Copper-catalyzed oxidative dehydrogenative dearomatization of indole derivatives: A new strategy to construct spirocyclic indolenines

Junli Chao, Yuanyuan Yue, Ke Wang, Xiaohui Guo, Chunying Sun, Yue Xu, Jianming Liu

yuanyuanyue@htu.cn (Y.Y.)
jmliu@htu.cn (J.L.)

Highlights

Copper-catalyzed oxidative dehydrogenative dearomatization of indole derivative

Affording a radical-cation intermediate by a single-electron-transfer oxidation

The reaction underwent the nucleophilic attack and dual deprotonation

Chao et al., iScience 25, 105669
December 22, 2022 © 2022 The Authors.
https://doi.org/10.1016/j.isci.2022.105669
Copper-catalyzed oxidative dehydrogenative dearomatization of indole derivatives: A new strategy to construct spirocyclic indolenines

Junli Chao, Yuanyuan Yue,* Ke Wang, Xiaohui Guo, Chunying Sun, Yue Xu, and Jianming Liu

SUMMARY
A concise copper-catalyzed oxidative dehydrogenative dearomatization of indole derivatives for the direct synthesis of spirocyclic indolenines containing fluorene and indeno[2,1-b]indole groups has been established. The utility of this method has also been successfully accomplished by dual oxidative dehydrogenative dearomatization to deliver the desired spirocyclic indolenines containing fluorene groups. According to mechanistic analyses, the C-H cleavage of the phenyl ring was not implicated in the rate-limiting phase. This transformation underwent a single-electron-transfer oxidation by copper(II) catalyst to afford a radical-cation intermediate, yielding the final product by nucleophilic attack and dual deprotonation.

INTRODUCTION
Spirocyclic indolenines serve as important core structural motifs in pharmaceutically relevant compounds and bioactive natural products, which indicate anti-infective, anti-tumor, and antiproliferative activity. Moreover, spiroindolenines have emerged as a promising scaffold for furnishing various synthetic transformations. The unique rigid structure of spiroindolenines makes them suitable candidates in organic optoelectronics. Consequently, numerous approaches have been developed to access functionalized spiroindolenines in synthetic chemistry and material science. Typically, the classical approaches to constructing these compounds generally require multistep sequences involving radical initiation, radical addition and cyclization. Of particular note, transition metal-catalyzed dearomatization of indole derivatives has been identified as a promising route for the synthesis of spiroindolenines. In 2012, You et al. developed an intramolecular Pd-catalyzed dearomatization arylation of 3-substituted indoles to generate various spiroindolenines (Scheme 1a). Subsequently, the Luan group reported an efficient Pd-catalyzed domino dearomatization reaction to deliver spiroindolenine-containing pentacyclic frameworks (Scheme 1b). Recently, an enantioselective Pd-catalyzed intermolecular dynamic kinetic asymmetric dearomatization of indole derivatives with internal alkynes was developed by Zhang et al. to access chiral spiroindolenines (Scheme 1c). Obviously, the pre-installing of those carbon-halide bonds in substrates for the Pd-catalyzed cross-couplings diminished their progress. Conceptually, the direct oxidative dehydrogenative dearomatization of indole derivatives to construct the spiroindolenines resolves some unique and challenging problems.

In the realm of synthetic chemistry, transition-metal-catalyzed oxidative coupling has been proven to be a powerful strategy for the field of synthetic chemistry. This strategy often utilizes simple, readily available reagents and avoids the tedious synthetic steps, which may assist organic synthesis by lowering costs and reducing waste. Among these reactions, copper has been recognized as an effective catalyst for oxidative coupling and aerobic oxidation to construct C-C bonds and C-O bonds as a cheap and abundant transition metal catalyst. In our efforts to develop copper-catalyzed oxidative annulation and aerobic oxidation transformations, we recognized that copper catalysts showed excellent activity in introducing different groups into heterocyclic compounds. Combining these two concepts, we envisioned that copper-catalyzed oxidative annulation furnished the dearomatization of indole derivatives to generate spiroindolenines containing fluorene and indeno[2,1-b]indole groups (Scheme 1d). To realize the dearomatization of indole derivatives through copper-catalyzed oxidative annulation, several major challenges must be addressed. First, the indole compound was easily decomposed under oxidative conditions. Second, the key to balancing the requirements for achieving oxidative dearomatization for the synthesis of spiroindolenine including fluorene and indeno[2,1-b]indole groups was judicious choice of catalyst system and careful design of indole...
substrate. We hypothesized that 2,2'-diphenyl-1\textsubscript{H},1'H-3,3'-biindole and 3-[(1',1'-biphenyl)-2-yl]-2-phenyl-1H-indole would be beneficial to furnish oxidative dehydrogenative dearomatization owing to their stability and conjugated system. This transformation underwent a single-electron-transfer oxidation by copper(II) catalyst to afford a radical-cation intermediate, which followed by nucleophilic attack and dual deprotonation to yield the final spiroindolenine. In this process, Cu(OAc)\textsubscript{2}/Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} could accomplish oxidative dehydrogenative dearomatization to avoid the decomposition of the indole substrate in the presence of TFA at 0°C. Herein, we will provide a straightforward route to construct spiroindolenines containing fluorene and indeno[2,1-b]indole groups with good atom and step economy.

RESULTS AND DISCUSSION

To validate our hypothesis, we commenced our studies by attempting the proposed 2,2'-diphenyl-1\textsubscript{H},1'H-3,3'-biindole (1a) as the substrate. Recent work had demonstrated that 2,2'-diphenyl-1\textsubscript{H},1'H-3,3'-biindole can be easily obtained from widely accessible 2-phenylindole through FeCl\textsubscript{3}-catalyzed oxidative dehydrogenative dearomatization.

Scheme 1. Transition-metal-catalyzed the dearomatization of indole derivatives
It is well known that Pd catalysts are effective in oxidative coupling and dearomatization. Hence, commercially available Pd(OAc)₂ was served as a contrast. To our delight, the reaction took place to afford the desired spiroindolenine in 25% yield in the presence of Na₂S₂O₈ (Table 1, entry 1). Then other commercially available Pd catalysts were investigated, which afforded moderate yields other than Pd(PPh₃)₂Cl₂ (Table 1, entries 2–5). Furthermore, we found that using Cu(OAc)₂ (10 mol %) instead of Pd(OAc)₂ allowed the reaction to proceed smoothly, leading the desired product in 36% yield (Table 1, entry 6). When the catalyst amount was increased to 20 mol % Cu(OAc)₂, the reaction efficiency was improved to 47% yield (Table 1, entry 7). Treatment of 1a with 20 mol % Cu(OAc)₂ delivered the corresponding product in 90% yield (Table 1, entry 8). When Cu(TFA)₂·xH₂O was used in the oxidative dearomatization of 1a, the desired product was obtained in 74% yield (Table 1, entry 9). Furthermore, oxidants such as (NH₄)₂S₂O₈ and K₂S₂O₈, were explored to generate the final product 2a in moderate yields (Table 1, entries 10 and 11). Finally, decreasing the temperature to 25°C had a negative impact on the formation of the product (Table 1, entry 12).

With the optimized reaction conditions in hand, we set out to explore the generality and robustness of copper-catalyzed oxidative dearomatization (Scheme 2). Various substituted 2,2'-diphenyl-1H,1'H-3,3'-biindoles could be accommodated in this transformation. The influence of the electron-donating substituents at the 4-position of the phenyl ring on the reaction outcome was investigated. 2,2'-Diphenyl-1H,1'H-3,3'-biindoles bearing methyl and methoxyl groups were suitable substrates, generating the desired spirocyclic indolenines in 64 and 48% yields, respectively (2b and 2c). Furthermore, substrates bearing functional groups such as chloro, bromo, and fluoro, were carried out under standard conditions to deliver the corresponding products in moderate yields (2d–2f). The tolerance for chlorides on the phenyl ring in this oxidative dearomatization proved to be valuable for further cross-coupling. In addition, the reaction of 2,2'-bis(2-fluorophenyl)-1H,1'H-3,3'-biindole produced the final product in lower yield, which demonstrated the negative effect of the fluoro group at 2-position of the phenyl ring (2g).

To demonstrate the synthetic utility of this transformation, this methodology was further applied to prepare spirocyclic indolenines containing fluorene groups (Scheme 3). In the process of optimizing the reaction conditions, we discovered that Cu(TFA)₂·xH₂O was the best catalyst for the oxidative dearomatization of 3-[(1,1'-biphenyl)-2-yl]-6,7-dimethyl-2-phenyl-1H-indole, and K₂S₂O₈ was the better oxidant in this transformation while optimizing the reaction conditions. Gratifyingly, 3-[(1,1'-biphenyl)-2-yl]-6,7-dimethyl-2-phenyl-1H-indole reacted smoothly under the optimized conditions, affording the desired spirocyclic indolenine in 61% yield (4a). The structure of 4a was unambiguously confirmed by a single-crystal X-ray diffraction analysis. Indole substrates bearing electron-donating groups, such as methyl, methoxy, and benzene, were compatible to generate the final products in 50–76% yields (4b–4d). Subjecting chloro- and fluoro-substituted indole substrates at the 4-position of the phenyl ring gave lower yields under standard conditions (4e and 4f). These results indicated that the substituent electronegativity had an

### Table 1. Optimization of reaction conditions

| Entry | Catalyst (mol %) | Oxidant     | Time (h) | T (°C) | Yield (%)<sup>b</sup> |
|-------|-----------------|-------------|----------|--------|---------------------|
| 1<sup>c</sup> | Pd(OAc)₂ (5 mol %) | Na₂S₂O₈    | 12       | 50     | 25                  |
| 2<sup>c</sup> | Pd(PPh₃)₂Cl₂ (5 mol %) | Na₂S₂O₈ | 12       | 50     | 0                   |
| 3<sup>c</sup> | Pd(TFA)₂ (5 mol %) | Na₂S₂O₈ | 12       | 50     | 35                  |
| 4<sup>c</sup> | PdCl₂ (5 mol %) | Na₂S₂O₈ | 12       | 50     | 30                  |
| 5<sup>c</sup> | Pd(acac)₂ (5 mol %) | Na₂S₂O₈ | 12       | 50     | 21                  |
| 6 | Cu(OAc)₂ (10 mol %) | Na₂S₂O₈ | 24       | 50     | 36                  |
| 7 | Cu(OAc)₂ (20 mol %) | Na₂S₂O₈ | 12       | 50     | 47                  |
| 8 | Cu(OAc)₂ (20 mol %) | Na₂S₂O₈ | 24       | 50     | 90                  |
| 9 | Cu(TFA)₂·xH₂O (20 mol %) | Na₂S₂O₈ | 24       | 50     | 74                  |
| 10 | Cu(OAc)₂ (20 mol %) | K₂S₂O₈ | 24       | 50     | 31                  |
| 11 | Cu(OAc)₂ (20 mol %) | (NH₄)₂S₂O₈ | 24       | 50     | 34                  |
| 12 | Cu(OAc)₂ (20 mol %) | Na₂S₂O₈ | 24       | 25     | 34                  |

<sup>a</sup>Standard condition: 1a (0.30 mmol), Cu(OAc)₂ (20 mol %), Na₂S₂O₈ (2.0 equiv), TFA (2.0 mL), N₂, 50°C, 24 h<sup>b</sup>Yield of isolated product. <sup>c</sup>The reaction is degassed by zero boiling.

<sup>02</sup>It is well known that Pd catalysts are effective in oxidative coupling and dearomatization. Hence, commercially available Pd(OAc)₂ was served as a contrast. To our delight, the reaction took place to afford the desired spiroindolenine in 25% yield in the presence of Na₂S₂O₈ (Table 1, entry 1). Then other commercially available Pd catalysts were investigated, which afforded moderate yields other than Pd(PPh₃)₂Cl₂ (Table 1, entries 2–5). Furthermore, we found that using Cu(OAc)₂ (10 mol %) instead of Pd(OAc)₂ allowed the reaction to proceed smoothly, leading the desired product in 36% yield (Table 1, entry 6). When the catalyst amount was increased to 20 mol % Cu(OAc)₂, the reaction efficiency was improved to 47% yield (Table 1, entry 7). Treatment of 1a with 20 mol % Cu(OAc)₂ delivered the corresponding product in 90% yield (Table 1, entry 8). When Cu(TFA)₂·xH₂O was used in the oxidative dearomatization of 1a, the desired product was obtained in 74% yield (Table 1, entry 9). Furthermore, oxidants such as (NH₄)₂S₂O₈ and K₂S₂O₈, were explored to generate the final product 2a in moderate yields (Table 1, entries 10 and 11). Finally, decreasing the temperature to 25°C had a negative impact on the formation of the product (Table 1, entry 12).

With the optimized reaction conditions in hand, we set out to explore the generality and robustness of copper-catalyzed oxidative dearomatization (Scheme 2). Various substituted 2,2'-diphenyl-1H,1'H-3,3'-biindoles could be accommodated in this transformation. The influence of the electron-donating substituents at the 4-position of the phenyl ring on the reaction outcome was investigated. 2,2'-Diphenyl-1H,1'H-3,3'-biindoles bearing methyl and methoxyl groups were suitable substrates, generating the desired spirocyclic indolenines in 64 and 48% yields, respectively (2b and 2c). Furthermore, substrates bearing functional groups such as chloro, bromo, and fluoro, were carried out under standard conditions to deliver the corresponding products in moderate yields (2d–2f). The tolerance for chlorides on the phenyl ring in this oxidative dearomatization proved to be valuable for further cross-coupling. In addition, the reaction of 2,2'-bis(2-fluorophenyl)-1H,1'H-3,3'-biindole produced the final product in lower yield, which demonstrated the negative effect of the fluoro group at 2-position of the phenyl ring (2g).

To demonstrate the synthetic utility of this transformation, this methodology was further applied to prepare spirocyclic indolenines containing fluorene groups (Scheme 3). In the process of optimizing the reaction conditions, we discovered that Cu(TFA)₂·xH₂O was the best catalyst for the oxidative dearomatization of 3-[(1,1'-biphenyl)-2-yl]-6,7-dimethyl-2-phenyl-1H-indole, and K₂S₂O₈ was the better oxidant in this transformation while optimizing the reaction conditions. Gratifyingly, 3-[(1,1'-biphenyl)-2-yl]-6,7-dimethyl-2-phenyl-1H-indole reacted smoothly under the optimized conditions, affording the desired spirocyclic indolenine in 61% yield (4a). The structure of 4a was unambiguously confirmed by a single-crystal X-ray diffraction analysis. Indole substrates bearing electron-donating groups, such as methyl, methoxy, and benzene, were compatible to generate the final products in 50–76% yields (4b–4d). Subjecting chloro- and fluoro-substituted indole substrates at the 4-position of the phenyl ring gave lower yields under standard conditions (4e and 4f). These results indicated that the substituent electronegativity had an
obvious impact on the formation of spirocyclic indolenine. Furthermore, substrates bearing heterocyclic substituents, such as benzofuran, benzothiophene and thiophene, were explored, furnishing the targeted spirocyclic indolenines from moderate to good yields (4g-4i). The reactions of substrates comprising dibenzofuran and dibenzothiophene units proceeded smoothly to deliver the corresponding products in 70% yields (4j and 4k). In addition, it was noted that the reaction seems sensitive to the effect of the 2-position of substituents on the phenyl ring (4l and 4m). Finally, indole substrates bearing different substituents on the indole ring readily underwent oxidative dehydrogenative dearomatization, delivering the desired products in 35–83% yields (4n-4q). Regrettably, 3-[[1,1'0-Biphenyl]-2-yl]-2-methyl-1H-indole 3s was carried out under the standard condition, no desired product 4s was observed.

