3**, 3-nitroso-pyridine species **6w** is transformed to **12** which is an analogue of hydroxylamine **11**.[14b] Then deoxygenation of **12** generates the aminate **13**,[14b] which is further translated into transition state **14** by coordinating with the catalytically active gold cation.[17] Finally, protonation of intermediate **15** to give the corresponding product **2w'**.



Standard condition: Substrate (0.2 mmol), NaO*t*Bu (2 equiv), IPrAuCl (2.5 mol%), B_2cat_2 (3.5 equiv) and CH_3CN (2 mL), at 100 °C under N_2, 12 h.

Scheme 4 Potential reaction intermediates.

Some extra experiments were implemented to obtain more information for the verification of the reaction mechanism. In our previous work,[7] 2-phenyl-1H-indol-1-ol **16** could be deoxygenated to produce 2-phenylindol **2a** (Scheme 4a). Not surprisingly, when 2-phenyl-1H-indol-1-ol **16** was subjected to standard conditions, 98% yield of 2-phenylindol **2a** was obtained. And 90% yield of 2-phenylindol **2a** was also achieved, when the reaction was performed without IPrAuCl (Scheme 4b), which suggests that oxygen-borane of species **5** might be formed in the absence of Au leading to the formation of the desired product. When the 2-(phenylethynyl)aniline **17** and (E)-2-styrylaniline **18** was used as substrates under standard conditions, no 2-phenylindol **2a** was observed (Scheme 4c, 4d), which verified that this reaction doesn't undergo the two-step process via reduction of 1-nitro-2-(phenylethynyl)benzene to amine first and subsequent cyclization of 2-ethynylaniline to lead to indoles.

3. Conclusions

In conclusion, we have disclosed a Au-catalyzed synthesis of 2-substituted indoles from 2-alkynylnitroarenes derivatives by using B_2cat_2 as a reductant. Our experiments suggest that this reaction undergoes reductive cyclization of 2-alkynylnitroarenes derivatives to render indole derivatives. Our future work is aimed at further mechanistic studies and synthetic application of this novel protocol.

4. Experimental section

4.1 General information

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All chemicals were purchased from Adamas Reagent, energy chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd and Tansoole. Unless stated otherwise, reactions were performed in oven-dried or flame-dried glassware using a Schlenk line under a nitrogen atmosphere. All solvents were commercially obtained, and reactions were performed without specific drying of solvents. Flash column chromatography was performed over silica gel (200-300 mesh).

^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 500 spectrometer (500 MHz ^{1}H, 125 MHz ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR , δ = 77.00 for ^{13}C-NMR) as an internal reference. Coupling constants (*J*) were reported in Hertz (Hz).The following abbreviations are used to indicate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. High resolution mass spectra were recorded using a Thermo Fisher Scientific LTQ FT Ultra or Waters Micromass GCT Premier instrument.

4.2 General procedure for starting materials (1)

To a solution of 1-nitro-2-iodobenzene (2.0 mmol) in triethylamine (10 ml) at room temperature was added $PdCl_2(PPh_3)_2$ (0.028 g, 0.02 mmol). The resultant suspension was stirred for 10 min followed by addition of alkynes (2.2 mmol) and then CuI (0.015 g, 0.04 mmol). This mixture was then stirred for 6 h. The reaction mixture was washed with NH_4Cl aq. (sat.) and brine, and dry over Na_2SO_4. The solvent were removed, and the residue was subjected to silica-gel column chromatography.

4.3 General process for the synthesis of 2-Substituted Indoles (2)

General procedure A. To a mixture of 1-nitro-2-alkynylbenezenes **1** (0.2 mmol, 1.0 equiv), B_2cat_2 (167 mg, 3.5 equiv) and IPrAuCl (3.1 mg, 2.5 mol%) was added NaO*t*Bu (38.4 mg, 2.0 equiv), MeCN (2 mL). The resulting mixture was heated to 100 °C. After 12 h, the mixture was cooled to room temperature. The solution was extracted with 3 × 10 mL of ethyl acetate. The combined organic phases were washed with 2 × 10 mL of brine. The resulting organic phase was dried over Na_2SO_4. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph to give the desired product **2**.

