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Ruthenium(II)-Catalyzed Direct Addition of Indole/Pyrrole C2−H Bonds to Alkynes

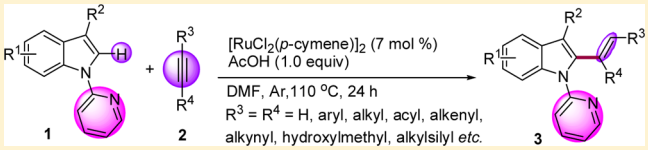
Libo Liang,[†,§] Shaomin Fu,[†,§] Dongen Lin,[†] Xiao-Qi Zhang,[‡] Yuanfu Deng,[†] Huanfeng Jiang,[†] and Wei Zeng*[,†]

[†]School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, China

[‡]College of Pharmacy, Jinan University, Guangzhou 510632, China

Supporting Information

ABSTRACT: A ruthenium-catalyzed C2-hydroindolation of alkynes has been achieved. This protocol provides a rapid and concise access to kinds of 2-alkenyl-substituted *N*-(2-pyridyl)-indoles in which the pyridyl moiety can be easily removed to afford free (N−H) indoles under mild conditions. Various arenes and alkynes, including electron-deficient and electron-rich internal alkynes and terminal alkynes, allow for this transformation.



INTRODUCTION

Transition-metal-catalyzed addition of aryl C−H bonds to alkynes belongs to a synthetically important C−C bond-forming reaction,[1] as this approach provides an atom- and step-economic strategy for constructing various alkenyl aromatic compounds directly from inactivated simple arenes instead of the conventional aryl halides or arylmetallic reagents.[2] Of these processes, hydroarylation of alkynes through chelation assistance has lately attracted increasing interest because it allows site-selective installation of alkenyl group into aromatic molecules.[3] For example, the groups of Ackermann,[4] Chang,[5] Yoshikai,[6] and Hiyama/Nakao[7] have revealed that transition-metal catalysts could effectively enhance addition of phenyl C−H[4−6] or pyridine C−H[7] bonds to alkynes with the aid of heteroatom-containing groups, but there are rare reported cases involved in hydroindolation of alkynes via C−H functionalization,[3a,d] although alkenyl-substituted indole nucleus can be found in natural products and complex biologically active molecules.[8]

Remarkably, in comparison with C2 position of indole, C3 position is an inherently nucleophilic reactive site, therefore Lewis acids could easily realize the addition of indole C3−H bonds to alkynes via a Friedel−Craft-type process.[9] Nevertheless, heteroatom-directed ortho-metalation reaction provides concise access to site-selective indole C2−H functionalization,[10] but there are very rare examples of C2-hydroindolation of alkynes. To date, the pioneering reports by Schipper et al.,[11] Ding and Yoshikai,[12] and Kanai and co-workers[13] described that Rh(III) (5 mol %) catalysts, Co(II) (10 mol %)/Grignard reagent (0.60 equiv) catalytical system, or Co(III) (5 mol %) catalyst, respectively, could enable effective intermolecular C2-hydroindolation of alkynes, in which *N*,*N*-dimethylcarbonyl or pyrimidyl group was employed as a directing group. Unfortunately, these protocols only allow the use of electron-rich internal alkynes or aryl-substituted terminal alkynes. Herein we demonstrated a valuable complementary approach to C2-hydroindolation of alkynes using ruthenium salts as catalyst, and the substrate scope can be further extended to electron-poor internal alkynes and acyl- or alkyl-substituted terminal alkynes.

RESULTS AND DISCUSSION

Initially, we investigated the effect of various Ru catalysts (5 mol %) on the addition of *N*-(2-pyridyl)indole (**1a**) C2−H to diphenylacetylene (**2a**) in the presence of $AgSbF_6$ (20 mol %) and PivOH (1.0 equiv) with 1,4-dioxane as solvent at 110 °C for 24 h (Table 1, entries 1−5), and we soon found that the dimeric species $[RuCl_2(p\text{-cymene})]_2$ provided 54% yield of the desired alkenylation product **3a**, whose structure was already unambiguously assigned by its single-crystal X-ray analysis (see Supporting Information for more details, and compare entries 1−4 with entry 5 in Table 1). Subsequently, further improvement of the reaction (83% yield of **3a**) was achieved when $AgBF_4$ and AcOH were employed as additive and proton source, respectively (compare entries 5−9 with entry 10 in Table 1). It is worth noting that only a trace of **3a** could be observed in the absence of $AgBF_4$ (compare entry 10 with entry 11 in Table 1).[14] To our delight, after various solvents including toluene, acetonitrile, and 1,2-dichloroethane (DCE) were evaluated for this transformation, the yield of product **3a** was significantly increased to 97% with the use of 7 mol % $[RuCl_2(p\text{-cymene})]_2$ in toluene (compare entries 10 and 12 with entry 13 in Table 1). Most importantly, a similar yield (98% yield of **3a**) could also be obtained in *N*,*N*-dimethylformamide (DMF) solvent system even when no silver salt additives were employed (compare entry 13 with entry 14 in Table 1). By the way, when DMF was used as solvent, the spots on the thin-layer chromatograpic (TLC) plate of the reaction mixture look very clean. On the contrary,

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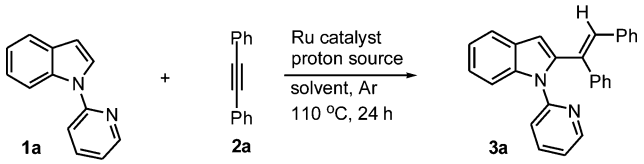
Table 1. Optimization of Reaction Parameters[a]



entry	Ru salts (5 mol %)	additive (20 mol %)	solvent	proton source	yield[b] (%)
1	$RuCl_3$	$AgSbF_6$	1,4-dioxane	PivOH	NR[c]
2	$Ru_3(CO)_{12}$	$AgSbF_6$	1,4-dioxane	PivOH	trace
3	A[d]	$AgSbF_6$	1,4-dioxane	PivOH	NR[c]
4	B[e]	$AgSbF_6$	1,4-dioxane	PivOH	NR[c]
5	C[f]	$AgSbF_6$	1,4-dioxane	PivOH	54
6	C	AgOAc	1,4-dioxane	PivOH	73
7	C	$AgPF_6$	1,4-dioxane	PivOH	40
8	C	$AgBF_4$	1,4-dioxane	PivOH	75
9	C	$AgBF_4$	1,4-dioxane	*i*-PrOH	19
10	C	$AgBF_4$	1,4-dioxane	AcOH	83
11	C		1,4-dioxane	AcOH	trace
12	C	$AgBF_4$	1,4-dioxane	AcOH	94[g]
13	C	$AgBF_4$	toluene	AcOH	97[g]
14	C		DMF[h]	AcOH	98[g]
15	C		CH_3CN	AcOH	73[g]
16	C		DCE[h]	AcOH	62[g]

[a]Unless otherwise noted, reactions were carried out by use of *N*-(2-pyridyl)indole (**1a**, 0.10 mmol) and alkyne (**2a**, 0.10 mmol) with Ru catalyst (5 mol %) in the presence of additive (20 mol %) and proton source (1.0 equiv) in 1,4-dioxane (2.0 mL) at 110 °C for 24 h under Ar in a sealed reaction tube, followed by flash chromatography on SiO_2. [b]Isolated yield. [c]No reaction. [d]A = $RuH_2(CO)(PPh_3)_2$. [e]B = $RuHCl(CO)(PPh_3)_3$. [f]C = $[RuCl_2(p\text{-cymene})]_2$. [g]Catalyst C (7 mol %) was used. [h]DMF = *N*,*N*-dimethylformamide; DCE = 1,2-dichloroethane.

alternative solvents afforded poorer results in the absence of silver additives (entries 15 and 16 in Table 1).