We next turned our attention to exploring the generality of the oxidative dearomatization of 3-[[1,1'-biphenyl]-2-yl]-2-phenyl-1H-indole (Scheme 4). Surprisingly, 3-[[1,1'-biphenyl]-2-yl]-2-phenyl-1H-indole underwent dual oxidative dehydrogenative dearomatization enabled by a copper catalyst to obtain the desired 6'-3([[1,1'-biphenyl]-4-yl]-2-phenyl-3H-indol-3-yl]-2'-(phenylspiro[fluorene-9,3'-indole] in 69% yield (6a). The structure of 6a was unambiguously confirmed by single-crystal X-ray diffraction analysis. 3-[[1,1'-Biphenyl]-2-yl]-2-phenyl-1H-indole (5a) underwent intramolecular oxidative dehydrogenative dearomatization to afford the corresponding indolenine. Then 3-[[1,1'-biphenyl]-2-yl]-2-phenyl-1H-indole (5a) reacted smoothly with indolenine via intramolecular oxidative dehydrogenative dearomatization to release final product 6a. Indole substrates bearing electron-donating groups could be successfully converted to the corresponding products in 50 and 53% yields (6b and 6c). Furthermore, indole substrates bearing electron-withdrawing groups proved to be suitable, affording the targeted product in 60% yield (6d). Finally, 3-[[1,1'-4',1''-terphenyl]-2-yl]-2-phenyl-1H-indole and 3-(2-(dibenzo[b,c]furan-3-yl)phenyl)-2-phenyl-1H-indole were carried out under the optimized conditions, enabling dual oxidative dehydrogenative dearomatization for the synthesis of spirocyclic indolenines in good yields (6e and 6f).
**Scheme 3. The scope of substituted 3-[(1,1'-biphenyl)-2-yl]-6,7-dimethyl-2-phenyl-1H-indole**

Reaction conditions: 3 (0.30 mmol), Cu(TFA)$_2$·H$_2$O (20 mol%), K$_2$S$_2$O$_8$ (2.0 equiv), TFA (1.0 mL), DCE (1.0 mL), N$_2$, 0°C, 24 h.
Notably, the oxidative dearomatization of 2,2'-diphenyl-1H,1'H-3,3'-biindole could be accomplished on the gram scale, proceeding smoothly to afford the desired products in 90% yield (Scheme 5). This result demonstrated that the scalability of copper-catalyzed oxidative dearomatization was compatible with this transformation.

Scheme 4. Dual oxidative dehydrogenative dearomatization of 3-[[1,1'-biphenyl]-2-yl]-2-phenyl-1H-indole derivatives
Reaction conditions: 5 (0.30 mmol), Cu(OAc)$_2$ (20 mol %), K$_2$S$_2$O$_8$ (2.4 equiv), TFA (1.0 mL), DCE (1.0 mL), N$_2$, 0°C, 24 h.
A series of control experiments were carried out to gain some insight into the mechanism of the oxidative dehydrogenative dearomatization (Scheme 6). First, when the radical scavenger 2,2,6,6-tetramethylpiperidinoxy (TEMPO) was applied to investigate the involvement of radical intermediates, the desired product (4a) was observed in 19% yield (Scheme 6a). Then we explored the effect of another radical scavenger, butylated hydroxytoluene (BHT) and obtained the corresponding product (4a) in 40% yield (Scheme 6b). These results suggested that a radical process may be ruled out in the copper-catalyzed oxidative dearomatization of indole derivatives. Moreover, kinetic isotope effect experiments were conducted under the optimized conditions (for more details, see SI). The observed kinetic isotope effect (\(k_H/k_D = 1.0\)) indicated that the C-H bond cleavage of the phenyl ring was not involved in the rate-limiting step of this transformation (Scheme 6c). This result also demonstrated that intramolecular electrophilic metatlation was not involved in the rate-limiting step. In addition, 3-methyl-2-phenyl-1H-indole and 2,3-bis(4-Methoxy-phenyl)-1H-indole were conducted under the optimized condition, the desired products were delivered in 57 and 40% yields by the copper(II) catalyzed intermolecular oxidative dehydrogenative dearomatization (Scheme 6d). The reaction site was occurred at 6-position of indole owing the highest electron density.

On the basis of the observed results and previous reports\(^{58,63–70}\), we proposed a plausible mechanism for this transformation (Scheme 7). First, 3-[(1,1'-biphenyl)-2-yl]-2-phenyl-1H-indole (5a) underwent a single-electron-transfer oxidation by copper(II) catalyst to afford a radical-cation intermediate I\(^{58,63,70}\), which followed by the deprotonation to yield intermediate II with the aid of CF\(_3\)CO\(_2\)/CO. After the second single-electron-transfer oxidation, an intramolecular capture of cation intermediate III could be well controlled by nucleophilic attack, affording intermediate IV. Intermediate V was easily obtained by the deprotonation. Furthermore, intermediate III could also capture with intermediate V to generate intermediate VI by second nucleophilic attack. After the next deprotonation, intermediate VI delivered final product 6a. In the above transformation, the copper-catalyzed dual oxidative dehydrogenative dearomatization of 5a could be successfully accomplished to give spirocyclic indolenines.

**Conclusion**

In summary, we have developed a copper-catalyzed oxidative dehydrogenative dearomatization of indole derivatives under mild conditions that offers a concise route to a wide array of spirocyclic indolenines containing fluorene and indeno[2,1-b]indole groups. Of particular note, this transformation could furnish the dual oxidative dehydrogenative dearomatization of 3-[(1,1'-biphenyl)-2-yl]-2-phenyl-1H-indole derivatives to deliver the desired spiroindolenines containing fluorene groups. Mechanistic studies indicated that the C-H bond cleavage of the phenyl ring was not involved in the rate-limiting step of this transformation. We also anticipate that this work will stimulate new interest in the development of copper-catalyzed dual oxidative dehydrogenative dearomatization of heterocyclic compounds and make a promising route for delivering a diverse array of spiroindolenines.

**Limitations of the study**

3-[(1,1'-Biphenyl)-2-yl]-2-methyl-1H-indole was not applicable in a copper-catalyzed oxidative dehydrogenative dearomatization to construct the desired spiroindolenine.

**STAR METHODS**

Detailed methods are provided in the online version of this paper and include the following:

- **KEY RESOURCES TABLE**
- **RESOURCE AVAILABILITY**
  - **Lead contact**
Scheme 6. Mechanistic studies

- Materials availability
- Data and code availability

**METHOD DETAILS**
- General information
- Synthesis of 2,2'-diphenyl-H-IH-3,3'-biindole derivatives
- Synthesis of 2,2'-biphenyl-H-IH-3,3'-biindole derivatives
- Synthesis of 3-(1,1'-biphenyl)-2-yl)-2-methyl-1H-indole
- Reaction profile of the standard reaction
- General procedure for the gram-scale synthesis of 2a
- Copper-catalyzed oxidative dehydrogenative dearomatization of 3a in the presence of TEMPO
- Copper-catalyzed oxidative dehydrogenative dearomatization of 3a in the presence of BHT
The preparation of d$_5$-6,7-dimethyl-2-phenyl-1H-indole
- Kinetic isotope effect experiment
- Synthesis of 3-methyl-2-phenyl-1H-indole
- Synthesis of 2,3-bis(4-methoxyphenyl)-1H-indole
- Copper(II)-catalyzed intermolecular oxidative dehydrogenative dearomatization of 3-methyl-2-phenyl-1H-indole
- Copper(II)-catalyzed intermolecular oxidative dehydrogenative dearomatization of 2,3-bis(4-methoxyphenyl)-1H-indole
- Characterization data of substrates
- Characterization data for the products

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105669.

ACKNOWLEDGMENTS
We are grateful for the financial support from National Natural Science Foundation of China (21573057), Key Scientific Research Project of Higher Education of Henan Province (23A150020), and Natural Science Foundation of Henan Province (212300410052). The authors thank Prof. Dr. Chao Liu, Prof. Dr. Shan Tang and Prof. Dr. Heng Zhang for helpful discussions.

AUTHOR CONTRIBUTIONS
Y.Y. and J.L. contributed to the conception and design of the experiments. J.L., Y.Y., K.W., X.G., C.S., and Y.Y. performed the experiments. Y.Y. and J.L. wrote the manuscript and all authors contributed to data analysis and scientific discussion.

DECLARATION OF INTERESTS
A patent has been filed on the reaction system under CN 114436943A. The authors declare no competing interests.

Received: September 21, 2022
Revised: October 29, 2022
Accepted: November 22, 2022
Published: December 22, 2022
67. Yuan, W., Huang, J., Xu, X., Wang, L., and Tang, X.-Y. (2021). Bi(CF₃)₃-catalyzed electron donor-acceptor complex-mediated aerobic sulfenylation of indoles under visible-light conditions. Org. Lett. 23, 7139–7143. https://doi.org/10.1021/acs.orglett.1c02553.

68. Uyanik, M., Tanaka, H., and Ishihara, K. (2020). Hypoiodite-catalyzed chemoselective tandem oxidation of homotryptamines to peroxyl and epoxytetrahydropyridindolenines. Org. Lett. 22, 8049–8054. https://doi.org/10.1021/acs.orglett.0c03001.

69. Liu, K., Song, W., Deng, Y., Yang, H., Song, C., Abdelilah, T., Wang, S., Cong, H., Tang, S., and Lei, A. (2020). Electrooxidation enables highly regioselective dearomatic annulation of indole and benzofuran derivatives. Nat. Commun. 11, 3. https://doi.org/10.1038/s41467-019-13829-4.

70. Tanaka, H., Ukegawa, N., Uyanik, M., and Ishihara, K. (2022). Hypoiodite-catalyzed oxidative umpolung of indoles for enantioselective dearomatization. J. Am. Chem. Soc. 144, 5756–5761. https://doi.org/10.1021/jacs.2c01852.
## STAR★METHODS

### KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins |
| Cu(TFA)$_2$·xH$_2$O | Aladdin | CAS: 123333-88-0 |
| Cu(OAc)$_2$ | Aladdin | CAS: 142-71-2 |
| Pd(TFA)$_2$ | Energy Chemical | CAS: 42196-31-6 |
| Pd(OAc)$_2$ | Energy Chemical | CAS: 3375-31-3 |
| Pd(PPh$_3$)$_2$Cl$_2$ | Energy Chemical | CAS: 13965-03-2 |
| PdCl$_2$ | Energy Chemical | CAS: 7647-10-1 |
| Pd(acac)$_2$ | Energy Chemical | CAS: 14024-61-4 |
| Na$_2$S$_2$O$_8$ | Aladdin | CAS: 7775-27-1 |
| K$_2$S$_2$O$_8$ | Aladdin | CAS: 7727-21-1 |
| (NH$_4$)$_2$S$_2$O$_8$ | Aladdin | CAS: 7727-54-0 |
| Trifluoroacetic acid | Aladdin | CAS: 76-05-1 |
| DCE | Aladdin | CAS: 107-06-2 |
| TEMPO | Energy Chemical | CAS: 2564-83-2 |
| BHT | Energy Chemical | CAS: 128-37-0 |
| Acetophenone | Energy Chemical | CAS: 98-86-2 |
| Polyphosphoric acid | Aladdin | CAS: 8017-16-1 |
| FeCl$_3$·6H$_2$O | Aladdin | CAS: 10025-77-1 |
| 2-Bromophenylacetic acid | Energy Chemical | CAS: 18698-97-0 |
| DCM | Energy Chemical | CAS: 75-09-2 |
| DMF | Energy Chemical | CAS: 68-12-2 |
| SOCl$_2$ | Energy Chemical | CAS: 7719-09-7 |
| Benzene | Aladdin | CAS: 71-43-2 |
| AlCl$_3$ | Aladdin | CAS: 7446-70-0 |
| Na$_2$CO$_3$ | Aladdin | CAS: 5968-11-6 |
| Triphenylphosphine | J&K Scientific | CAS: 603-35-0 |
| Phenylboric acid | Energy Chemical | CAS: 98-80-6 |
| 2,3-Dimethylhydrazine hydrochloride | Macklin | CAS: 56737-75-8 |
| Phenylhydrazine | Aladdin | CAS: 100-63-0 |
| Bis[2-diphenylphosphino)phenyl] ether | Energy Chemical | CAS: 166330-10-5 |
| LiOH·H$_2$O | Energy Chemical | CAS: 1310-66-3 |
| 2-Methylindole | Energy Chemical | CAS: 95-20-5 |
| 2-Bromobiphenyl | Energy Chemical | CAS: 2052-07-5 |
| 4-Tolyboronic acid | Leyan | CAS: 5720-05-8 |
| 4-Methoxyphenylboronic acid | Leyan | CAS: 5720-07-0 |
| 4-Chlorophenylboronic acid | Leyan | CAS: 1679-18-1 |
| 4-Biphenylboronic acid | Leyan | CAS: 5122-94-1 |
| 4-Fluorobenzeneboronic acid | Leyan | CAS: 1765-93-1 |
| Benzo[b]thiophene-3-boronic acid | Leyan | CAS: 113893-08-6 |
| 2-Thiopheneboronic acid | Leyan | CAS: 6165-68-0 |
| Dibenzofuran-4-boronic acid | Leyan | CAS: 100124-06-9 |

(Continued on next page)
RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Jianming Liu (jmliu@htu.cn).

Materials availability
All materials generated in this study are available in the article and supplemental information or from the lead contact without restriction upon reasonable request.

Data and code availability
- All original crystal structures have been deposited at CCDC and are publicly available as of the date of publication. CCDC numbers are listed in the key resources table.
- This paper does not report original code.
- Any additional information required to reanalyze the data reported in this paper can be obtained from the lead contact upon request.

METHOD DETAILS

General information
All the chemicals and solvents were used as received without further purification. Silica gel (200–300 mesh) was purchased from Sinopharm Chemical Reagent Co., Ltd. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 100–200 mesh silica gel. High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF-QII mass spectrometer (ESI). The 1H (400 MHz), 13C (101 MHz), and 19F NMR (376 MHz) data were recorded on a Bruker Avance TM spectrometer operating at 400 MHz and 600 MHz using CDCl3 or DMSO-d6. For CDCl3, 1H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) as the internal reference; 13C NMR spectra were recorded with CDC13 (δ = 77.00 ppm) as the internal reference. For DMSO-d6, 1H NMR spectra were recorded with DMSO (δ = 2.50 ppm) as the internal reference; 13C NMR spectra were recorded with DMSO (δ = 39.50 ppm) as the internal reference.

Synthesis of 2,2′-diphenyl-1H,1′H-3,3′-biindole derivatives

\[
\text{Ph} + \text{PhNHNNH}_2 \xrightarrow{\text{Polyphosphoric acid}} \text{Ph} - \text{NPh}_2 \text{Ph} \quad 110 \, ^\circ \text{C, 4.0 h}
\]
(1) Acetophenone (583 μL, 5.0 mmol), phenylhydrazine (744 μL, 7.5 mmol), and polyphosphoric acid (15.5 g) were added to a 100 mL round-bottom flask and heated at 100–110°C for 4 hours. After completing the reaction, the obtained solution was poured into ice water (50 mL), neutralized by KOH solution, and extracted with EtOAc (3 × 50 mL). The combined organic phase was dried by anhydrous Na₂SO₄ and concentrated. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate (v/v = 40:1) as an eluent to afford the desired product.

(2) 2-Phenylindole (193.2 mg, 1.0 mmol) and FeCl₃·6H₂O (81.1 mg, 30 mol %) were added into a 25 mL flame-dried Schlenk tube equipped with a stir bar. Toluene (4.0 mL) was injected into a 25 mL flame-dried Schlenk tube. Then, the tube was heated at 120°C for 12 hours. After cooling to room temperature, the reaction mixture were concentrated in vacuum. Then, the residue was purified by chromatography on a silica gel column with petroleum ether/ethyl acetate (v/v = 10:1) as an eluent to afford the desired product (1a-1g). Products 1b-1g were prepared according to the above procedure.