General procedure B. To a mixture of 1-nitro-2-alkynylbenezenes **1** (0.2 mmol, 1.0 equiv), B_2cat_2 (167 mg, 3.5 equiv) and IPrAuCl (3.1 mg, 2.5 mol%) was added NaO*t*Bu (38.4mg, 2 equiv), MeCN (2 mL). The resulting mixture was heated to 100 °C. After 12 h, the mixture was cooled to room temperature. The solution was extracted with 3 × 10 mL of ethyl acetate. The combined organic phases were washed with 5 × 10 mL of K_2CO_3 aq. (sat.). The resulting organic phase was dried over Na_2SO_4. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph to give the desired product **2**.

4.4 Characterization data for products

2-phenyl-1H-indole (2a).[18] Compound **2a** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.67 (dt, *J* = 7.5, 4.0 Hz, 3H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.41 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.25 – 7.18 (m, 1H), 7.18 – 7.10 (m, 1H), 6.89 – 6.80 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 136.8, 132.4, 129.3, 129.1, 127.8, 125.2, 122.4, 120.7, 120.3, 110.9, 100.0.

2-(4-fluorophenyl)-1H-indole (2b).[18] Compound **2b** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.69 – 7.57 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.11 (m, 3H), 6.77 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.1 Hz), 137.0, 136.8, 129.3, 128.7, 126.9 (d, *J* = 8.0 Hz), 122.4, 120.7, 120.4, 116.1 (d, *J* = 21.8 Hz), 110.9, 100.0.

2-(4-chlorophenyl)-1H-indole (2c).[18] Compound **2c** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.40 (t, *J* = 8.7 Hz, 3H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 136.7, 133.4, 130.9, 129.2, 129.1, 126.3, 122.7, 120.7, 120.4, 110.9, 100.4.

2-(4-(trifluoromethyl)phenyl)-1H-indole (2d).[18] Compound **2d** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.68 (dd, *J* = 18.4, 8.1 Hz, 3H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 1.7 Hz, 1H). ^{13}C NMR (125 MHz, DMSO) δ 137.9, 136.5, 136.3, 128.8, 127.7 (d, *J* = 31.3 Hz), 126.31 (d, *J* = 3.8 Hz), 125.8, 124.8 (d, *J* = 270.0 Hz), 122.9, 121.0, 120.2, 112.0, 101.2.

2-(4-methoxyphenyl)-1H-indole (2e).[6] Compound **2e** was prepared according to the general procedure B (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a white solid in 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.60 (dd, *J* = 7.8, 5.6 Hz, 3H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.14 (dt, *J* = 30.3, 7.3 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.72 (s, 1H), 3.86 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 138.0, 136.7, 129.4, 126.5, 125.2, 121.9, 120.4, 120.2, 114.5, 110.7, 98.9, 55.4.

2-(4-(pentyloxy)phenyl)-1H-indole (2f).[19] Compound **2f** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 55% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.72 (s, 1H), 4.00 (t, *J* = 6.6 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.48 – 1.39 (m, 4H), 1.29 (d, *J* = 12.3 Hz, 2H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 138.1, 136.6, 129.5, 126.5, 125.0, 121.9, 120.3, 120.2, 115.0, 110.7, 98.7, 68.2, 29.0, 28.2, 22.5, 14.1.

2-(p-tolyl)-1H-indole (2g).[18] Compound **2g** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.40 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 6.80 (dd, *J* = 2.1, 0.7 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 137.7, 136.7, 129.7, 129.6, 129.4, 125.1, 122.1, 120.5, 120.2, 110.8, 99.4, 21.3.

2-(4-ethylphenyl)-1H-indole (2h). Compound **2h** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15 (td, *J* = 7.6, 0.9 Hz, 1H), 6.82 (s, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.32 – 1.29 (m, 3H). ^{13}C NMR (125

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MHz, $CDCl_3$) δ 144.1, 138.1, 136.7, 129.8, 129.4, 128.6, 125.2, 122.1, 120.6, 120.2, 110.9, 99.5, 28.7, 15.6. HRMS (ESI, m/z): calculated for $C_{16}H_{15}N$ $[M+H]^+$: 222.1277; found: 222.1279.