With an optimized catalytic system in hand, we first investigated the reactivity of various *N*-(2-pyridyl)indole derivatives. As shown in Table 2, all 5-, 6-, or 7-substituted indole substrates exhibited excellent reactivity with exclusive *E*-stereochemistry, no matter whether electron-withdrawing (such as 5-CN, 5-NO_2, 5-CO_2Me, 5-halide, 6-halide, etc.) or electron-donating groups (such as 5-MeO, 7-Me, etc.) are introduced to the benzene ring. For example, C2-hydroindolation of diphenylacetylene (**2a**) with 5-ethoxycarbonyl-*N*-(2-pyridyl) indole (**1h**) and 7-methyl-*N*-(2-pyridyl)indole (**1k**) could afford the desired alkenylation products **3h** and **3k** in 91% and 94% yield, respectively (entries 8 and 11 in Table 2). On the contrary, the substituted group (R^2) at C3 position of indole showed significant electronic effects. The substrate (**1l**) with electron-donating group (3-Me) on the indole ring produced 96% yield of **3l**; however, 3-acetyl-*N*-(2-pyridyl)-indole (**1m**) underwent obviously worse conversion and provided lower yield of **3m** (25%; see entries 12 and 13 in Table 2). Moreover, this reaction protocol could also smoothly convert *N*-(2-pyridyl)pyrrole (**1n**) to the corresponding 2,5-bis-alkenylation pyrrole derivative **3n** (40% yield) and 2-alkenylation pyrrole product **3o** (52% yield), possibly due to a double migratory insertion of alkyne **2a** into Ru(II) intermediate (entry 14 in Table 2), respectively. For the *N*-(2-pyrimidyl)indole (**1o**), the desired 2-alkenylation derivatives **3p** could also be obtained in 83% yield (entry 15 in Table 2).

Subsequently, we further investigated the scope of C2-hydroarylation of *N*-(2-pyridyl)indole (**1a**) by employing differently substituted alkynes. It was found that this transformation tolerated a variety of electron-rich internal alkynes, such as diarylacetylene (**2a**), aryl alkyl alkyne (**2c**), aryl hydroxymethyl alkyne (**2d**), aryl methoxymethyl internal alkyne (**2e**), dialkyl alkyne (**2g**), silyl-substituted alkyne (**2h**), aryl alkenyl alkyne (**2j**), and aryl alkynyl alkyne (**2k**), could couple with **1a** in good to excellent yields (entries 15, 17−19, 21, 22, 24, and 25 in Table 2). It is worth noting that unsymmetric internal alkyne **2c** gave two products **3s** and **3t** in around 2:1 ratio where the reaction was under steric control (entry 17 in Table 2). In contrast, aryl hydroxymethyl internal alkyne **2d** and aryl methoxymethyl internal alkyne **2e** provided **3u** (89% yield) and **3v** (83% yield) with high regioselectivity, probably due to the weak coordination between Ru(II) and ether or alcohol oxygen atom (entries 18 and 19 in Table 2). Importantly, this reaction protocol remarkably tolerated electron-poor internal aryl methoxycarbonyl alkyne (**2f**), and gave the desired alkenylation product **3w** in 93% yield (entry 20 in Table 2). Moreover, electron-rich and electron-poor terminal alkynes (**2b** and **2i**) also allowed for this transformation and afforded the corresponding 1,1-disubstituted alkene (**3q**) and 1, 2-disubstituted alkene **3y** (54% yield) with high regioselectivity (entries 16 and 23 in Table 2), which is different from the Ru-catalyzed alkenylation of *N*,*N*-dimethylbenzamide with terminal alkynes.[15] Surprisingly, when hept-1-yne (**2l**) was applied to this reaction system, the major product was the C2-alkylation compounds **3zb** and **3zc** (**3zb**/**3zc** = 6.7) which were possibly derived from the C2-alkenylation indole intermediates via a reduction process, in which DMF acts as a reducing agent (entry 26 in Table 2).[16] On the contrary, employing toluene as solvent furnished the desired C2-alkenylation products **3zd** and **3ze** in an overall yield of 86% (entry 27 in Table 2).

Finally, we easily removed the pyridyl group on the alkenylation product **3** under CH_3OTf/NaOH conditions to provide the corresponding free (N−H) indole derivative **4**—several examples are shown in Table 3 (see Supporting Information for more details)—which could be used for further synthetic transformations.[12]

To further investigate the mechanism, the H/D exchange of 3-methyl-*N*-(2-pyridyl)indole **1l** was conducted in Ru(II)/CD_3OD system for 96 h in the absence of alkyne **2a**, and 95% deuterium incorporation at C2 position was observed (eq 1 in Scheme 1). Notably, 82% (C7 position of indole) and 95% (C6 position of pyridine) deuterium incorporation was also observed (see Supporting Information for more details about the ^{1}H NMR spectra).[17,18] On the other hand, the content of C2-deuterium in **D-1la** under Ru(II)/CH_3OH system[19] and Ru(II)/AcOH system was decreased from 95% to 5% and 18%, respectively (eqs 2 and 3 in Scheme 1; see Supporting Information for more details about the corresponding ^{1}H NMR spectra of **D-1la**, **D-1lb**, and **D-1lc**). These results clearly

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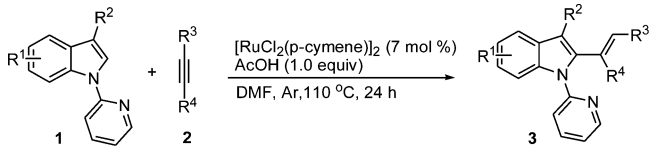
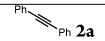
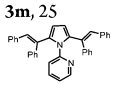
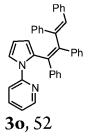
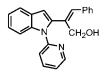
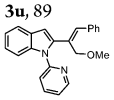
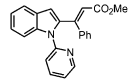
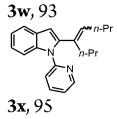
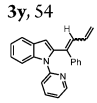
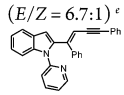
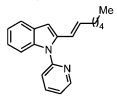
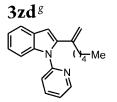
Table 2. Ru(II)-Catalyzed Addition of Indole C2−H Bonds to Alkynes[a]



entry	indole **1**	alkyne **2**	**3**, yield (%)[b]
1	**1a**, $R^1 = R^2 = H$	 **2a**	**3a**, 98
2	**1b**, R^1 = 5-MeO, $R^2 = H$	2a	**3b**, 97
3	**1c**, R^1 = 5-F, $R^2 = H$	2a	**3c**, 80
4	**1d**, R^1 = 5-Cl, $R^2 = H$	2a	**3d**, 94
5	**1e**, R^1 = 5-Br, $R^2 = H$	2a	**3e**, 95
6	**1f**, R^1 = 5-NO_2, $R^2 = H$	2a	**3f**, 74
7	**1g**, R^1 = 5-CN, $R^2 = H$	2a	**3g**, 94
8	**1h**, R^1 = 5-CO_2Me, $R^2 = H$	2a	**3h**, 91
9	**1i**, R^1 = 6-F, $R^2 = H$	2a	**3i**, 85
10	**1j**, R^1 = 6-Cl, $R^2 = H$	2a	**3j**, 86
11	**1k**, R^1 = 7-Me, $R^2 = H$	2a	**3k**, 94
12	**1l**, $R^1 = H$, R^2 = 3-Me	2a	**3l**, 96
13	**1m**, $R^1 = H$, R^2 = 3-Ac	2a	**3m**, 25  **3n**, 40
14	 1n	2a	 **3o**, 52
15	 1o	2a	 **3p**, 83
16	**1a**, $R^1 = R^2 = H$	 2b	 **3q**  **3r** **3q** + **3r** = 81[c] (**3q** /**3r** = 1:4)[d]
17	**1a**, $R^1 = R^2 = H$	 2c	 **3s**, 62  **3t**, 34
18	**1a**, $R^1 = R^2 = H$	 **2d**	 **3u**, 89
19	**1a**, $R^1 = R^2 = H$	 **2e**	 **3v**, 83
20	**1a**, $R^1 = R^2 = H$	 **2f**	 **3w**, 93
21	**1a**, $R^1 = R^2 = H$	 **2g**	 **3x**, 95 (*E*/*Z* = 4.2:1)[e]
22	**1a**, $R^1 = R^2 = H$	 **2h**	 **3q**  **3r** **3q** + **3r** = 98[c] **3q**/**3r** = 1:19[d]
23	**1a**, $R^1 = R^2 = H$	 2i	 **3y**, 54
24	**1a**, $R_1 = R_2 = H$	 **2j**	 **3z**, 81 (*E*/*Z* = 6.7:1)[e]
25	**1a**, $R^1 = R^2 = H$	 **2k**	 **3za**, 88
26	**1a**, $R^1 = R^2 = H$	 **2l**	 **3zb**[f]  **3zc**[f] **3zb** + **3zc** = 76 **3zb**/**3zc** = 6.7:1
27	**1a**, $R^1 = R^2 = H$	 **2l**	 **3zd**[g]  **3ze**[g] **3zd** + **3ze** = 86 **3zd**/**3ze** = 2.3:1