**Synthesis of 2,2'-biphenyl-1H,1'H-3,3'-biindole derivatives**

(1) A 2-bromophenylacetic acid (10.75 g, 50 mmol) was dissolved in 100 mL DCM, a few drops of DMF were added, and then SOCl₂ (7.2 g, 4.41 mL, 60 mmol) was added drop by drop under stirring at 0°C. The reaction mixture was refluxed at 50°C for 2 hours. After cooling to room temperature, the reaction mixture was reduced in vacuum and volatile substances were removed. The residue was dried under vacuum and redissolved in DCM (150 mL), then benzene (39 g, 500 mmol) was added to the solution. The resulting mixture was cooled to 0°C, and AlCl₃ (7.2 g, 56 mmol) was gradually added to make the internal temperature of the solution below 10°C. The mixture was stirred at room temperature for 2.0 h and quenched with cold 3.0 M HCl (200 mL). The water layer was extracted with DCM (50 mL). The combined organic layer was washed with 5.0% sodium bicarbonate and brine and then dried with anhydrous sodium sulfate. The solvent was removed by decompression, and the residue was recrystallized from ethanol to produce a yellowish solid.

(2) In a 25 mL flame-dried Schlenk tube equipped with a stir bar, 2-(2-bromophenyl)-1-phenylethylketone (274 mg, 1 mmol), phenylboric acid (182.9 mg, 1.5 mmol), Pd(OAc)₂ (11.2 mg, 5 mol %), PPh₃ (26.2 mg, 10 mol %), and Na₂CO₃ (276.4 mg, 2.0 mmol) were added and charged with N₂ three times. A mixture of isopropanol (4.0 mL) and water (1.0 mL) was injected into a 25 mL flame-dried Schlenk tube. The Schlenk tube was then allowed to stir at 80°C for 24 h. After cooling to room temperature, the reaction mixture was extracted by ethyl acetate (3 × 20 mL) and water (20 mL). The organic phase was dried by anhydrous sodium sulfate and concentrated under reduced pressure.
The residue was purified by silica gel column chromatography with the appropriate proportion of petroleum ether and ethyl acetate (v/v = 30:1) as eluents to afford the desired 2-[(1,1'-biphenyl)-2-yl]-1-phenylethan-1-one.

(3) 2-[(1,1'-Biphenyl)-2-yl]-1-phenylethan-1-one (1.362 g, 5.0 mmol) was added to a 25 mL flame-dried Schlenk tube equipped with a stir bar and the tube was sealed. Then 2,3-dimethylhydrazine hydrochloride (1.295 g, 7.5 mmol), hydrochloric acid (813 μL, 10 mmol) and anhydrous ethanol (10 mL) were injected into a Schlenk tube. The Schlenk tube was then allowed to stir at 90°C for 12 h. After cooling to room temperature, the reaction mixture was extracted by dichloromethane (3 x 50 mL). The organic phase was dried by anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with petroleum ether and ethyl acetate (v/v = 100:1) as an eluent to afford the desired 2,2'-diphenyl-1'H,1'H-3,3'-biindole.

Synthesis of 3-[(1,1'-biphenyl)-2-yl]-2-methyl-1H-indole
A 25 mL flame-dried Schlenk tube was charged with 2-methylindole (131 mg, 1.0 mmol), Pd(OAc)₂ (11.2 mg, 0.05 mmol), LiOH$\cdot$H₂O (126 mg, 3.0 mmol), and dppm (19.2 mg, 0.05 mmol). Then, H₂O (2.0 mL) and 2-bromobiphenyl (268 mg, 1.2 mmol) was injected into the Schlenk tube with a syringe. The tube was degassed by freeze-pump-thaw using liquid N₂. The Schlenk tube contents were then allowed to stir at 110°C for 18 h. After cooling to room temperature, the solvent was concentrated in vacuum and the residue purified by chromatography on silica gel with petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 50:1, v/v) as eluent to afford the desired product in 86% yield.

Reaction profile of the standard reaction
(a) In a 25 mL flame-dried Schlenk flask equipped with a stir bar, 2,2'-biphenyl-1'H,1'H-3,3'-biindole 1a (115.2 mg, 0.30 mmol), Cu(OAc)₂ (10.9 mg, 20 mol %) and Na₂S₂O₈ (142.9 mg, 0.60 mmol) were added, and the tube was then sealed. The Schlenk tube was purged three times with N₂. Next, TFA (2.0 mL) was injected into the Schlenk tube with a syringe. Subsequently, the Schlenk flask was allowed to stir at 50°C for 24 h. After cooling to room temperature, the mixture was extracted with saturated sodium bicarbonate solution (30 mL) and dichloromethane (3 x 30 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuum. Then, the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 50:1, v/v) as an eluent to afford the desired product in 90% yield.

(b) A 25 mL flame-dried Schlenk tube was charged with 3-[(1,1'-biphenyl)-2-yl]-6,7-dimethyl-2-phenyl-1H-indole 3a (111.9 mg, 0.30 mmol), Cu(TFA)$_2$·xH₂O (17.4 mg, 20 mol %), K₂S₂O₅ (97.3 mg, 0.36 mmol), DCE (1.0 mL) and TFA (1.0 mL). Then, the tube was degassed by freeze-pump-thaw using liquid N₂. The contents of the Schlenk tube were then allowed to stir at 0°C for 24 h. Next, the mixture was extracted with saturated sodium bicarbonate solution (30 mL) and dichloromethane (3 x 30 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuum. Then, the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 4:1) as an eluent to afford the desired product in 61% yield.

(c) A 25 mL flame-dried Schlenk tube was charged with 3-[(1,1'-biphenyl)-2-yl]-2-phenyl-1H-indole 5a (103.5 mg, 0.30 mmol), Cu(OAc)₂ (5.5 mg, 20 mol %), K₂S₂O₅ (97.3 mg, 0.36 mmol), DCE (1.0 mL) and TFA (1.0 mL). Then the tube was degassed by freeze-pump-thaw using liquid N₂. The contents of Schlenk tube were then allowed to stir at 0°C for 24 h. Then, the mixture was extracted with saturated sodium bicarbonate solution (30 mL) and dichloromethane (3 x 30 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuum. Then, the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 4:1) as an eluent to afford the desired product in 69% yield.
General procedure for the gram-scale synthesis of 2a

In a 100 mL flame-dried Schlenk flask equipped with a stir bar, 2,2'-biphenyl-1H,1'H-3,3'-biindole (1.538 g, 4.0 mmol), Cu(OAc)_2 (145.3 mg, 20 mol %) and Na_2S_2O_8 (1.905 g, 8.0 mmol) were combined and the tube was then sealed. The Schlenk tube was purged three times with N_2. Next, TFA (20 mL) was injected into the Schlenk tube with a syringe. Subsequently, the Schlenk flask was allowed to stir at 50°C for 24 h. After cooling to room temperature, the mixture was extracted with saturated sodium bicarbonate solution (100 mL) and dichloromethane (3 × 100 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuum. Then, the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 4:1) as an eluent to afford the desired product in 90% yield.

Copper-catalyzed oxidative dehydrogenative dearomatization of 3a in the presence of TEMPO

A 25 mL flame-dried Schlenk tube was charged with 3-((1,1'-biphenyl)-2-yl)-6,7-dimethyl-2-phenyl-1H-indole 3a (111.9 mg, 0.30 mmol), Cu(TFA)_2·xH_2O (17.4 mg, 20 mol %), TEMPO (93.6 mg, 0.60 mmol), K_2S_2O_8 (97.3 mg, 0.36 mmol) and TFA (2.0 mL). Then the tube was degassed by freeze-pump-thaw using liquid N_2. The contents of Schlenk tube were then allowed to stir at 0°C for 24 h. Then, the mixture was extracted with saturated sodium bicarbonate solution (30 mL) and dichloromethane (3 × 30 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuum. Then, the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 4:1) as an eluent to afford the desired product in 19% yield.

Copper-catalyzed oxidative dehydrogenative dearomatization of 3a in the presence of BHT

A 25 mL flame-dried Schlenk tube was charged with 3-((1,1'-biphenyl)-2-yl)-6,7-dimethyl-2-phenyl-1H-indole 3a (111.9 mg, 0.30 mmol), Cu(TFA)_2·xH_2O (17.4 mg, 20 mol %), BHT (132 mg, 0.60 mmol), K_2S_2O_8 (97.3 mg, 0.36 mmol) and TFA (2.0 mL). Then the tube was degassed by freeze-pump-thaw using liquid N_2. The contents of Schlenk tube were then allowed to stir at 0°C for 24 h. Then, the mixture was extracted with saturated sodium bicarbonate solution (30 mL) and dichloromethane (3 × 30 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuum. Then, the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 4:1) as an eluent to afford the desired product in 40% yield.

The preparation of d_5-6,7-dimethyl-2-phenyl-1H-indole

(1) In a 25 mL flame-dried Schlenk tube equipped with a stir bar, 2-(2-bromophenyl)-1-phenylethyl-ketone (274 mg, 1 mmol), phenyl-d_5-boric acid (190.5 mg, 1.5 mmol), Pd(OAc)_2 (11.2 mg, 5 mol %), PPh_3 (26.2 mg, 10 mol %), and Na_2CO_3 (276.4 mg, 2.0 mmol) were added and the tube was then sealed. A mixture of isopropanol (4.0 mL) and water (1.0 mL) was injected into a 25 mL flame-dried Schlenk tube. The Schlenk tube was then allowed to stir at 80°C for 24 h. After cooling to room temperature, the reaction mixture was extracted by ethyl acetate (3 × 20 mL) and water (20 mL). The organic phase was dried by anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with the appropriate proportion of petroleum ether and ethyl acetate (v/v = 30:1) as eluents to afford the desired 2-((1,1'-biphenyl)-2-yl)-1-phenylethan-1-one.

(2) 2-((1,1'-Biphenyl)-2-yl-2',3',4',5',6'-d_5)-1-phenylethyl-1-one (1.387 g, 5.0 mmol) was added to a 25 mL flame-dried Schlenk tube equipped with a stir bar and sealed the tube. Then, 2,3-dimethylhydrazine hydrochloride (1.295 g, 7.5 mmol), hydrochloric acid (813 µL, 10 mmol) and anhydrous ethanol (10 mL) were injected into a Schlenk tube. The Schlenk tube was then allowed to stir at 90°C for 12 h. After cooling to room temperature, the reaction mixture was extracted by dichloromethane.
(3 x 50 mL). The organic phase was dried by anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with petroleum ether and ethyl acetate (v/v = 100:1) as an eluent to afford the desired 2,2'-diphenyl-1H,1'H-3,3'-biindole (48%).

3-[[1',1'-biphenyl]-2-yl]-2',3',4',5',6'-d5]-6,7-dimethyl-2-phenyl-1H-indole

\[
\text{\begin{center}
\includegraphics[width=0.2\textwidth]{structure1.png}
\end{center}}
\]

\(^1\text{H NMR (400 MHz, DMSO-\text{d}_{6}) \delta 10.74 (br, 1H), 7.43–7.35 (m, 5H), 7.19 (s, 4H), 6.91 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H).}
\]

Kinetic isotope effect experiment

(a) A 25 mL flame-dried Schlenk tube was charged with 3-[[1',1'-biphenyl]-2-yl]-6,7-dimethyl-2-phenyl-1H-indole 3a (111.9 mg, 0.30 mmol), Cu(TFA)\(_2\)-xH\(_2\)O (17.4 mg, 20 mol %), K\(_2\)S\(_2\)O\(_8\) (97.3 mg, 0.36 mmol) and TFA (2.0 mL). Then, the tube was degassed by freeze-pump-thaw using liquid N\(_2\). The contents of Schlenk tube were then allowed to stir at 0°C for 1.0, 1.5 and 2.0 h. Then, the mixture was extracted with saturated sodium bicarbonate solution (30 mL) and dichloromethane (3 x 30 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuum. Then, the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 4:1) as an eluent to afford the desired product.

(b) A 25 mL flame-dried Schlenk tube was charged with 3-[[1',1'-biphenyl]-2-yl]-d5-6,7-dimethyl-2-phenyl-1H-indole 3a (111.9 mg, 0.30 mmol), Cu(TFA)\(_2\)-xH\(_2\)O (17.4 mg, 20 mol %), K\(_2\)S\(_2\)O\(_8\) (97.3 mg, 0.36 mmol) and TFA (2.0 mL). Then, the tube was degassed by freeze-pump-thaw using liquid N\(_2\). The contents of Schlenk tube were then allowed to stir at 0°C for 1.0, 1.5 and 2.0 h. Then, the mixture was extracted with saturated sodium bicarbonate solution (20 mL) and dichloromethane (3 x 20 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuum. Then, the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 4:1) as an eluent to afford the desired product.

6',7'-dimethyl-2'-phenylspiro[fluorene-9,3'-indole]-1,2,3,4-d\(_4\)

\[
\text{\begin{center}
\includegraphics[width=0.2\textwidth]{structure2.png}
\end{center}}
\]

\(^1\text{H NMR (400 MHz, CDCl}_3\) \delta 7.92 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.41 (td, J = 7.6, 0.8 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.16–7.10 (m, 3H), 6.68 (d, J = 7.6 Hz, 2H), 6.38 (d, J = 7.2 Hz, 1H), 2.77 (s, 3H), 2.37 (s, 3H); \(^{13}\text{C}(^1\text{H}) \text{NMR (101 MHz, CDCl}_3\) \delta 176.6, 155.0, 145.5, 145.3, 141.7, 141.7, 140.5, 137.1, 132.9, 130.4, 129.8, 128.4, 128.3, 128.2, 128.0, 127.9, 124.0, 123.6, 120.8, 118.8, 72.0, 19.8, 14.2.}
**Synthesis of 3-methyl-2-phenyl-1H-indole**

A mixture of phenylhydrazine (14.1 mL, 0.143 mol), propiophenone (17.3 mL, 0.130 mol) and concentrated sulfuric acid (13.9 mL, 0.260 mol) in 120 mL ethanol was placed under inert atmosphere and heated to reflux at 90°C overnight until complete consumption of the starting ketone. The resulting mixture was cooled to room temperature and precipitated in a 10-fold excess of ice water. The formed precipitate was filtered off and dried in a vacuum oven to give a beige powder, which was recrystallized from water:ethanol 1:2 to yield 3a as a yellow solid (93% yield).

3-Methyl-2-phenyl-1H-indole (5g)

![Chemical Structure of 3-Methyl-2-phenyl-1H-indole](image)

Yellow solid, 93% yield; m.p. 88–90°C. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 11.14 (br, 1H), 7.67 (d, $J = 7.6$ Hz, 2H), 7.54–7.49 (m, 3H), 7.37–7.33 (m, 2H), 7.11 (t, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 2.41 (s, 3H); $^{13}$C{^1}H NMR (101 MHz, DMSO-d$_6$) $\delta$ 136.4, 134.2, 133.6, 129.9, 129.2, 128.0, 127.4, 122.0, 119.1, 119.0, 111.5, 107.3, 10.3. HRMS, calculated for C$_{15}$H$_{14}$N (M + H$^+$): 208.1121, found 208.1116.