2-(4-propylphenyl)-1H-indole (2i).[20] Compound **2i** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 1.3 Hz, 1H), 2.68 – 2.60 (m, 2H), 1.74 – 1.63 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 138.1, 136.7, 129.8, 129.4, 129.1, 125.1, 122.1, 120.5, 120.2, 110.8, 99.4, 37.8, 24.5, 13.9.

2-(4-(tert-butyl)phenyl)-1H-indole (2j).[21] Compound **2j** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.65 – 7.60 (m, 3H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.13 (dd, *J* = 10.9, 3.8 Hz, 1H), 6.81 (d, *J* = 1.4 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 138.0, 136.7, 129.6, 129.4, 126.0, 124.9, 122.1, 120.6, 120.2, 110.9, 99.5, 34.7, 31.3.

2-(m-tolyl)-1H-indole (2k).[22] Compound **2k** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 77% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.17 (ddd, *J* = 23.9, 11.5, 7.1 Hz, 3H), 6.83 (d, *J* = 2.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.0, 136.8, 132.3, 129.3, 128.9, 128.5, 125.9, 122.3, 122.2, 120.6, 120.2, 110.9, 99.9, 21.6.

2-(3-fluorophenyl)-1H-indole (2l).[18] Compound **2l** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.36 – 7.31 (m, 1H), 7.24 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.06 – 7.00 (m, 1H), 6.90 – 6.81 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (d, *J* = 244.5 Hz), 136.9, 136.6 (d, *J* = 2.6 Hz), 134.6 (d, *J* = 8.2 Hz), 130.6 (d, *J* = 8.6 Hz), 129.1, 122.9, 120.9, 120.7 (d, *J* = 2.8 Hz), 120.5, 114.5 (d, *J* = 21.1 Hz), 112.0 (d, *J* = 22.6 Hz), 111.1, 100.9.

2-(3-chlorophenyl)-1H-indole (2m).[23] Compound **2m** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.68 – 7.60 (m, 2H), 7.56 – 7.49 (m, 1H), 7.43 – 7.33 (m, 2H), 7.29 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.15 (td, *J* = 7.6, 0.9 Hz, 1H), 6.85 (dd, *J* = 2.1, 0.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.0, 136.3, 135.0, 134.2, 130.3, 129.1, 127.6, 125.2, 123.2, 122.9, 120.9, 120.5, 111.0, 101.0.

2-(naphthalen-1-yl)-1H-indole (2n).[23] Compound **2n** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a yellow solid in 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.97 – 7.85 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.65 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.58 – 7.50 (m, 3H), 7.46 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.26 (dd, *J* = 15.2, 1.2 Hz, 1H), 7.22 – 7.16 (m, 1H), 6.82 (dd, *J* = 2.0, 0.7 Hz, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 136.4, 133.9, 131.5, 131.1, 128.9, 128.6, 128.5, 127.2, 126.7, 126.2, 125.7, 125.4, 122.2, 120.6, 120.2, 110.9, 103.7.

2-(naphthalen-2-yl)-1H-indole (2o).[24] Compound **2o** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.07 (s, 1H), 7.97 – 7.80 (m, 4H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.99 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 137.0, 133.5, 132.8, 129.6, 129.3, 128.7, 128.0, 127.8, 126.7, 126.1, 123.8, 123.0, 122.5, 120.7, 120.3, 110.9, 100.6.

3-(1H-indol-2-yl)quinoline (2p).[25] Compound **2p** was prepared according to the general procedure B (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 70% yield. ^{1}H NMR (500 MHz, DMSO) δ 11.86 (s, 1H), 9.47 (d, *J* = 2.3 Hz, 1H), 8.74 (d, *J* = 2.1 Hz, 1H), 8.07 – 7.98 (m, 2H), 7.76 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.66 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.48 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.22 (d, *J* = 1.4 Hz, 1H), 7.17 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.06 (td, *J* = 7.5, 0.9 Hz, 1H).^{13}C NMR (125 MHz, DMSO) δ 148.5, 146.6, 137.5, 134.7, 129.8, 129.3, 128.8, 128.6, 128.1, 127.6, 127.4, 125.5, 122.3, 120.4, 119.7, 111.5, 100.5.