[a]Unless otherwise noted, reactions were carried out by use of N-substituted indole or pyrrole (**1**, 0.10 mmol) and alkyne (**2**, 0.20 mmol) with $[RuCl_2(p\text{-cymene})]_2$ catalyst (7 mol %) in the presence of AcOH (1.0 equiv) in DMF (2.0 mL) at 110 °C for 24 h under Ar in a sealed reaction tube, followed by flash chromatography on SiO_2. [b]Isolated yield. [c]Total isolated yield of mixture **3q** and **3r**. [d]The **3q**/**3r** ratio was determined by ^{1}H NMR spectroscopy. [e]The *E*/*Z* ratio was determined by ^{1}H NMR spectroscopy. [f]When PivOH was used as the source of H atoms, the overall yield of **3zb** and **3zc** decreased to 56%. [g]The solvent (DMF) was changed to toluene.

demonstrate that the first step of a reversible C(sp^2)−H bond cleavage process was involved in the transformation. Subsequently, the intermolecular isotope effect (K_H/K_D = 0.99) further indicated that the reversible C(sp^2)−H bond-breaking was not the rate-limiting step of the reaction (eq 4 in Scheme 1).

On the basis of the above observations, we proposed the possible mechanism shown in Scheme 2. The transformation is initiated by coordination of the nitrogen atom from the pyridine ring to the cationic ruthenium center, followed by an electrophilic substitution to produce the five-membered cycloruthenium complexes B with concomitant loss of a

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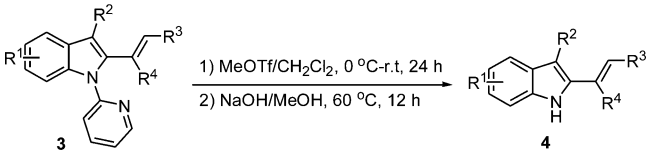
Table 3. Several Examples of Removal of Pyridine Directing Group[a]

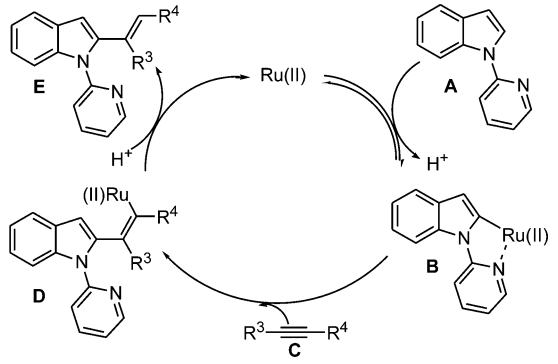


entry	*N*-(2-pyridyl)indole **3**	free (N-H) indole **4**	yield (%)[b]
1	**3a**	**4a**	90
2	**3b**	**4b**	82
3	**3e**	**4c**	86
4	**3l**	**4d**	86

[a]CH_2Cl_2 (7.5 mL) solution of *N*-(2-pyridyl)indole **3** (0.3 mmol) with MeOTf (0.36 mmol) was stirred from 0 °C to room temperature for 24 h. After removal of the solvent, aqueous NaOH (2.0 M, 1.8 mL) and MeOH (3.6 mL) were added to the corresponding mixture, respectively, and then stirred at 60 °C for 12 h under Ar atmosphere, followed by flash chromatography on SiO_2. [b]Isolated yield.

proton.[17b,20] Of course, the possibility of OAc-assisted deprotonative cyclometalation pathway also could not be ruled out.[4,21] Subsequently, alkynes (C) insertion into ruthenium−C2 (indole) bond would lead to alkenyl Ru intermediates D, which would be further protonated to afford alkenylation product E and regenerate the ruthenium catalyst.

Scheme 2. Proposed Catalytic Cycle

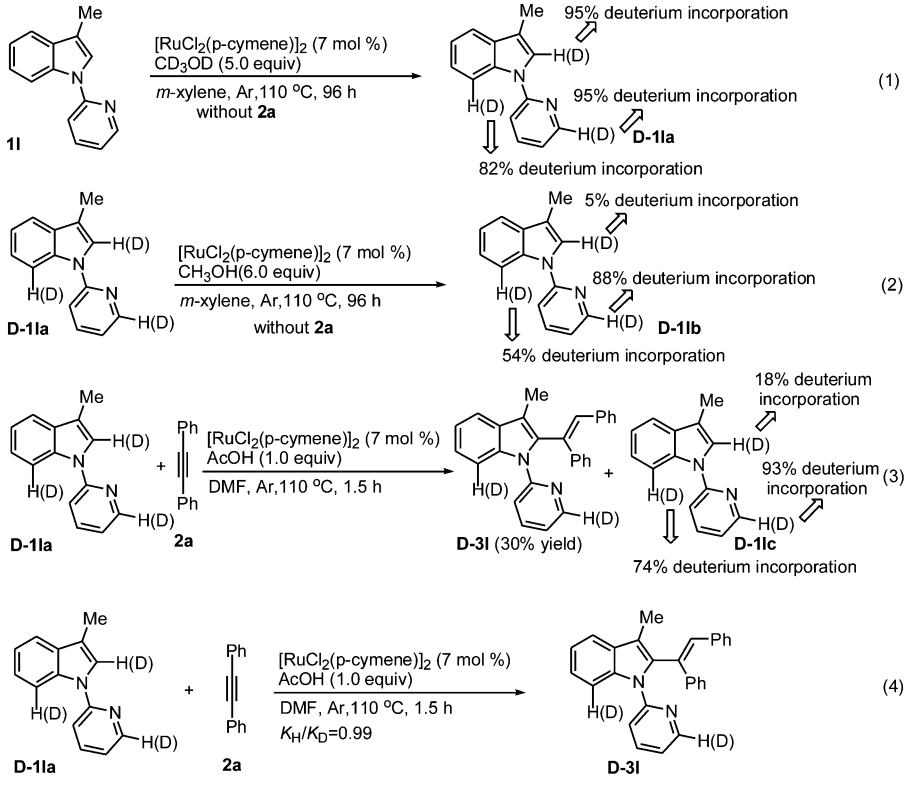


In summary, we have developed the first ruthenium-catalyzed C2-hydroindolation of alkynes, which provides efficient access to various alkenylation indoles.[22] This new approach tolerates a variety of arenes and alkynes, especially electron-poor internal alkynes and acyl- or alkyl-substituted terminal alkynes, which have not been easily accessible through existing synthetic methods.[11−13] Moreover, the pyridyl moiety could also be easily removed to produce free (N−H) indoles that can be further broadly used in organic transformations.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. Solvents were

Scheme 1. Preliminary Mechanistic Studies



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treated with 4 Å molecular sieves or sodium and distilled prior to use. Flash chromatography was performed on silica gel (40−63 mm) by standard techniques. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), or quartet (q). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Low-resolution mass spectra were recorded on a HPLC−mass spectrometer. High-resolution exact mass measurements (HRMS) were performed on a TOF spectrometer. Infrared spectra are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. Crystal data were obtained by employing graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 293 (2) K and operating in the $\varphi-\omega$ scan mode. Structures were solved by direct methods in SHELXS-97. Indole substrates including 1-(pyridin-2-yl)-1*H*-indole (**1a**),[23] 5-methoxy-1-(pyridin-2-yl)-1*H*-indole (**1b**),[23] 5-chloro-1-(pyridin-2-yl)-1*H*-indole (**1d**),[24] 5-bromo-1-(pyridin-2-yl)-1*H*-indole (**1e**),[23] 1-(pyridin-2-yl)-1*H*-indole-5-carbonitrile (**1g**),[25] methyl 1-(pyridin-2-yl)-1*H*-indole-5-carboxylate (**1h**),[26] 7-methyl-1-(pyridin-2-yl)-1*H*-indole (**1k**),[27] 3-methyl-1-(pyridin-2-yl)-1*H*-indole (**1l**),[23] 1-[1-(pyridin-2-yl)-1*H*-indol-3-yl]ethanone (**1m**),[25] 2-(1*H*-pyrrol-1-yl)pyridine (**1n**),[28] and 1-(pyrimidin-2-yl)-1*H*-indole (**1o**)[23] were prepared by previously reported procedures. All the alkyne substrates are commercially available.