**Synthesis of 2,3-bis(4-methoxyphenyl)-1H-indole**

A mixture of phenylhydrazine (5.6 mL, 56.2 mmol), 1,2-bis(4-methoxyphenyl)ethanone (12.0 g, 46.8 mmol) and 4N hydrochloric acid in dioxane (24 mL) in 96 mL anhydrous ethanol was placed under inert atmosphere and heated to reflux at 90°C for 24 h until complete consumption of the starting ketone. The resulting mixture was cooled to room temperature and diluted with 80 mL ethyl acetate before being washed with aqueous saturated sodium bicarbonate solution (2×15 mL) and brine (2×15 mL). The organic phase was dried on magnesium sulfate and evaporated in vacuo to give a brown oil, which was purified by means of column chromatography to give 2,3-bis(4-methoxyphenyl)-1H-indole 5g as a brown oil (73% yield).

2,3-Bis(4-Methoxyphenyl)-1H-indole (5h)

![Chemical Structure of 2,3-Bis(4-Methoxyphenyl)-1H-indole](image)

Brown oil, 73% yield. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 11.37 (br, 1H), 7.42–7.38 (m, 4H), 7.26–7.23 (m, 2H), 7.14–7.10 (m, 1H), 7.00–6.93 (m, 5H), 3.78 (s, 3H), 3.76 (s, 3H); $^{13}$C{^1}H NMR (101 MHz, DMSO-d$_6$) $\delta$ 159.1, 158.1, 136.4, 134.2, 131.3, 129.8, 128.9, 128.1, 125.5, 122.0, 119.9, 118.8, 114.6, 114.5, 112.6, 111.7, 55.6, 55.4. HRMS, calculated for C$_{22}$H$_{20}$NO$_2$ (M + H$^+$): 330.1489, found 330.1484.

**Copper(II)-catalyzed intermolecular oxidative dehydrogenative deamination of 3-methyl-2-phenyl-1H-indole**

A 25 mL flame-dried Schlenk tube was charged with 3-methyl-2-phenyl-1H-indole (124.3 mg, 0.60 mmol), Cu(TFA)$_2$·xH$_2$O (17.4 mg, 10 mol %), K$_2$S$_2$O$_8$ (194.6 mg, 0.72 mmol), DCE (2.0 mL) and TFA (2.0 mL). Then, the tube was degassed by freeze-pump-thaw using liquid N$_2$. The contents of the Schlenk tube were then allowed to stir at 0°C for 24 h. Next, the mixture was extracted with saturated sodium
bicarbonate solution (30 mL) and dichloromethane (3 × 30 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuum. Then, the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 4:1) as an eluent to afford the desired product (6g) in 57% yield.

3,3'-dimethyl-2,2'-diphenyl-1'H,3H-3,6'-biindole (6g)

Yellow solid, 57% yield; m.p. 134–136°C. 1H NMR (400 MHz, DMSO-<i>d</i><sub>6</sub>) δ 11.04 (br, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.44–7.39 (m, 3H), 7.37–7.34 (m, 3H), 7.20–7.15 (m, 3H), 6.73 (d, J = 8.4 Hz, 1H), 2.35 (s, 3H), 1.87 (s, 3H); 13C{1H} NMR (101 MHz, DMSO-<i>d</i><sub>6</sub>) δ 182.8, 153.3, 150.0, 136.7, 134.7, 130.9, 133.4, 132.5, 131.2, 129.2, 129.0, 128.1, 127.9, 127.5, 126.6, 122.5, 121.2, 119.7, 116.9, 108.1, 107.3, 60.9, 55.4, 22.4, 10.2. HRMS, calculated for C<sub>30</sub>H<sub>25</sub>N<sub>2</sub> (M + H<sup>+</sup>): 413.2012, found 413.2014.

Copper(II)-catalyzed intermolecular oxidative dehydrogenative dearomatization of 2,3-bis(4-methoxyphenyl)-1H-indole

A 25 mL flame-dried Schlenk tube was charged with 3-methyl-2-phenyl-1H-indole (197.5 mg, 0.60 mmol), Cu(TFA)<sub>2</sub>·xH<sub>2</sub>O (17.4 mg, 10 mol %), K<sub>2</sub>SO<sub>8</sub> (194.6 mg, 0.72 mmol), DCE (2.0 mL) and TFA (2.0 mL). Then, the tube was degassed by freeze-pump-thaw using liquid N<sub>2</sub>. The contents of the Schlenk tube were then allowed to stir at 0°C for 24 h. Next, the mixture was extracted with saturated sodium bicarbonate solution (30 mL) and dichloromethane (3 × 30 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuum. Then, the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 4:1) as an eluent to afford the desired product (6h) in 57% yield.

2,2',3,3'-Tetrakis(4-methoxyphenyl)-1'H,3H-3,6'-biindole (6h)

Yellow solid, 40% yield; m.p. 46–49°C. 1H NMR (400 MHz, DMSO-<i>d</i><sub>6</sub>) δ 11.26 (br, 1H), 7.95 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.65–7.29 (m, 5H), 7.25–7.20 (m, 5H), 7.15 (t, J = 7.6 Hz, 1H), 6.98–6.87 (m, 9H), 3.76–3.70 (m, 12H); 13C{1H} NMR (101 MHz, DMSO-<i>d</i><sub>6</sub>) δ 181.1, 161.6, 159.1, 158.7, 158.1, 153.9, 149.9, 136.2, 134.7, 133.7, 132.4, 131.5, 131.2, 130.2, 129.5, 128.3, 127.9, 127.8, 126.5, 125.8, 125.2, 123.9, 120.9, 120.5,
Characterization data of substrates

2,2'-diphenyl-1H,1’H-3,3'-biindole (1a)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 480.5 mg, 50% yield; m.p. 172–174°C. 1H NMR (400 MHz, DMSO-d6) δ 11.58 (br, 2H), 7.55–7.52 (m, 4H), 7.48 (dt, J = 8.0, 0.8 Hz, 2H), 7.21–7.17 (m, 4H), 7.14–7.08 (m, 4H), 6.94 (d, J = 7.8 Hz, 2H), 6.85–6.81 (m, 2H); 13C{1H} NMR (101 MHz, DMSO-d6) δ 136.5, 134.6, 133.0, 129.4, 128.3, 126.9, 126.3, 121.8, 119.3, 111.3, 106.3. HRMS, calculated for C28H21N2 (M + H+): 385.1699, found 385.1696.

2,2'-Di-p-tolyl-1H,1’H-3,3'-biindole (1b)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 473 mg, 47% yield; m.p. 111–113°C. 1H NMR (400 MHz, DMSO-d6) δ 11.50 (br, 2H), 7.48–7.45 (m, 6H), 7.10–7.06 (m, 2H), 7.01 (d, J = 8.0 Hz, 4H), 6.89 (d, J = 8.0 Hz, 2H), 6.81 (t, J = 7.6 Hz, 2H), 2.19 (s, 6H); 13C{1H} NMR (101 MHz, DMSO-d6) δ 136.4, 136.2, 134.7, 130.2, 129.5, 129.0, 126.2, 121.5, 119.1, 119.0, 111.2, 105.9, 20.7. HRMS, calculated for C30H24N2Na (M + Na+): 435.1832, found 435.1830.

2,2'-Bis(4-methoxyphenyl)-1H,1’H-3,3'-biindole (1c)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a light green solid, 659 mg, 70% yield; m.p. 139–142°C. 1H NMR (400 MHz,
DMSO-$d_6$ δ 11.44 (br, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.09–7.05 (m, 2H), 6.92 (d, $J = 8.0$ Hz, 2H), 6.84 (d, $J = 7.2$ Hz, 2H), 6.79 (d, $J = 9.2$ Hz, 2H), 3.67 (s, 6H); $^{13}$C{1H} NMR (101 MHz, DMSO-$d_6$) δ 158.3, 136.3, 134.7, 129.7, 127.6, 125.6, 121.3, 119.0, 118.9, 113.9, 111.1, 105.2, 55.0. HRMS, calculated for C$_{30}$H$_{24}$N$_2$NaO$_2$ (M + Na$^+$): 467.1730, found 467.1727.

2,2'-Bis(4-chlorophenyl)-1H,1'H-3,3'-biindole (1d)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 583.9 mg, 53% yield; m.p. 110–113°C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 11.67 (br, 2H), 7.48 (dd, $J = 8.8, 2.0$ Hz, 6H), 7.28–7.25 (m, 4H), 7.13 (td, $J = 6.8, 1.2$ Hz, 2H), 6.96 (d, $J = 8.0$ Hz, 2H), 6.86 (t, $J = 7.4$ Hz, 2H); $^{13}$C{1H} NMR (101 MHz, DMSO-$d_6$) δ 136.7, 133.4, 131.7, 131.5, 128.9, 128.4, 128.0, 122.2, 119.4, 119.3, 111.5, 106.5. HRMS, calculated for C$_{28}$H$_{18}$Cl$_2$N$_2$ (M + Na$^+$): 475.0739, found 475.0733.

2,2'-Bis(4-bromophenyl)-1H,1'H-3,3'-biindole (1e)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a brick red solid, 793 mg, 58% yield; m.p. 143–145°C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 11.65 (br, 2H), 7.48 (d, $J = 8.8$ Hz, 2H), 7.44–7.38 (m, 8H), 7.13 (t, $J = 7.6$ Hz, 2H), 6.95 (d, $J = 8.0$ Hz, 2H), 6.86 (t, $J = 7.6$ Hz, 2H); $^{13}$C{1H} NMR (101 MHz, DMSO-$d_6$) δ 136.6, 133.4, 130.0, 131.3, 128.9, 128.3, 122.1, 120.1, 119.3, 119.3, 111.5, 106.5. HRMS, calculated for C$_{28}$H$_{19}$Br$_2$N$_2$ (M + H$^+$): 540.9909, found 540.9905.

2,2'-Bis(4-fluorophenyl)-1H,1'H-3,3'-biindole (1f)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 498 mg, 57% yield; m.p. 119–121°C. $^1$H NMR (400 MHz,
DMSO-d$_6$ δ 11.59 (br, 2H), 7.50–7.46 (m, 6H), 7.11 (t, $J$ = 7.6 Hz, 2H), 7.05 (t, $J$ = 8.8 Hz, 4H), 6.97 (d, $J$ = 8.0 Hz, 2H), 6.86 (t, $J$ = 7.6 Hz, 2H); $^{13}$C{1H} NMR (101 MHz, DMSO-d$_6$) δ 161.1 (d, $J$ = 245.4 Hz), 136.5, 133.8, 129.5 (d, $J$ = 3.0 Hz), 129.1, 128.5 (d, $J$ = 8.1 Hz), 121.9, 119.3, 119.2, 115.3 ($J$ = 22.2 Hz), 111.4, 105.9. HRMS, calculated for C$_{28}$H$_{19}$F$_2$N$_2$ (M + H$^+$): 421.1511, found 421.1508.

2,2'-Bis(2-fluorophenyl)-1H,1'H-3,3'-biindole (1g)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 367.6 mg, 35% yield; m.p. 223–226°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.37 (br, 2H), 7.45 (d, $J$ = 8.0 Hz, 2H), 7.23–7.17 (m, 4H), 7.14–7.01 (m, 6H), 6.95–6.90 (m, 4H); $^{13}$C{1H} NMR (101 MHz, DMSO-d$_6$) δ 159.0 (d, $J$ = 248.5 Hz), 136.4, 130.8 (d, $J$ = 3.0 Hz), 129.4, 129.2 ($J$ = 8.1 Hz), 127.9, 123.9 ($J$ = 3.0 Hz), 121.6, 120.9 ($J$ = 14.1 Hz), 119.4, 118.8, 115.5 ($J$ = 22.2 Hz), 111.4, 107.1. HRMS, calculated for C$_{28}$H$_{19}$F$_2$N$_2$ (M + H$^+$): 421.1511, found 421.1508.

3-[[1,1'-Biphenyl]-2-yl]-6,7-dimethyl-2-phenyl-1H-indole (3a)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.142 g, 61% yield; m.p. 165–167°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.69 (br, 1H), 7.55 (d, $J$ = 6.4 Hz, 1H), 7.38–7.28 (m, 3H), 7.07–7.00 (m, 3H), 6.90–7.85 (m, 5H), 6.81 (t, $J$ = 7.2 Hz, 2H), 6.66 (d, $J$ = 7.2 Hz, 2H), 2.34 (s, 3H), 2.31 (s, 3H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$) δ 142.5, 141.9, 136.2, 134.3, 133.2, 132.3, 130.6, 128.9, 128.4, 127.5, 127.3, 127.0, 125.7, 123.1, 117.8, 117.0, 19.5, 13.2. HRMS, calculated for C$_{28}$H$_{24}$N (M + H$^+$): 374.1903, found 374.1904.

6,7-Dimethyl-3-[[4'-methyl-[1,1'-biphenyl]-2-yl]-2-phenyl-1H-indole (3b)
The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.098 g, 57% yield, m.p. 134–136°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.72 (br, 1H), 7.41–7.30 (m, 5H), 7.23–7.18 (m, 5H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.77 (s, 3H), 6.73 (d, $J = 8.0$ Hz, 1H), 2.42 (s, 3H), 2.29 (s, 3H), 2.13 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) $\delta$ 141.7, 138.6, 136.1, 134.8, 133.9, 133.7, 132.6, 132.1, 130.2, 128.7, 128.0, 127.9, 127.4, 127.2, 127.1, 126.6, 122.1, 118.3, 115.7, 113.6, 20.5, 19.1, 13.3. HRMS, calculated for C$_{29}$H$_{26}$N (M + H$^+$): 388.2060, found 388.2063.

3-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-6,7-dimethyl-2-phenyl-1H-indole (3c)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.094 g, 54% yield; m.p. 202–204°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (br, 1H), 7.61 (d, $J = 7.2$ Hz, 1H), 7.44–7.30 (m, 4H), 7.14 (d, $J = 6.8$ Hz, 3H), 7.00–6.97 (m, 3H), 6.67 (d, $J = 8.4$ Hz, 2H), 6.45 (d, $J = 8.0$ Hz, 2H), 3.69 (s, 3H), 2.43 (s, 6H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 157.8, 136.3, 134.5, 134.1, 133.3, 132.3, 130.5, 129.9, 128.3, 127.3, 127.1, 127.0, 123.1, 117.8, 117.1, 113.0, 55.3, 19.5, 13.3. HRMS, calculated for C$_{29}$H$_{25}$NNaO (M + Na$^+$): 426.1828, found 426.1824.

3-(1,1':4',1''-Tetrphenyl)-2-yl)-6,7-dimethyl-2-phenyl-1H-indole (3d)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a brick red solid, 1.288 g, 57% yield; m.p. 142–144°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.80 (br, 1H), 7.53–7.51 (m, 2H), 7.44–7.37 (m, 6H), 7.30 (d, $J = 7.2$ Hz, 1H), 7.24 (d, $J = 8.4$ Hz, 1H), 7.19–7.15 (m, 5H), 6.98 (d, $J = 8.0$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 2H), 6.78 (d, $J = 8.0$ Hz, 1H), 2.42 (s, 3H), 2.30 (s, 6H); $^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) $\delta$ 141.2, 140.6, 139.7, 137.4, 136.3, 134.2, 133.7, 132.7, 132.1, 130.2, 128.8, 128.8, 128.7, 127.9, 127.6, 127.6, 127.3, 127.2, 127.1, 126.7, 126.3, 125.5, 122.3, 118.5, 115.6, 113.2, 19.2, 13.3. HRMS, calculated for C$_{34}$H$_{28}$N (M + H$^+$): 450.2216, found 450.2212.