2-(thiophen-2-yl)-1H-indole (2q).[26] Compound **2q** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a yellow solid in 56% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 7.16 – 7.12 (m, 1H), 7.10 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.80 – 6.67 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 135.6, 132.4, 129.1, 128.0, 124.6, 122.9, 122.6, 120.6, 120.5, 110.8, 100.4.

6-methyl-2-phenyl-1H-indole (2r).[18] Compound **2r** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.68 – 7.61 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.34 – 7.29 (m, 1H), 7.19 (d, *J* = 0.5 Hz, 1H), 6.98 (dd, *J* = 8.0, 0.9 Hz, 1H), 6.80 (dd, *J* = 2.1, 0.8 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3, 137.2, 132.6, 132.3, 129.0, 127.5, 127.1, 125.0, 122.1, 120.3, 110.9, 99.8, 21.9.

6-fluoro-2-phenyl-1H-indole (2s).[27] Compound **2s** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.54 (dd, *J* = 8.1, 5.5 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 9.2 Hz, 1H), 6.91 (t, *J* = 8.5 Hz, 1H), 6.80 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0 (d, *J* = 236.6 Hz), 138.4, 136.7 (d, *J* = 12.4 Hz), 132.1, 129.1, 127.8, 125.8, 125.0, 121.4 (d, *J* = 10.0 Hz), 109.1 (d, *J* = 24.3 Hz), 99.9, 97.3 (d, *J* = 25.9 Hz).

6-chloro-2-phenyl-1H-indole (2t).[27] Compound **2t** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 44% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 18.0, 10.6 Hz, 2H), 7.09 (dd, *J* = 8.4, 1.5 Hz, 1H), 6.80 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 137.1, 131.9, 129.1, 128.0, 127.8, 125.2, 121.5, 121.0, 110.8, 100.0, 99.9.

5-fluoro-2-phenyl-1H-indole (2u).[18] Compound **2u** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.69 – 7.63 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.26 (m, 3H), 6.95 (td, *J* = 9.1, 2.5 Hz, 1H), 6.79 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2 (d, *J* = 233.3 Hz), 139.7, 133.3, 132.0, 129.6 (d, *J* = 10.4 Hz), 129.1, 128.0, 125.2, 111.5 (d, *J* = 9.7 Hz), 110.6 (d, *J* = 26.3 Hz), 105.4 (d, *J* = 23.3 Hz), 100.1 (d, *J* = 4.7 Hz).

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6-methyl-2-(p-tolyl)-1H-indole (2v). Compound **2v** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a white solid in 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.56 – 7.50 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.17 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.77 – 6.73 (m, 1H), 2.49 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 137.4, 137.2, 132.0, 129.8, 129.7, 127.2, 124.9, 122.0, 120.2, 110.8, 99.2, 21.8, 21.3. HRMS (ESI, m/z): calculated for $C_{16}H_{15}N$ $[M+H]^+$: 222.1277; found: 222.1282.

(E)-2-styrylpyridin-3-amine (2w').[28] Compound **2w'** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 50:1 v/v). The product was obtained as a yellow solid in 33% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 3.6, 2.4 Hz, 1H), 7.66 (d, *J* = 15.7 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.37 (dd, *J* = 10.4, 4.7 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.20 (d, *J* = 15.7 Hz, 1H), 7.03 – 6.99 (m, 2H), 3.82 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 140.4, 140.0, 137.1, 133.1, 128.7, 128.1, 127.0, 123.4, 123.0, 122.0.

2-cyclopropyl-1H-indole (2x).[29] Compound **2x** was prepared according to the general procedure A (petroleum ether/ethyl acetate = 100:1 v/v). The product was obtained as a colorless oil in 36% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.57 (d, *J* = 5.8 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.20 – 7.10 (m, 2H), 6.21 (s, 1H), 2.00 – 1.93 (m, 1H), 1.01 (d, *J* = 7.2 Hz, 2H), 0.82 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 135.8, 128.8, 121.0, 119.8, 119.7, 110.3, 97.7, 8.9, 7.4.

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Competing financial interests

The authors declare no competing financial interests.

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