Procedures for Preparation of Indole Substrates 1c, 1f, 1i, and 1j. *Procedure A:*[23] *Synthesis of **1c** and **1f**.* A mixture of indole starting material (5.0 mmol), 2-bromopyridine (6.0 mmol), and KOH (0.70 g, 12.5 mmol) in dimethyl sulfoxide (DMSO, 6 mL) was vigorously stirred at 120 °C under argon atmosphere for 30 h. After the mixture was cooled to ambient temperature, it was diluted with EtOAc (40 mL) and washed with H_2O (2 × 30 mL). The aqueous phase was extracted with EtOAc (3 × 30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents in vacuum, the crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give the desired indole derivatives.

*5-Fluoro-1-(pyridin-2-yl)-1H-indole (**1c**).* Light yellow solid; mp = 62−64 °C; 869 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56−8.55 (m, 1H), 8.23 (dd, *J* = 9.1, 4.6 Hz, 1H), 7.83−7.79 (m, 1H), 7.72 (d, *J* = 3.5 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.16 (ddd, *J* = 7.3, 4.9, 0.7 Hz, 1H), 7.02 (td, *J* = 9.1, 2.6 Hz, 1H), 6.66 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.6 (d, *J* = 236.7 Hz), 152.4, 148.9, 138.5, 131.8, 131.0 (d, *J* = 10.1 Hz), 127.3, 120.2, 114.5 (d, *J* = 9.2 Hz), 114.1, 111.2 (d, *J* = 25.4 Hz), 106.0 (d, *J* = 23.4 Hz), 105.4 (d, *J* = 4.3 Hz). IR (KBr, cm^{-1}) 3057, 1589, 1474, 1343, 1264, 1208, 1145, 741. HRMS (electrospray ionization time-of-flight, ESI-TOF) calcd for $[M + H]^+$ $C_{13}H_{10}FN_2$ 213.0823, found 213.0825.

*5-Nitro-1-(pyridin-2-yl)-1H-indole (**1f**).* Yellow solid; mp = 88−90 °C; 789 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.63−8.61 (m, 1H), 8.60 (d, *J* = 2.2 Hz, 1H), 8.33 (d, *J* = 9.2 Hz, 1H), 8.18 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.90 (td, *J* = 8.2, 1.9 Hz, 1H), 7.82 (d, *J* = 3.5 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.29 (ddd, *J* = 7.4, 4.9, 0.7 Hz, 1H), 6.88 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.7, 149.1, 142.6, 138.9, 138.0, 129.7, 129.0, 121.4, 118.4, 117.7, 114.8, 113.5, 107.0. IR (KBr, cm^{-1}) 3052, 1586, 1510, 1465, 1343, 1211, 1140, 967, 743. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{13}H_{10}N_3O_2$ 240.0768, found 240.0766.

Procedure B:[22] *Synthesis of **1i** and **1j**.* NaH (60% dispersion in mineral oil, 180 mg, 4.5 mmol) was added in portions at 0 °C to a stirred solution of indole starting material (3.0 mmol) in DMF (10 mL). After the mixture was stirred for 30 min at 0 °C, 2-bromopyridine (0.95 g, 6.0 mmol) was added and the mixture was stirred at 110 °C for 18 h. After the mixture was cooled to ambient temperature, it was diluted with EtOAc (40 mL) and washed with H_2O (2 × 30 mL). The aqueous phase was extracted with EtOAc (3 × 30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give the desired indole derivatives.

*6-Fluoro-1-(pyridin-2-yl)-1H-indole (**1i**).* White solid; mp = 86−88 °C; 339 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57−8.56 (m, 1H), 8.06 (dd, *J* = 10.8, 2.1 Hz, 1H), 7.82 (td, *J* = 8.2, 1.8 Hz, 1H), 7.66 (d, *J* = 3.5 Hz, 1H), 7.55 (dd, *J* = 8.6, 5.5 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.17 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.97 (td, *J* = 9.0, 2.3 Hz, 1H), 6.68 (d, *J* = 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.5 (d, *J* = 237.8 Hz), 152.4, 148.9, 138.5, 135.2 (d, *J* = 12.8 Hz), 126.7, 126.0 (d, *J* = 3.8 Hz), 121.5 (d, *J* = 10.1 Hz), 120.2, 114.0, 109.9 (d, *J* = 24.5 Hz), 105.6, 100.6 (d, *J* = 28.2 Hz). IR (KBr, cm^{-1}) 3013, 1699, 1591, 1530, 1462, 1346, 1267, 1206, 930, 756. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{13}H_{10}FN_2$ 213.0823, found 213.0822.

*6-Chloro-1-(pyridin-2-yl)-1H-indole (**1j**).* White solid; mp = 110−112 °C; 393 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.59−8.57 (m, 1H), 8.33 (m, 1H), 7.83 (td, *J* = 8.2, 1.9 Hz, 1H), 7.67 (d, *J* = 3.5 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.21−7.16 (m, 2H), 6.68 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.2, 148.9, 138.6, 135.5, 129.1, 128.9, 126.4, 121.9, 121.7, 120.4, 114.2, 113.7, 105.6. IR (KBr, cm^{-1}) 3057, 1640, 1520, 1445, 1340, 1266, 1203, 1152, 895, 742. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{13}H_{10}ClN_2$ 229.0527, found 229.0528.

General Procedure for Synthesis of 3a−3z and 3za−3ze. $[RuCl_2(p\text{-cymene})]_2$ (0.007 mmol, 7 mol %), AcOH (0.1 mmol, 1.0 equiv), 1-(pyridin-2-yl)-1*H*-indole **1a** (0.1 mmol, 1.0 equiv), and 1,2-diphenylethyne **2a** (0.2 mmol, 2.0 equiv) were dissolved in 2.0 mL of DMF in a tube, and then the tube was sealed under Ar and heated at 110 °C in an oil bath for 24 h. The reaction progress was monitored by thin-layer chromatography (TLC): after the starting material disappeared, the corresponding reaction mixture was then cooled down and solvent was removed in vacuum. The given residue was purified by column chromatography to give **3a**.

*(E)-2-(1,2-Diphenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3a**).* White solid; mp = 149−151 °C; 35.0 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44−8.43 (m, 1H), 7.64−7.62 (m, 1H), 7.55 (td, *J* = 7.8, 1.8 Hz, 1H), 7.42−7.40 (m, 1H), 7.19−7.02 (m, 14H), 6.92 (s, 1H), 6.75 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.9, 149.1, 142.9, 138.7, 138.6, 137.6, 136.8, 134.2, 130.6, 130.2, 129.5, 128.2, 128.0, 127.9, 127.3, 127.0, 123.1, 121.7, 121.5, 121.1, 120.7, 110.9, 107.4. IR (KBr, cm^{-1}) 3057, 1584, 1454, 1355, 1265, 1208, 1148, 744, 701, 552. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{21}N_2$ 373.1699, found 373.1703.

*(E)-2-(1,2-Diphenylvinyl)-5-methoxy-1-(pyridin-2-yl)-1H-indole (**3b**).* Yellow solid; mp = 160−162 °C; 39.0 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43−8.42 (m, 1H), 7.55 (td, *J* = 7.9, 1.9 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.15−7.00 (m, 13H), 6.88 (s, 1H), 6.83 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.67 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.2, 152.0, 149.0, 143.4, 138.6, 137.7 136.8, 134.3, 134.0, 130.6, 130.3, 129.5, 128.8, 128.0, 128.0, 127.4, 127.1, 121.5, 121.4, 113.2, 111.9, 107.5, 102.4, 55.9. IR (KBr, cm^{-1}) 3059, 2924, 2851, 1586, 1462, 1339, 1268, 1215, 1160, 1032, 748. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{28}H_{23}N_2O$ 403.1805, found 403.1816.

*(E)-2-(1,2-Diphenylvinyl)-5-fluoro-1-(pyridin-2-yl)-1H-indole (**3c**).* Light yellow solid; mp = 158−160 °C; 31.2 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44−8.42 (m, 1H), 7.56 (td, *J* = 7.8, 1.9 Hz, 1H), 7.35 (dd, *J* = 9.0, 4.5 Hz, 1H), 7.26 (dd, *J* = 8.7, 2.9 Hz, 1H), 7.15−7.00 (m, 12H), 6.93−6.88 (m, 2H), 6.70 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.7 (d, *J* = 235.9 Hz), 151.8, 149.1, 144.5, 138.4, 137.8, 136.7, 135.3, 134.0, 131.3, 130.2, 129.6, 128.7 (d, *J* = 9.9 Hz), 128.1, 127.5, 127.3, 121.8, 121.7, 111.9 (d, *J* = 9.4 Hz), 111.3 (d, *J* = 26.0 Hz), 107.2 (d, *J* = 4.4 Hz), 105.5 (d, *J* = 23.6 Hz). IR (KBr, cm^{-1}) 3058, 1584, 1456, 1266, 1202, 1153, 855, 743. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}FN_2$ 391.1605, found 391.1604.