3-(4'-Chloro-[1,1'-biphenyl]-2-yl)-6,7-dimethyl-2-phenyl-1H-indole (3e)
The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.413 g, 69% yield; m.p. 133–135°C. 1H NMR (400 MHz, CDCl₃) δ 7.79 (br, 1H), 7.64 (dd, J = 7.2, 1.2 Hz, 1H), 7.45 (td, J = 7.6, 1.6 Hz, 1H), 7.38 (td, J = 7.6, 1.6 Hz, 1H), 7.33–7.26 (m, 2H), 7.14–7.09 (m, 3H), 6.97 (d, J = 8.0 Hz, 1H), 6.91 (dd, J = 7.4, 2.2 Hz, 2H), 6.83–6.80 (m, 2H), 6.59–6.56 (m, 2H), 6.43 (s, 3H), 2.40 (s, 3H); 13C{1H} NMR (101 MHz, CDCl₃) δ 141.2, 140.3, 136.3, 134.3, 133.5, 133.1, 132.3, 131.7, 130.4, 130.2, 130.2, 128.4, 127.9, 127.7, 127.4, 127.3, 127.1, 123.3, 118.0, 116.9, 114.1, 19.5, 13.2. HRMS, calculated for C₂₈H₂₃ClN (M + H⁺): 408.1514, found 408.1511.

3-(4'-Fluoro-[1,1'-biphenyl]-2-yl)-6,7-dimethyl-2-phenyl-1H-indole (3f)

![Structure of 3f](image)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.250 g, 64% yield; m.p. 136–138°C. 1H NMR (400 MHz, DMSO-d₆) δ 10.81 (br, 1H), 7.43–7.38 (m, 3H), 7.34–7.32 (m, 1H), 7.20–7.14 (m, 5H), 6.95 (d, J = 8.0 Hz, 1H), 6.79–6.75 (m, 5H), 2.44 (s, 3H), 2.31 (s, 3H); 13C{1H} NMR (101 MHz, DMSO-d₆) δ 160.7 (d, J = 243.4 Hz), 140.5, 137.7 (d, J = 4.0 Hz), 136.3, 134.2, 133.7, 132.6, 132.1, 130.2, 130.5, 130.0 (d, J = 8.1 Hz), 128.9, 127.9, 127.5, 127.3, 127.0, 126.8, 122.3, 118.5, 115.6, 114.1 (d, J = 22.2 Hz), 113.0, 19.2, 13.3. HRMS, calculated for C₂₈H₂₂FNNa (M + Na⁺): 414.1628, found 414.1616.

3-(2-(Benzofuran-2-yl)phenyl)-6,7-dimethyl-2-phenyl-1H-indole (3g)

![Structure of 3g](image)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 395.7 mg, 19% yield; m.p. 67–69°C. 1H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 7.6 Hz, 2H), 7.49–7.45 (m, 1H), 7.38–7.34 (m, 3H), 7.29–7.26 (m, 3H), 7.22–7.20 (m, 1H), 7.16–7.12 (m, 4H), 7.05–7.01 (m, 2H), 6.87 (d, J = 8.4 Hz, 1H), 6.07 (d, J = 1.2 Hz, 1H), 2.49 (s, 3H), 2.41 (s, 6H); 13C{1H} NMR (101 MHz, CDCl₃) δ 154.9, 154.2, 136.3, 133.3, 133.2, 132.7, 131.2, 130.5, 129.6, 128.7, 128.6, 127.7, 127.6, 127.4, 127.0, 124.0, 123.5, 122.4, 121.1, 117.9, 117.2, 115.3, 110.9, 104.8, 19.5, 13.4. HRMS, calculated for C₃₀H₂₃NNaO (M + Na⁺): 436.1672, found 436.1674.
3-(2-(Benzo[b]thiophen-3-yl)phenyl)-6,7-dimethyl-2-phenyl-1H-indole (3h)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.319 g, 61% yield; m.p. 116–118°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.71 (br, 1H), 7.76 (d, $J$ = 8.0 Hz, 1H), 7.52–7.46 (m, 3H), 7.41 (d, $J$ = 6.8 Hz, 1H), 7.28 (d, $J$ = 8.0 Hz, 1H), 7.19–7.12 (m, 5H), 7.09–7.03 (m, 2H), 6.97 (d, $J$ = 8.0 Hz, 1H), 6.73 (d, $J$ = 8.0 Hz, 1H), 6.62 (s, 1H), 2.37 (s, 3H), 2.27 (s, 3H); $^{13}$C ($^1$H) NMR (101 MHz, DMSO-$d_6$) $\delta$ 138.7, 137.9, 136.4, 136.1, 135.4, 135.1, 134.2, 132.6, 132.4, 130.8, 129.6, 128.8, 128.6, 128.2, 127.9, 127.8, 127.4, 127.1, 126.9, 126.8, 123.8, 123.7, 123.5, 122.3, 122.2, 118.3, 115.4, 113.2, 19.1, 13.2. HRMS, calculated for C$_{30}$H$_{24}$NS (M + H$^+$): 430.1624, found 430.1624.

6,7-Dimethyl-2-phenyl-3-(2-(thiophen-2-yl)phenyl)-1H-indole (3i)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a brown solid, 487.5 mg, 33% yield; m.p. 136–138°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.96 (br, 1H), 7.70 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.42 (dd, $J$ = 7.6, 1.6 Hz, 1H), 7.38–7.33 (m, 3H), 7.26–7.18 (m, 5H), 6.93 (dd, $J$ = 3.6, 1.2 Hz, 1H), 6.77 (dd, $J$ = 5.0, 3.8 Hz, 1H), 6.71 (s, 2H), 2.48 (s, 3H), 2.30 (s, 3H); $^{13}$C ($^1$H) NMR (101 MHz, DMSO-$d_6$) $\delta$ 142.4, 136.2, 134.5, 134.3, 133.3, 132.7, 132.5, 129.9, 128.9, 128.1, 127.6, 127.5, 127.4, 127.3, 126.9, 126.4, 126.3, 125.2, 122.3, 118.4, 115.6, 113.3, 19.2, 13.3. HRMS, calculated for C$_{26}$H$_{21}$NNaS (M + Na$^+$): 402.1287, found 402.1279.

3-(2-(Dibenzo[b,d]furan-4-yl)phenyl)-6,7-dimethyl-2-phenyl-1H-indole (3j)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a brick red solid, 1.481 g, 64% yield; m.p. 90–92°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.68 (br, 1H), 7.96 (d, $J$ = 8.0 Hz, 1H), 7.76 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.61–7.58 (m, 1H), 7.51–7.47 (m, 3H), 7.40–7.36 (m, 1H), 7.30–7.24 (m, 4H), 7.06 (t, $J$ = 7.6 Hz, 2H), 6.99 (t, $J$ = 8.0 Hz, 2H), 6.86 (dd, $J$ = 16.4, 8.4 Hz, 2H), 6.69 (d, $J$ = 8.0 Hz, 1H), 2.34 (s, 3H), 2.24 (s, 3H); $^{13}$C ($^1$H)
NMR (101 MHz, DMSO-d<sub>6</sub>) δ 155.2, 152.9, 136.2, 136.1, 135.0, 134.1, 132.2, 131.3, 128.5, 128.1, 127.9, 127.6, 127.5, 127.0, 126.9, 126.8, 126.3, 125.9, 123.7, 123.3, 122.5, 122.1, 122.0, 120.7, 119.2, 118.3, 115.6, 113.2, 111.2, 19.1, 13.2. HRMS, calculated for C<sub>34</sub>H<sub>26</sub>NO (M + H<sup>+</sup>): 464.2009, found 464.2010.

3-(2-(Dibenzo[b,d]thiophen-4-yl)phenyl)-6,7-dimethyl-2-phenyl-1H-indole (3k)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.408 g, 47% yield; m.p. 114–116°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (dd, <i>J</i> = 5.6, 2.8 Hz, 1H), 7.81 (d, <i>J</i> = 8.0 Hz, 1H), 7.76–7.68 (m, 4H), 7.58–7.48 (m, 3H), 7.41–7.37 (m, 3H), 7.02 (t, <i>J</i> = 8.0 Hz, 2H), 6.94 (s, 4H), 6.74 (d, <i>J</i> = 8.0 Hz, 1H), 2.41 (s, 3H), 2.36 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 140.3, 139.9, 139.8, 136.4, 136.1, 135.7, 134.5, 134.3, 133.0, 130.2, 129.3, 128.4, 128.3, 128.0, 127.4, 127.2, 126.9, 126.3, 123.9, 123.1, 121.3, 119.4, 117.7, 117.0, 19.5, 13.2. HRMS, calculated for C<sub>34</sub>H<sub>26</sub>NS (M + H<sup>+</sup>): 480.1780, found 480.1782.

3-(2'-Methoxy-[1,1'-biphenyl]-2-yl)-6,7-dimethyl-2-phenyl-1H-indole (3l)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.020 g, 50% yield; m.p. 138–140°C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.65 (br, 1H), 7.36–7.34 (m, 2H), 7.33–7.29 (m, 4H), 7.23–7.19 (m, 3H), 6.99–6.95 (m, 1H), 6.91 (d, <i>J</i> = 8.0 Hz, 1H), 6.71 (d, <i>J</i> = 8.0 Hz, 1H), 6.65 (d, <i>J</i> = 8.0 Hz, 2H), 6.51 (t, <i>J</i> = 7.6 Hz, 1H), 3.22 (s, 3H), 2.41 (s, 3H), 2.28 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-d<sub>6</sub>) δ 155.9, 138.8, 136.0, 135.1, 133.6, 132.7, 131.7, 131.4, 130.4, 130.1, 128.3, 127.8, 127.7, 127.6, 127.2, 126.5, 126.2, 121.8, 119.4, 118.1, 115.9, 114.0, 110.5, 54.5, 19.1, 13.2. HRMS, calculated for C<sub>29</sub>H<sub>26</sub>NO (M + H<sup>+</sup>): 404.1780, found 404.1782.

3-(2'-Fluoro-[1,1'-biphenyl]-2-yl)-6,7-dimethyl-2-phenyl-1H-indole (3m)
The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1,269 g, 65% yield; m.p. 139–141°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 10.75 (br, 1H), 7.48–7.39 (m, 4H), 7.35–7.33 (m, 1H), 7.21–7.19 (m, 4H), 7.06–7.01 (m, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.84–6.78 (m, 1H), 6.76–6.72 (m, 2H), 6.68 (td, J = 7.6, 2.0 Hz, 1H), 2.41 (s, 3H), 2.29 (s, 3H); $^{13}$C{1H} NMR (101 MHz, DMSO-d$_6$) δ 158.9 (d, J = 245.4 Hz), 136.1, 135.5, 135.0, 134.2, 132.5, 132.0, 131.1 (d, J = 4.0 Hz), 128.8, 128.7, 128.4 (d, J = 8.1 Hz), 128.1, 128.0, 127.6, 126.9 (d, J = 6.1 Hz), 126.7, 123.3 (d, J = 3.0 Hz), 122.1, 118.4, 115.5, 115.0 (d, J = 23.2 Hz), 112.9, 19.2, 13.3. HRMS, calculated for C$_{28}$H$_{22}$FNNa (M + Na$^+$): 414.1628, found 414.1625.

3-[[1,1'-Biphenyl]-2-yl]-7-chloro-6-fluoro-2-phenyl-1H-indole (3n)

![Image of 3-[[1,1'-Biphenyl]-2-yl]-7-chloro-6-fluoro-2-phenyl-1H-indole (3n)]

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.023 g, 51% yield; m.p. 137–139°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.65 (br, 1H), 7.45 (td, J = 7.2, 2.0 Hz, 1H), 7.42–7.37 (m, 3H), 7.24–7.22 (m, 3H), 7.20–7.19 (m, 2H), 7.07 (dd, J = 8.4, 4.8 Hz, 1H), 7.00–6.96 (m, 3H), 6.91 (dd, J = 7.8, 1.8 Hz, 2H); $^{13}$C{1H} NMR (101 MHz, DMSO-d$_6$) δ 154.0 (d, J = 238.4 Hz), 141.8, 141.2, 136.7, 135.2, 132.8, 132.0, 131.8, 130.4, 128.3, 128.2, 127.8, 127.4, 126.6, 126.1, 118.1 (d, J = 9.1 Hz), 114.1, 108.6 (d, J = 23.2 Hz), 102.1 (d, J = 21.2 Hz). HRMS, calculated for C$_{26}$H$_{17}$ClFNNa (M + Na$^+$): 420.0926, found 420.0927.

3-[[1,1'-Biphenyl]-2-yl]-6-bromo-2-phenyl-1H-indole (3o)

![Image of 3-[[1,1'-Biphenyl]-2-yl]-6-bromo-2-phenyl-1H-indole (3o)]

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 770.4 mg, 36% yield; m.p. 171–173°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.51 (br, 1H), 7.50 (d, J = 1.6 Hz, 1H), 7.45 (td, J = 6.8, 2.0 Hz, 2H), 7.40 (dd, J = 4.8, 2.0 Hz, 2H), 7.24–7.21 (m, 3H), 7.20–7.17 (m, 2H), 7.07–7.02 (m, 2H), 6.98–6.96 (m, 3H), 6.84–6.82 (m, 2H); $^{13}$C{1H} NMR (101 MHz, DMSO-d$_6$) δ 141.8, 141.2, 136.7, 135.2, 132.8, 132.0, 131.8, 130.4, 128.3, 128.2, 127.8, 127.7, 127.4, 127.3, 127.0, 126.0, 122.2, 120.4, 114.2, 113.6, 113.0. HRMS, calculated for C$_{26}$H$_{19}$BrN (M + H$^+$): 424.0695, found 424.0692.

3-[[1,1'-Biphenyl]-2-yl]-6-methyl-2-phenyl-1H-indole (3p)

![Image of 3-[[1,1'-Biphenyl]-2-yl]-6-methyl-2-phenyl-1H-indole (3p)]

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 770.4 mg, 36% yield; m.p. 171–173°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.51 (br, 1H), 7.50 (d, J = 1.6 Hz, 1H), 7.45 (td, J = 6.8, 2.0 Hz, 2H), 7.40 (dd, J = 4.8, 2.0 Hz, 2H), 7.24–7.21 (m, 3H), 7.20–7.17 (m, 2H), 7.07–7.02 (m, 2H), 6.98–6.96 (m, 3H), 6.84–6.82 (m, 2H); $^{13}$C{1H} NMR (101 MHz, DMSO-d$_6$) δ 141.8, 141.2, 136.7, 135.2, 132.8, 132.0, 131.8, 130.4, 128.3, 128.2, 127.8, 127.7, 127.4, 127.3, 127.0, 126.1, 122.2, 120.4, 114.2, 113.6, 113.0. HRMS, calculated for C$_{26}$H$_{18}$BrN (M + H$^+$): 424.0695, found 424.0692.
The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.003 g, 50% yield; m.p. 137–139°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.12 (br, 1H), 7.45–7.37 (m, 4H), 7.20–7.16 (m, 5H), 7.14 (s, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.98–6.92 (m, 3H), 6.86–6.83 (m, 2H), 6.73 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H); $^{13}$C$^1$(H) NMR (101 MHz, DMSO-d$_6$) δ 141.7, 141.4, 136.3, 133.7, 133.5, 132.5, 132.0, 130.7, 130.3, 128.1, 128.1, 127.5, 127.3, 127.3, 126.8, 126.7, 126.7, 125.9, 121.0, 118.4, 112.8, 111.0, 21.4. HRMS, calculated for C$_{27}$H$_{22}$N (M + H$^+$): 360.1747, found 360.1743.

3-(2-(Benzo[b]thiophen-3-yl)phenyl)-2-phenyl-1H-indole (3q)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.239 g, 62% yield; m.p. 150–152°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.22 (br, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.59–7.43 (m, 4H), 7.30 (d, J = 8.4 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.17–7.03 (m, 8H), 6.98 (t, J = 7.6 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.90 (s, 1H); $^{13}$C$^1$(H) NMR (101 MHz, DMSO-d$_6$) δ 138.6, 137.8, 136.4, 135.8, 135.5, 134.9, 134.5, 132.4, 132.3, 131.0, 128.9, 128.1, 128.1, 127.1, 127.1, 126.9, 124.0, 123.7, 123.4, 122.3, 122.2, 121.6, 119.4, 118.5, 112.7, 111.2. HRMS, calculated for C$_{29}$H$_{20}$NS (M + H$^+$): 402.1311, found 402.1311.

3-(1,1'-Biphenyl)-2-phenyl-1H-indole (5a)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.354 g, 79% yield; m.p. 150–153°C. $^1$H NMR (600 MHz, DMSO-d$_6$) δ 11.34 (br, 1H), 7.46–7.42 (m, 3H), 7.41–7.38 (m, 2H), 7.21–7.17 (m, 6H), 7.08 (t, J = 7.2 Hz, 1H), 6.98–6.90 (m, 4H), 6.86 (d, J = 6.6 Hz, 2H); $^{13}$C$^1$(H) NMR (101 MHz, DMSO-d$_6$) δ 141.9, 141.4, 136.0, 134.3, 133.6, 132.5, 132.2, 130.4, 128.9, 128.2, 127.6, 127.5, 127.4, 127.0, 126.0, 121.7, 119.4, 118.7, 113.0, 111.3. HRMS, calculated for C$_{26}$H$_{20}$N (M + H$^+$): 346.1590, found 346.1585.

3-(4'-Methyl-[1,1'-biphenyl]-2-yl)-2-phenyl-1H-indole (5b)
The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.446 g, 80% yield; m.p. 76–78°C. $^1$H NMR (600 MHz, DMSO-$d_6$) δ 11.32 (br, 1H), 7.45–7.35 (m, 6H), 7.23 (d, J = 6.0 Hz 4H), 7.12 (d, J = 7.8 Hz 1H), 7.07 (t, J = 7.2 Hz 1H), 6.89 (t, J = 7.8 Hz 1H), 6.79–6.76 (m, 4H), 2.11 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) δ 141.9, 138.6, 135.9, 135.1, 134.1, 133.6, 132.5, 132.2, 130.4, 129.0, 128.3, 128.1, 127.5, 127.4, 127.0, 126.9, 121.8, 119.4, 118.8, 113.2, 111.3, 20.6. HRMS, calculated for C$_{27}$H$_{22}$N (M + H$^+$): 360.1747, found 360.1742.

3-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-2-phenyl-1H-indole (5c)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.591 g, 85% yield; m.p. 190–192°C. $^1$H NMR (600 MHz, DMSO-$d_6$) δ 11.33 (br, 1H), 7.43–7.36 (m, 5H), 7.25–7.19 (m, 5H), 7.12 (d, J = 7.8 Hz 1H), 7.07 (t, J = 7.8 Hz 1H), 6.90 (t, J = 7.2 Hz 1H), 6.81 (d, J = 8.4 Hz 2H), 6.53 (d, J = 8.0 Hz 2H), 3.59 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) δ 157.7, 141.6, 136.0, 134.1, 133.8, 133.5, 132.5, 132.2, 130.3, 129.3, 128.9, 128.3, 127.5, 127.2, 127.1, 126.9, 121.8, 119.4, 118.8, 113.3, 113.0, 111.3, 54.9. HRMS, calculated for C$_{26}$H$_{22}$NO (M + H$^+$): 376.1696, found 376.1693.

3-(4'-Fluoro-[1,1'-biphenyl]-2-yl)-2-phenyl-1H-indole (5d)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 1.526 g, 84% yield; m.p. 162–164°C. $^1$H NMR (600 MHz, DMSO-$d_6$) δ 11.35 (br, 1H), 7.46–7.44 (m, 3H), 7.38–7.36 (m, 2H), 7.22–7.18 (m, 4H), 7.16–7.14 (m, 3H), 7.09 (td, J = 6.6, 1.2 Hz, 1H), 6.93 (t, J = 7.2 Hz 1H), 6.80–6.75 (m, 4H); $^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) δ 160.7 (d, J = 244.4 Hz), 140.7, 137.7 (d, J = 3.0 Hz), 136.0, 134.4, 133.5, 132.4, 132.1, 130.3, 130.1 (d, J = 7.1 Hz), 128.7, 127.8, 127.5, 127.1, 127.0, 121.8, 119.5, 118.6, 114.1 (d, J = 21.2 Hz), 112.6, 114.4. HRMS, calculated for C$_{26}$H$_{20}$FN (M + H$^+$): 364.1496, found 364.1494.

3-(4'-Chloro-[1,1'-biphenyl]-2-yl)-2-phenyl-1H-indole (5e)
The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a beige solid, 1.626 g, 86% yield; m.p. 153–155°C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 11.36 (br, 1H), 7.48–7.5 (m, 3H), 7.39–7.37 (m, 2H), 7.21–7.18 (m, 4H), 7.14 (dd, $J = 7.8, 2.4$ Hz, 2H), 7.10 (t, $J = 7.8$ Hz, 1H), 6.99 (d, $J = 7.8$ Hz, 2H), 6.94 (t, $J = 7.8$ Hz, 1H), 6.77 (d, $J = 8.4$ Hz, 2H); $^{13}$C{1H} NMR (101 MHz, DMSO-$d_6$) $\delta$ 140.4, 140.2, 136.0, 134.4, 133.5, 132.4, 132.2, 130.9, 130.2, 130.0, 128.7, 128.3, 128.1, 127.6, 127.3, 127.1, 127.0, 121.9, 119.5, 118.6, 112.4, 111.4. HRMS, calculated for C$_{26}$H$_{19}$ClN (M + H$^+$): 380.1201, found 380.1202.

3-(1,1':4,1''-Terphenyl)-2-phenyl-1H-indole (5f)

![Structure](image)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a brown solid, 1.712 g, 81% yield; m.p. 178–180°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.34 (br, 1H), 7.51–7.43 (m, 6H), 7.40–7.36 (m, 3H), 7.30–7.19 (m, 9H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 141.3, 140.5, 139.7, 137.4, 136.0, 134.4, 133.5, 132.4, 132.1, 130.2, 128.8, 128.7, 128.1, 127.7, 124.7, 127.0, 126.9, 126.3, 125.5, 121.7, 119.4, 118.6, 112.7, 111.2. HRMS, calculated for C$_{32}$H$_{24}$N (M + H$^+$): 422.1903, found 422.1905.

3-(2-(Dibenzo[b,d]furan-4-yl)phenyl)-2-phenyl-1H-indole (5g)

![Structure](image)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 2.007 g, 92% yield; m.p. 87–89°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.13 (br, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 7.8$ Hz, 1H), 7.61–7.59 (m, 1H), 7.55 (t, 1H), 7.37–7.33 (m, 1H), 7.30–7.23 (m, 4H), 7.19 (d, $J = 7.2$ Hz, 2H), 7.14 (d, $J = 8.4$ Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 2H), 7.03–6.97 (m, 2H), 6.95–6.83 (m, 4H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 155.1, 152.8, 136.4, 135.7, 134.9, 134.2, 132.1, 132.0, 131.3, 128.7, 128.2, 127.9, 127.0, 126.9, 126.6, 125.8, 123.5, 123.2, 122.5, 122.1, 121.5, 120.7, 119.2, 119.0, 118.6, 112.7, 111.0. HRMS, calculated for C$_{32}$H$_{22}$NO (M + H$^+$): 436.1696, found 436.1687.

Synthesis of 3-(1,1'-biphenyl)-2-yl)-2-methyl-1H-indole

A 25 mL flame-dried Schlenk tube was charged with 2-methylindole (131 mg, 1.0 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), LiOH·H$_2$O (126 mg, 3.0 mmol), and dppm (19.2 mg, 0.05 mmol). Then, H$_2$O (2.0 mL) was injected into the Schlenk tube with a syringe. The tube was degassed by freeze-pump-thaw using liquid N$_2$. The Schlenk tube contents were then allowed to stir at 110°C for 18 h. After cooling to room temperature, the solvent was concentrated in vacuum and the residue purified by chromatography on silica gel with petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 50:1, v/v) as eluent to afford the desired product in 86% yield.
3-([1,1’-Biphenyl]-2-yl)-2-methyl-1H-indole (2s)

Yellow solid, 86% yield; m.p. 142–144°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.85 (br, 1H), 7.41 (d, $J = 3.6$ Hz, 3H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.17–7.06 (m, 7H), 6.97 (t, $J = 7.2$ Hz, 1H), 6.86 (t, $J = 7.4$ Hz, 1H), 1.77 (s, 3H); $^{13}$C ($^1$H) NMR (101 MHz, DMSO-$d_6$) $\delta$ 142.1, 141.6, 135.4, 133.4, 132.4, 132.2, 130.4, 128.7, 128.3, 128.0, 127.4, 127.2, 126.4, 120.4, 118.9, 117.8, 112.1, 110.7, 12.0. ESI-MS: 283.

Characterization data for the products

$^Z$-Phenyl-5H-spiro[indeno[1,2-b]indole-10,3’-indole] (2a)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 103.7 mg, 90% yield; m.p. 257–259°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.07 (br, 1H), 8.10 (d, $J = 8.1$ Hz, 1H), 8.04 (d, $J = 7.2$ Hz, 1H), 7.90 (dd, $J = 7.6$, 1.2 Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.75 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.59–7.52 (m, 2H), 7.47–7.36 (m, 3H), 7.23 (td, $J = 8.0$, 1.2 Hz, 1H), 7.15 (td, $J = 8.0$, 1.2 Hz, 1H), 7.09–7.04 (m, 3H), 6.76–6.74 (m, 2H); $^{13}$C ($^1$H) NMR (151 MHz, DMSO-$d_6$) $\delta$ 183.5, 155.5, 142.1, 140.5, 137.2, 133.5, 131.7, 130.4, 129.4, 128.8, 128.5, 128.1, 127.0(3), 126.9(8), 126.7, 126.4, 126.2, 125.5, 122.6, 122.1, 121.1, 120.5, 119.8, 112.4, 110.4, 65.2. HRMS, calculated for C$_{38}$H$_{29}$N$_2$ (M + H$^+$): 383.1543, found 383.1537.

2-Methyl-2’-(p-tolyl)-5H-spiro[indeno[1,2-b]indole-10,3’-indole] (2b)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 79.0 mg, 64% yield; m.p. 127–135°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.00 (br, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 8.02 (d, $J = 7.2$ Hz, 1H), 7.78–7.72 (m, 3H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.43 (td, $J = 5.6$, 1.2 Hz, 1H), 7.39–7.33 (m, 2H), 7.21 (td, $J = 8.0$, 1.2 Hz, 1H), 7.14 (td, $J = 8.0$, 1.2 Hz, 1H), 6.86 (d, $J = 8.4$ Hz, 2H), 6.60 (d, $J = 8.4$ Hz, 2H), 2.35 (s, 3H), 2.06 (s, 3H); $^{13}$C ($^1$H) NMR (101 MHz, DMSO-$d_6$) $\delta$ 183.7, 155.5, 142.3, 137.6, 137.3, 136.9, 136.1, 133.6, 132.1, 129.3, 129.2, 128.2, 127.7.
2-Methoxy-2'-(4-methoxyphenyl)-5H-spiro[indeno[1,2-b]indole-10,3'-indole] (2c)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 64.0 mg, 48% yield; m.p. 155–162°C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.18 (br, 1H), 7.98–7.93 (m, 2H), 7.83 (d, $J$ = 7.2 Hz, 1H), 7.63–7.60 (m, 2H), 7.46 (dd, $J$ = 7.2, 1.8 Hz, 1H), 7.37 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.23–7.16 (m, 3H), 7.13 (dd, $J$ = 8.6, 2.6 Hz, 1H), 6.76–6.74 (m, 2H), 6.65–6.63 (m, 2H), 3.91 (s, 3H), 3.54 (s, 3H); $^{13}$C{1H} NMR (101 MHz, DMSO-$d_6$) δ 179.6, 158.9, 157.9, 157.0, 142.1, 141.5, 141.0, 137.9, 135.0, 128.3, 126.6, 126.1, 125.0, 124.7, 124.2, 123.1, 121.4, 120.4, 120.0, 119.9, 114.3, 113.9, 112.4, 111.9, 106.4, 66.0, 55.5, 54.9. HRMS, calculated for C$_{30}$H$_{23}$N$_2$O$_2$ (M + H$^+$): 433.1754, found 433.1752.

2-Chloro-2'-(4-chlorophenyl)-5H-spiro[indeno[1,2-b]indole-10,3'-indole] (2d)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 70.8 mg, 52% yield; m.p. 290–292°C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.16 (br, 1H), 8.07 (t, $J$ = 8.4 Hz, 2H), 7.90–7.87 (m, 2H), 7.77 (dd, $J$ = 7.6, 0.8 Hz, 1H), 7.65 (dd, $J$ = 8.2, 2.2 Hz, 1H), 7.54 (d, $J$ = 8.0 Hz, 1H), 7.47 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.41 (td, $J$ = 7.4, 1.2 Hz, 1H), 7.24 (td, $J$ = 7.6, 1.0 Hz, 1H), 7.18–7.13 (m, 3H), 6.73–6.70 (m, 2H); $^{13}$C{1H} NMR (101 MHz, DMSO-$d_6$) δ 181.5, 155.1, 141.5, 138.9, 137.2, 132.6, 132.4, 131.9, 131.6, 130.7, 129.1, 128.9, 128.8, 127.4, 127.3, 126.6, 126.3, 125.9, 124.1, 123.0, 121.5, 120.7, 119.8, 112.5, 110.1, 64.5. HRMS, calculated for C$_{28}$H$_{17}$Cl$_2$N$_2$ (M + H$^+$): 451.0763, found 451.0762.

2-Bromo-2'-(4-bromophenyl)-5H-spiro[indeno[1,2-b]indole-10,3'-indole] (2e)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 62.0 mg, 38% yield; m.p. 301–303°C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.19 (br, 1H), 8.03 (t, $J$ = 8.4 Hz, 2H), 7.90–7.87 (m, 2H), 7.77 (dd, $J$ = 7.6, 0.8 Hz, 1H), 7.65 (dd, $J$ = 8.2, 2.2 Hz, 1H), 7.54 (d, $J$ = 8.0 Hz, 1H), 7.47 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.41 (td, $J$ = 7.4, 1.2 Hz, 1H), 7.24 (td, $J$ = 7.6, 1.0 Hz, 1H), 7.18–7.13 (m, 3H), 6.73–6.70 (m, 2H); $^{13}$C{1H} NMR (101 MHz, DMSO-$d_6$) δ 181.5, 155.1, 141.5, 138.9, 137.2, 132.6, 132.4, 131.9, 131.6, 130.7, 129.1, 128.9, 128.8, 127.4, 127.3, 126.6, 126.3, 125.9, 124.1, 123.0, 121.5, 120.7, 119.8, 112.5, 110.1, 64.5. HRMS, calculated for C$_{29}$H$_{21}$Br$_2$N$_2$ (M + H$^+$): 451.0771, found 451.0762.
DMSO-d$_6$  12.18 (br, 1H), 8.07 (t, $J$ = 7.0 Hz, 2H), 8.01 (s, 1H), 7.81 (s, 2H), 7.77 (dd, $J$ = 7.8, 1.0 Hz, 1H), 7.53 (d, $J$ = 8.0 Hz, 1H), 7.48 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.41 (dd, $J$ = 7.4, 1.2 Hz, 1H), 7.32–7.28 (m, 2H), 7.25 (td, $J$ = 7.6, 1.0 Hz, 1H), 7.15 (t, $J$ = 7.6 Hz, 1H), 6.66–6.62 (m, 2H); 13C{1H} NMR (151 MHz, DMSO-d$_6$) δ 181.4, 155.1, 141.4, 139.3, 137.3, 134.5, 132.6, 131.9, 130.9, 129.4, 128.8, 128.7, 127.8, 127.3, 126.6, 126.3, 124.3, 123.1, 121.5, 120.8, 120.7, 120.5, 119.8, 112.5, 110.1, 64.6. HRMS, calculated for C$_{28}$H$_{17}$Br$_2$N$_2$ (M + H$^+$): 419.1354, found 419.1353.