*(E)-5-Chloro-2-(1,2-diphenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3d**).* Light yellow solid; mp = 129−131 °C; 38.3 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43−8.42 (m, 1H), 7.59−7.54 (m, 2H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.13−6.98 (m, 13H), 6.92 (s, 1H), 6.69 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.5, 149.2, 144.2, 138.3, 137.9, 137.1, 136.6, 133.8, 131.4, 130.2, 129.6, 129.3, 128.1, 127.5, 127.3, 126.7, 123.3, 121.9, 121.7, 120.0, 112.2, 106.7. IR (KBr, cm^{-1}) 3056,

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1588, 1443, 1370, 1323, 1266, 1207, 1068, 866, 750, 702. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}ClN_2$ 407.1310, found 407.1322.

*(E)-5-Bromo-2-(1,2-diphenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3e**).* Light yellow solid; mp = 176−178 °C; 42.8 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43−8.42 (m, 1H), 7.75 (d, J = 1.4 Hz, 1H), 7.56 (td, J = 7.9, 1.8 Hz, 1H), 7.29−7.23 (m, 2H), 7.13−6.98 (m, 12H), 6.92 (s, 1H), 6.69 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.5, 149.2, 144.1, 138.3, 137.9, 137.3, 136.6, 133.8, 131.4, 130.2, 129.9, 129.6, 128.1, 127.5, 127.3, 125.9, 123.1, 121.9, 121.7, 114.3, 112.6, 106.5. IR (KBr, cm^{-1}) 3058, 1586, 1445, 1369, 1323, 1266, 1207, 750, 702. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}BrN_2$ 451.0804, found 451.0791.

*(E)-2-(1,2-Diphenylvinyl)-5-nitro-1-(pyridin-2-yl)-1H-indole (**3f**).* Yellow solid; mp = 187−189 °C; 30.9 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.58 (d, J = 2.1 Hz, 1H), 8.46−8.44 (m, 1H), 8.07 (dd, J = 9.1, 2.2 Hz, 1H), 7.61 (td, J = 7.8, 1.9 Hz, 1H), 7.38 (d, J = 9.1 Hz, 1H), 7.16−7.02 (m, 10H), 6.99−6.95 (m, 3H), 6.92 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.7, 149.4, 146.3, 142.7, 141.2, 138.1, 137.8, 136.1, 133.1, 132.4 130.0, 129.6, 128.2, 128.1, 127.6, 127.6, 127.5, 122.6, 121.8, 118.5, 117.5, 111.0, 107.9. IR (KBr, cm^{-1}) 3058, 1641, 1512, 1464, 1330, 1269, 1071, 743, 700. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}N_3O_2$ 418.1550, found 418.1556.

*(E)-2-(1,2-Diphenylvinyl)-1-(pyridin-2-yl)-1H-indole-5-carbonitrile (**3g**).* Light yellow solid; mp = 171−173 °C; 37.3 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.45−8.43 (m, 1H), 7.98 (s, 1H), 7.60 (td, J = 7.7, 1.8 Hz, 1H), 7.43−7.38 (m, 2H), 7.14−7.02 (m, 10H), 6.98−6.95 (m, 3H), 6.82 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.8, 149.3, 145.4, 140.0, 138.1, 137.9, 136.2, 133.2, 132.2, 130.0, 129.6, 128.2, 128.1, 128.0, 127.6, 127.5, 125.9, 122.5, 121.8, 120.5, 111.9, 106.8, 104.2. IR (KBr, cm^{-1}) 3060, 2220, 1580, 1462, 1368, 1327, 1267, 885, 751. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{28}H_{20}N_3$ 398.1652, found 398.1653.

*(E)-Methyl 2-(1,2-diphenylvinyl)-1-(pyridin-2-yl)-1H-indole-5-carboxylate (**3h**).* Light yellow solid; mp = 168−170 °C; 39.1 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44−8.43 (m, 1H), 8.39 (d, J = 1.1 Hz, 1H), 7.87 (dd, J = 8.7, 1.5 Hz, 1H), 7.58 (td, J = 7.8, 1.9 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 7.14−6.96 (m, 13H), 6.85 (s, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.0, 151.3, 149.2, 144.4, 141.0, 138.2, 137.9, 136.5, 133.7, 131.4, 130.1, 129.6, 128.0, 127.8, 127.4, 127.3, 124.4, 123.5, 123.1, 122.1, 121.8, 110.5, 107.8, 51.9. IR (KBr, cm^{-1}) 3058, 2924, 2851, 1710, 1644, 1438, 1310, 1262, 1182, 1133, 1088, 742. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{29}H_{23}N_2O_2$ 431.1754, found 431.1755.

*(E)-2-(1,2-Diphenylvinyl)-6-fluoro-1-(pyridin-2-yl)-1H-indole (**3i**).* Light yellow solid; mp = 88−90 °C; 33.2 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44−8.43 (m, 1H), 7.59−7.51 (m, 2H), 7.17−7.01 (m, 13H), 6.92 (td, J = 9.2, 2.2 Hz, 2H), 6.88 (s, 1H), 6.71 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.7 (d, J = 239.2 Hz), 151.7, 149.1, 143.4 (d, J = 3.8 Hz), 138.8 (d, J = 12.3 Hz), 138.4, 137.9, 136.7, 134.0, 130.7, 130.2, 129.6, 128.1, 127.5, 127.2, 124.7, 121.8, 121.5, 121.4 (d, J = 10.3 Hz), 109.8 (d, J = 24.5 Hz), 107.4, 97.9 (d, J = 27.0 Hz). IR (KBr, cm^{-1}) 3011, 1703, 1579, 1473, 1351, 1268, 755, 702. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}FN_2$ 391.1605, found 391.1605.

*(E)-6-Chloro-2-(1,2-diphenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3j**).* Light yellow solid; mp = 143−145 °C; 35.0 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.45−8.43 (m, 1H), 7.57 (td, J = 7.8, 1.9 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.42 (s, 1H), 7.14−6.98 (m, 13H), 6.91 (s, 1H), 6.72 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.4, 149.2, 143.7, 139.0, 138.3, 137.9, 136.6, 133.9, 131.1, 130.2, 129.6, 129.1, 128.1, 127.5, 127.3, 126.8, 121.9, 121.9, 121.6, 121.5, 111.2, 107.2. IR (KBr, cm^{-1}) 3053, 1643, 1451, 1336, 1268, 1206, 818, 754, 699. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}ClN_2$ 407.1310, found 407.1309.

*(E)-2-(1,2-Diphenylvinyl)-7-methyl-1-(pyridin-2-yl)-1H-indole (**3k**).* White solid; mp = 124−126 °C; 36.3 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35−8.34 (m, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.13−6.86 (m, 15H), 6.74 (s, 1H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.5, 148.3, 144.4, 139.0, 137.7, 136.9, 136.8, 134.4, 131.5, 129.9, 129.6, 128.7, 128.1, 128.0, 127.2, 127.1, 125.6, 125.1, 122.9, 121.7, 120.7, 118.8, 106.1, 19.6. IR (KBr, cm^{-1}) 3059, 2925, 2850, 1588,1471, 1433, 1347, 1266, 1150, 745. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{28}H_{23}N_2$ 387.1856, found 387.1856.

*(E)-2-(1,2-Diphenylvinyl)-3-methyl-1-(pyridin-2-yl)-1H-indole (**3l**).* Light yellow solid; mp = 136−138 °C; 37.1 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38−8.37 (m, 1H), 7.67−7.62 (m, 1H), 7.51 (td, J = 7.9, 1.9 Hz, 1H), 7.45−7.40 (m, 1H), 7.22−7.17 (m, 2H), 7.14−7.11 (m, 6H), 7.01−6.93 (m, 4H), 6.88−6.86 (m, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.0, 148.9, 138.8, 138.6, 137.5, 137.2, 137.0, 133.5, 132.7, 130.1, 129.5, 129.5, 128.1, 127.8, 127.1, 123.4, 121.2, 121.1, 120.6, 119.2, 114.5, 110.8, 10.0. IR (KBr, cm^{-1}) 3056, 2922, 2856, 1584, 1459, 1358, 1266, 751, 699. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{28}H_{23}N_2$ 387.1856, found 387.1859.