2-Fluoro-2’-(4-fluorophenyl)-5H-spiro[indeno[1,2-b]indole-10,3’-indole] (2f)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 38.1 mg, 30% yield; m.p. 218–224°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.21 (br, 1H), 8.07 (t, $J$ = 7.2 Hz, 2H), 7.92 (dd, $J$ = 8.8, 5.2 Hz, 1H), 7.78 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.73 (dd, $J$ = 2.8, 8.8 Hz, 1H), 7.53 (d, $J$ = 8.0 Hz, 1H), 7.51–7.46 (m, 2H), 7.41 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.25–7.21 (m, 1H), 7.17–7.13 (m, 1H), 6.97–6.92 (m, 2H), 6.67–6.73 (m, 2H); 13C{1H} NMR (151 MHz, DMSO-d$_6$) δ 182.1, 161.6 (d, $J$ = 246.1 Hz), 161.1 (d, $J$ = 244.6 Hz), 155.1, 141.9, 137.1, 136.1, 132.8, 131.3 (d, $J$ = 7.6 Hz), 128.7, 127.5 (d, $J$ = 7.6 Hz), 127.2, 127.0, 126.6, 126.2, 124.5 (d, $J$ = 7.6 Hz), 122.6, 121.4, 120.6, 119.7, 118.7 (d, $J$ = 22.7 Hz), 115.7 (d, $J$ = 22.7 Hz), 113.3 (d, $J$ = 24.2 Hz), 112.3, 109.5, 64.4; $^{19}$F NMR (376 MHz, DMSO-d$_6$) δ −112.43, −115.40 ppm. HRMS, calculated for C$_{28}$H$_{17}$F$_2$N$_2$ (M + H$^+$): 419.1354, found 419.1353.

4-Fluoro-2’-(2-fluorophenyl)-5H-spiro[indeno[1,2-b]indole-10,3’-indole] (2g)

The title compound was prepared according to the general procedure (A) and purified by flash column chromatography to give a yellow solid, 34.9 mg, 28% yield; m.p. 218–224°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.70 (br, 1H), 8.03 (d, $J$ = 8.0 Hz, 1H), 7.97 (d, $J$ = 7.6 Hz, 1H), 7.51–7.70 (m, 2H), 7.45 (d, $J$ = 8.0 Hz, 1H), 7.48–7.44 (m, 3H), 7.39 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.24–7.11 (m, 3H), 6.99 (td, $J$ = 7.6, 1.2 Hz, 1H), 6.94–6.89 (m, 2H); 13C{1H} NMR (101 MHz, DMSO-d$_6$) δ 180.6 (d, $J$ = 4.0 Hz), 158.6 (d, $J$ = 248 Hz), 156.3 (d, $J$ = 249.5 Hz), 156.0, 139.3, 137.2, 132.2 (d, $J$ = 5.1 Hz), 130.0, 129.9, 129.6, 129.5, 129.4, 128.9, 128.6, 127.8 (d, $J$ = 13.1 Hz), 126.7, 126.3, 126.1, 124.9 (d, $J$ = 4.0 Hz), 122.7, 122.6 (d, $J$ = 2.0 Hz), 121.0, 120.7, 119.3, 118.7 (d, $J$ = 20.2 Hz), 117.6 (d, $J$ = 14.1 Hz), 115.7 (d, $J$ = 22.2 Hz), 113.0, 109.9, 61.6; $^{19}$F NMR (376 MHz, DMSO-d$_6$) δ −114.27, −117.49 ppm. HRMS, calculated for C$_{28}$H$_{17}$F$_2$N$_2$ (M + H$^+$): 419.1354, found 419.1353.
6',7'-Dimethyl-2'-phenylspiro[fluorene-9,3'-indole] (4a)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 68.4 mg, 61% yield; m.p. 178–183°C. 1H NMR (400 MHz, DMSO-d6) δ 8.11 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 7.2 Hz, 2H), 7.28–7.24 (m, 1H), 7.15 (t, J = 8.0 Hz, 4H), 6.86 (d, J = 7.6 Hz, 1H), 6.75 (d, J = 7.6 Hz, 2H), 6.25 (d, J = 7.6 Hz, 1H), 2.65 (s, 3H), 2.29 (s, 3H); 13C{1H} NMR (101 MHz, DMSO-d6) δ 175.4, 154.3, 144.7, 141.1, 140.0, 136.8, 132.1, 130.7, 129.1, 128.4 (4), 128.3 (6), 127.8, 127.3, 123.3, 121.4, 118.4, 71.3, 19.3, 13.8. HRMS, calculated for C28H22N (M+H+): 372.1747, found 372.1749.

2,6',7'-Trimethyl-2'-phenylspiro[fluorene-9,3'-indole] (4b)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 76.6 mg, 66% yield; m.p. 231–236°C. 1H NMR (400 MHz, CDCl3) δ 7.88 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.54 (dd, J = 7.2, 2.0 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.26–7.21 (m, 2H), 7.15–7.09 (m, 3H), 6.87 (dd, J = 7.6, 16.0 Hz, 2H), 6.69 (s, 1H), 6.41 (d, J = 7.6 Hz, 1H), 2.79 (s, 3H), 2.38 (s, 3H), 2.22 (s, 3H); 13C{1H} NMR (101 MHz, CDCl3) δ 176.8, 154.9, 145.5, 145.2, 141.8, 140.7, 139.1, 138.4, 137.1, 132.9, 130.4, 129.7, 128.4, 128.3, 128.0, 127.8, 124.5, 123.9, 120.5, 118.9, 71.8, 21.6, 19.8, 14.2. HRMS, calculated for C29H24N (M+H+): 386.1903, found 386.1900.

2-Methoxy-6',7'-dimethyl-2'-phenylspiro[fluorene-9,3'-indole] (4c)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 89.6 mg, 76% yield; m.p. 215–218°C. 1H NMR (400 MHz, CDCl3) δ 7.76 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.31 (td, J = 7.6, 1.2 Hz, 1H), 7.20–7.15 (m, 1H), 7.08 (t, J = 7.6 Hz, 2H), 7.00 (td, J = 7.6, 1.2 Hz, 1H), 6.91 (dd, J = 8.4, 2.4 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.37–6.35 (m, 2H), 3.57 (s, 3H), 2.72 (s, 3H), 2.32 (s, 3H); 13C{1H} NMR (101 MHz, CDCl3) δ 176.7, 160.3, 155.0, 147.2, 145.0, 141.7, 140.7, 137.1, 134.6, 132.9, 130.4, 129.7, 128.4, 128.2,
The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 67.3 mg, 50% yield; m.p. 233–237°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (dd, \(J = 16.0, 8.0\) Hz, 2H), 7.62 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.50 (d, \(J = 7.6\) Hz, 2H), 7.40–7.34 (m, 3H), 7.26 (t, \(J = 7.6\) Hz, 2H), 7.21–7.14 (m, 2H), 7.11–7.06 (m, 4H), 6.84–6.81 (m, 2H), 6.38 (d, \(J = 7.6\) Hz, 1H), 2.73 (s, 3H), 2.31 (s, 3H); \(^{13}\)C \(^1\)H NMR (101 MHz, CDCl\(_3\)) \(\delta\) 176.6, 155.1, 146.2, 145.8, 141.4, 141.3, 140.9, 140.6, 140.4, 137.2, 132.9, 130.5, 129.8, 128.7, 128.4, 128.3, 128.0, 127.9, 127.4, 127.3, 127.2, 124.0, 122.5, 121.1, 120.9, 118.9, 72.1, 19.8, 14.2. HRMS, calculated for C\(_{34}\)H\(_{26}\)N (M + H\(^+\)): 448.2060, found 448.2053.

2-Chloro-6',7'-dimethyl-2',2'-phenylspiro[fluorene-9,3'-indole] (4e)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 40.0 mg, 31% yield; m.p. 233–234°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 7.6\) Hz, 1H), 7.81 (d, \(J = 8.0\) Hz, 1H), 7.46 (d, \(J = 7.6\) Hz, 2H), 7.43–7.35 (m, 2H), 7.23 (t, \(J = 7.6\) Hz, 1H), 7.17–7.11 (m, 3H), 6.88–6.83 (m, 3H), 6.36 (d, \(J = 7.6\) Hz, 1H), 2.74 (s, 3H), 2.36 (s, 3H); \(^{13}\)C \(^1\)H NMR (101 MHz, CDCl\(_3\)) \(\delta\) 175.8, 155.0, 147.2, 145.4, 140.6, 140.3, 139.7, 137.5, 133.9, 132.7, 130.6, 130.1, 128.7, 128.6, 128.5, 128.4, 128.0, 124.3, 124.1, 121.7, 120.9, 118.8, 71.7, 19.8, 14.2. HRMS, calculated for C\(_{28}\)H\(_{21}\)ClN (M + H\(^+\)): 406.1357, found 406.1358.

2-Fluoro-6',7'-dimethyl-2',2'-phenylspiro[fluorene-9,3'-indole] (4f)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 41.1 mg, 35% yield; m.p. 187–192°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86–7.83 (m, 2H), 7.48 (d, \(J = 7.2\) Hz, 2H), 7.40 (t, \(J = 7.6\) Hz, 1H), 7.26–7.21 (m, 1H), 7.15–7.07 (m, 4H), 6.87 (dd, \(J = 10.4, 7.6\) Hz, 2H), 6.57 (dd, \(J = 8.4, 2.4\) Hz, 1H), 6.37 (d, \(J = 7.6\) Hz, 1H), 2.74 (s, 3H), 2.36 (s,
6,7-Dimethyl-2-phenylspiro[indeno[2,1-b]benzofuran-6,3'-indole] (4g)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 59.7 mg, 48% yield; m.p. 216–218°C. 1H NMR (400 MHz, CDCl3) 8.14 (dd, J = 6.8, 2.0 Hz, 1H), 8.00 (dd, J = 7.6, 1.6 Hz, 1H), 7.92 (dd, J = 7.2, 2.0 Hz, 1H), 7.48–7.33 (m, 5H), 7.10–7.02 (m, 4H), 6.83 (dd, J = 8.0, 2.4 Hz, 2H), 2.71 (s, 3H), 2.38 (s, 3H); 13C{1H} NMR (101 MHz, CDCl3) 177.2, 158.7, 156.2, 142.3, 140.5, 138.9, 137.5, 130.3, 128.7, 128.0, 127.8, 127.5, 127.3, 127.0, 126.3, 125.7, 124.8, 124.3, 124.2, 122.0, 121.9, 112.7, 111.7, 68.2, 19.8, 14.2. HRMS, calculated for C30H22NO (M + H+): 412.1696, found 412.1692.

6,7-Dimethyl-2-phenylspiro[benzo[b]indeno[1,2-d]thiophene-6,3'-indole] (4h)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 80.1 mg, 63% yield; m.p. 189–191°C. 1H NMR (400 MHz, CDCl3) 8.21 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.6 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.34–7.26 (m, 2H), 7.13 (t, J = 7.2 Hz, 1H), 7.04 (t, J = 7.6 Hz, 2H), 6.97 (t, J = 7.2 Hz, 1H), 6.79 (dd, J = 13.2, 7.6 Hz, 2H), 6.37 (d, J = 7.6 Hz, 1H), 2.66 (s, 3H), 2.27 (s, 3H); 13C{1H} NMR (101 MHz, CDCl3) 174.8, 155.0, 149.0, 148.5, 145.8, 141.6, 139.1, 138.3, 137.8, 132.9, 132.9, 130.7, 130.1, 128.6, 128.2, 128.1, 127.8, 126.1, 125.1, 124.6, 124.2, 123.4, 122.3, 120.0, 118.8, 70.1, 19.8, 14.2. HRMS, calculated for C30H22NS (M + H+): 428.1466, found 428.1466.

6,7-Dimethyl-2-phenylspiro[indeno[2,1-b]thiophene-8,3'-indole] (4i)
The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 34.2 mg, 30% yield; m.p. 196–197°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 7.6$ Hz, 1H), 7.51 (d, $J = 7.2$ Hz, 2H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.26–7.22 (m, 2H), 7.15 (t, $J = 7.6$ Hz, 2H), 7.01 (t, $J = 8.0$ Hz, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 7.6$ Hz, 1H), 6.57 (d, $J = 4.8$ Hz, 1H), 6.43 (d, $J = 7.6$ Hz, 1H), 2.72 (s, 3H), 2.35 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 175.4, 155.1, 148.9, 148.2, 144.0, 138.5, 137.9, 137.4, 133.1, 130.6, 129.9, 128.9, 128.5, 128.3, 127.9, 127.8, 126.5, 123.8, 121.5, 119.8, 118.7, 69.3, 19.8, 14.1. HRMS, calculated for C$_{26}$H$_{17}$NS ($M + H^+$): 378.1311, found 378.1309.

$\delta^6,7^0$-Dimethyl-$2^0$-phenylspiro[fluoreno[$4,3-b$]benzofuran-7,3$^0$-indole] (4j)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 94.8 mg, 70% yield; m.p. 225–227°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.47 (d, $J = 7.6$ Hz, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.76 (d, $J = 16.0$, 8.0 Hz, 2H), 7.56–7.52 (m, 2H), 7.39 (t, $J = 7.2$ Hz, 1H), 7.24–7.19 (m, 2H), 7.11 (t, $J = 7.6$ Hz, 2H), 6.96 (d, $J = 7.6$ Hz, 1H), 6.89 (d, $J = 7.6$, 4.0 Hz, 2H), 6.42 (d, $J = 7.6$ Hz, 1H), 2.81 (s, 3H), 2.38 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 176.3, 156.9, 155.1, 145.9, 144.4, 140.9, 140.0, 139.7, 138.5, 133.1, 130.5, 129.9, 128.6, 128.4, 128.3, 128.0, 127.4, 126.0, 125.0, 124.3, 124.0, 123.8, 123.2, 120.8, 120.3, 118.9, 118.4, 112.1, 72.7, 19.8, 14.2. HRMS, calculated for C$_{34}$H$_{24}$NO ($M + H^+$): 462.1852, found 462.1853.

$\delta^6,7^0$-Dimethyl-$2^0$-phenylspiro[benzo[$b$]fluoreno[$3,4-d$]ay]thiophene-7,3$^0$-indole] (4k)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 96.3 mg, 70% yield; m.p. 255–257°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (t, $J = 8.0$ Hz, 2H), 8.01 (d, $J = 7.6$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.57–7.47 (m, 5H), 7.24–7.17 (m, 2H), 7.08 (t, $J = 7.6$ Hz, 2H), 7.00–6.95 (m, 2H), 6.86 (d, $J = 7.6$ Hz, 1H), 6.37 (d, $J = 7.6$ Hz, 1H), 2.79 (s, 3H), 2.37 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 176.3, 155.1, 145.9, 144.4, 140.9, 140.0, 139.7, 137.4, 136.7, 135.9, 135.2, 132.9, 132.8, 130.6, 130.0, 128.5, 128.3, 128.0, 128.0, 127.1, 125.0, 123.9, 123.2, 122.9, 121.9, 121.4, 120.1, 118.9, 72.5, 19.8, 14.3. HRMS, calculated for C$_{34}$H$_{24}$NS ($M + H^+$): 478.1624, found 478.1623.
4-Methoxy-6',7'-dimethyl-2'-phenylspiro[fluorene-9,3'-indole] (4l)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 36.4 mg, 30% yield; m.p. 158–161°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (d, $J$ = 7.6 Hz, 1H), 7.51 (d, $J$ = 7.6 Hz, 2H), 7.39 (t, $J$ = 7.6 Hz, 1H), 7.21 (t, $J$ = 7.2 Hz, 1H), 7.14–7.07 (m, 4H), 6.91 (d, $J$ = 8.4 Hz, 1H), 6.86–6.81 (m, 2H), 6.47 (d, $J$ = 7.6 Hz, 1H), 6.37 (d, $J$ = 8.4 Hz, 1H), 4.09 (s, 3H), 2.75 (s, 3H), 2.35 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 176.6, 156.3, 155.0, 147.1, 144.6, 141.1, 140.6, 137.1, 133.0, 130.4, 129.7, 129.6, 129.3, 128.4, 128.2, 128.0, 127.9, 127.4, 124.5, 123.3, 118.8, 116.1, 110.3, 72.2, 55.6, 19.8, 14.2. HRMS, calculated for C$_{28}$H$_{24}$NO (M + H$^+$): 402.1852, found 402.1851.

4-Fluoro-6',7'-dimethyl-2'-phenylspiro[fluorene-9,3'-indole] (4m)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 29.2 mg, 25% yield; m.p. 213–216°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J$ = 8.0 Hz, 1H), 7.47 (dd, $J$ = 8.0, 0.8 Hz, 2H), 7.42 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.25–7.21 (m, 1H), 7.18–7.07 (m, 5H), 6.86 (t, $J$ = 6.8 Hz, 2H), 6.66–6.42 (m, 1H), 6.37 (d, $J$ = 7.6 Hz, 1H), 2.74 (s, 3H), 2.35 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 176.0, 158.6 (d, $J$ = 252.5 Hz), 154.9, 148.1, 148.0, 144.8, 140.0, 138.8 (d, $J$ = 3.0 Hz), 137.5, 132.7, 130.7, 130.0, 129.6 (d, $J$ = 7.1 Hz), 129.0, 128.8, 128.6, 128.5 (3), 128.4 (8), 128.0 (3), 128.0 (0), 124.3 (d, $J$ = 6.1 Hz), 123.8, 119.7 (d, $J$ = 4.0 Hz), 118.8, 115.4 (d, $J$ = 20.2 Hz), 72.3, 19.8, 14.2; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -118.77. HRMS, calculated for C$_{28}$H$_{23}$FN (M + H$^+$): 390.1653, found 390.1654.

7'-Chloro-6'-fluoro-2'-phenylspiro[fluorene-9,3'-indole] (4n)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 19.2 mg, 20% yield; m.p. 189°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (d, $J$ = 7.6 Hz, 1H), 7.51 (d, $J$ = 7.6 Hz, 2H), 7.39 (t, $J$ = 7.6 Hz, 1H), 7.21 (t, $J$ = 7.2 Hz, 1H), 7.14–7.07 (m, 4H), 6.91 (d, $J$ = 8.4 Hz, 1H), 6.86–6.81 (m, 2H), 6.47 (d, $J$ = 7.6 Hz, 1H), 6.37 (d, $J$ = 8.4 Hz, 1H), 4.09 (s, 3H), 2.75 (s, 3H), 2.35 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 176.0, 158.6 (d, $J$ = 252.5 Hz), 154.9, 148.1, 148.0, 144.8, 140.0, 138.8 (d, $J$ = 3.0 Hz), 137.5, 132.7, 130.7, 130.0, 129.6 (d, $J$ = 7.1 Hz), 129.0, 128.8, 128.6, 128.5 (3), 128.4 (8), 128.0 (3), 128.0 (0), 124.3 (d, $J$ = 6.1 Hz), 123.8, 119.7 (d, $J$ = 4.0 Hz), 118.8, 115.4 (d, $J$ = 20.2 Hz), 72.3, 19.8, 14.2; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -118.77. HRMS, calculated for C$_{28}$H$_{23}$FN (M + H$^+$): 390.1653, found 390.1654.
The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 91.8 mg, 77% yield; m.p. 138–141°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J = 8.4$ Hz, 2H), 7.49 (dd, $J = 8.0$, 1.2 Hz, 2H), 7.43 (td, $J = 7.6$, 0.8 Hz, 2H), 7.26–7.22 (m, 1H), 7.17–7.09 (m, 4H), 6.86–6.80 (m, 3H), 6.66–6.62 (m, 1H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 181.0, 158.8 (d, $J = 247.5$ Hz), 154.4, 144.0, 141.7, 139.8 (d, $J = 3.0$ Hz), 131.9, 131.6, 128.8, 128.6, 128.5, 123.9, 121.1, 120.3 (d, $J = 9.1$ Hz), 114.1 (d, $J = 23.2$ Hz), 113.8 (d, $J = 20.2$ Hz), 72.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –117.5 ppm. HRMS, calculated for C$_{26}$H$_{16}$ClFN (M + H$^+$): 396.0950, found 396.0949.

6′-Bromo-2′-phenylspiro[fluorene-9,3′-indole] (4o)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 97.5 mg, 78% yield; m.p. 210–212°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J = 2.0$ Hz, 1H), 7.93 (d, $J = 8.0$ Hz, 2H), 7.47–7.41 (m, 4H), 7.24 (t, $J = 8.0$ Hz, 1H), 7.20–7.10 (m, 5H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.50 (d, $J = 8.0$ Hz, 1H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 179.7, 157.5, 144.2, 142.2, 141.8, 132.0, 131.2, 129.4, 128.7, 128.5, 128.2, 124.3, 123.9, 123.3, 121.9, 121.1, 71.4. HRMS, calculated for C$_{26}$H$_{17}$BrN (M + H$^+$): 422.0539, found 422.0537.

6′-Methyl-2′-phenylspiro[fluorene-9,3′-indole] (4p)

The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 37.8 mg, 35% yield; m.p. 178–181°C. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.12 (d, $J = 7.6$ Hz, 2H), 7.64 (s, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.34 (d, $J = 7.2$ Hz, 2H), 7.27 (t, $J = 6.8$ Hz, 2H), 7.19–7.14 (m, 4H), 6.90 (d, $J = 7.6$ Hz, 1H), 6.74 (d, $J = 7.6$ Hz, 2H), 6.43 (d, $J = 7.2$ Hz, 1H), 2.38 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, DMSO-d$_6$) $\delta$ 176.9, 155.8, 144.4, 141.2, 139.8, 138.1, 131.9, 130.9, 128.5, 128.4, 127.3, 123.2, 121.5, 121.2, 70.6, 21.1. HRMS, calculated for C$_{27}$H$_{20}$N (M + H$^+$): 358.1590, found 358.1589.

2′-Phenylspiro[benzo[b]indeno[1,2-d]thiophene-6,3′-indole] (4q)
The title compound was prepared according to the general procedure (B) and purified by flash column chromatography to give a yellow solid, 99.9 mg, 83% yield; m.p. 139–142°C. ¹H NMR (400 MHz, CDCl₃) δ 8.32 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.61–7.54 (m, 3H), 7.46–7.36 (m, 3H), 7.24 (t, J = 7.2 Hz, 1H), 7.16–7.06 (m, 4H), 6.85 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 7.2 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 176.4, 156.0, 148.4, 147.8, 145.8, 142.0, 141.1, 139.2, 132.8, 132.4, 131.1, 129.0, 128.6, 128.4, 127.9, 126.9, 126.2, 125.2, 124.7, 124.2, 123.4, 122.4, 122.0, 121.2, 120.1, 69.7. HRMS, calculated for C₂₈H₁₈NS (M + H⁺): 400.1154, found 400.1153.

6'-{(3-{[1,1'-Biphenyl]-4-yl})-2-phenyl-3H-indol-3-yl}-2'-phenylspiro[fluorene-9,3'-indole] (6a)

The title compound was prepared according to the general procedure (C) and purified by flash column chromatography to give a yellow solid, 71.4 mg, 69% yield; m.p. 289–290°C. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 7.2 Hz, 5H), 7.76 (d, J = 8.0 Hz, 1H), 7.40–7.24 (m, 14H), 6.18 (t, J = 7.2 Hz, 2H), 7.13–7.05 (m, 4H), 7.03–6.95 (m, 4H), 6.84–6.76 (m, 3H), 6.38 (d, J = 8.0 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 180.3, 178.5, 155.9, 144.6, 144.4, 143.3, 142.2, 141.7, 141.7, 139.6, 138.4, 132.6, 132.3, 130.9, 130.7, 129.7, 129.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.5, 127.2, 126.8, 126.2, 124.3, 124.1, 121.4, 122.6, 121.8, 121.4, 120.9, 71.4. HRMS, calculated for C₅₂H₃₅N₂ (M + H⁺): 687.2795, found 687.2790.

2-Methyl-6'-{(3'{-4'-methyl-}[1,1'-biphenyl]-4-yl})-2-phenyl-3H-indol-3-yl}-2'-phenylspiro[fluorene-9,3'-indole] (6b)

The title compound was prepared according to the general procedure (C) and purified by flash column chromatography to give a yellow solid, 57.2 mg, 53% yield; m.p. 258–259°C. ¹H NMR (400 MHz, CDCl₃) δ 7.86–7.71 (m, 7H), 7.41–7.26 (m, 14H), 6.58 (d, J = 8.4 Hz, 2H), 6.41–6.37 (m, 1H), 2.20 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 180.3, 178.6, 156.8, 155.9, 154.3, 148.0, 145.0, 144.8, 144.7, 144.5, 144.5, 143.4, 142.6, 142.3, 141.9, 141.8, 141.0, 139.2, 139.1, 139.0, 138.6, 138.4, 138.4, 136.7, 136.1, 134.7, 132.7, 132.3, 130.8, 130.8, 130.7, 130.4, 129.6, 129.4, 129.4, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.8, 127.3, 127.1,
2-Methoxy-6’-(3-(4’-methoxy-[1,1’-biphenyl]-4-yl)-2-phenyl-3H-indol-3-yl)-2’-phenylspiro[fluorene-9,3’-indole] (6c)

The title compound was prepared according to the general procedure (C) and purified by flash column chromatography to give a yellow solid, 56.4 mg, 50% yield; m.p. 232–235°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.85–7.79 (m, 3H), 7.75 (dd, J = 8.4, 2.4 Hz, 3H), 7.41–7.24 (m, 13H), 7.19 (t, J = 7.2 Hz, 2H), 7.09–6.89 (m, 7H), 6.76–6.71 (m, 1H), 6.40 (d, J = 8.0 Hz, 1H), 6.30–6.27 (m, 2H), 3.69 (s, 3H), 3.60 (s, 3H); \(^{13}\)C{\(^1\)H} NMR (101 MHz, CDCl\(_3\)) \(\delta 180.3, 178.6, 160.2, 158.3, 155.8, 146.4, 144.1, 143.0, 142.3, 141.7, 138.9, 134.6, 134.6, 132.9, 132.3, 132.1, 130.9, 130.7, 129.6, 128.5, 128.3, 128.1, 127.4, 127.2, 127.1, 126.2, 124.3, 124.3, 123.9, 122.5, 122.4, 121.7, 121.7, 121.5, 120.0, 114.5, 111.9, 109.5, 71.3, 55.6, 55.2. HRMS, calculated for C\(_{54}\)H\(_{39}\)N\(_2\)O\(_2\) (M + H\(^+\)): 747.3006, found 747.3006.

2-Chloro-6’-(3-(4’-chloro-[1,1’-biphenyl]-4-yl)-2-phenyl-3H-indol-3-yl)-2’-phenylspiro[fluorene-9,3’-indole] (6d)

The title compound was prepared according to the general procedure (C) and purified by flash column chromatography to give a white solid, 68.4 mg, 60% yield; m.p. 273–274°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.94 (d, J = 7.6 Hz, 2H), 7.87 (dd, J = 8.4, 2.8 Hz, 1H), 7.79 (d, J = 4.4 Hz, 1H), 7.60–7.51 (m, 1H), 7.44–7.21 (m, 15H), 7.16–7.02 (m, 5H), 6.89 (t, J = 7.2 Hz, 1H), 6.82–6.75 (m, 4H), 6.52 (dd, J = 18.4, 8.0 Hz, 2H); \(^{13}\)C{\(^1\)H} NMR (101 MHz, CDCl\(_3\)) \(\delta 180.7, 148.4, 142.3, 142.2, 141.1, 140.1, 140.0, 138.6, 138.1, 135.6, 135.5, 132.9, 132.8, 132.5, 132.3, 132.3, 132.2, 131.8, 131.3, 130.9, 130.4, 130.4, 130.2, 130.1, 129.9, 129.8, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.3, 127.2, 127.2, 126.5, 126.1, 124.2, 123.8, 123.5, 121.7, 119.2, 113.4, 113.4, 111.2, 111.1, 71.4, 29.8. HRMS, calculated for C\(_{52}\)H\(_{33}\)Cl\(_2\)N\(_2\) (M + H\(^+\)): 755.2015, found 755.2015.
The title compound was prepared according to the general procedure (C) and purified by flash column chromatography to give a yellow solid, 62.1 mg, 49% yield; m.p. 197–201°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00–7.83 (m, 6H), 7.61 (t, $J$ = 6.4 Hz, 1H), 7.50–7.20 (m, 22H), 7.15–6.96 (m, 11H), 6.77 (s, 1H), 6.47–6.40 (m, 1H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 180.1, 178.5, 155.9, 148.0, 145.3, 144.9, 144.8, 143.1, 142.0, 141.3, 140.8, 140.5, 140.4, 139.1, 138.6, 138.2, 134.5, 132.4, 132.2, 131.1, 130.9, 130.4, 129.9, 129.6, 129.3, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 127.9, 127.5, 127.1, 126.9, 126.1, 126.0, 125.0, 124.1, 124.1, 122.6, 122.5, 121.6, 121.2, 120.9, 71.2. HRMS, calculated for C$_{64}$H$_{43}$N$_2$ (M + H$^+$): 839.3421, found 839.3426.

The title compound was prepared according to the general procedure (C) and purified by flash column chromatography to give a yellowish brown solid, 71.4 mg, 55% yield; m.p. 235–239°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.37–8.33 (m 1H), 8.07–8.04 (m, 3H), 7.97 (d, $J$ = 8.4 Hz, 1H), 7.85–7.78 (m, 1H), 7.74–7.62 (m, 3H), 7.57 (dd, $J = 14.4$, 7.6 Hz, 2H), 7.49–7.16 (m, 15H), 7.12–6.91 (m, 8H), 6.84 (d, $J = 8.0$ Hz, 1H), 6.77–6.67 (m, 2H), 6.46–6.30 (m, 2H), 6.19–6.00 (m, 1H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 180.0, 179.9, 178.2, 178.1, 156.8, 156.0, 155.9, 155.5, 153.4, 152.6, 152.4, 150.8, 148.1, 146.2,
144.5, 144.4, 144.0, 143.9, 142.3, 141.7, 141.4, 139.5, 139.2, 138.4, 137.7, 136.9, 134.5, 133.2, 132.6, 132.2,
131.3, 130.9, 130.5, 129.9, 129.7, 129.2, 128.8, 128.8, 128.6, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9,
127.4, 127.4, 127.3, 127.0, 126.6, 126.4, 126.2, 125.9, 125.1, 124.9, 124.5, 124.5, 124.4, 124.2, 124.1, 124.0,
124.0, 123.8, 123.2, 122.5, 122.4, 122.3, 121.7, 121.6, 121.4, 121.3, 121.2, 120.7, 120.4, 120.3, 120.1,
119.9, 118.4, 112.0, 111.8, 111.6, 71.9, 71.4. HRMS, calculated for C_{64}H_{38}N_{2}NaO_{2} (M + Na^{+}): 889.2825,
found 889.2833.