*(E)-1-(2-(1,2-Diphenylvinyl)-1-(pyridin-2-yl)-1H-indol-3-yl)-ethanone (**3m**).* Light yellow solid; mp = 176−178 °C; 10.4 mg, 25% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (d, J = 8.0 Hz, 1H), 8.36−8.35 (m, 1H), 7.51 (td, J = 7.8, 1.8 Hz, 1H), 7.39−7.33 (m, 3H), 7.30−7.24 (m, 6H), 7.16−7.12 (m, 5H), 7.00−6.98 (m, 2H), 6.84 (d, J = 8.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9, 149.9, 149.2, 143.0, 140.5, 137.6, 137.1, 135.9, 134.0, 131.9, 128.8, 128.7, 128.6, 128.4, 128.1, 127.1, 126.7, 124.1, 123.4, 123.1, 122.9, 121.5, 117.7, 111.2, 29.8. IR (KBr, cm^{-1}) 3065, 2923, 2850, 1646, 1574, 1454, 1392, 1179, 757, 689. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{29}H_{23}N_2O$ 415.1805, found 415.1805.

*2-{2,5-Bis[(E)-1,2-diphenylvinyl]-1H-pyrrol-1-yl}pyridine (**3n**).* Yellow solid; mp = 191−193 °C; 20.0 mg, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, J = 4.5 Hz, 1H), 7.09 (t, J = 7.7 Hz, 1H), 7.03−6.96 (m, 12H), 6.91−6.87 (m, 8H), 6.77−6.74 (m, 1H), 6.68 (s, 2H), 6.60 (d, J = 7.9 Hz, 1H), 6.35 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.3, 148.3, 139.2, 139.0, 137.2, 136.6, 134.5, 130.0, 129.4, 128.8, 127.8, 127.8, 126.8, 126.5, 123.7, 121.7, 111.8. IR (KBr, cm^{-1}) 3063, 1668, 1534, 1462, 1310, 1277, 1223, 1143, 822, 741. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{37}H_{28}N_2Na$ 523.2145, found 523.2149.

*2-{2-[(1Z,3E)-1,2,3,4-Tetraphenylbuta-1,3-dienyl]-1H-pyrrol-1-yl}-pyridine (**3o**).* Yellow solid; mp = 183−185 °C; 26.0 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, J = 4.6 Hz, 1H), 7.28−7.24 (m, 4H), 7.22−7.14 (m, 4H), 7.11 (d, J = 7.6 Hz, 2H), 7.04−6.99 (m, 9H), 6.93 (d, J = 7.5 Hz, 2H), 6.79 (s, 1H), 6.73−6.69 (m, 2H), 6.44 (d, J = 3.4 Hz, 1H), 6.33 (d, J = 8.0 Hz, 1H), 6.20 (d, J = 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.6, 148.1, 142.2, 139.7, 138.3, 137.6, 137.4, 136.3, 134.4, 133.9, 133.9, 131.1, 130.1, 129.4, 129.3, 128.2, 128.1, 128.0, 127.8, 127.4, 127.3, 127.2, 127.0, 126.4, 122.2, 121.3, 112.9, 111.1. IR (KBr, cm^{-1}) 3066, 1671, 1533, 1466, 1302, 1263, 1219, 1139, 810, 744. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{37}H_{28}N_2Na$ 523.2145, found 523.2147.

*(E)-2-(1,2-Diphenylvinyl)-1-(pyrimidin-2-yl)-1H-indole (**3p**).*[29] White solid; mp = 150−152 °C; 31.0 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.53 (d, J = 4.8 Hz, 2H), 8.04 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.28−7.20 (m, 2H), 7.13−7.10 (m, 7H), 7.04−7.00 (m, 4H), 6.89−6.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.0, 157.6, 142.8, 138.6, 137.9, 137.2, 135.5, 130.5, 129.7, 128.9, 128.0, 127.7, 127.2, 127.0, 123.8, 122.1, 120.7, 117.1, 112.9, 110.1. IR (KBr, cm^{-1}) 3055, 1703, 1545, 1430, 1346, 1264, 744. MS (ESI) m/z 374.2 $[M + H]^+$.

*2-(1-Phenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3q**).* Obtained as a 4:1 mixture with its regioisomer (*E*)-1-(pyridin-2-yl)-2-styryl-1*H*-indole **3r**; yellow oil; 24.0 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73−8.72 (m, 1H, **3q**), 8.63−8.62 (m, 1H, **3r**), 7.89 (td, J = 7.8, 1.9 Hz, 1H, **3q**), 7.79 (td, J = 7.9, 1.9 Hz, 1H, **3r**), 7.65−7.61 (m, 1H, **3q**), 7.57 (d, J = 8.3 Hz, 1H, **3r**), 7.51−7.49 (m, 1H, **3q** and **3r**), 7.42−7.39 (m, 3H, **3q** and **3r**), 7.36−7.29 (m, 3H, **3q** and **3r**), 7.24−7.21 (m, 1H, **3q** and **3r**), 7.19−7.14 (m, 2H, **3q** and **3r**), 7.10 (d, J = 4.4 Hz, 2H, **3q**), 6.98 (s, 1H, **3q**), 6.62 (s, 1H, **3r**), 6.58 (d, J = 12.3 Hz, 1H, **3r**), 6.45 (d, J = 12.2 Hz, 1H, **3r**). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.4, 151.3, 149.7, 149.3, 138.4, 138.2, 138.0, 137.9, 137.2, 137.2, 137.0, 135.6, 131.8, 130.6, 128.8, 128.7, 128.7, 128.4, 127.8, 127.6, 126.6, 123.0, 123.0, 122.1, 121.6, 121.6, 121.5, 121.2, 121.2, 120.8, 120.6, 120.2, 118.5, 111.3, 111.0, 105.5, 102.4. IR (KBr,

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cm^{-1}) 3052, 1584, 1463, 1344, 1263, 1213, 1140, 956, 741, 694. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{21}H_{17}N_2$ 297.1386, found 297.1389.

*(E)-2-(1-Phenylbut-1-enyl)-1-(pyridin-2-yl)-1H-indole (**3s**).* Yellow oil; 20.1 mg, 62% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.46−8.45 (m, 1H), 7.60−7.56 (m, 2H), 7.41−7.40 (m, 1H), 7.15−7.07 (m, 7H), 7.01−6.99 (m, 2H), 6.62 (s, 1H), 5.98 (t, J = 7.4 Hz, 1H), 2.19 (p, J = 7.5 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.0, 149.0, 142.7, 138.7, 138.2, 137.6, 135.8, 132.9, 129.7, 128.4, 127.6, 126.9, 122.7, 121.8, 121.5, 121.0, 120.5, 110.9, 106.1, 22.8, 14.4. IR (KBr, cm^{-1}) 3059, 2924, 2856, 1644, 1527, 1457, 1345, 1265, 742. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{23}H_{21}N_2$ 325.1699, found 325.1699.

*(E)-2-(1-Phenylbut-1-en-2-yl)-1-(pyridin-2-yl)-1H-indole (**3t**).* Yellow oil; 11.0 mg, 34% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.58−8.57 (m, 1H), 7.67 (td, J = 7.8, 1.9 Hz, 1H), 7.57−7.54 (m, 2H), 7.25−7.07 (m, 9H), 6.67 (s, 1H), 6.45 (s, 1H), 2.35 (q, J = 7.5 Hz, 2H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.7, 149.2, 141.8, 138.5, 138.0, 137.4, 136.0, 131.4, 128.6, 128.5, 128.3, 126.8, 123.0 121.7, 121.3, 121.3, 120.4, 111.4, 105.5, 24.2, 13.5. IR (KBr, cm^{-1}) 3054, 2923, 2852, 1638, 1522, 1460, 1342, 1266, 743. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{23}H_{20}N_2Na$ 347.1519, found 347.1521.

*(Z)-3-Phenyl-2-[1-(pyridin-2-yl)-1H-indol-2-yl]prop-2-en-1-ol (**3u**).* Brown solid; mp = 78−80 °C; 29.0 mg, 89% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.57 (d, J = 4.7 Hz, 1H), 7.88 (t, J = 7.7 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.34−7.30 (m, 2H), 7.28−7.19 (m, 6H), 6.77 (s, 1H), 6.43 (s, 1H), 4.58 (s, 2H), 4.47 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.3, 148.9, 140.8, 138.7, 137.4, 136.2, 134.4, 133.2, 128.9, 128.7, 128.4, 127.6, 123.0, 121.9, 121.5, 121.2, 120.9, 110.6, 105.0, 62.2. IR (KBr, cm^{-1}) 3374, 3058, 2925, 2855, 1705, 1537, 1457, 1346, 1264, 1012, 742. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{22}H_{19}N_2O$ 327.1492, found 327.1492.

*(Z)-2-(3-methoxy-1-phenylprop-1-en-2-yl)-1-(pyridin-2-yl)-1H-indole (**3v**).* Light yellow oil; 26.2 mg, 83% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.66 (d, J = 4.5 Hz, 1H), 7.78 (t, J = 7.7 Hz, 1H), 7.63 (d, J = 7.3 Hz, 2H), 7.33 (dd, J = 13.0, 7.3 Hz, 3H), 7.29−7.13 (m, 6H), 6.85 (s, 1H), 6.63 (s, 1H), 4.18 (s, 2H), 3.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.6, 149.1, 140.8, 138.6, 138.0, 136.4, 135.6, 130.0, 128.9, 128.6, 128.3, 127.5, 123.2, 122.0, 121.7, 121.3, 120.7, 111.4, 105.7, 70.7, 58.5. IR (KBr, cm^{-1}) 3053, 2922, 2844, 1569, 1471, 1333, 1260, 1203, 1142, 1014, 741. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{23}H_{21}N_2O$ 341.1648, found 341.1647.

*(E)-Methyl 3-phenyl-3-(1-(pyridin-2-yl)-1H-indol-2-yl)acrylate (**3w**).* Yellow solid; mp = 88−90 °C; 32.9 mg, 93% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.48−8.47 (m, 1H), 7.85 (s, 1H), 7.69−7.66 (m, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.31−7.12 (m, 9H), 6.61 (s, 1H), 3.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.6, 151.3, 149.1, 143.5, 137.8, 136.7, 134.4, 133.5, 130.3, 129.6, 128.7, 128.4, 124.1, 123.1, 121.2, 121.1, 121.1, 119.2, 111.6, 106.7, 52.3. IR (KBr, cm^{-1}) 3057, 2924, 2851, 1713, 1638, 1457, 1382, 1253, 1201, 745, 688. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{23}H_{19}N_2O_2$ 355.1441, found 355.1442.

*(E)-2-(Oct-4-en-4-yl)-1-(pyridin-2-yl)-1H-indole (**3x**).* Obtained as a 4.2:1 mixture with its stereoisomer (*Z*)-2-(oct-4-en-4-yl)-1-(pyridin-2-yl)-1*H*-indole; yellow oil; 28.9 mg, 95% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.65−8.64 [m, 1H, **3x**(*E*) and **3x**(*Z*)], 7.75 [td, J = 7.8, 1.4 Hz, 1H, **3x**(*E*) and **3x**(*Z*)], 7.58−7.56 [m, 2H, **3x**(*E*) and **3x**(*Z*)], 7.26−7.21 [m, 2H, **3x**(*E*) and **3x**(*Z*)], 7.17−7.11 [m, 2H, **3x**(*E*) and **3x**(*Z*)], 6.55 [s, 1H, **3x**(*E*) and **3x**(*Z*)], 5.56 [t, J = 7.4 Hz, 1H, **3x**(*E*)], 5.51 [t, J = 7.4 Hz, 1H, **3x**(*Z*)], 2.13−2.05 [m, 4H, **3x**(*E*) and **3x**(*Z*)], 1.38−1.26 [m, 4H, **3x**(*E*) and **3x**(*Z*)], 0.91−0.79 [m, 6H, **3x**(*E*) and **3x**(*Z*)]. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.8, 149.1, 149.1, 142.7, 142.6, 138.1, 137.8, 137.8, 135.1, 133.7, 132.3, 131.7, 128.6, 122.5, 121.5, 121.5, 121.4, 121.0, 120.2, 111.3, 111.2, 104.4, 32.5, 31.0, 30.4, 30.2, 22.7, 21.9, 21.6, 14.1, 14.0, 13.9, 13.9. IR (KBr, cm^{-1}) 3059, 2954, 2863, 1580, 1459, 1348, 1264, 1210, 784, 740. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{21}H_{25}N_2$ 305.2012, found 305.2027.

*2-(1-Phenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3q**).* Obtained as a 19:1 mixture with its regioisomer (*E*)-1-(pyridin-2-yl)-2-styryl-1*H*-indole **3r**; yellow oil; 29.0 mg, 98% yield; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.72 (d, J = 4.6 Hz, 1H), 7.88 (t, J = 7.7 Hz, 1H), 7.64−7.62 (m, 1H), 7.51−7.49 (m, 1H), 7.42−7.39 (m, 3H), 7.36−7.29 (m, 3H), 7.23−7.15 (m, 3H), 7.11 (s, 1H), 7.09 (s, 1H), 6.98 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.4, 149.7, 138.4, 138.1, 137.9, 137.2, 130.6, 128.8, 128.7, 127.8, 126.6, 123.0, 122.1, 121.6, 121.4, 120.6, 118.4, 111.0, 102.4. IR (KBr, cm^{-1}) 3054, 1582, 1459, 1345, 1267, 1212, 1150, 956, 744, 695. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{21}H_{16}N_2Na$ 319.1206, found 319.1214.

*(E)-Ethyl 3-(1-(pyridin-2-yl)-1H-indol-2-yl)acrylate (**3y**).* Yellow oil; 15.8 mg, 54% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.70 (d, J = 4.4 Hz, 1H), 7.91 (t, J = 7.7 Hz, 1H), 7.71−7.65 (m, 2H), 7.46 (d, J = 8.2 Hz, 1H), 7.40−7.35 (m, 2H), 7.25−7.16 (m, 2H), 7.12 (s, 1H), 6.35 (d, J = 15.9 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.9, 150.6, 149.9, 138.7, 138.6, 134.9, 133.9, 128.1, 124.5, 122.5, 121.8, 121.5, 121.5, 118.6, 111.1, 106.6, 60.5, 14.3. IR (KBr, cm^{-1}) 3051, 2923, 2848, 1717, 1628, 1451, 1388, 1257, 1189, 751. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{18}H_{16}N_2O_2Na$ 315.1104, found 315.1107.

*(E)-2-(1-Phenylbuta-1,3-dienyl)-1-(pyridin-2-yl)-1H-indole (**3z**).* Obtained as a 6.7:1 mixture with its stereoisomer (*Z*)-2-(1-phenylbuta-1,3-dienyl)-1-(pyridin-2-yl)-1*H*-indole; yellow oil; 26.1 mg, 81% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.58 (d, J = 4.7 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.70−7.64 (m, 2H), 7.36−7.30 (m, 4H), 7.27−7.14 (m, 5H), 7.07−7.03 (m, 1H), 6.75 (d, J = 8.2 Hz, 3H), 5.27 (d, J = 17.4 Hz, 1H), 5.14 (d, J = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.3, 149.0, 139.5, 137.8, 137.6, 136.7, 133.6, 133.5, 132.7, 129.5, 128.4, 128.3, 127.5, 123.1, 121.3, 121.3, 120.6, 120.5, 119.8, 111.7, 107.2. IR (KBr, cm^{-1}) 3055, 1592, 1466, 1353, 1255, 1218, 1144, 742. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{23}H_{18}N_2Na$ 345.1362, found 345.1369.

*(E)-2-(1,4-Diphenylbut-1-en-3-ynyl)-1-(pyridin-2-yl)-1H-indole (**3za**).* Brown oil; 34.8 mg, 88% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.68 (d, J = 4.4 Hz, 1H), 7.95 (d, J = 7.7 Hz, 2H), 7.79 (t, J = 7.7 Hz, 1H), 7.68 (t, J = 8.2 Hz, 2H), 7.42 (dd, J = 14.0, 7.5 Hz, 3H), 7.36−7.22 (m, 9H), 7.13 (s, 1H), 6.96 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.2, 149.3, 139.6, 138.5, 138.0, 137.3, 136.3, 131.4, 129.1, 128.7, 128.5, 128.4, 128.3, 128.2, 123.4, 122.9, 121.8, 121.5, 121.4, 120.8, 113.9, 111.3, 106.0, 97.3, 87.7. IR (KBr, cm^{-1}) 3058, 2196, 1641, 1456, 1363, 1264, 1208, 1150, 743, 688. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{29}H_{21}N_2$ 397.1699, found 397.1697.

*2-Heptyl-1-(pyridin-2-yl)-1H-indole (**3zb**).* Obtained as a 6.7:1 mixture with its regioisomer 2-(heptan-2-yl)-1-(pyridin-2-yl)-1*H*-indole (**3zc**); yellow oil; 22.2 mg, 76% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.58 (d, J = 4.7 Hz, 1H, **3zb** and **3zc**), 7.73 (t, J = 7.7 Hz, 1H, **3zb** and **3zc**), 7.55−7.53 (m, 1H, **3zb** and **3zc**), 7.34−7.28 (m, 2H, **3zb** and **3zc**), 7.20−7.17 (m, 1H, **3zb** and **3zc**), 7.11−7.08 (m, 2H, **3zb** and **3zc**), 6.44 (s, 1H, **3zc**), 6.42 (s, 1H, **3zb**), 3.22−3.13 (m, 1H, **3zc**), 2.81 (t, J = 7.7 Hz, 2H, **3zb**), 1.57−1.50 (m, 2H, **3zb** and **3zc**), 1.26−1.20 (m, 8H, **3zb**; 6H, **3zc**), 0.86−0.77 (m, 3H, **3zb**; 6H, **3zc**). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.7, 149.7, 141.9, 138.3, 137.4, 128.8, 122.1, 121.6, 121.2, 120.6, 119.9, 110.1, 102.1, 31.8, 29.3, 29.1, 28.7, 27.5, 22.7, 14.2. IR (KBr, cm^{-1}) 3055, 2936, 2845, 1582, 1461, 1345, 1246, 1216, 743. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{20}H_{25}N_2^+$ 293.2012, found 293.1995.

*(E)-2-(hept-1-enyl)-1-(pyridin-2-yl)-1H-indole (**3zd**).* Obtained as a 2.3:1 mixture with its regioisomer 2-(hept-1-en-2-yl)-1-(pyridin-2-yl)-1*H*-indole (**3ze**); yellow oil; 24.9 mg, 86% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.62 (s, 1H, **3zd** and **3ze**), 7.77−7.71 (m, 1H, **3zd** and **3ze**), 7.62−7.50 (m, 1H, **3zd**; 2H, **3ze**), 7.45−7.44 (m, 1H, **3zd**), 7.30−7.26 (m, 1H, **3zd** and **3ze**), 7.23−7.10 (m, 3H, **3zd** and **3ze**), 6.73 (s, 1H, **3zd**), 6.69 (s, 1H, **3ze**), 6.32 (d, J = 15.9 Hz, 1H, **3zd**), 6.25−6.18 (m, 1H, **3zd** and **3ze**), 5.76−5.70 (m, 1H, **3ze**), 2.47 (dd, J = 14.1, 7.0 Hz, 2H, **3ze**), 2.14 (dd, J = 13.8, 6.8 Hz, 2H, **3zd**), 1.51−1.28 (m, 6H, **3zd** and **3ze**), 0.91−0.86 (m, 3H, **3zd** and **3ze**). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.5, 149.5, 149.5, 138.5, 138.1, 138.1, 137.5, 136.9, 136.0, 135.2, 134.2, 128.8, 128.8, 122.8, 122.4, 121.9, 121.9, 121.6, 121.6, 121.2, 121.1, 120.5, 120.2, 120.0, 118.9, 111.2,

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110.9, 105.3, 101.3, 33.3, 31.8, 31.5, 29.6, 29.4, 28.9, 22.7, 22.6, 14.2. IR (KBr, cm^{-1}) 3066, 2955, 2867, 1592, 1463, 1336, 1258, 1203, 962, 887, 744. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{20}H_{22}N_2Na$ 313.1675, found 313.1678.

Several Examples of Removal of Pyridyl Group of 3. Methyl trifluoromethanesulfonate (0.36 mmol, 1.2 equiv) was added dropwise to a solution of **3** (0.30 mmol, 1.0 equiv) in CH_2Cl_2 (7.5 mL) at 0 °C, and the resulting solution was stirred for 24 h at room temperature. Then the solvent was removed under vacuum, and the residue was dissolved in MeOH (3.6 mL). A 2 M aqueous NaOH solution (1.8 mL) was added, and stirring was continued at 60 °C for 12 h. The solvents were removed, and the resulting residue was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography to afford **4**.

*(E)-2-(1, 2-Diphenylvinyl)-1H-indole (**4a**).*[29,30] Light yellow solid; mp = 137−139 °C; 80.0 mg, 90.4% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.41−7.40 (m, 3H), 7.35−7.34 (m, 2H), 7.29 (d, J = 8.1 Hz, 1H), 7.17−7.06 (m, 6H), 7.01−6.99 (m, 2H), 6.43 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 140.2, 138.4, 136.7, 136.6, 134.0, 130.2, 129.6, 129.0, 128.9, 128.2, 128.2, 127.1, 125.9, 122.7, 120.7, 120.3, 110.8, 103.1. IR (KBr, cm^{-1}) 3455, 3096, 1622, 1489, 1332, 1251, 1201, 1143, 741. MS (ESI) m/z 296.1 $[M + H]^+$.

*(E)-2-(1,2-Diphenylvinyl)-5-methoxy-1H-indole (**4b**).*[22d] Brown solid; mp = 142−145 °C; 80.3 mg, 82.4% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (s, 1H), 7.39 (m, 3H), 7.33 (m, 2H), 7.16 (d, J = 8.8 Hz, 1H), 7.12−7.07 (m, 3H), 7.04 (s, 1H), 7.00−6.98 (m, 3H), 6.82 (d, J = 8.7 Hz, 1H), 6.37 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.4, 140.9, 138.3, 136.6, 134.0, 131.9, 130.2, 129.5, 129.3, 129.0, 128.1, 128.1, 127.0, 125.7, 113.0, 111.5, 102.6, 102.2, 55.8. IR (KBr, cm^{-1}) 3458, 3098, 2934, 2862, 1618, 1493, 1335, 1266, 1210, 1163, 744. MS (ESI) m/z 326.2 $[M + H]^+$.

*(E)-5-Bromo-2-(1,2-diphenylvinyl)-1H-indole (**4c**).* Yellow solid; mp = 161−163 °C; 96.8 mg, 86.3% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (s, 1H), 7.64 (s, 1H), 7.42−7.41 (m, 3H), 7.33 (m, 2H), 7.22 (d, J = 10.0 Hz, 1H), 7.15−7.12 (m, 4H), 7.08 (s, 1H), 7.01−6.99 (m, 2H), 6.39 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.4, 138.0, 136.2, 135.2, 133.4, 130.6, 130.1, 129.5, 129.1, 128.3, 128.2, 127.3, 126.8, 125.3, 123.0, 113.3, 112.1, 101.9. IR (KBr, cm^{-1}) 3453, 3091, 1621, 1493, 1340, 1256, 1201, 1138, 742, 698. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{22}H_{17}BrN^+$ 374.0539, found 374.0514.

*(E)-2-(1,2-diphenylvinyl)-3-methyl-1H-indole (**4d**).* Light yellow solid; mp = 120−122 °C; 79.7 mg, 86.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (s, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.33 (m, 3H), 7.28 (m, 2H), 7.21−7.05 (m, 8H), 6.91 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.9, 136.9, 135.6, 135.4, 134.4, 130.3, 129.9, 129.6, 129.5, 128.9, 128.1, 128.0, 126.9, 122.6, 119.4, 118.9, 110.8, 110.6, 10.2. IR (KBr, cm^{-1}) 3457, 3098, 2925, 2854, 1624, 1493, 1338, 1243, 1155, 746. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{23}H_{20}N^+$ 310.1590, found 310.1587.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional text with details on experimental conditions, six tables listing single-crystal data for **3a**, text and 13 figures describing mechanistic details, and ^{1}H and ^{13}C NMR spectra for starting materials and products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail zengwei@scut.edu.cn.

Author Contributions

§L. Liang and S. Fu contributed equally to this work.

Notes

The authors declare no competing financial interest.

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